First-principle investigations of nanoscale carbon-based materials for their electronic properties and potential applications

Wang, Min

2011

Wang, M. (2011). First-principle investigations of nanoscale carbon-based materials for their electronic properties and potential applications. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/46301>

<https://doi.org/10.32657/10356/46301>

**First-Principle Investigations of Nanoscale Carbon-Based
Materials for Their Electronic Properties and Potential
Applications**

Wang Min

School of Chemical and Biomedical Engineering

A thesis submitted to the

Nanyang Technological University

in fulfillment of the requirement for the degree of

Doctor of Philosophy

2011

Acknowledgement

I would like to express my greatest appreciation to my supervisor Prof. Li Chang Ming, for his warm encouragement and patient instruction. All my research work is under his kind guidance and inspirations. He also imparts his knowledge and experience to me and gives me many good suggestions for my research. I also want to thanks for his help in writings, including all the journal publications and the thesis, and for his financial support during my PhD program.

Further, thanks all the group members for their kind helps. I also want to thank the School of Chemical and Biomedical Engineering for the resource supports.

Last but not least, I would like to express my sincere appreciation to my parents for their love, support and dedication.

Table of content

Acknowledgement	i
Table of content.....	ii
List of Figures	v
List of Tables.....	xiii
Abstract	xiv
Chapter 1 Introduction.....	1
1.1 Background	1
1.2 Motivations	2
1.3 Objectives	4
1.4 Organization.....	6
Chapter 2 Literature Review.....	8
2.1 Overview of Carbon.....	8
2.2 Allotropes.....	9
2.3 Graphene	10
2.3.1 Electronic properties of graphene	11
2.3.2 Electronic properties of graphene nanoribbons	12
2.3.3 Graphene oxide	16
2.4 Carbon Nanobuds.....	18
2.5 Electron and spin transport properties of carbon-based systems	22
2.5.1 Transport in carbon nanotubes and graphene nanoribbons.....	23
2.5.2 Negative differential resistance (NDR).....	24
2.5.3 Spin transport in zigzag graphene nanoribbons	27
2.6 Other works.....	29
2.6.1 Experimental syntheses.....	29
2.6.2 Experiments of magnetism in graphene materials	33
2.6.3 Experimental and theoretical works for the outlook parts	35

Chapter 3	First Principle Theory	38
3.1	Schrödinger Equation.....	38
3.2	Density Functional Theory (DFT)	39
3.2.1	Hohenberg and Kohn Theorems	39
3.2.2	Kohn-Sham equation	40
3.2.3	Local density approximation (LDA).....	41
3.3	Computation methods in the thesis	41
3.3.1	Computation methods for electronic property	41
3.3.2	Calculation methods for electronic transport property	42
Chapter 4	Magnetism in Oxidized Graphene with Hydroxyl Groups	44
4.1	Introduction.....	44
4.2	Computation models	45
4.3	Results and Discussion	47
4.3.1	Comparison in different magnetic configurations	47
4.3.2	Band structures and spin densities	48
4.3.3	Hybridization analysis	51
4.4	Conclusion	54
4.5	Appendix.....	55
4.5.1	Two-epoxy-group structures	55
4.5.2	One-epoxy-and-one-hydroxyl-group structures.....	56
Chapter 5	Magnetism in Oxidized Zigzag Graphene Nanoribbons	58
5.1	Introduction.....	58
5.2	Structures of epoxy pairs on the zigzag graphene ribbons.....	59
5.3	Results and discussion	60
5.3.1	Ordered and random epoxy-group structures	60
5.3.2	Analysis between n-ZGNR and n-ZGO-0	61
5.3.3	Analysis between a set of 16-ZGO-m.....	65
5.3.4	Analysis from orbitals' hybridization	67
5.3.5	Discussion between this work and related reported experiments	69
5.4	Conclusions.....	69

Chapter 6	Negative Differential Resistance in Oxidized Zigzag Graphene Nanoribbons	71
6.1	Introduction	71
6.2	The structures for electron transport studies	72
6.3	Results and Discussion	75
6.3.1	<i>I-V</i> characteristics	75
6.3.2	Bias dependent transmission curves	77
6.3.3	Schematic model for NDR mechanism	79
6.4	Conclusions	82
Chapter 7	Magnetic properties of all-carbon graphene-fullerene nanobuds	83
7.1	Introduction	83
7.2	Models of nanobuds	84
7.3	Results and Discussion	88
7.3.1	Energy analysis	88
7.3.2	Spin-polarized band structures	89
7.3.3	Orbitals' hybridization analysis	93
7.3.4	Spin densities and bond lengths in nanobuds	94
7.3.5	Comparing CNT-based with graphene-based nanobuds	97
7.4	Conclusion	99
Chapter 8	General Conclusion and Outlook	101
8.1	General conclusion	101
8.2	Outlook	103
Abbreviations		106
Publications		107
References		108

List of Figures

Figure 2.2.1. Structures of the different allotropes of carbon: (a) diamond, (b) graphite (3D), (c) graphene, (d) C ₆₀ (fullerene) and (e) carbon nanotube.	10
Figure 2.3.1. (a) Lattice structure of graphene in real space. (b) Energy band structure of graphene. The energy bands become cone shaped at the corners of Brillouin zone. (c) Tight-binding model with non-orthogonal orbital. Reprinted with permission from the reference [57].	11
Figure 2.3.2. (a) Schemes of an 11-AGNR and (b) a 6-ZGNR. The solid black and cyan rectangles and the empty circles denote carbon atoms of different sublattices and hydrogen atoms, respectively. The variations of band gaps in N_a -AGNRs calculated by (c) TB and (d) LDA methods. (e) Band structures of N_a -AGNRs with $N_a=12, 13$, and 14 , respectively. (f) Spin density distributions of a 12-ZGNR (plotted from $\rho_\alpha(r)-\rho_\beta(r)$). (g) The band structure of a 12-ZGNR with degenerate α - and β -spin states. The direct band gap of Δ_z^0 and the energy splitting of Δ_z^1 at $kd_z=\pi$ are denoted, respectively. (h) The variation of Δ_z^0 and Δ_z^1 with different widths of N_z -ZGNRs. Reprinted with permission from the reference [58].	13
Figure 2.3.3. (a) ZGNRs in the electric field. The field is applied along x axis. (b) Dependence of band gaps of α -spin and β -spin with the variation of external field E_{ext} for n -ZGNRs, $n=8, 11, 16$, and 32 , denoted as filled circles, open circles, squares and triangles, respectively. The insert is the rescaled gaps $\delta_{\alpha,\beta}=\Delta_{\alpha,\beta}/\Delta_0(w)$ vs wE_{ext} . (c) The spin-polarized band structures with the external electric field from small (left) to large (right). Schematic diagrams of the electric states (top) and spin distributions (bottom) of ZGNRs (d) without and (e) with an applied external field. Reprinted with permission from the reference [59].	14
Figure 2.3.4. (a) Left: an epoxy group situates on carbon-carbon bond on the left. Right:	

the carbon-carbon bond breaks. (b) The progress for two or more epoxy groups aligned on the coronene molecules. (c) The reaction path for one free oxygen atom to bind on one oxidized coronene molecule. (d) Oxidized graphene sheet: (d-1) an epoxy chain, and (d-2) one epoxy pair or (d-3) one carbonyl pair in the epoxy chain. (e) Reaction paths in the initial epoxy pair (ep), transition state (TS), and carbonyl pair (cp): (e-1) the first and (e-2) the next formation of carbonyl pair. Reprinted with permissions from the references [66] and [67].17

Figure 2.4.1. (a) Low- and (b) intermediate-magnification TEM images of sample. (c)-(e) HRTEM images of samples. (g)-(k) Different bonding methods of fullerenes on SWNTs. The atoms are colored due to the relative binding energy. Reprinted with permission from the reference [28].19

Figure 2.4.2. (a) UV-vis absorption spectra of C_{60} (dotted line), C_{70} (dashed line) and nanobuds (solid line) in hexane (black) and toluene (red). (b) Field emission properties of nanobuds in the presence of 65, 100 and 150 ppm of water, comparing with SWNT. (c) and (d) Structures of nanobuds with two different connections between fullerenes and CNTs. Spin densities in two magnetic nanobuds: (e) (10,10) and (f) (17,0) CNT-nanobud. Reprinted with permissions from the references [28] and [77].20

Figure 2.4.3. (a-1)-(e-1) Nanobuds of different fragmental sizes of fullerene fusing with graphene sheets, denoted by the numbers of carbon atoms: C_{254} , C_{248} , C_{224} , C_{218} and C_{200} , respectively (a-2)-(e-2) Electronic band structures and density of states of five mentioned graphene nanobuds, respectively. Reprinted with permission from the reference [78].21

Figure 2.5.1. The electronic band structures and conductances of (a) (5,5) CNT, (b) (9,0) CNT, (c) (10,0) CNT, (d) (8,2) CNT, (e) 16-AGNR, and (f) 17-AGNR. Reprinted with permission from the reference [79].23

Figure 2.5.2. (a) (5,5) CNT-molecule-(5,5) CNT transport system [47]. Phenylethynyl (PE) / pyrrolo pyrrole (PP) is connected symmetrically/asymmetrically between two CNTs in the calculations. (b) I-V curves for the CNT-PP/PE-CNT systems[47]. (c) (4,4) CNT-molecule-(4,4) CNT transport system[45]. Anthracene molecule is covalent or non-covalent adsorbed on two CNT electrodes. (d) I-V curves for the

CNT-anthracene-CNT junction with covalent/non-covalent adsorption. Reprinted with permission from the reference [45].25

Figure 2.5.3. (a) Schematic AGNRs device for transport study. The nitrogen ('N') doping sites are colored as blue dots. The width and length of AGNR is numbered on the left and bottom, respectively. (b) The band structures and density of states of the undoped and doped AGNRs and isolated scattering region. (c) I-V curves for AGNR transport systems with different widths and lengths. Reprinted with permission from the reference [83]26

Figure 2.5.4. (a) ZGNR is connected with two FM electrodes with applied magnetic field along the arrow direction, resulting in (b) the spin orientations along edges. (c) I-V curves for FM (black square) at 300K and 5K, and those for AFM at 300K (red ring) and 5K (blue triangle). (d) Transmission curves in AFM for α -spin (red) and β -spin (blue). Log-scale plots of MR vs bias V_b for different n-ZGNRs at (e)300K and (f)5K, with n=8,16, 24 and 32, colored in black, red, blue and green lines respectively. In the 32-ZGNR with AFM configuration: (g) different spin orientation currents vs bias characteristics. (h) I_α / I_{total} (red) and I_β / I_{total} (blue). (i) ZTG and V_{th} vs $1/(W_0 + W)$, where W is the width of ZGNR and W_0 is the fitting parameter. (j) Energy difference per edge atom between FM and AFM configuration in ZGNRs. (k)With an external magnetic field the domain wall (DW) formation energy as a function of various DW widths. Reprinted with permission from the reference [84].28

Figure 2.6.1. (a) Graphene visualized by atomic force microscopy. The heights (9 Å and 13 Å) indicate the folded region. (b) Transmission electron microscopy image of suspended graphene sheet on a metallic scaffold. (c) Scanning electron microscope images of the growth graphene films on Ni (inset) layers by CVD. (d) Transmission electron microscopy image of few-layer graphene by CVD. (e) Graphene devices prepared on oxidized Si wafer visualized by scanning electron microscope. Reprinted with permissions from the references [6], [14] and [85].30

Figure 2.6.2. Schematic structure for graphene oxide. Reprinted with permission from the reference [89].32

Figure 2.6.3. (a)-(d) TEM images of the opening of the multiwalled carbon nanotubes step by step. (e) Schematic steps of the unzipping of carbon nanotube. (f) The proposed

chemical reactions in unzipping carbon nanotube. Reprinted with permission from the reference [62].	32
Figure 2.6.4. (a) Magnetization hysteresis loops. Samples annealing at 400 (square) and 600 °C (filled ring). M vs H loop at 300 K with the samples annealing at (b) 400 and (c) 600 °C. The ESR spectra measured at 4.2 K on (d) OGNRS, (e) RGNRs and (f) HGNRs. Reprinted with permission from the references [36-37].	34
Figure 2.6.5. (a) Graphene/Si p-n junction solar cell and its principle (right, bottom). (b) Graphene oxide in polymer solar cells. Reprinted with permission from the references [90] and [91].	36
Figure 2.6.6. Schematic illustrations (a) to represent the experiments, and (b) to clarify the proposed MWNT oscillators. (c) The oscillatory motion in DWNT. (d) Structure of C ₆₀ @SWNT oscillator. (e)-(f) oscillatory behavior based on different armchair SWNTs and different lengths of SWNTs. (g) Kinetic and potential energies during 120-170 ps. Reprinted with permission from the references[24], [92], [93], [96], and [97].	37
Figure 3.3.1. The model of the scattering region between two semi-infinite electrodes: left (L) and right (R) electrodes.	42
Figure 4.2.1. Geometric structures of three oxidized graphenes. Two hydroxyl groups connect with two (a) neighbored carbon atoms, (b) non-neighbored carbon atoms having one carbon atom between or (c) non-neighbored carbon atoms having two carbon atoms between in a hexagonal ring in the top and side view, respectively. Carbon, oxygen and hydrogen atoms are colored in grey, green and orange, respectively. The blue triangles display the unseen connections between carbon atoms and hydroxyl groups on the back side.	46
Figure 4.3.1. Electronic non spin-polarized band structures in (a) Case A and (c) Case C, and spin-polarized band structures in (b) Case B. The majority- (up-) spin bands are plotted at the right part with red color, while the minority- (down-) spin bands are plotted at the left part with black color. The up (or down) olive arrows denotes for up- (or down-) spin bands. The Fermi energy is set to zero. The band structure in Case C is also presented to illustrate details near the Fermi surface in the insert of (c). K ($2\pi/3a$, $2\pi/3a$, 0), X (0, π/a , 0), and Γ (0, 0, 0).	49

Figure 4.3.2. Isosurfaces of spin densities ($0.1 e / \text{\AA}^3$) in Case B denoted by red lobes in (a) top view and (b) side view. The axes x, y, and z are presented as black, blue and red arrows. Carbon, oxygen and hydrogen atoms are colored in grey, green and orange, respectively.

.....50

Figure 4.3.3. (a) Cyan and green circles show two sublattices in graphene, respectively. All bonds in graphene are equivalent. Schematic chemical bonds in blue for association of graphene and hydroxyl group: (b) one bond formed and left one unpaired electron colored as a small pink circle, (c) two chemical bonds formed from two neighbored carbon atoms, (d) two chemical bonds formed from two non-neighbored carbon atoms with one atom between, left two unpaired electrons, and (e) two chemical bonds formed from two non-neighbored carbon atoms with two atoms between, and left two unpaired electrons, which form a double bond.53

Figure 5.2.1. (a) Schematic illustrations of n-ZGNR, (b) n-ZGO-0 and (c) n-ZGO-2 in the top and side view. The orange balls denote hydrogen atoms, passivating the edge of carbon atoms colored in gray. The oxygen atoms are illustrated in red. The green dashed rectangle denotes a single unit cell. Blue numbers 1 to n are denoted as the width of nanoribbons. The pink numbers 0 to m point out the positions for epoxy pairs during our studies.60

Figure 5.3.1. [Rotate right 90°] (i) Electronic spin-polarized band structures, (ii) projected density of states (DOS) and (iii) top- and side-view spin density plots of (a) 16-ZGNR, (b) 16-ZGO-0, (c) 16-ZGO-1, (d) 16-ZGO-2, and (e) 16-ZGO-3. In band structures, the majority- (up-) spin bands are plotted at right parts with red color, while minority- (down-) spin bands are plotted at left parts with black color. The up (or down) pink arrows denotes for up- (or down-) spin bands. In projected DOS structures, the red (black) lines and blue (cyan) lines denote as the majority- (minority-) spin projected DOS of whole devices and oxygen atoms, respectively. The Fermi energy is set to zero. Isosurfaces of spin density ($\pm 0.01 e / \text{\AA}^3$) are denoted by blue (positive) and red (negative) lobes. The positions of epoxy-pair chains are pointed out with red arrows.64

Figure 5.3.2. (a) Structures of graphene. All bonds in graphene are equivalent, and the double bonds are marked for convenience of comparison with others. Structures of (b)

zigzag edges passivated by hydrogen atoms, and (c) oxygen atoms located in the zigzag direction of graphene. Schematic chemical forming: (e) C-H bonds and (f) C-O bonds from (d) graphene. The red and blue balls in (b) and (c) are represented as α -C and β -C atoms.

.....68

Figure 6.2.1. Schematic illustrations of (a) n-ZGNR, (b) n-ZGO-0 and (c) n-ZGO-2 in the top- and side- view. The green dashed rectangle is presented as one unit cell. Blue numbers 1 to n are denoted as the width of zigzag nanoribbons. The pink numbers 0 to m point out the positions for epoxy pairs. Schematic plots of (d) 16-ZGO-0 and (e) 16-ZGO-2 devices for electron transports in top view. Blue, pink and green parts are denoted as left electrode, scattering region and right electrode, respectively. Left and right electrodes are applied with the voltages of $V/2$ and $-V/2$, respectively. Hydrogen, carbon and oxygen atoms are colored in orange, gray and red, respectively.73

Figure 6.2.2. (i) Electronic spin-polarized band structures, (ii) projected density of states (DOS) and (iii) top- and side-view spin density plots of (a) 16-ZGO-0 and (b) 16-ZGO-2. The majority- (up-) spin bands are plotted at right parts with red color, while the minority- (down-) spin bands are plotted at left parts with black color. The up (or down) pink arrows denotes for up- (or down-) spin bands. Each band line is from Γ (0, 0, 0) to X (π/a , 0, 0) (a is the unit cell length). In projected DOS structures, the red (black) lines and blue (cyan) lines denote as the majority- (minority-) spin projected DOS of whole devices and oxygen atoms, respectively. The Fermi energy is set to zero. Isosurfaces of spin densities ($\pm 0.01 e/\text{\AA}^3$) are denoted by blue (positive) and red (negative) lobes. The positions of epoxy-pair chains are pointed out with red arrows.74

Figure 6.3.1. I - V characteristics of (a) 16-ZGO-0 (ring), (b) 16-ZGO-2 (square), and (c) 8-ZGO-0 (triangle) NDR devices. The red and black symbols are denoted as majority- (up-) spin and minority- (down-) spin I - V characteristics, respectively.76

Figure 6.3.2. Bias dependent transmission curves of (a) majority-, (b) minority- spin in 16-ZGO-0 device and (c) majority-, (d) minority- spin in 16-ZGO-2 device. In each section, eleven different color curves are presented from bias 0.0 V to 1.0 V with an increment of 0.1 V. The balls point out the position of left and right chemical potentials (μ_L and μ_R respectively). The red words A-1 to D-1, and A-2 to D-2 in (a) ~ (d) are marked with

red arrows to point out the critical positions for NDR's occurrences and terminations....78

Figure 6.3.3. (a) Majority-spin density of states (DOS) in 16-ZGO-0 device. The Fermi energy is set to zero. (b)-(d) Schematic illustration for NDR mechanism. The pink and blue rectangles represent the DOS of two electrodes, and two red lines in between indicate the positions of the HOMO and LUMO for scattering region with the bias voltages of 0.0, 0.2 and 1.0 V, respectively.81

Figure 7.2.1. Geometric structures of four nanobuds. (a) and (c) The associated carbon atoms in pink are the connected location in Case A and B. The green atoms are expected as the host of unpaired spin. (b) The blue and green carbon atoms are the associated positions in Case C and D, respectively. (c) Three of the pink atoms are labeled as **u**, **v** and **w** for the topological connection of Case A and B. (d) The structure of C₅₄. Two green atoms labeled as **p** and **q**. Atoms (**u,v**) and (**v,w**) connect with (**p,q**) to form Case A and B, respectively. (e)-(h) Geometric structures in the top and side view in Case A-D respectively. C₅₄, graphene and the associated carbon atoms are colored in olive, cyan and pink, respectively. The top view of (e) and (f) nanobuds display the location of mirror planes illustrated as blue line, which can also be observed from different rotations of three yellow bonds.85

Figure 7.2.2. Geometric structures of (a) Case A and (b) Case B. The green colored atoms of fullerene, pink associated atoms and cyan atoms of graphene exhibit (a) six- and nine-membered rings for Case A; and (b) seven- and eight- membered rings for Case B.88

Figure 7.3.1. Electronic spin-polarized band structures in (a) Case A and (b) Case B, and non spin-polarized band structures in (c) Case C and (d) Case D. The majority- (up-) spin bands are plotted at right parts with red color, while the minority- (down-) spin bands are plotted at left parts with black color. The Fermi energy is set to zero. The up (or down) olive arrows denotes for up- (or down-) spin bands. The up-spin band structures in Case A and B are also presented to illustrate details near the Fermi surface.....91

Figure 7.3.2. (a) - (d) projected DOS for Case A - D, respectively. For Case A and B, the pink, blue, cyan, red and olive lines in (a) and (b) denote the projected DOS of atoms C2-C4-C5, atoms C1-C3-C6, C₅₄ fullerene structures, nanobuds and graphenes, respectively. In (c) and (d), the projected DOS of C₅₄ fullerene structures, nanobuds and graphenes are presented as blue, red, and cyan lines, respectively for Case C and D.....92

Figure 7.3.3. (a) Cyan and green circles show two sublattices in graphene, respectively. All bonds in graphene are equivalent. Schematic chemical bonds in blue for association of graphene and fullerene: (b) one bond formed and left one unpaired electron colored as a small pink circle, (c) two chemical bonds formed from two nearest carbon atoms, (d) two chemical bonds forming from two next-nearest atoms of the same sublattice, left two unpaired electrons, and (e) two chemical bonds binding two furthest atoms of different sublattice separately, and left two unpaired electrons, which form a double bond.....	94
Figure 7.3.4. Isosurfaces of (a) [or (b)] spin density ($0.2 e / \text{\AA}^3$) for Case A [or Case B] denoted by red lobes. In (a) and (b), the C_{54} structures are shown in olive.....	96
Figure 7.3.5. The bond lengths ($\text{\AA}$) in Case A-D are marked in (a)-(d), respectively. The pink carbon atoms are denoted as associated positions. The green carbon atoms in (a) and (b) are presented the spin positions.	97
Figure 8.2.1. Diagram of a FET working as a gas sensor. The pink dots are presented as the functionalized groups on the P/N materials.	104

List of Tables

Table 4.3.1. The energy data: NM, AFM, FM and the related formation reactions. The binding energy E_b is defined as $E_{GO}-E_{OH}-E_{graphene}$, E_{GO} , E_{OH} , and $E_{graphene}$ are the energies of oxidized graphene, hydroxyl group, and graphene, respectively.	48
Table 5.3.1. Energy data of a set of n-ZGO-0 and n-ZGNR structures containing NM, FM and AFM states. Each total energy result is listed inside parentheses. The total energy differences of NM and AFM states are compared with corresponding FM ones. The total energy differences of “16-ZGO-random” and “16-ZGO- $\perp$ ” are compared with NM state of 16-ZGO.	62
Table 5.3.2. Energy data of a set of 16-ZGO-m (m= 0, 1, 2, and 3) and 16-ZGNR structures containing NM, FM and AFM states. Each total energy result is listed inside parentheses. The total energy differences of NM and AFM states are compared with corresponding FM ones. Each total magnetic moment is listed as the value of corresponding favorable ground state.	66
Table 7.3.1. The energy data of four kinds of nanobuds : NM, AFM, FM and the related formation reactions. The binding energy E_b is defined as $E_{nanobuds}-E_{C54}-E_{graphene}$, where $E_{nanobuds}$, E_{C54} , and $E_{graphene}$ are the energies of nanobud, C ₅₄ , and graphene, respectively. The energy differences of AFM and FM states are compared with corresponding NM ones.	89

Abstract

New materials and devices at nanoscale are greatly required to overcome Moore's limits in engineering and technology. Recently, nanoscale carbon-based materials, have received considerable attention, due to their unique electronic, optical, and mechanical properties. All of the works in my PhD thesis are devoted to the following topic: first-principle investigations of carbon materials for their electronic properties and potential applications.

First, three oxidized graphene structures with hydroxyl groups have been investigated through the spin-polarized density functional theory. The results reveal that in a graphene hexagonal ring structure, only chemical bond formation by two non-neighbored hydroxyl-bonded carbon atoms but with one carbon atom between can cause unpaired spins to produce a magnetic moment of $1.2 \mu_B$, while other two structures are nonmagnetic. This work paves the way for the controllable synthesis or/and oxidized graphene with hydroxyl groups at specific carbon positions for magnetic properties.

Second, a series of structures with an epoxy-pair chain at various positions on zigzag graphene nanoribbons are considered. The results show that this kind of graphene oxide is ferromagnetic at ground state, providing great promise in the field of spintronics. In comparison with zigzag graphene nanoribbons of the same width, this graphene oxide is metallic and its spin density distribution is modified by epoxy pairs at different locations, thus offering some fundamental insights into graphene-based materials.

Third, the electronic transport property of an epoxy-pair chain on zigzag graphene nanoribbons (ZGO) is studied theoretically. The results indicate that this graphene oxide can have a negative differential resistance (NDR) phenomenon, supported by bias dependent transmission curves of different orientation spins. This discovery may provide great potential for applications in NDR-based nanoelectronics by using modified graphene materials.

Fourth, four proposed all-carbon graphene-fullerene nanobuds have been investigated through spin-polarized density functional theory. Two nanobuds possess nearly magnetic moments of $6 \mu_B$, originating from unpaired spins due to the chemical bond formation from two next-nearest atoms in graphene. In two other nanobuds, the connections of two atoms in different sublattices of graphene cannot generate unpaired spins, resulting in non-magnetic states. The magnetic nanobuds gain great promise for new spintronics and guide controllable experimental synthesis for desired geometries.

In brief, all of the accomplishments discussed above have been achieved to explain and describe the magnetism of carbon materials including graphene nanobuds and graphene oxide. Moreover, the discovery of ZGOs could provide great potential applications in NDR nanoelectronics.

Chapter 1 Introduction

1.1 Background

The well-known ‘Moore’s law’ pointed out in 1965 predicts the ‘scaling’ limit, and thus indicates that the trend for performance enhancement in traditional electronic devices, particularly silicon-based devices, cannot continue indefinitely [1]. A worldwide intensive endeavor has been undertaken to develop alternative devices including materials and technologies to conquer Moore’s limit. One approach is to explore novel nanomaterials and nanodevices.

Carbon, as a singular element in the universe, possesses a rather unique property of forming complicated chains or central cores in molecules, thus creating new materials and the basis for the existence of life [2]. Carbon is one of the most miscellaneous elements to form different types of chemical bonds with many other elements. It can form different allotropes and enable the existence of complicated organic molecules. The various properties of carbon directly arises from different arrangements of electrons in carbon atoms: three kinds of sp-hybridizations [3], determining the geometries and properties of carbon-based materials. Besides the conventional diamond and graphite, new carbon allotropes – fullerene [4], carbon nanotube (CNT) [5], and graphene [6] – have been discovered.

Graphene, as a new carbon allotrope, is one of the most interesting investigated materials,

playing an important role of carbon, as it can be thought of as the basis of other carbon allotropes - fullerene, CNT, and graphite. Graphene possesses novel electronic properties including near-ballistic transport [6], massless Dirac fermions [7], Berry's phase [8], quantum Hall effect [7-8], and high mobility [7], showing great promise for nanoelectronics [9-13]. Due to its optically transparent and conductive properties, graphene is also ideal for electrodes [14-15] and photonics [16-19]. Furthermore, two or more carbon materials can be experimentally synthesized together. For example, the so-called carbon peapod [20-25], which consists of trapped fullerenes inside CNTs, possesses interesting magnetic properties with heating and irradiating [26-27]. In recent years, another interesting type of hybrid carbon nanostructures called the nanobud, was reported by Nasibulin *et al* [28], who synthesized the fullerenes on the outer surface of single-walled carbon nanotubes. These low-dimensional carbon nanostructures, possessing sp^2 hybridized carbon atoms, have played critical roles in nanoscience and nanoengineering.

1.2 Motivations

Recently, investigations of advanced carbon-based materials have been the focus of great efforts in nanoscience and nanoengineering to meet the needs of potential industrial applications. How to design these nanostructures and how to further investigate the unique electronic properties of these nanostructures are very challenging questions. Some of these nanostructures may not be easy to study experimentally. Thus, theoretical

modeling not only can provide important fundamentals, but also can give guidelines and knowledge for the design of practical experiments.

For example, graphene, as one of the most investigated materials, is gapless and needed to modify for various potential applications [29-33]. A functionalized approach is one of the usual methods to treat graphene. The use of strong acid to treat graphene can introduce oxygen groups on the surface or the edges of graphene. With the oxidative process, graphene oxide exists widely as a critical intermediate during fabrications and modifications of graphene. It is fundamentally and practically valuable to study the electronic properties of graphene oxide and its incorporation into graphene layers, which could facilitate an atomistic understanding of formation mechanisms for graphene and modified graphene materials.

Moreover, the question of how to design nanostructures from recently well-known and other experimentally accessible materials is also very challenging. The composite structure - carbon peapod - has been investigated in terms of the physical and chemical properties coming from both carbon nanotube and fullerene[34]. Another recent experimental structure – nanobud, can also display impressive applications, as carbon structures with the hybridization of two or more materials can display not only their components' properties but also new features. It is theoretically advantageous to investigate the electronic properties of these composite carbons, which could provide new experimental designs and give guidance for the development of accessible hybridized carbons including optics, high current density and thermal transport.

Another promising application of carbon-based materials is to fabricate magnetic devices - spintronics - carrying information arising from electron spin and magnetism of materials besides electron charge. Given that, in most instances, magnetic materials are mainly based on d and f elements for technological applications, it is essential to extend new materials possessing magnetic ordering without opening d and f shells. Spintronics have now attracted enormous research efforts in carbon-based structures. How to treat carbons for high-performance spintronics is not easy to approach without an understanding of the fundamentals of physical and chemical insights. On the other hand, carbon materials can be used as transport devices by the tools of first-principle studies, including both charges and spins. Promising spintronics and transport nanoelectronics could be designed and predicted.

1.3 Objectives

The objective of this research is to investigate the electronic properties of carbon materials to extend potential applications. The objectives are listed below:

1. Graphene oxide, one solution-processable graphene material, is one of the most important approaches to fabricate and/or modify graphene-based materials [35]. Recently, experimental evidences of ferromagnetism in oxidized graphenes have been reported [36-38]. Though oxide groups including hydroxyl or/and epoxy groups are considered on the graphene surface and finally induce the magnetism, it is still not clear how to and where to connect can determine the origination of magnetism. In the

thesis project, several hydroxyl/epoxy groups connecting on graphene surface are considered to perform first principle simulation for the study of the origination of magnetism and electronic properties.

2. Graphene nanoribbons are elongated strips of graphene with edges and sketch a predominant type of graphene materials [9, 39-43]. Normally, there are two kinds of graphene nanoribbons, the armchair and zigzag types. Zigzag graphene nanoribbons (ZGNRs) display antiferromagnetism and can be tuned by the external electric field. The oxygen groups connecting on the surfaces of ZGNRs could affect the magnetic properties. In this project, a series of structures are studied with the factors of the positions of oxygen groups and the lengths of the ZGNRs.
3. With the investigations of oxygen groups on the graphene or ZGNRs, several structures can be used as candidates for transport nanoelectronics. Transport properties have been discussed in various molecular junctions[44] between carbon nanotubes[45-50] and other metal electrodes such as gold [51-55]. Due to their magnetic properties, graphene materials can also provide spin current for transport devices. Thus, in this project, the transport properties of graphene materials are theoretically investigated for potential nanoelectronics.
4. The experimentally accessible carbon structures – nanobuds – as the hybridization of carbon nanotube and fullerene have possessed unique properties. Graphene, as a new carbon material, has many potential applications. The composition of graphene and fullerene to form a new nanobud could also be possible for experimental synthesis and

could provide other interesting features. Thus, for this part, the first-principle theory is used to study several proposed graphene-fullerene nanobuds, and consider the effects of different connections between graphene and fullerene. The electronic properties of the composite structures can guide the experimental applications.

1.4 Organization

The thesis is organized as follows:

Chapter 1 generally introduces the topic of the thesis and briefly describes the motivations and objectives.

Chapter 2 reviews carbon-based materials, including experimental observations and theoretical investigations.

Chapter 3 presents first principle theory and the detailed computation methods in the thesis.

Chapter 4 describes the magnetic properties of oxidized graphene with hydroxyl groups.

Chapter 5 discusses the ferromagnetism of oxidized zigzag graphene nanoribbons.

Chapter 6 describes the electronic transport properties of oxidized zigzag graphene nanoribbons.

Chapter 7 introduces the magnetism of graphene-fullerene nanobuds.

Chapter 8 summarizes the thesis and gives an outlook on carbon-based materials.

Chapter 2 Literature Review

2.1 Overview of Carbon

Carbon is one of the most miscellaneous elements to form different types and number of bonds with many other elements. It can form different allotropes and also enable the existence of complicated organic molecules.

The various properties of carbon directly arise from different arrangements of electrons in carbon atoms: sp-hybridizations [3]. Depending on the number of involved p orbitals, three different ways can be formed:

- (i) A 2s orbital and one of the 2p orbitals can form two hybridized sp^1 orbitals with an angle of 180° linearly. Thus, one sp^1 hybridization carbon atom can make two σ bonds and two π bonds.
- (ii) When a 2s orbital hybridizing with two 2p orbitals, three sp^2 orbitals are formed with an angle of 120° on the same plane. As a result, one sp^2 hybridized carbon atom owns three σ bonds and one π bond.
- (iii) One 2s orbital pairs with three 2p orbitals, forming four sp^3 orbitals with tetrahedral arrangements with the mutual angle of 109.5° . Thus, in one sp^3 hybridized carbon atom, four σ bonds are formed.

Therefore, based on these three types of hybridizations, the geometries and properties of carbon-based materials such as allotropes are determined by the number and nature of the hybridized bonds. This capability of complicated bonding behavior is also the basis for organic chemistry and the existence of life [2].

2.2 Allotropes

In the carbon family, two classical carbon allotropes – diamond and graphite (see Figure 2.2.1(a) and (b)) have been well known from ancient times. Sp^3 hybridized carbon atoms are bonded to four others in the diamond, yielding the hardness, thermal transport, insulator and optical transparent properties. Graphite is made up of layered planar sheets in a hexagonal network by sp^2 hybridized carbon atoms. As each carbon atom bonds with three other atoms, electrons can move freely due to the unpaired π orbital, which is perpendicular to the sheets, giving rise to conductivity.

During the last few decades of 20th century, the carbon allotropy family was enriched by the discovery of several new carbon materials, including 0-dimensional (0D) “buckyball” C_{60} fullerene reported by Smalley et al in 1985 [4] and 1D carbon nanotube (CNT) reported by Iijima in 1991 [5] (see Figure 2.2.1(d) and (e)). In 2004, Novoselov *et al* reported graphene (see Figure 2.2.1(c)) — a 2D single layer of graphite [6]. These low-dimensional carbon nanostructures, possessing sp^2 hybridized carbon atoms, have played critical roles in nanoscience and nanoengineering.

Figure 2.2.1. Structures of the different allotropes of carbon: (a) diamond, (b) graphite (3D), (c) graphene, (d) C_{60} (fullerene) and (e) carbon nanotube.

2.3 Graphene

Graphene is a one-atom-thick planar sheet of carbon atoms that can be viewed as an individual atomic plane extracted from graphite. Though it was first experimentally discovered in 2004, it has been studied for more than sixty years theoretically, which serves as a good model system to describe and investigate various carbon structures such as CNTs. This two dimensional structure was believed to be unstable for a long time and preferred to form curved structures such as fullerene and CNTs. So when this structure became reality, a lot of experiments and theoretical works followed. To honor their pioneering work in the study of graphene, Geim and Novoselov were awarded the 2010 Nobel Prize in Physics.

2.3.1 Electronic properties of graphene[56-57]

Graphene has a honeycomb lattice structure (Figure 2.3.1 (a)) of carbon atoms in sp^2 hybridization state. In a unit cell, there are two carbon atoms. Each atom contributes one free electron. The Brillouin zone of graphene is hexagonal in shape. The unhybridized $2p_z$ orbital gives rise to valence and conduction bands (see the blue lines in Figure 2.3.1 (c)). The energy band structure of graphene is shown in Figure 2.3.1 (b) and the tight binding model of graphene is shown in Figure 2.3.1 (c). The energy bands become cone shaped at the corners of Brillouin zone, as shown in the insert of Figure 2.3.1 (b) and (c).

Figure 2.3.1. (a) Lattice structure of graphene in real space. (b) Energy band structure of graphene. The energy bands become cone shaped at the corners of Brillouin zone. (c) Tight-binding model with non-orthogonal orbital. Reprinted with permission from the reference [57].

It attracted a great deal of attentions immediately after its discovery. In graphene, electrons, obtaining a linear dispersion relation, behave like massless relativistic particles. Thus, plenty of unique electronic properties, including an anomalous quantum Hall effect and the absence of localization, have been observed. It also acts as a good material for the area of quantum electrodynamics, and opens new perspectives for carbon electronics.

2.3.2 Electronic properties of graphene nanoribbons [58-59]

As a simple variation of graphene, graphene nanoribbons (GNRs) with nanometer sized widths have been studied [41, 60-62]. GNRs with armchair shaped edges (AGNRs) are classified by the number of carbon atoms (N_a) along the ribbon width (W_a) (Figure 2.3.2(a)), named N_a -AGNR. Similarly, ribbons with zigzag shaped edges are classified by the number of carbon atoms (N_z) with the ribbon width (W_z) (Figure 2.3.2 (b)), denoted as N_z -ZGNR.

The band structures of N_a -AGNRs are shown in Figure 2.3.2 (e) for $N_a = 12, 13$, and 14 , exhibiting direct band gaps at $kd_a=0$ for all cases. The N_a -AGNRs are semiconductors with energy gaps that decrease as a function of increasing ribbon widths $\Delta_{N_a} \sim W_a^{-1}$. The gap of a N_a -AGNR (Δ_{N_a}) displays three family behaviors (see Figure 2.3.2 (c) and (d)) with a hierarchy of gap size: $\Delta_{3p} \geq \Delta_{3p+1} > \Delta_{3p+2} (=0)$ for all p 's (where p is a positive integer).

Figure 2.3.2. (a) Schemes of an 11-AGNR and (b) a 6-ZGNR. The solid black and cyan rectangles and the empty circles denote carbon atoms of different sublattices and hydrogen atoms, respectively. The variations of band gaps in N_a -AGNRs calculated by (c) TB and (d) LDA methods. (e) Band structures of N_a -AGNRs with $N_a=12, 13$, and 14 , respectively. (f) Spin density distributions of a 12-ZGNR (plotted from $\rho_\alpha(r)-\rho_\beta(r)$). (g) The band structure of a 12-ZGNR with degenerate α - and β -spin states. The direct band gap of Δ_z^0 and the energy splitting of Δ_z^1 at $kd_z=\pi$ are denoted, respectively. (h) The variation of Δ_z^0 and Δ_z^1 with different widths of N_z -ZGNRs. Reprinted with permission from the reference [58].

Figure 2.3.3. (a) ZGNRs in the electric field. The field is applied along x axis. (b) Dependence of band gaps of α -spin and β -spin with the variation of external field E_{ext} for n -ZGNRs, $n=8, 11, 16$, and 32 , denoted as filled circles, open circles, squares and triangles, respectively. The insert is the rescaled gaps $\delta_{\alpha, \beta} = \Delta_{\alpha, \beta} / \Delta_0(w)$ vs wE_{ext} . (c) The spin-polarized band structures with the external electric field from small (left) to large (right). Schematic diagrams of the electric states (top) and spin distributions (bottom) of ZGNRs (d) without and (e) with an applied external field. Reprinted with permission from the reference [59].

Spin-polarized first principle calculation is chosen and predicts doubly degenerate of α - and β -spin in ZGNRs, an antiferromagnetic ground state with the same spin ordering at each sublattice and opposite spin orientations between the two sublattices. The spin density distributions in the case of 12-ZGNR are plotted in Figure 2.3.2 (f), where one is labeled as α -spin (red) and the other β -spin (blue). The energy difference between ferromagnetic and antiferromagnetic configurations decreases with an increase of N_z . The degenerate band structure of 12-ZGNR is displayed in Figure 2.3.2(g). Thus, ZGNRs are also semiconductors. The direct band gap of Δ_z^0 ($\frac{2\pi}{3} < kd_z < \pi$, d_z =unit cell length shown in Figure 2.3.2 (b)) decreases with the increase of W_z (Figure 2.3.2(h)).

As the edge states and their linear combinations in ZGNRs are near Fermi level (E_F), it is expected to apply an external electric field to significantly tune these states (see Figure 2.3.3 (a)). With applied electric field, the spin-polarized band structures are shown in Figure 2.3.3 (c). In α -spin, the valence and conduction bands near E_F move further apart, and the gap between them widens, whereas in β -spin, the gap between valence and conduction bands becomes narrower and finally is closed indirectly (the insert of Figure 2.3.3 (c)). Thus, with an appropriate external field, the ZGNR has a coexistence of metallic and insulating behaviors for two spins separately. The half-metallic property originates from the induced energy-level shifts of two opposite spins by the applied external electric field (E_{ext}). The effects of the external field on the two spins are opposite, resulting in moving the valence and conduction energy levels in β -spin closer and those in α -spin further apart (see Figure 2.3.3 (e)). The critical electric field to approach

half-metallic property in ZGNRs decreases with the increase of the width of ribbons (w). The variation of the energy gap is dependent on wE_{ext} , as shown in Figure 2.3.3 (b).

2.3.3 Graphene oxide

To fabricate and/or modify graphene-based materials, oxidation has become an important approach. For example, graphene can be cut into different sizes with oxygen plasma etching to produce nanoribbons [10] and quantum dots [63-64]. In solution processing, graphene nanoribbons can also be generated by reducing graphene oxide [32]. Recently, graphene nanoribbons have even been fabricated by unzipping carbon nanotubes with a simple oxidative process [62]. With an oxygen plasma treatment reported by Gokus *et al* [65], photoluminescence (PL) was first observed in single graphene layers. With the oxidative process, graphene oxide exists widely as a critical intermediate during fabrications and modifications of graphene.

Based on the first principle study, several structures of graphene oxide [66-67] have been proposed. Graphene is often functionalized by epoxy and hydroxyl groups during the fabrication and/or modification process. The epoxy groups have been suggested to align in a line on graphene (see Figure 2.3.4 (d-1)) or carbon nanotubes, and rupture carbon-carbon bonds to form ordered structures [66], as shown in Figure 2.3.4 (a)-(c). During the further oxidation process, the epoxy-pair structure illustrated in Figure 2.3.4(d-2) is more favorable (a lower energy of 2.71 eV) than the scenario where an extra epoxy group is situated far from the existing epoxy chain [67].

Figure 2.3.4. (a) Left: an epoxy group sits on carbon-carbon bond on the left. Right: the carbon-carbon bond breaks. (b) The progress for two or more epoxy groups aligned on the coronene molecules. (c) The reaction path for one free oxygen atom to bind on one oxidized coronene molecule. (d) Oxidized graphene sheet: (d-1) an epoxy chain, and (d-2) one epoxy pair or (d-3) one carbonyl pair in the epoxy chain. (e) Reaction paths in the initial epoxy pair (ep), transition state (TS), and carbonyl pair (cp): (e-1) the first and (e-2) the next formation of carbonyl pair. Reprinted with permissions from the references [66] and [67].

It is also noted [67] that an energy of just 0.1 eV is required to form one epoxy pair or add an epoxy group to extend the epoxy chain on graphene. It has been found that there is a high energy barrier of 0.76 eV [67] for the reaction of one epoxy pair to form one carbonyl pair, depicted in Figure 2.3.4 (d-3), though the existence of one carbonyl pair is

0.45 eV lower than one epoxy pair [67]. The detailed reaction path is plotted in Figure 2.3.4 (e-1). Moreover, the energy barrier to break two neighboring epoxy pairs into two carbonyl pairs approaches 1.07 eV [67] as shown in Figure 2.3.4 (e), indicating that the alignment of epoxy pairs on graphene could be a relatively stable state. It may be possible to observe this state experimentally, as a similar graphene oxide has been found to be relatively stable, which can only become nanoribbons by sonochemical cutting[68]. The electronic and transport properties of this kind of graphene oxide have been discussed in Chapters 5 and 6 of this thesis.

2.4 Carbon Nanobuds

The electronic, optical and mechanical properties of carbon allotropes have been widely investigated, especially in fullerenes, CNTs and graphenes. To extend their potential applications, the intrinsic properties could be modified including vacancies and doping, to approach opportune characteristics including magnetic, catalytic thermal, mechanical and optical capabilities. Various nanostructures of carbons are accessible. One method is to hybridize two or more materials.

In 2007, one interesting type of hybrid carbon nanostructures called a nanobud, was reported by Nasibulin *et al* [28], who synthesized the fullerenes on the outer surface of single-walled carbon nanotubes (SWNT). TEM images and related schematic bonding results, indicating the formation of nanobuds, are shown in Figure 2.4.1.

Figure 2.4.1. (a) Low- and (b) intermediate-magnification TEM images of sample. (c)-(e) HRTEM images of samples. (g)-(k) Different bonding methods of fullerenes on SWNTs. The atoms are colored due to the relative binding energy. Reprinted with permission from the reference [28].

It is expected that the nanobuds' properties can be modified by the interaction between fullerene and SWNT or even better than them. From experimental result [28], the UV-vis absorption of nanobuds and C_{60}/C_{70} in toluene and hexane are shown in Figure 2.4.2 (a),

contributed by both fullerenes and SWNTs (above 650 nm[69-70]). The field emission property of nanobud is better than that of SWCNT, especially in the presence of small amounts of added water vapor (see Figure 2.4.2 (b)). Up to date, various possible nanobuds[71-73], mainly consisting of CNTs and fullerenes, have been investigated in nonmagnetic (NM) [74-76] and magnetic electronic properties[77]. Both fullerene and SWNT are not magnetic. Sp^2 hybridization of CNT is modified at the joint positions, resulting in magnetism, which has been studied with density functional theory. The spin densities in two kinds of magnetic nanobuds are plotted in Figure 2.4.2 (e) and (f).

Figure 2.4.2. (a) UV-vis absorption spectra of C₆₀ (dotted line), C₇₀ (dashed line) and nanobuds (solid line) in hexane (black) and toluene (red). (b) Field emission properties of nanobuds in the presence of 65, 100 and 150 ppm of water, comparing with SWNT. (c)

and (d) Structures of nanobuds with two different connections between fullerenes and CNTs. Spin densities in two magnetic nanobuds: (e) (10,10) and (f) (17,0) CNT-nanobud. Reprinted with permissions from the references [28] and [77].

Figure 2.4.3. (a-1)-(e-1) Nanobuds of different fragmental sizes of fullerene fusing with graphene sheets, denoted by the numbers of carbon atoms: C254, C248, C224, C218 and C200, respectively (a-2)-(e-2) Electronic band structures and density of states of five mentioned graphene nanobuds, respectively. Reprinted with permission from the reference [78].

So far, the material design of graphene nanobuds, has been investigated theoretically [78].

Full or fragmented fullerene is fused with the graphene sheet, as shown in Figure 2.4.3 (a-1)-(e-1). Due to Stones-Wales defects, curvature occurs and gives rise to modified graphene nanobuds. Five nanobuds are investigated from full-size to smallest-fragment-size of fullerene fusing with defected graphene, denoted as C254, C248, C224, C218, and C200 respectively. C254 means that the number of carbon atoms in this nanobud is 254. Under ab initio molecular dynamics simulation, it was found that these nanobuds are quite stable without bonds breaking or forming up to 800K. According to the band structures and density of states of five nanobuds, they are all semimetallic despite the different fragmentation level of fullerenes. Two bands near Fermi level contact with each other at the K point, originating from the graphene monolayer, see Figure 2.4.3 (a-2)-(e-2).

2.5 Electron and spin transport properties of carbon-based systems

Investigating and understanding the electron and spin transport properties of nanoscale systems are among the challenging works for recent rapid progress of nanoscience and nanotechnology. As experimental results alone are not straightforward and sufficient to give correct understanding of transport in systems, today more and more theoretical efforts are being invested to predict and explain various phenomena. Transport in a low-dimensional system can be investigated by non-equilibrium Green's function and Landauer-Büttiker formalism. The corresponding conductance and current can be evaluated from the transmission.

2.5.1 Transport in carbon nanotubes and graphene nanoribbons [79]

The conductance of carbon nanotubes (CNTs) is in agreement with the calculated band structures (or density of states). The (5,5) armchair CNT is metallic with two bands crossing at the Fermi level, leading to a plateau of conductance (see Figure 2.5.1 (a)). The electronic and corresponding conductance of (9,0) and (10,0) zigzag CNTs are presented in Figure 2.5.1 (b) and (c). The calculated conductance of (9,0) CNT around the Fermi level confirms the feature of electronic bands as well. In (10,0) CNT, the conductance exhibits semiconducting behavior, in agreement with its electric band structure. The band structure and conductance of (8,2) CNT are shown in Figure 2.5.1 (d).

Figure 2.5.1. The electronic band structures and conductances of (a) (5,5) CNT, (b) (9,0)

CNT, (c) (10,0) CNT, (d) (8,2) CNT, (e) 16-AGNR, and (f) 17-AGNR. Reprinted with permission from the reference [79].

In armchair graphene nanoribbons (AGNRs), the band gap depends on the width of ribbons. 16-AGNR exhibits a direct band gap of 0.8 eV, while 17-AGNR has a very small gap of 0.2 eV. The corresponding conductances are illustrated in Figure 2.5.1 (e) and (f). The conductance around Fermi level regions is zero in AGNRs and the zero-region is reduced with the decrease of band gaps.

2.5.2 Negative differential resistance (NDR)

Transport properties including negative differential resistance (NDR) have been discussed in various molecular junctions [44] between carbon nanotubes [45-50] and other metal electrodes such as gold [51-55]. In these transport studies, different materials have been used for two electrodes and a scattering region. It has been found that the conducting properties are sensitive to the torsion geometries between electrodes and scattering regions.

In the scattering region part, symmetric or asymmetric connection [47] and covalent or non-covalent adsorption [45] between two electrodes can result in quite different transport properties. In Ref. [47], phenylethynyl (PE) / pyrrolo pyrrole (PP) are used in a (5,5) CNT-molecule-(5,5) CNT transport system, as shown in Figure 2.5.2 (a). In the I-V curves (see Figure 2.5.2 (b)), only PP system has the NDR property. In Ref. [45], it is found that the junction can possess NDR phenomena when anthracene molecule is

non-covalently adsorbed on two (4,4) CNT electrodes, shown in Figure 2.5.2 (c)-(d). Thus, NDR can only be observed under asymmetric connection[47] or non-covalent adsorption[45].

Figure 2.5.2. (a) (5,5) CNT-molecule-(5,5) CNT transport system [47]. Phenylethynyl (PE) / pyrrolo pyrrole (PP) is connected symmetrically/asymmetrically between two CNTs in the calculations. (b) I-V curves for the CNT-PP/PE-CNT systems[47]. (c) (4,4) CNT-molecule-(4,4) CNT transport system[45]. Anthracene molecule is covalent or non-covalent adsorbed on two CNT electrodes. (d) I-V curves for the CNT-anthracene-CNT junction with covalent/non-covalent adsorption. Reprinted with permission from the reference [45].

A procedure that involves using the same material for the three parts at first and then

doping electrode is considered [80-82]. Graphene has been one of the most explored host materials in recent years. Related transport properties have also been widely investigated. It has been reported that armchair graphene nanoribbons (AGNRs) are semiconductors. With the substituted atoms “N” in the AGNRs, the introduced doping state could make ribbons effective electrodes (see Figure 2.5.3 (a)-(b)). This AGNR transport system can present NDR phenomena, as shown in Figure 2.5.3(c). Additionally, the peak and valley currents can be tuned with different widths and lengths of AGNRs.

Figure 2.5.3. (a) Schematic AGNRs device for transport study. The nitrogen (‘N’) doping sites are colored as blue dots. The width and length of AGNR is numbered on the left and bottom, respectively. (b) The band structures and density of states of the undoped and

doped AGNRs and isolated scattering region. (c) I-V curves for AGNR transport systems with different widths and lengths. Reprinted with permission from the reference [83]

2.5.3 Spin transport in zigzag graphene nanoribbons [84]

It is reported that zigzag graphene nanoribbons (ZGNRs) are antiferromagnetic (AFM) at the ground state [58]. With the increase of the ZGNRs' width, the energy difference between AFM and ferromagnetic (FM) decreases rapidly [84], as plotted in Figure 2.5.4 (j). Moreover, in the presence of the external magnetic field, the FM configuration can be more stable [84], as shown in Figure 2.5.4 (k). Besides, a ZGNR with an FM configuration is metallic [84] while a ZGNR with an AFM configuration is a semiconductor. The ZGNR device is attached with electrodes and can be operated as an FM/AFM configuration with the same /opposite external magnetic fields on two ferromagnetic electrodes, as illustrated in Figure 2.5.4 (a)-(b). Based on such a system, spin-based electronics, i.e. spintronics, can be predicted and designed.

Figure 2.5.4. (a) ZGNR is connected with two FM electrodes with applied magnetic field along the arrow direction, resulting in (b) the spin orientations along edges. (c) I-V curves for FM (black square) at 300K and 5K, and those for AFM at 300K (red ring) and 5K (blue triangle). (d) Transmission curves in AFM for α -spin (red) and β -spin (blue). Log-scale plots of MR vs bias V_b for different n-ZGNRs at (e)300K and (f)5K, with $n=8,16, 24$ and 32 , colored in black, red, blue and green lines respectively. In the 32-ZGNR with AFM configuration: (g) different spin orientation currents vs bias characteristics. (h) I_α / I_{total} (red) and I_β / I_{total} (blue). (i) ZTG and V_{th} vs $1/(W_0 + W)$, where W is the width of ZGNR and W_0 is the fitting parameter. (j) Energy difference per edge atom between FM and AFM configuration in ZGNRs. (k) With an external magnetic field the domain wall (DW) formation energy as a function of various DW widths. Reprinted with permission from the reference [84].

Recently, Kim et al [84] theoretically investigated a bias-dependent spin-valve device exhibiting large magnetoresistance (MR). The MR is defined as $MR = (R_{AFM} - R_{FM}) / R_{FM}$, where $R_{AFM/FM}$ is the resistance within FM/AFM configuration. From the I-V curves of FM (or parallel, ‘P’) and AFM (or antiparallel, ‘AP’) shown in Figure 2.5.4(c), MR thousands times larger than before can be observed with different widths of ZGNRs under different temperatures, as shown in Figure 2.5.4 (d)-(e). The super MR originates from the unique symmetry of orbitals of ZGNRs. Moreover, the filtering effect (measured by the ratio: I_α / I_{total}) based on two different spin orientation currents (I_α, I_β) can also be evaluated in ZGNR with AFM configuration

devices, as shown in Figure 2.5.4 (g)-(h). With the increase of bias, the α -spin current increases a lot, while the β -spin current is not changed a lot (see Figure 2.5.4 (g)). Thus, the ratio I_{α} / I_{total} increases gradually to nearly 100% with a bias of 0.15 V (see Figure 2.5.4 (h)). The zero transmission gap (ZTG) and the threshold voltage (V_{th}), which is defined as the voltage to produce 99% spin-polarized current, are scaled by the ZGNRs' widths in Figure 2.5.4 (i). With the control of the widths of ribbons, it is possible to design a realistic nanoscale device based on predicted MR and the filter spin-current effect of ZGNRs.

2.6 Other works

In this section, other important experimental works are discussed, containing the following parts: 1) the synthesis of graphene, 2) the magnetism of graphene and graphene oxide, and 3) other experimental and theoretical works for the outlook part.

2.6.1 Experimental syntheses

The preparation of high quality carbon materials with desirable size in a low cost way is essential for the fabrication of devices. Graphite is stacked by many-layered graphene sheets attracting with weak van der Waals (vdW) force. Exfoliation and cleavage by physical and chemical tools can break the interaction of vdW force and separate individual graphene sheets.

Figure 2.6.1. (a) Graphene visualized by atomic force microscopy. The heights (9 Å and 13 Å) indicate the folded region. (b) Transmission electron microscopy image of suspended graphene sheet on a metallic scaffold. (c) Scanning electron microscope images of the growth graphene films on Ni (inset) layers by CVD. (d) Transmission electron microscopy image of few-layer graphene by CVD. (e) Graphene devices prepared on oxidized Si wafer visualized by scanning electron microscope. Reprinted with permissions from the references [6], [14] and [85].

The micromechanical cleavage of graphite is one of the commercially available ways to produce highly oriented graphene sheet, which is also mentioned in the discovery of

graphene [6]. The graphite is put on a photoresist and baked to stick to the photoresist. Then a scotch tape is used to peel off layers from the graphite sheet and repeat several times. Thus, single- to few-layer graphene sheets, shown in Figure 2.6.1 (a) and (b), can be released in acetone from photoresist. The released graphene is transferred on oxidized Si substrate to form the transistor device (Figure 2.6.1 (e)).

Chemical vapor deposition (CVD) is another most used techniques for the synthesis of graphene [14]. For example, in the CVD chamber, a gas mixture of H_2 , CH_4 , and Ar with the ratio of 1:0.15:2 is used as the precursor. At a temperature of $1000^\circ C$ and followed by a rapid cooling, the nucleation growth of graphene is formed on the Ni film Figure 2.6.1 (c) and (d). The high cooling rate determines the number of the graphene layers and also affects the efficient transfer of graphene layers onto other substrate.

Graphene oxide (GO) is mainly prepared from the oxidation of graphite through chemical exfoliation methods, such as Brodie [86], Staudenmaier [87] and Hummer [88] methods. Brodie and Staudenmaier methods use potassium chlorate ($KClO_3$) and nitric acid (HNO_3) to oxide graphite, while Hummer method uses potassium permanganate ($KMnO_4$) and sulfuric acid (H_2SO_4). These strong acids also act as precursors during oxidation to GO. The oxygen groups are connected with graphene, rendering GO hydrophilic, thus GO can be exfoliated in the solvents and also disperses well in water. With stirring and typically sonication, the dispersion of GO platelets can be obtained in solvents. The proposed GO structure [89] is schematically shown in Figure 2.6.2. With chemical reduction, such as ascorbic acid, sodium borohydride, hydroquinone, reduced graphene oxide or pristine graphene can be obtained.

Figure 2.6.2. Schematic structure for graphene oxide. Reprinted with permission from the reference [89].

Figure 2.6.3. (a)-(d) TEM images of the opening of the multiwalled carbon nanotubes step by step. (e) Schematic steps of the unzipping of carbon nanotube. (f) The proposed chemical reactions in unzipping carbon nanotube. Reprinted with permission from the reference [62].

Moreover, the oxidized graphene nanoribbons can be obtained from similar treatment as Hummer method. First suspend multiwalled carbon nanotubes (MWCNTs) in the concentrated H_2SO_4 , followed by 500wt% KMnO_4 for one hour at room temperature and

another hour at 55-70°C (see Figure 2.6.3 (f)), then with the isolation, the formation of oxidized graphene nanoribbon from the unzipping of carbon nanotube can be obtained [62]. The TEM images of the stepwise opening of MWCNTs shown in Figure 2.6.3 (a)-(d) and schematic illustration shown in Figure 2.6.3 (e) are well describe the unzipping phenomenon, and also provide some background and support for the following experimental and theoretical investigations.

2.6.2 Experiments of magnetism in graphene materials

Recently, the magnetism of graphene materials investigated by SQUID (superconducting quantum interference device) and electron spin resonance (ESR) [36] are reported.

In Ref. [37], the authors first synthesize graphene oxide from Hummer method. GO film contains many oxygen groups (see Figure 2.6.2) and then annealed under an argon environment at different temperatures (such as 400, 600 and 800 °C) to form the final graphene samples. Then the magnetization measurements on the samples are performed by SQUID magnetometer. Two samples, annealing at the temperatures of 400 and 600 °C, are measured at the room temperature (300 K). The magnetization hysteresis loops can be observed (see Figure 2.6.4 (a)-(c)), and clearly present the ferromagnetic ordering of these samples. With a lower measured temperature such as 2K, the saturation magnetization can be significantly increased. Using the reduction and annealing for the preparation of samples, most of the oxygen groups could be removed from the graphene surface, but the rest oxygen groups should play an important role in the ferromagnetism, due to

nonmagnetism of the pristine graphene. The possible mechanism about the magnetic property in this experiment is investigated in Chapter 4.

Figure 2.6.4. (a) Magnetization hysteresis loops. Samples annealing at 400 (square) and 600 °C (filled ring). M vs H loop at 300 K with the samples annealing at (b) 400 and (c) 600 °C. The ESR spectra measured at 4.2 K on (d) OGNRS, (e) RGNRs and (f) HGNRs. Reprinted with permission from the references [36-37].

In Ref. [36], graphene nanoribbons (GNRs), which are gained from unzipping of MWCNTs, are further prepared to form three kinds of GNRs - the oxidized GNRs (OGNRs), the reduced GNRs (RGNRs) and hydrogenated GNRs (HGNRs). They are

performed by ESR measurement at 4.2 K. The ESR signals with symmetric shapes (Figure 2.6.4 (d)-(f)) are located at the g values (g_c) of 2.0029, 2.0032, and 2.0031 respectively, indicating the paramagnetic features. The people also find that the paramagnetic center can arise from oxygen functionalization on the samples. With the reduction of OGNRs by N_2H_4 , RGNRs' ESR signals are similar to OGNR's, indicating that some of the oxygen groups are not removed to keep the magnetic features. The possible mechanism about the magnetic result in graphene nanoribbon is investigated in Chapter 5.

2.6.3 Experimental and theoretical works for the outlook parts

Since graphene material is thin and optical transparence, people begin to use it in thin film devices, such as solar cells and transistors. The performance can match or even better than conventional devices. For example, with a built-in electric field, modified graphene can be tuned as a p-type material. The thin sheet is deposited onto an n-type Si wafer as a hole transporting layer to form a Schottky junction solar cell with a contact printing transfer (Figure 2.6.5 (a)). A graphene oxide film, used as a hole transport and electron blocking layer, is spin-coated on ITO in an P3HT/PCBM-organic solar cell (Figure 2.6.5 (b)). The power conversion efficiency of the device with GO can meet the one with PEDOT:PSS as the electron blocking layer.

Figure 2.6.5. (a) Graphene/Si p-n junction solar cell and its principle (right, bottom). (b) Graphene oxide in polymer solar cells. Reprinted with permission from the references [90] and [91].

Another kind of device is the CNT-based oscillatory system experimentally developed by Zettl *et al* [92]. In the experiment, a very small frictional force $\sim 10^{-14} \text{ N}\cdot\text{\AA}^{-1}$ exists in MWNT when the inner core is pulled out by tips, then released back into the outer shell and retracted inside the outer shell quickly, schematically shown in Figure 2.6.6 (a). Motivated by these interesting experimental results, Zheng and Jiang [93] proposed the MWNT as a nanoscale oscillator with frequency in the gigahertz range (see Figure 2.6.6 (b)). Legoas *et al* [94] presented a molecular dynamics (MD) simulation and investigated a 38 GHz oscillator with a (9,0) CNT inside an (18,0) CNT (see Figure 2.6.6 (c)). Furthermore, Su *et al* [24] and Liu *et al* [95] employed a C₆₀ molecule instead of an inner nanotube inside a single-walled carbon nanotube (SWNT) (see Figure 2.6.6 (d)), obtaining an oscillator with a higher frequency. Moreover, the frequency could be tuned by different outer CNTs or different lengths of CNTs, as shown in Figure 2.6.6 (e-g).

Figure 2.6.6. Schematic illustrations (a) to represent the experiments, and (b) to clarify the proposed MWNT oscillators. (c) The oscillatory motion in DWNT. (d) Structure of C₆₀@SWNT oscillator. (e)-(f) oscillatory behavior based on different armchair SWNTs and different lengths of SWNTs. (g) Kinetic and potential energies during 120-170 ps. Reprinted with permission from the references[24], [92], [93], [96], and [97].

Chapter 3 First Principle Theory

To predict new physical and chemical properties of different materials and design new materials, the first principle theory is widely explored in the realms of chemistry, physics and biology on an atomic scale. The Schrödinger equation describes the electronic properties of molecular systems with high accuracy at *ab initio* level.

3.1 Schrödinger Equation

To investigate the properties of a many-body electronic structure of N_e electrons and N_n nuclei, the Schrödinger equation is used to describe this system with a wavefunction

$\Psi_{MB}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{N_e}; \vec{R}_1, \vec{R}_2, \dots, \vec{R}_{N_n})$:

$$\hat{H}\Psi_{MB} = E\Psi_{MB}, \quad (1)$$

Where $\hat{H}$ is the Hamiltonian operator:

$$\begin{aligned} \hat{H} = \hat{T} + \hat{V} = & -\frac{\hbar^2}{2} \left(\sum_{i=1}^{N_e} \nabla_{\vec{r}_i}^2 + \sum_{I=1}^{N_n} \frac{1}{M_I} \nabla_{\vec{R}_I}^2 \right) \\ & + \left(\frac{1}{2} \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|} - e^2 \sum_{\vec{r}_i, \vec{R}_I} \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \right). \end{aligned} \quad (2)$$

In Eq.(2), $\hat{T}$ and $\hat{V}$ are kinetic and potential energy operators, the coordinates of electrons and nuclei are $\vec{r}_i$ and $\vec{R}_I$, and the masses and the charges of nuclei are M_I .

Based on the Born-Oppenheimer approximation [98], the nuclei can be treated as classical particles and considered to be fixed. The many-body problem is reduced to concern the electrons moving in external potentials $V_{ext}(\vec{r}_i)$, which is the external field induced by the interaction between the electrons and nuclei. The Schrödinger equation is then

$$\hat{H}_e(r) = -\frac{\hbar^2}{2} \sum_{i=1}^{N_e} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_{i=1}^{N_e} V_{ext}(\vec{r}_i), \quad (3)$$

3.2 Density Functional Theory (DFT)

To solve many-body Schrödinger equation (Eq.(3)) analytically is not possible, while numerical solution is perfectly possible in theory. Density functional theory (DFT) provides one computationally feasible way to solve many-body Schrödinger equation. Its main idea is that the ground state of an interacted many electron system in an external potential is only determined by the electron density $n(r)$.

3.2.1 Hohenberg and Kohn Theorems [99]

In history, Hohenberg and Kohn proved two important theorems and introduced the fundamental references for the DFT.

Theorem I: If the electrons in two different systems, one trapped in a external potential

$V_{ext,1}(r)$ and the other in $V_{ext,2}(r)$ have the same ground state electronic density $n(r)$ then necessarily $V_{ext,1}(r) - V_{ext,2}(r) = \text{const.}$

Theorem II: For any N and potential $V_{ext}(r)$, the ground state energy E_0 can be determined by minimize the density functional:

$$E[n(r)] = F[n(r)] + \int V_{ext}(r') n(r') dr', \quad (4)$$

If and only if the charge density $n(r)$ is exact the ground state charge density $n_0(r)$, the function is minimized. $F[n(r)]$ is independent on V_{ext} .

3.2.2 Kohn-Sham equation[100]

The function $F[n(r)]$ is expressed by Kohn and Sham as:

$$F[n] = T_0[n] + \frac{1}{2} \int n(r) V_H(r) dr + E_{xc}[n], \quad (5)$$

where the first term is the kinetic energy, $V_H(r) = e^2 \int \frac{n(r')}{|r - r'|} dr'$ in the second term is

Hartree potential, and the third term is related to the exchange and correlation potential.

Based on Eq. (4) and (5), the Schrödinger equation in Eq. (3) can be rewritten as following:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{ext}(r) + V_H(r) + V_{xc}(r) \right] \psi_i(r) = \epsilon_i \psi_i(r), \quad (6)$$

where the exchange correlation potential is denoted as $V_{xc}(r) = \frac{\delta E_{xc}[n(r)]}{\delta n(r)}$.

The Eq. (6) can be solved through a self-consistent method.

3.2.3 Local density approximation (LDA) [101]

The exchange and correlation function E_{xc} is still unknown and now variant approximations are used to approach. One of the widely used methods is the local density approximation (LDA), which is derived from homogeneous electron gas model:

$$E_{xc}^{LDA}[n(r)] = \int n(r) \mathcal{E}_{xc}[n(r)] dr. \quad (7)$$

where $\mathcal{E}_{xc}$ is exchange and correlation energy density as a function of the electronic density $n(r)$.

3.3 Computation methods in the thesis

3.3.1 Computation methods for electronic property

In some chapters of the thesis, I investigate the magnetism of different materials. The spin polarized calculation along the periodic direction is chosen based on *ab initio* pseudopotential density functional theory (DFT) within local density approximation (LDA) [101] by using SIESTA package [102]. A double- ζ plus polarization basis set is

employed for calculation. The proper energy cutoff for real-space mesh size is chosen such as 300 Ry. The initial structures are relaxed until the force on each atom is less than $0.04 \text{ eV/\AA}$ normally. The proper Monkhorst-Pack k -point grid along the periodic axis is chosen to sample Brillouin zone (BZ) in the corresponding chapters.

3.3.2 Calculation methods for electronic transport property

In the non-equilibrium electronic system, the left and right electrodes are semi-infinite with the middle contact part - the scattering region (see Figure 3.3.1). In the thesis, these three parts are described by single- ζ plus polarization basis sets and local density approximation [101], implemented in the SIESTA package [102] at first to get related density matrix elements. Then the electronic transport properties are studied by non-equilibrium Green's functions with TRANSIESTA package[103]. 30 points of contour integration on the imaginary plane is used to obtain the density matrix from the Green's function. A proper cut off energy for the grid mesh is employed to have the converged transmission values such as 300 Ry.

Figure 3.3.1. The model of the scattering region between two semi-infinite electrodes: left (L) and right (R) electrodes.

Then the current-voltage (I-V) characteristics are calculated with Landauer-Büttiker formalism[104] by integrating the transmission coefficient $T(E, V_b)$ within the energy (E) region and bias voltage (V_b):

$$I = \frac{2e}{h} \int dE T(E, V_b) [f_L(E - \mu_L) - f_R(E - \mu_R)], \quad (8)$$

where f_L and f_R are the Fermi distribution of the left and right electrodes, respectively. μ_L and μ_R , the chemical potentials of the left and right electrodes:

$$\mu_L - \mu_R = eV_b, \quad (9)$$

$$\mu_L = E_F + \frac{eV_b}{2}, \quad (10)$$

$$\mu_R = E_F - \frac{eV_b}{2}, \quad (11)$$

where E_F is the Fermi level.

$T(E, V_b)$ can be calculated as

$$T(E, V_b) = \text{Tr}[\Gamma_L(E) G^R(E) \Gamma_R(E) G^A(E)], \quad (12)$$

where Γ_L and Γ_R are contact broadening functions of left and right electrodes, respectively.

They depend on the electrodes' surface Green's function and contact bonding. $G^R(E)$ and $G^A(E)$ are retard and advanced Green's functions of scattering region, respectively.

Chapter 4 Magnetism in Oxidized Graphene with Hydroxyl Groups¹

4.1 Introduction

Graphene has fueled up significant research efforts [57] since its first report in 2004 [6]. However, because of its gapless property, it is important to modify graphene to possess different electronic properties for various potential applications [13, 16, 41-42, 105-108].

One promising applications of carbon-based materials is to fabricate magnetic devices – spintronics, carrying information arising from electron spin and magnetism of materials besides electron charge. Spintronics have now attracted enormous research efforts in carbon-based structures such as fullerene [109-110], carbon nanotube [111-112], composited carbon structures-peapod [23-25, 27] and nanobuds [77], and organic molecule [113] based materials. More carbon-based magnetic structures are expected to be explored and fabricated for spintronics. The predicted investigations of magnetic ordering in graphene-based materials have been reported in the presence of impurities[114-115], certain edges [60, 116] or defects [33] as well, due to the nonmagnetism in graphene.

In experiments, since it is difficult to prepare pristine graphene naturally, graphene oxide, one solution-processable graphene material, is synthesized from graphite first and then

¹ Reprinted with permission from the reference: [Wang M, Huang W, Chan-Park M B and Li C M 2011 *Nanotechnology* **22** 105702]. Copyright (2011) by Institute of Physics (IOP).

reduced for further graphene-based experimental investigations [117]. Such oxidation is one of the most important approaches to fabricate and/or modify graphene-based materials [35]. Recently, experimental evidences of ferromagnetism in oxidized graphene have been reported [36-38]. Though the oxide groups including hydroxyl or/and epoxy groups are considered on the graphene and finally induce the magnetism, it is still not clear how and where to connect with to determine the origination of magnetism. When one epoxy group is connected with two nearest carbon atoms, the sp^2 hybridization of carbon atoms could be turned into sp^3 bonds, resulting in no possibility of unpaired electrons (or spins), as shown in Scheme 1 and the appendix of this chapter (Figure S 1 and Figure S 3). In this work, I consider the hydroxyl groups connecting on graphene surface, and perform first principle method to study the magnetic properties.

Scheme 1. (a) graphene and (b) one epoxy group connected with graphene.

4.2 Computation models

The oxidized graphene sheets have a layer height of around 6.7 Å from the recent atomic force microscope image [118], indicating that the oxide groups likely appear on both sides of graphene. Hence, two-sided configurations are considered. When one carbon

atom binds with a hydroxyl group, due to symmetry, there are three positions to form a second bond in one hexagonal ring. Two hydroxyl groups can locate on the two neighbored or non-neighbored carbon atoms with one or two carbon atoms between in a hexagonal ring shown in Figure 4.2.1 (a)-(c), respectively. The blue triangles marked in Figure 4.2.1 represent the unseen connections between carbon atoms and hydroxyl groups on the back side. In the side view of three structures, the torsions can be observed in oxidized graphenes. Two hydroxyl groups locate on the surface of a 9-unit-cell graphene structure, and the Monkhorst-Pack k-point grid of $21 \times 21 \times 1$ is chosen to sample Brillouin zone. The lengths along two periodic directions are $7.38 \text{ \AA}$.

Figure 4.2.1. Geometric structures of three oxidized graphenes. Two hydroxyl groups connect with two (a) neighbored carbon atoms, (b) non-neighbored carbon atoms having one carbon atom between or (c) non-neighbored carbon atoms having two carbon atoms

between in a hexagonal ring in the top and side view, respectively. Carbon, oxygen and hydrogen atoms are colored in grey, green and orange, respectively. The blue triangles display the unseen connections between carbon atoms and hydroxyl groups on the back side.

4.3 Results and Discussion

4.3.1 Comparison in different magnetic configurations

With consideration of the spin polarization, the antiferromagnetic (AFM), ferromagnetic (FM) and nonmagnetic (NM) configurations are considered to have the favorable ground states. The energy data of the three configurations are listed in Table 4.3.1. In Case A and C, it is found that only NM could be observed though different FM and AFM configurations are chosen as the initial spin distributions for the calculation. The energies of the three configurations are compared; however, the energy differences could be smaller than the numerical error ($\sim 10^{-5}$ eV), and moreover, the net spin of each atom generated from the charge difference between up spin and down spin ($\rho_{\uparrow}-\rho_{\downarrow}$) is nearly zero ($\sim 10^{-6}$), that is, the final FM and AFM configurations are just NM one actually.. Hence, we consider that nonmagnetic configurations are the ground states in Case A and C. In Case B, FM has a lower energy (~ 0.027 eV/*per atom*) than NM and AFM. Therefore, in comparison with three kinds of oxidized graphene, only Case B has the potential application for spintronics.

To assume the reaction of graphene and hydroxyl group (OH) into oxidized graphene

(GO), the binding energy E_b is studied and should be defined as $E_{GO}-E_{OH}-E_{graphene}$, where E_{GO} , E_{OH} , and $E_{graphene}$ are the energies of oxidized graphene, hydroxyl group, and graphene, respectively. The positive binding energy means that the reaction is endothermic. Therefore, Case A is the most stable state for the least requirement of the binding energy.

Table 4.3.1. The energy data: NM, AFM, FM and the related formation reactions. The binding energy E_b is defined as $E_{GO}-E_{OH}-E_{graphene}$, E_{GO} , E_{OH} , and $E_{graphene}$ are the energies of oxidized graphene, hydroxyl group, and graphene, respectively.

	NM	FM	AFM	E_b
	(eV/per atom)	(eV/per atom)	(eV/per atom)	(eV/per atom)
Case A ^a	-3691.838912	--	--	-0.31
Case B	-3689.869835	-3689.896493	-3689.868222	-0.22
Case C ^a	-3691.080541	--	--	-0.28

^aThe initial FM and AFM configurations are set for simulation, but the distributions of final FM and AFM states only present NM configurations. The energies of FM and AFM are also nearly the same as that in NM (error $<10^{-5}$ eV). Hence, we determine that only NM can be observed and stable.

4.3.2 Band structures and spin densities

The properties of three oxidized graphene structures could be determined by their geometric factors. The band structures are first considered. Three points - K ($2\pi/3a$, $2\pi/3a$, 0) (a is the unit length), X (0 , π/a , 0), and Γ (0 , 0 , 0) are investigated in each band line. To determine the properties, we mainly focus on the bands near Fermi level (E_F). In Case A

and C, the non-polarized band structures are plotted in Figure 4.3.1 (a) and (c), respectively. A small indirect bandgap is shown near E_F in Case A, that is, it is a semiconductor. A value of about 110 meV in the lowest conduction band locates above E_F between Γ and K points. The highest valence band locates below Fermi level with about 63 meV below E_F at Γ point. As shown in the insert of Figure 4.3.1 (c) for Case C, most of the highest valence band locates below Fermi level, but it is about 22 meV higher than E_F at Γ point. Meanwhile, the valley point of the conduction band stands between Γ and K points with a value of 55 meV above E_F . Thus, Case C is semimetallic.

Figure 4.3.1. Electronic non spin-polarized band structures in (a) Case A and (c) Case C, and spin-polarized band structures in (b) Case B. The majority- (up-) spin bands are plotted at the right part with red color, while the minority- (down-) spin bands are plotted at the left part with black color. The up (or down) olive arrows denotes for up- (or down-) spin bands. The Fermi energy is set to zero. The band structure in Case C is also presented to illustrate details near the Fermi surface in the insert of (c). K ($2\pi/3a$, $2\pi/3a$, 0), X (0 , π/a , 0), and Γ (0 , 0 , 0).

The spin-polarized band structures in Case B is metallic as illustrated in Figure 4.3.1 (b). In the down-spin part, parts of the highest valence band near Fermi level locate below E_F . The valley point between K and Γ is about 64 *meV* below E_F , while that between X and K is about 9 *meV* below Fermi level. In the up-spin part, the lowest conduction band near Fermi level has the peak value of about 288 *meV* at Γ point. From the spin-polarized band structure in Case B, the net magnetic moment could be estimated as 1~2 μ_B . Indeed, Case B has the magnetic moment of 1.2 μ_B with the integration in Brillouin zone. In Figure 4.3.2, the spin densities are plotted in top and side view. The isosurface is chosen as 0.1 $e/\text{\AA}^3$, labeled as red lobes. The unpaired spins are mostly located on the graphene. The carbon atoms which connect with hydroxyl groups possess little spin densities shown in Figure 4.3.2.

Figure 4.3.2. Isosurfaces of spin densities ($0.1 e/\text{\AA}^3$) in Case B denoted by red lobes in (a) top view and (b) side view. The axes x, y, and z are presented as black, blue and red arrows. Carbon, oxygen and hydrogen atoms are colored in grey, green and orange, respectively.

4.3.3 Hybridization analysis

Here, we notice that the distributions of spin densities in graphene only locate on the carbon atoms of the same sublattice, different from the sublattice that includes two carbon atoms connecting with hydroxyl groups. To explain the magnetic properties, we try to analyze and estimate the possible models for the results from the carbon orbitals' hybridization. Different sp -hybridized orbitals could be form in carbon atoms[3]. In graphene, each carbon atom possesses three sp^2 bonds: three σ orbitals placed in the plane and one unpaired electron in the π orbital is in perpendicular direction. During the graphene oxidization, breaking of π bonds and producing of new σ bonds exist, resulting in the formation of sp^3 hybridization from sp^2 hybridization. During this transformation, unpaired electrons could possibly generate (Case B), leading to the origination for the magnetic properties.

In graphene, two sublattices are equivalent, labeled as two different color balls in Figure 4.3.3 (a). When one carbon atom of graphene binds with $-OH$ group shown in Figure 4.3.3 (b), there are three positions to form a second bond in a hexagonal ring. In Figure 4.3.3 (c), when two bonds are formed from the neighbored carbon atoms of the hexagonal ring, the former double bond between two neighbored carbon atoms transforms into single one. Two unpaired electrons participate in the formation of covalent bonds with hydroxyl groups. Two non-neighbored hydroxyl-carbon bonds with two carbon atoms between are shown in Figure 4.3.3 (e), and similar situation can be seen: two unpaired electrons form a double bond. Thus these two situations cannot generate unpaired spins. In Figure 4.3.3 (d), two bonds are formed from two non-neighbored carbon atoms with

one atom between, producing two unpaired electrons, to possess strong ferromagnetic coupling[33]. Thus, the ferromagnetism could be observed from this kind of bond formations and two carbon atoms gain little spin as well. Comparing with the analysis based on Figure 4.3.3 (c)-(e), Case A-C in Figure 4.2.1 have the same chemical bond formation of hydroxyl groups and carbon atoms in graphene, respectively. The magnetism of Case B comes from the unpaired spin by this kind bond formation. Due to the effects of oxygen atoms and sp^2/sp^3 hybridization between carbon atoms, the total magnetic moment in Case B is delocalized and smaller than $2 \mu_B$.

It is worthy of a note that the magnetism is also possible in the presence of one epoxy group and one hydroxyl group positing on both sides of oxidized graphene. The electronic properties of two related structures without/with a carbon atom in the middle of the epoxy group and the hydroxyl group as shown in Figure S 3 (a) and (b) respectively are investigated. The data of energy differences indicate that their ground states are FM. The spin-polarized band structures and spin densities are plotted in Figure S 4 and Figure S 5, respectively. The magnetic moments of $0.61 \mu_B$ and $0.38 \mu_B$ are obtained in the two structures, which can also be explained by the carbon orbitals' hybridization process shown in Figure 4.3.3 (g) and (h). As the same analysis above, the unpaired spin can be observed, and is affected by two oxygen groups, finally resulting in a magnetic moment of $0.61 \mu_B$ in the structure shown in Figure 4.3.3 (g) and Figure S 3 (a), while the unpaired spin between two oxygen groups shown in Figure 4.3.3 (h) and Figure S 3 (b) is more influenced to gain a smaller magnetic moment of $0.38 \mu_B$.

From the hybridization analyses, it also explains that the distribution of spin density only locates on the atoms of the same sublattice of graphene (see the bottom of Figure 4.3.3).

The double bond can be considered as two unpaired spins shown in Figure 4.3.3 (i), one of which forms a new double bond with the nearest carbon atom having unpaired spin (Figure 4.3.3 (j)). Thus the unpaired spin in one atom shown in Figure 4.3.3 (b) can “transport” to another atom in the same sublattice represented in Figure 4.3.3 (j), resulting in the distribution of spin density only on the atoms in the same sublattice.

Figure 4.3.3. (a) Cyan and green circles show two sublattices in graphene, respectively.

All bonds in graphene are equivalent. Schematic chemical bonds in blue for association of graphene and hydroxyl group: (b) one bond formed and left one unpaired electron colored as a small pink circle, (c) two chemical bonds formed from two neighbored carbon atoms, (d) two chemical bonds formed from two non-neighbored carbon atoms with one atom between, left two unpaired electrons, and (e) two chemical bonds formed from two non-neighbored carbon atoms with two atoms between, and left two unpaired electrons,

which form a double bond.

4.4 Conclusion

The magnetic properties of three oxidized graphene structures with hydroxyl groups have been investigated through spin-polarized density functional theory. In terms of geometric positions, Case A and C are nonmagnetic, and Case B is ferromagnetic. With further analysis of the chemical bond formation, a magnetic moment of $1.2 \mu_B$ in Case B originates from unpaired spins due to the chemical bond formed from two non-neighbored hydroxyl-bonded carbon atoms but connected with one carbon atom between in the ring. While in Case A and C, the chemical bond formation cannot generate unpaired spins for non-magnetic states. The magnetic oxidized graphene gains great promise for new spintronics. This work could provide fundamentals to guide the controllable experimental synthesis for desired geometric distributions of the hydroxyl-bonded carbon atoms.

4.5 Appendix

4.5.1 Two-epoxy-group structures

Figure S 1. Geometric structures of three oxidized graphenes by two epoxy groups. The blue triangles display the unseen connections between carbon atoms and epoxy groups on the back side. The carbon and oxygen atoms are denoted as gray and red balls respectively.

Table S 1. Energy data of NM states.

	NM (eV/per atom)
(a) in Figure S 1 ^a	-3657.208944
(b) in Figure S 1 ^a	-3657.292315
(c) in Figure S 1 ^a	-3656.241868

(^a The initial FM and AFM configurations are set for simulation, but the distributions of final FM and AFM states only present NM configurations. The energies of FM and AFM are also nearly the same as that in NM (error $<10^{-5}$ eV), and moreover, the net spin of each atom generated from the charge difference between up spin and down spin ($\rho_{\uparrow}-\rho_{\downarrow}$) is nearly zero ($\sim 10^{-6}$), that is, the final FM and AFM configurations are just NM one actually. Hence, we determine that only NM can be observed and stable.)

Figure S 2. Electronic non spin-polarized band structures. The Fermi energy is set to zero.

K ($2\pi/3a$, $2\pi/3a$, 0), X (0 , π/a , 0), and Γ (0 , 0 , 0).

4.5.2 One-epoxy-and-one-hydroxyl-group structures

Figure S 3. Geometric structures of two oxidized graphenes by one epoxy group and one hydroxyl group. The blue triangles display the unseen connections between carbon atoms and epoxy groups on the back side. The carbon, oxygen and hydrogen atoms are denoted as gray, green, and orange balls respectively.

Table S 2. The energy data: NM, AFM and FM.

	NM (eV/per atom)	FM (eV/per atom)	AFM (eV/per atom)
(a) in Figure S 3	-174.959363	-174.959982	-174.959299
(b) in Figure S 3	-174.922140	-174.922290	-174.922089

Figure S 4. Electronic spin-polarized band structures in (a) and (b). The majority- (up-) spin bands are plotted at the right part with red color, while the minority- (down-) spin bands are plotted at the left part with black color. The up (or down) olive arrows denotes for up- (or down-) spin bands. The Fermi energy is set to zero. K ($2\pi/3a$, $2\pi/3a$, 0), X (0, π/a , 0), and Γ (0, 0, 0).

Figure S 5. Isosurfaces of spin densities ($0.1 e/\text{\AA}^3$) for the structures of Figure S 3 (a) and (b) respectively.

Chapter 5 Magnetism in Oxidized Zigzag Graphene Nanoribbons²

5.1 Introduction

Graphene becomes the subject of significant research efforts immediately after its first report in 2004 [6]. To enable various potential applications, it is important to modify graphene to possess unique electronic properties. With the oxidative process, graphene oxide exists widely as a critical intermediate during fabrications and modifications of graphene. Based on the first principle study, several structures of graphene oxide [66-67] have been proposed. Graphene is often functionalized by epoxy and hydroxyl groups during fabrication and/or modification process. The epoxy groups have been suggested to align in a line on graphene or carbon nanotubes, and rupture carbon-carbon bonds to form ordered structures [66]. During the further oxidation process, the epoxy-pair structure is more favorable. This state could be possible to be experimentally observed, since a similar graphene oxide has been found relatively stable, which can only become nanoribbons by sonochemically cutting[68]. Some experimental works on magnetism of oxidized graphene nanoribbons[36] and oxidized graphite[119] have been studied very recently. One related work based on proposed carbon nanotube (CNT) with epoxy chains also represents magnetic properties [120]. Furthermore, some reports have shown that

² Reprinted with permission from the reference: [Wang M and Li C M 2010 *New Journal of Physics* **12** 083040]. Copyright (2010) by Institute of Physics (IOP).

carbon-based structures could offer potential applications for spintronics [121-122], including fullerene[109-110], carbon nanotube [111-112], and hybrid carbon structures [26-27, 77]. In this work, we perform theoretical studies of an epoxy-pair chain on zigzag graphene nanoribbons along the nanoribbon direction, particularly the magnetic properties of some unique graphene oxide structures, providing a family of graphene oxide as excellent candidates for magnetic nanoelectronics.

5.2 Structures of epoxy pairs on the zigzag graphene ribbons

The spin polarized electronic structure of zigzag graphene nanoribbon (ZGNR) with an epoxy-pair chain along the periodic direction is studied. The Monkhorst-Pack $41 \times 1 \times 1$ k -point grid is chosen to sample Brillouin zone (BZ). The unit length along x axis is $2.46 \text{ \AA}$. In accordance with previous report [58], the classification of ZGNRs is defined by the number of zigzag chains ‘ n ’ to form the width, termed as ‘ n -ZGNR’ (see blue numbers in Figure 5.2.1 (a)). The positions for one epoxy pair per unit cell are labeled by blue dashed lines, and classified by the pink numbers ‘ m ’ to describe graphene oxide, finally termed as ‘ n -ZGO- m ’ in this paper (Figure 5.2.1 (b) and (c)). Here, we only discuss ZGOs, which contains even rings per unit cell labeled by green dashed rectangle, obtaining maximum $m = n / 4 - 1$. Thus, when an epoxy pair locates at $m=0$ position, the n -ZGO-0 also has mirror plane (see blue dashed line in Figure 5.2.1 (b)) comparing with n -ZGNR.

Figure 5.2.1. (a) Schematic illustrations of n-ZGNR, (b) n-ZGO-0 and (c) n-ZGO-2 in the top and side view. The orange balls denote hydrogen atoms, passivating the edge of carbon atoms colored in gray. The oxygen atoms are illustrated in red. The green dashed rectangle denotes a single unit cell. Blue numbers 1 to n are denoted as the width of nanoribbons. The pink numbers 0 to m point out the positions for epoxy pairs during our studies.

5.3 Results and discussion

5.3.1 Ordered and random epoxy-group structures

To study the electronic properties of graphene oxide, we need to consider its stability. The total energy of the ordered epoxy-group structured-graphene oxide and several structures

with a random distribution of epoxy groups in graphene are calculated as shown “16-ZGO-random” in Table 5.3.1, revealing that the latter has a higher energy than the former by ~ 1.4 eV/unit cell, indication that the random structure is much less stable than an ordered one. Another structure of graphene oxide with an epoxy group alignment in smaller chains perpendicular to the axis of the nanoribbon is also calculated and is found out to have a higher energy than an ordered structure with the epoxy chain alignment along nanoribbon direction by ~ 1.2 eV/unit cell (see “16-ZGO- $\perp$ ” in Table 5.3.1), and to have less stability than the latter. Thus, in this work we focus our study on the relatively stable structure, the ordered structure with the epoxy chain alignment along nanoribbon direction.

5.3.2 Analysis between n-ZGNR and n-ZGO-0

The width ‘n’ and oxidation position ‘m’ are two main factors in ZGO. The width effect in ‘n-ZGO-0’ type structures is firstly studied. As a comparison, ‘n-ZGNR’ and ‘n-ZGO-0’, both processing mirror symmetries, are examined. With consideration of the spin polarization, the antiferromagnetic (AFM), ferromagnetic (FM) and nonmagnetic (NM) configurations are considered to have the favorable ground states. The energy data of the three configurations are listed in Table 5.3.1. The energy differences of AFM and NM states are compared with corresponding FM states. In Table 5.3.1, both 12-ZGNR and 16-ZGNR are AFM in terms of the reported results [58-59], presenting a strong spin-orbital interaction. However, with the epoxy pairs, n-ZGO-0 devices exhibit FM

states. The energy difference between non-spin-polarized and spin-polarized states is larger than 50 *meV*, and that between ferromagnetic and antiferromagnetic configuration is much smaller, decreasing as the width ‘n’ of graphene oxide increases. The energy differences between FM and AFM states per unit cell are 15.7 *meV*, 7.0 *meV*, 6.6 *meV* and 5.0 *meV*, for 8-ZGO-0, 12-ZGO, 16-ZGO, and 20-ZGO, respectively.

Table 5.3.1. Energy data of a set of n-ZGO-0 and n-ZGNR structures containing NM, FM and AFM states. Each total energy result is listed inside parentheses. The total energy differences of NM and AFM states are compared with corresponding FM ones. The total energy differences of “16-ZGO-random” and “16-ZGO- $\perp$ ” are compared with NM state of 16-ZGO.

Structure	NM (meV/unit cell)	FM (meV/unit cell)	AFM (meV/ unit cell)
8-ZGO-0	53.9 (-3378074.9)	0.0 (-3378128.8)	15.7 (-3378113.1)
12-ZGO-0	51.8 (-4620068.2)	0.0 (-4620120.0)	7.0 (-4620113.0)
16-ZGO-0	57.7 (-5862022.3)	0.0 (-5862080.0)	6.6 (-5862073.4)
20-ZGO-0	60.1 (-7103982.8)	0.0 (-7104042.9)	5.9 (-7104037.0)
16-ZGO-random	1352.8(-5860669.5)	--	--
16-ZGO-$\perp$	1194.0(-5860828.3)	--	--
12-ZGNR	47.4 (-3755969.3)	0.0 (-3756016.7)	-3.2 (-3756019.9)
16-ZGNR	52.2 (-4997919.4)	0.0 (-4997971.6)	-4.0 (-4997975.6)

Geometrical factors often determine the electronic properties. To further study, we compare the differences between 16-ZGNR and 16-ZGO-0 at first and then between

16-ZGO-m structures. The spin-polarized band structures are first considered. Each band line is from Γ (0, 0, 0) to X (π/a , 0, 0), (a is the unit cell length) shown in Figure 5.3.1. Thus, 16-ZGNR is semiconductor and its direct band gap is 140 *meV*. In 16-ZGO-0, the band lines are 104 *meV* and 262 *meV* above Fermi energy level in majority-spin and minority-spin segments respectively, demonstrating metallic property for 16-ZGO-0. In the isosurface of the spin density for 16-ZGNR, it clearly presents that the majority and minority spins appear in two different sublattices as shown in Figure 5.3.1 (a). Thus, a stronger antiferromagnetic coupling exists in 16-ZGNR[58]. Evidently, the magnetic moment of each spin in each sublattice of 16-ZGNR is around 0.44 μ_B , in agreement with the previous work[59]. However, in 16-ZGO-0, with the existence of oxygen atoms, the favorable ground state is ferromagnetic, and moreover, it also shows that the large spin density locates at oxygen atoms as shown in Figure 5.3.1 (b). The oxygen atoms divide ZGO into two parts. Each part could be considered as a ‘new’ zigzag graphene nanoribbon. Opposite spin states occupy different sublattices originated from staggered sublattice potentials [123-124]. Then in each part, the majority and minority spins also appear in two different sublattices. The magnetic moments of majority and minority spins in their corresponding sublattice of each part are 0.60 μ_B and -0.10 μ_B . Each oxygen atom contains a magnetic moment of 0.05 μ_B .

Figure 5.3.1. [Rotate right 90°] (i) Electronic spin-polarized band structures, (ii) projected density of states (DOS) and (iii) top- and side-view spin density plots of (a) 16-ZGNR, (b) 16-ZGO-0, (c) 16-ZGO-1, (d) 16-ZGO-2, and (e) 16-ZGO-3. In band structures, the majority- (up-) spin bands are plotted at right parts with red color, while minority- (down-) spin bands are plotted at left parts with black color.

spin bands are plotted at left parts with black color. The up (or down) pink arrows denotes for up- (or down-) spin bands. In projected DOS structures, the red (black) lines and blue (cyan) lines denote as the majority- (minority-) spin projected DOS of whole devices and oxygen atoms, respectively. The Fermi energy is set to zero. Isosurfaces of spin density ($\pm 0.01 e / \text{\AA}^3$) are denoted by blue (positive) and red (negative) lobes. The positions of epoxy-pair chains are pointed out with red arrows.

5.3.3 Analysis between a set of 16-ZGO-m

In addition, with different epoxy-pair sites, a set of ‘16-ZGO-m’ is investigated. Regardless of 16-ZGO-0, other sites could break such a mirror symmetry shown in Figure 5.2.1 (b). The ferromagnetic states are also favorable for their ground states obtaining from the energy differences between FM, NM and AFM configurations (see Table 5.3.2). Moreover, the energy difference between non-spin-polarized and spin-polarized states is still large, while the energy difference between ferromagnetic and antiferromagnetic configuration is much smaller. The energy differences between FM and AFM states per unit cell are 6.6 *meV*, 8.2 *meV*, 1.7 *meV* and 0.8 *meV* for 16-ZGO-0, 16-ZGO-1, 16-ZGO-2 and 16-ZGO-3, respectively. Comparing the FM energies in 16-ZGO-m devices, 16-ZGO-0 is more stable.

The band lines near Fermi level of the minority-spin part in Figure 5.3.1 (b) move upward as the epoxy-pair sites increase in (c) ~ (e). Meanwhile, from their projected density of states (DOS), the minority-spin peaks near Fermi level have generally shrunk (see black lines in Figure 5.3.1 (b)-(ii) ~ (e)-(ii)) while the contribution of oxygen atoms for

projected DOS (see blue and cyan lines in Figure 5.3.1 (b)-(ii) ~ (e)-(ii)) does not change too much.

Table 5.3.2. Energy data of a set of 16-ZGO-m (m= 0, 1, 2, and 3) and 16-ZGNR structures containing NM, FM and AFM states. Each total energy result is listed inside parentheses. The total energy differences of NM and AFM states are compared with corresponding FM ones. Each total magnetic moment is listed as the value of corresponding favorable ground state.

Structure	NM (meV/unit cell)	FM (meV/unit cell)	AFM (meV/unit cell)
16-ZGO-0	57.7 (-5862022.3)	0.0 (-5862080.0)	6.6 (-5862073.4)
16-ZGO-1	44.5(-5862029.8)	0.0(-5862074.3)	8.2(-5862066.1)
16-ZGO-2	56.3(-5862002.9)	0.0(-5862059.2)	1.7(-5862057.5)
16-ZGO-3	68.4(-5861897.5)	0.0(-5861965.9)	0.8(-5861965.1)
16-ZGNR	52.2 (-4997919.4)	0.0 (-4997971.6)	-4.0 (-4997975.6)

Thus, the different epoxy-pair site changes the spin density distribution of carbon atoms. Since the oxygen atoms divide the graphene nanoribbons into ‘upper’ and ‘bottom’ parts, the magnetic moments of the two parts are clearly not the same unless oxygen atoms locate at the middle. Obviously, the upper part of 16-ZGO-m (except 16-ZGO-0) gains more spin density distributions [see Figure 5.3.1 (c) ~ (e)], while the majority and minority spins appear in two different sublattices of each part as well. To clarify the trend from different epoxy-pair sites, the magnetic moments of majority and minority spins in

two parts are calculated, which can also be observed from the spin density isosurfaces in Figure 5.3.1. In the upper part, the magnetic moment of the majority spin increases while the absolute value of the minority spin decreases as the site of epoxy pair moves upwards. In the other hand, the trend is just different in the bottom part. The oxygen atoms tend to gain more up-spins as their locations are closer to the upper edge.

5.3.4 Analysis from orbitals' hybridization

To consider the different magnetic configurations in '16-ZGNR' and '16-ZGO-m', the magnetism from orbitals' hybridization is analyzed and estimated. First, two $2s$ and two $2p$ electrons in carbon atoms could form different sp -hybridized orbitals[3]. In graphene, four orbitals of each carbon atom are hybridized to form sp^2 bonding, with its typical sp^2 C-C bond length of 1.42 Å. Meanwhile, three σ orbitals placed in the graphene plane with a value of 120° for bond angle, and one unpaired electron are expected in the π orbital, which is along z axis in perpendicular direction. Mostly, the process of breaking of π bonds and producing of new σ bonds result in the transformation of sp^2 hybridization to sp^3 hybridization, which is the mechanism of the magnetic properties in carbon nanostructure. Clearly, a change of bond length and angles exists in the transformation of sp^2 hybridization to sp^3 hybridization. For ideal sp^3 hybridization, the C-C bond length is 1.54 Å. The bond length between α -C (C_α) and β -C (C_β) atoms of graphene oxide in Figure 5.3.2 (c) and (f) is around 1.47 Å, between 1.42 and 1.54 Å. Then, an intermediate character of this hybridization is between sp^2 and sp^3 . However, the net magnetic moment

of C_α is nearly 0.00 in ZGO. Therefore, the hybridization of C_β is sp^2 rather than sp^3 and C_β atom gains a larger net magnetic moment. In the other hand, in zigzag graphene nanoribbon passivated by hydrogen atoms, see Figure 5.3.2 (b) and (e), the bond between C_α and C_β atoms is 1.40 Å, resulting in sp^2 hybridization and a larger net magnetic moment locates on C_α atom.

Figure 5.3.2. (a) Structures of graphene. All bonds in graphene are equivalent, and the double bonds are marked for convenience of comparison with others. Structures of (b) zigzag edges passivated by hydrogen atoms, and (c) oxygen atoms located in the zigzag direction of graphene. Schematic chemical forming: (e) C-H bonds and (f) C-O bonds from (d) graphene. The red and blue balls in (b) and (c) are represented as α -C and β -C atoms.

5.3.5 Discussion between this work and related reported experiments

During formation of graphene oxide in a solution process, $\text{KMnO}_4/\text{H}_2\text{SO}_4$ solution treatment to unzip carbon nanotube is reported by Kosynkin *et al* [62] recently. A very newly published paper experimentally reveals paramagnetism in this kind of oxidized graphene nanoribbons [36], which is close to our proposed structure, thus well supporting our calculations. Antiferromagnetism of one type of graphene oxide has been reported [51]. Since it has a structure different from our studied one, it is understandable for their different properties exhibited.

To experimentally realize the proposed structure in this work is also important. In discussion, we choose 16-ZGO mainly with a width of ~ 3.5 nm, which size can be experimentally realized in graphene. Moreover, the selectivity of the epoxy-pair chain position has many choices, since all ZGO discussed here have ferromagnetic properties. Once the epoxy chain exists, it is easy to form an epoxy pair or add a new epoxy group to extend the chain on graphene with an energy of 0.1 eV [67].

5.4 Conclusions

In conclusion, spin-polarized first-principle calculations of proposed graphene oxide structures have been conducted. A series of structures with the epoxy-pair chain at various positions on zigzag graphene nanoribbons are considered. This kind graphene oxide is ferromagnetic at ground state, providing great promise in the field of spintronics.

Moreover, with a comparison of the same width of ZGNR, ZGO is metallic. The spin density distribution can be modified with different sites of epoxy pairs. These discoveries can also render some fundamental insights of graphene materials.

Chapter 6 Negative Differential Resistance in Oxidized Zigzag Graphene Nanoribbons³

6.1 Introduction

Graphene's novel electronic properties[57], sheet-like, optical transparent and conductive have great potential applications for nanoelectronics, flexible photonics and electrodes. Since graphene is gapless, its modifications can form unique structures to possess various specific electronic properties. Based on the first principle studies of graphene oxide in the last chapter, the structures of an epoxy-pair chain on zigzag graphene nanoribbons (ZGO) could be ferromagnetic as ground states. Then, in this chapter, the transport property is mainly discussed. The results indicate that this kind of graphene oxide can have a negative differential resistance (NDR) phenomenon, thus providing great promise in nanoelectronics.

It is noted that a model of zigzag graphene nanoribbon (ZGNR) exhibits semiconductor nature[58], while the ZGO is metallic[116]. Since ZGNR is an antiferromagnetic semiconductors[58], it cannot be used as an electrode directly[83-84]. However, in terms of our calculation, ZGOs are metallic[116], which can function as an “electrode” for itself. Such a connection is reported in metallic

³ Reprinted with permission from the reference [Wang M and Li C M 2011 *Phys. Chem. Chem. Phys.* **13** 1413]. Copyright (2011) by The Royal Society of Chemistry.

armchair graphene nanoribbons[125]. Thus, the system in this work could potentially provide a kind of useful junctions. Moreover, due to its ferromagnetic and NDR properties, ZGO systems can be used as promising spin-valve devices with magnetoresistance as well. Very recently, one interesting work on the graphitic memory switch was reported by Tour *et al* [126], in which devices were treated by UV-ozone to remove useless carbon from several graphite layers. Based on our results, we doubt that graphene oxide structures exist in their experimental device and negative differential resistance phenomena may give some contributions for the memory switch. The related experimental result could be an evidence of this kind of GO for NDR's nanoelectronics applications.

6.2 The structures for electron transport studies

We first consider the electronic properties of a zigzag graphene nanoribbon (ZGNR) with an epoxy-pair chain, termed as 'n-ZGO-m' to represent the width 'n' of zigzag nanoribbon (Figure 6.2.1 (a)) and epoxy-pair position 'm' (Figure 6.2.1 (a)-(c)). ZGOs, which are discussed here, contain even rings per unit cell labelled by green dashed rectangle, obtaining maximum $m = n / 4 - 1$. With spin-polarization calculations of a series of ZGOs structures, n-ZGOs (n=8,12,16,20) are ferromagnetic[116] as their ground states. Moreover, the experimental investigation on GO's magnetism has reported very recently[36, 119]. ZGOs also process metallic properties from their band structures.

Figure 6.2.1. Schematic illustrations of (a) n-ZGNR, (b) n-ZGO-0 and (c) n-ZGO-2 in the top- and side- view. The green dashed rectangle is presented as one unit cell. Blue numbers 1 to n are denoted as the width of zigzag nanoribbons. The pink numbers 0 to m point out the positions for epoxy pairs. Schematic plots of (d) 16-ZGO-0 and (e) 16-ZGO-2 devices for electron transports in top view. Blue, pink and green parts are denoted as left electrode, scattering region and right electrode, respectively. Left and right

electrodes are applied with the voltages of $V/2$ and $-V/2$, respectively. Hydrogen, carbon and oxygen atoms are colored in orange, gray and red, respectively.

Figure 6.2.2. (i) Electronic spin-polarized band structures, (ii) projected density of states (DOS) and (iii) top- and side-view spin density plots of (a) 16-ZGO-0 and (b) 16-ZGO-2. The majority- (up-) spin bands are plotted at right parts with red color, while the minority- (down-) spin bands are plotted at left parts with black color. The up (or down) pink arrows denotes for up- (or down-) spin bands. Each band line is from Γ (0, 0, 0) to X (π/a , 0, 0) (a is the unit cell length). In projected DOS structures, the red (black) lines and blue (cyan) lines denote as the majority- (minority-) spin projected DOS of whole devices and oxygen atoms, respectively. The Fermi energy is set to zero. Isosurfaces of spin

densities ($\pm 0.01 \text{ e } / \text{\AA}^3$) are denoted by blue (positive) and red (negative) lobes. The positions of epoxy-pair chains are pointed out with red arrows.

Thus, we mainly choose 16-ZGO-0 and 16-ZGO-2 structures (Figure 6.2.1 (b) and (c)) for our following transport discussions. The metallic property is evidently by density of states (DOS) as well (see Figure 6.2.2 (a)-(ii) and (b)-(ii)). Thus, to consider the electron transport in ZGO devices, the same ZGO structure can be used in three parts: left electrode (blue), scattering part (pink), and right electrode (green), schematically illustrated in Figure 6.2.1 (d) and (e). Left and right electrodes are applied with the voltages of $V/2$ and $-V/2$, respectively. The electronic transport properties are studied by non-equilibrium Green's functions (NEGF) with using TRANSIESTA package[103].

6.3 Results and Discussion

6.3.1 I - V characteristics

The spin currents with different orientations are obtained in 16-ZGO-0 and 16-ZGO-2 devices as shown in Figure 6.3.1 (a) and (b), respectively, exhibiting robust negative differential resistance (NDR) phenomena, in which current decreases with the increase of voltage. In 16-ZGO-0 device, the peak and valley currents for majority spins are $9.14 \mu\text{A}$ at 0.2 V bias voltage and $3.71 \mu\text{A}$ at $V_b = 0.9 \text{ V}$, while those for minority spins are $24.16 \mu\text{A}$ at $V_b = 0.4 \text{ V}$ and $12.47 \mu\text{A}$ at $V_b = 0.9 \text{ V}$, respectively. In 16-ZGO-2, the peak and valley

currents of majority spins are $8.27 \mu\text{A}$ with a bias of 0.2 V and $4.06 \mu\text{A}$ at $V_b = 0.6 \text{ V}$, and those of minority spins are $24.74 \mu\text{A}$ at $V_b = 0.4 \text{ V}$ and $16.35 \mu\text{A}$ at $V_b = 0.7 \text{ V}$, respectively. In a comparison with other widths of ZGOs, the I - V characteristic of 8-ZGO-0 system is also plotted in Figure 6.3.1 (c). The NDR phenomena could be observed as well. The peak and valley currents for majority spins are $6.89 \mu\text{A}$ at 0.2 V bias voltage and $2.17 \mu\text{A}$ at $V_b = 0.8 \text{ V}$, while those for minority spins are $25.59 \mu\text{A}$ at $V_b = 0.4 \text{ V}$ and $7.35 \mu\text{A}$ at $V_b = 0.8 \text{ V}$, respectively.

Figure 6.3.1. I - V characteristics of (a) 16-ZGO-0 (ring), (b) 16-ZGO-2 (square), and (c) 8-ZGO-0 (triangle) NDR devices. The red and black symbols are denoted as majority-

(up-) spin and minority- (down-) spin I - V characteristics, respectively.

6.3.2 Bias dependent transmission curves

To clarify the NDR mechanism, in Figure 6.3.2, the bias dependent transmission curves ($T(E, V_b)$) are presented for these two systems at first. Since the ZGO system is metallic, the peak of $T(E, V_b)$ around Fermi level is contributed from both HOMO and LUMO. The left shift of the transmission peaks corresponding to the HOMO level, E_{HOMO} , with a shift along μ_L could be observed with increase of the bias voltage. Thus, the carrier hopping between the left electrode and the scattering region is good for transport. However, the peaks of E_{LUMO} appear on the right of μ_R at first, and then touch the right chemical potential μ_R , and finally appear on the left of μ_R (more clearly in Figure 6.3.2 (c) and (d)). Thus, the hopping becomes difficult due to the large gap between LUMO and μ_R . Consequently, the critical bias for the peak and μ_R to touch together is near the voltage of the peak current in Figure 6.3.1. In the right edge of the bias-dependent transmission, corresponding to the LUMO level, E_{LUMO} shift right (see Figure 6.3.2 (c) and (d)), and after certain bias, the transmission peaks, corresponding to the LUMO+1 level, E_{LUMO+1} , appear and have a left shift (also see the analysis below in Figure 6.3.3). When the peaks of E_{LUMO+1} touch or move close to the right chemical potential, the carrier hopping becomes good again and the systems end NDR phenomena and the currents begin to increase from their valley values in Figure 6.3.1. Thus, the current is suppressed by LUMO resulting in NDR and finally the increase of current after NDR comes from LUMO+1's contribution.

Figure 6.3.2. Bias dependent transmission curves of (a) majority-, (b) minority- spin in 16-ZGO-0 device and (c) majority-, (d) minority- spin in 16-ZGO-2 device. In each section, eleven different color curves are presented from bias 0.0 V to 1.0 V with an

increment of 0.1 V. The balls point out the position of left and right chemical potentials (μ_L and μ_R respectively). The red words A-1 to D-1, and A-2 to D-2 in (a) ~ (d) are marked with red arrows to point out the critical positions for NDR's occurrences and terminations.

In Figure 6.3.2, the critical positions for right chemical potential for NDR's occurrences and terminations are marked as A-1 ($V_b = 0.2$ V) and A-2 ($V_b = 1.0$ V) for majority spin in 16-ZGO-0, B-1 ($V_b = 0.3$ V) and B-2 ($V_b = 1.0$ V) for minority spin in 16-ZGO-0, C-1 ($V_b = 0.2$ V) and C-2 ($V_b = 0.7$ V) for up-spin in 16-ZGO-2, and D-1 ($V_b = 0.4$ V) and D-2 ($V_b = 0.7$ V) for down-spin in 16-ZGO-2, respectively. These bias voltages are quite close to the peak and valley values in Figure 6.3.1. Thus, the analysis of bias-dependent transmissions with consideration of different spin orientations lead to NDR features of I - V characteristics.

6.3.3 Schematic model for NDR mechanism

To further elucidate the NDR mechanism and the occurrence of $T(E, V_b)$, a schematic model of DOS under different bias voltages is illustrated in Figure 6.3.3 (b) - (d). The pink and blue rectangles represent the conduction and valence bands of two electrodes respectively. Two red lines between them indicate the positions of the HOMO and LUMO for the scattering region. For simplification, here we just consider the majority spin part in 16-ZGO-0 system. Since we choose the same materials for electrodes and scattering

regions, under zero bias voltage, the density of states (DOS) of these three parts are the same as shown in Figure 6.3.3 (a). The marked labels peak A, B and C with black arrows indicate the HOMO, LUMO and LUMO+1 in 16-ZGO-0 structures. The rectangles represented as DOS of electrodes shift up and down at applied bias voltages for left and right electrodes, respectively. For further simplification, we assume that the positions of HOMO and LUMO in scattering region do not obviously change with applied bias voltages. With zero bias voltage, the HOMO and LUMO of the scattering region match the valence and conduction bands of two electrodes (see Figure 6.3.3 (b)), resulting in high and large transmission peaks located at Fermi level as shown in Figure 6.3.2 (a). With a voltage of 0.2 V applied, an up-/down- shift of 0.1 V appears in DOS for left/right electrodes. Thus, the LUMO of the scattering region just catches the upper edge of conduction band of the right electrode (Figure 6.3.3 (c)), corresponding with A-1 in Figure 6.3.2 (a). Both hole and electron hoppings occur at this moment. Since there is an energy gap between LUMO (peak B) and LUMO+1 (peak C) in 16-ZGO-0, the right electrode also has an energy gap between the conduction and the second conduction bands. Thus, even with an increased bias voltage, the current cannot increase with no overlap between the conduction band of the right electrode and the LUMO of the scattering region, leading to negligible transmission coefficients above Fermi level (see the region between A-1 to A-2 in Figure 6.3.2 (a)). Thus at a bias of 1.0 V, the shift of the right electrode's DOS causes the overlap between the second conduction band (or peak C) and the LUMO of the scattering region to produce a transmission peak (A-2) and an increased current again. This analysis is in agreement with 16-ZGO-2 due to the shifts of conduction bands of right electrodes to generate NDR with non-zero bias voltages. Since

in DOS the energy gaps between LUMO and LUMO+1 are different in these two ZGO systems (refer to Figure 6.2.2. (a)-(ii) and (b)-(ii)), the bias voltages of peak current and valley current of 16-ZGO-2 system are larger and smaller than those of 16-ZGO-0, respectively. Moreover, the peak current is possibly dependent on the width and the position of epoxy pair in the calculated system (see Figure 6.3.1 (a) - (c)), and the peak-to-valley ratio of our suggested ZGO system could also be modified, which broadens the potential applications of NDR. In discussions, it is naturally considered if there is an energy gap between HOMO and HOMO-1, by which when the DOS of the left electrode shifts up with non-zero bias voltage, this kind of NDR could appear as well. It is reported by Ren *et al*[83] that a NDR device has also been obtained by such a gap formation between HOMO and HOMO-1 through doping the electrode parts differently.

Figure 6.3.3. (a) Majority-spin density of states (DOS) in 16-ZGO-0 device. The Fermi energy is set to zero. (b)-(d) Schematic illustration for NDR mechanism. The pink and blue rectangles represent the DOS of two electrodes, and two red lines in between indicate the positions of the HOMO and LUMO for scattering region with the bias voltages of 0.0, 0.2 and 1.0 V, respectively.

6.4 Conclusions

In summary, the calculated spin currents in ZGOs have negative differential resistance phenomena (NDR), supported by bias dependent transmission curves of different orientation spins. Non-zero bias voltages make the density of states (DOS) of the right electrodes shifting down. Because of an energy gap between LUMO and LUMO+1 in ZGOs, with a certain bias, the conduction band of the right electrode cannot match the LUMO of the scattering region, then NDR occurs. With a larger bias, NDR ends when the second conduction band of the right electrode covers the LUMO of the scattering region. The NDR can be widely observed in ZGO devices since most of the ZGO systems possess such an energy gap between LUMO and LUMO+1. This discovery may provide great potential applications in NDR-based nanoelectronics using modified graphene materials.

Chapter 7 Magnetic properties of all-carbon graphene-fullerene nanobuds⁴

7.1 Introduction

A worldwide intensive endeavor is inspired to develop alternative devices including materials and technologies to conquer the Moore's limit on silicon device. One approach is to explore novel nanomaterials such as nanoscale carbons. The known low-dimensional carbon nanostructures including fullerene, CNT and graphene, possessing with sp^2 hybridized carbon atoms, have played critical roles in the nanoscience and nanoengineering.

In the carbon family, though the existence of strong covalence inhibits unpaired spins, various mechanisms of ordered magnetic states have been proposed to explore new materials. Various factors including vacancies [127-128], adatoms [129], terminal groups at the edges [31], and negative Gaussian curvature[130], are generally considered to affect the magnetism in carbon structures. Some experimentally observed magnetism[131-132] in carbon materials can partly support the proposed mechanism; however, the fundamental mechanisms of magnetism is still not very clear. In addition, different approaches are used to access various nanostructures of carbons for potential applications. One method is to hybridize two or more materials

⁴ Reprinted with permission from the reference [Wang M and Li C M 2011 *Phys. Chem. Chem. Phys.* **13** 5945]. Copyright (2011) by The Royal Society of Chemistry.

together. Such a hybrid carbon structure has widely potential applications due to its unique features such as optical transparent, flexible, high current density, and its experimental accessibility as well. In recent years, one interesting type of hybrid carbon nanostructures called nanobud, is reported by Nasibulin *et al* [28], who synthesize the fullerenes on the outer surface of single-walled carbon nanotubes (SWCNT). Up to date, various possible nanobuds [71-73], mainly consisting with CNTs and fullerenes, have been investigated in nonmagnetic (NM) [74-76] and magnetic electronic properties [77]. Considering excellent versatile applications of both graphene [57] and fullerene [133], the use of graphenes instead of CNTs to form nanobuds with fullerene [78] also seems possible to exhibit a carbon magnetic nanostructures. In this paper, we investigate this kind of nanobuds for all-carbon structures by density functional theory, which is the most popular and reliable method to theoretically study physical and chemical properties of the materials for good agreement with experimental results [99-100, 134-135].

7.2 Models of nanobuds

In this work, four kinds of nanobuds are studied, and named as Case A, B, C and D, of which the geometrical structures are presented in Figure 7.2.1. Normal fullerene C_{60} misses a six ring to establish C_{54} structure (see Figure 7.2.1(d)), which associates with graphene to produce the nanobud. In this work, four kinds of connection positions in graphene are selected for discussion.

Figure 7.2.1. Geometric structures of four nanobuds. (a) and (c) The associated carbon atoms in pink are the connected location in Case A and B. The green atoms are expected as the host of unpaired spin. (b) The blue and green carbon atoms are the associated positions in Case C and D, respectively. (c) Three of the pink atoms are

labeled as **u**, **v** and **w** for the topological connection of Case A and B. (d) The structure of C₅₄. Two green atoms labeled as **p** and **q**. Atoms (**u,v**) and (**v,w**) connect with (**p,q**) to form Case A and B, respectively. (e)-(h) Geometric structures in the top and side view in Case A-D respectively. C₅₄, graphene and the associated carbon atoms are colored in olive, cyan and pink, respectively. The top view of (e) and (f) nanobuds display the location of mirror planes illustrated as blue line, which can also be observed from different rotations of three yellow bonds.

In Case A and B, the six carbon atoms of graphene shown as pink color in Figure 7.2.1 (a) and (c) form covalent bonds with the fullerene. These atoms in graphene are converted from sp^2 character into sp^3 when forming the nanobud. The unpaired spins are expected to appear in the nearby atoms colored as green in Figure 7.2.1 (a) and (c). To illustrate these two associations, we label two atoms in C₅₄ as **p** and **q** in Figure 7.2.1 (d), and the carbon atoms in graphene are labeled as **u**, **v** and **w** in Figure 7.2.1 (c). The (**p**, **q**) atoms are connected with (**u**, **v**) in Case A and with (**v**, **w**) to form Case B, shown in Figure 7.2.1 (e) and (f), respectively. In Case C and D, the associated carbon atoms of the graphene are colored as blue and green, respectively (Figure 7.2.1 (b)). The geometric symmetry has no difference whether atoms (**p**, **q**) connect with atoms (**u**, **v**) or (**v**, **w**) because of equivalence. Though the graphenes in these two cases (Figure 7.2.1(g) and (h)) apply the same point group symmetries with the former two cases, the electric properties could be quite different.

From geometric perspective, the top- and side-view structures of four cases are shown in Figure 7.2.1 (e)-(h). C_{54} , graphene and the associated carbon atoms are colored in olive, cyan and pink, respectively. To illustrate the geometric differences between Case A and B, the blue lines denoted as mirror planes in the side view display the same mirror planes' locations in the top-view plotted in Figure 7.2.1 (e) and (f). In Case A, when (**p,q**) atoms bond to (**u,v**), nine- and six-membered rings form between the connection parts (termed as 9-6 [77]), while in Case B, eight- and seven-member rings (termed as 8-7 [77]) appear with the binding between (**p, q**) and (**v, w**), shown in Figure 7.2.2 (a) and (b). This kind of symmetry can also be observed by different orientations of three yellow-colored bonds in the center of the figures.

In Case C, the associated six atoms in graphene are lifted up for more favorable connection with C_{54} structure through the side view in Figure 7.2.1 (g). Besides the size of hexagon ring is nearly the same as that of C_{54} in the top view. In Case D, the associated six atoms locate much further than those of Case C; from the top view these atoms cannot be seen due to nearly completely coverage by C_{54} . The nanobuds are analyzed by density functional theory (DFT) calculations. Each nanobud consists of a 49-unit-cell graphene and a C_{54} fullerene ball structure, and the Monkhorst-Pack $11 \times 11 \times 1$ k-point grid is chosen to sample Brillouin zone (BZ). The unit lengths of nanobuds along two periodic directions (x and y axes) are 17.22 Å.

Figure 7.2.2. Geometric structures of (a) Case A and (b) Case B. The green colored atoms of fullerene, pink associated atoms and cyan atoms of graphene exhibit (a) six- and nine-membered rings for Case A; and (b) seven- and eight- membered rings for Case B.

7.3 Results and Discussion

7.3.1 Energy analysis

The energy data of nonmagnetic (NM), antiferromagnetic (AFM), ferromagnetic (FM) states and the related formation reactions are listed in Table 7.3.1. The energy differences of AFM and FM states are compared with corresponding NM ones. From the table, it is important to figure out that the ground states in Case A and B are ferromagnetic, while those of Case C and D are nonmagnetic. To assume the fusion of graphene and C_{54} into a nanobud, the binding energy E_b is studied and defined as

$E_{\text{nanobuds}} - E_{\text{C54}} - E_{\text{graphene}}$, where E_{nanobuds} , E_{C54} , and E_{graphene} are the energies of nanobuds, C₅₄, and graphene, respectively. The energy of C₅₄ is defined as $E_{\text{C54}} = 54 \times E_{\text{C60}} / 60$. The positive binding energy means that the reaction is endothermic. Case D is more stable, since it requires the least binding energy.

Table 7.3.1. The energy data of four kinds of nanobuds : NM, AFM, FM and the related formation reactions. The binding energy E_b is defined as $E_{\text{nanobuds}} - E_{\text{C54}} - E_{\text{graphene}}$, where E_{nanobuds} , E_{C54} , and E_{graphene} are the energies of nanobud, C₅₄, and graphene, respectively. The energy differences of AFM and FM states are compared with corresponding NM ones.

Case	E_{NM} (meV/per atom)	E_{AFM} (meV/ per atom)	E_{FM} (meV/per atom)	E_b (meV /per atom)
A	0.0 (-154969.8)	-2.2 (-154972.0)	-4.0 (-154973.8)	57.0
B	0.0 (-154974.1)	-0.6 (-154974.7)	-2.5 (-154976.6)	54.1
C	0.0 (-154997.1)	0.7 (-154996.4)	0.7 (-154996.4)	33.7
D	0.0 (-155003.5)	0.3 (-155003.2)	0.3 (-155003.2)	27.3

7.3.2 Spin-polarized band structures

Geometrical factors are determinant to study the properties of nanobuds. To study these, we first consider the band structures of the four cases. Each band line is from K ($2\pi/3a, 2\pi/3a, 0$) (a is the unit length), to X ($0, \pi/a, 0.0000$), to Γ ($0, 0, 0$), and last to

K. In Case A and B, the associated atoms in graphene are the same, but due to different connections with atoms of C_{54} , the spin-polarized band structures in Case A is semiconducting as illustrated in Figure 7.3.1 (a), while that in Case B is semimetallic as shown in Figure 7.3.1 (b). Here we mainly focus on the bands near Fermi level (E_F). In Case A, the highest occupied up-spin band is totally below Fermi level, gradually from 98 meV below E_F at K point to 27 meV below E_F at Γ point. The lowest unoccupied down-spin band locates above Fermi level, with 79 meV above E_F at K point and 38 meV above E_F at Γ point. In Case B, the lowest unoccupied up-spin band locates gradually from 120 meV below Fermi level at K point to 11 meV above E_F at Γ point. Most of the highest occupied up-spin band is below Fermi level, and only some partition around Γ point is above E_F . While most of the highest occupied down-spin band is above Fermi level, only some parts around K point is 22 meV below E_F . In both Case A and B, the flatbands around 0.5 eV above E_F in both majority and minority parts are contributed from fullerene (see Figure 7.3.2 (a) and (b)), which are in agreement with results reported by Su *et al* [77]. In Case C and D, the non-polarized band structures are plotted in Figure 7.3.1 (c) and (d), respectively. Two bands meet on the Fermi level at K points in both cases, and thus both nanobuds are semimetallic [78]. Due to symmetry, Case C and D have the conic Dirac points even with the chemical attachment of C_{54} . Similar phenomena have also been reported by Zeng *et al* [78]. The formations of nanobuds provide additional states of fullerene (see Figure 7.3.2 (c) and (d)) into pure graphene's band structures and also possibilities for doping other functional groups on nanobuds.

Figure 7.3.1. Electronic spin-polarized band structures in (a) Case A and (b) Case B, and non spin-polarized band structures in (c) Case C and (d) Case D. The majority- (up-) spin bands are plotted at right parts with red color, while the minority- (down-) spin bands are plotted at left parts with black color. The Fermi energy is set to zero. The up (or down) olive arrows denotes for up- (or down-) spin bands. The up-spin band structures in Case A and B are also presented to illustrate details near the Fermi surface.

To further describe the contribution of each component in the nanobud, the projected densities of states (DOS) of fullerene (C_{54}), graphene, and nanobud are plotted in Figure 7.3.2 (a)-(d) for the four cases respectively. It clearly illustrates that around Fermi level, the graphene contributes to DOS more than fullerene in Case A and B, while fullerene contributes more in Case C and D. The flat bands in the band structure are denoted as the contribution of fullerene, evidently supported by a large project DOS of fullerene at the same energy level.

Figure 7.3.2. (a) - (d) projected DOS for Case A - D, respectively. For Case A and B, the pink, blue, cyan, red and olive lines in (a) and (b) denote the projected DOS of atoms C2-C4-C5, atoms C1-C3-C6, C_{54} fullerene structures, nanobuds and graphenes,

respectively. In (c) and (d), the projected DOS of C_{54} fullerene structures, nanobuds and graphenes are presented as blue, red, and cyan lines, respectively for Case C and D.

7.3.3 Orbitals' hybridization analysis

To consider the net magnetic moment in each case, the orbitals' hybridization can be used to generally analyze and estimate the results. Carbon atoms, consisting of two $2s$ and two $2p$ electrons, could form different sp -hybridized orbitals [3]. In graphene, sp^2 bonding is hybridized in each carbon atom. Carbon atoms in graphene process three σ orbitals placed in the graphene plane and one unpaired electron in the π orbital along z axis in perpendicular direction. The process of the breaking of π bonds and the producing of new σ bonds thus results in a transformation of sp^2 hybridization in graphene to sp^3 hybridization in nanobuds, which is the mechanism of the magnetic properties in hybrid carbon nanostructures. In graphene, two sublattices are equivalent, labeled as two different color balls in Figure 7.3.3 (a). When one carbon atom of graphene binds with the atom of fullerene shown in Figure 7.3.3 (b), in one hexagonal ring, there are three positions to form a second bond. In Figure 7.3.3 (c), when two bonds are formed from the nearest carbon atoms of graphene, the former double bond between two nearest carbon atoms transforms into single one. Two unpaired electrons participate in formation of covalent bonds with the atoms of fullerene. In the case of a second binding with the furthest atom as shown in Figure 7.3.3 (e), a similar situation can be seen: two unpaired electrons form a double bond. In Figure 7.3.3 (d), this situation is quite different. A second bond is formed from the

next-nearest carbon atom of graphene, producing two unpaired electrons, which possess strong ferromagnetic coupling [33]. The magnetic moment of $1 \mu_B$ could be obtained from each bond formation.

Figure 7.3.3. (a) Cyan and green circles show two sublattices in graphene, respectively. All bonds in graphene are equivalent. Schematic chemical bonds in blue for association of graphene and fullerene: (b) one bond formed and left one unpaired electron colored as a small pink circle, (c) two chemical bonds formed from two nearest carbon atoms, (d) two chemical bonds forming from two next-nearest atoms of the same sublattice, left two unpaired electrons, and (e) two chemical bonds binding two furthest atoms of different sublattice separately, and left two unpaired electrons, which form a double bond.

7.3.4 Spin densities and bond lengths in nanobuds

Based on such analysis for the formations of chemical bonds, it could be easy to estimate the net magnetic moment for the four kinds of nanobuds. Comparing with

connections, in Case C and Case D the associated bonds as shown in Figure 7.3.3 (c) and (e) produce no unpaired electron, resulting in non-magnetic states. However, in Case A and B, the associated bonds coming from the next-nearest atoms, which provide strong ferromagnetic coupling, result in the approximate net magnetic moment of $6 \mu_B$, which could also be obtained from spin-polarized band structures exhibited in Figure 7.3.1 (a) and (b) evidently. With the integration in BZ, indeed, the nanobuds of Case A and Case B are found to have the magnetic moments of $5.76 \mu_B$ and $5.55 \mu_B$, respectively. The spin densities of two cases are plotted in Figure 7.3.4. The isosurface of the spin density is chosen as $0.2 e / \text{\AA}^3$. The locations of unpaired spins on the graphenes, labeled as red lobes in Figure 7.3.4, are in agreement with the above analysis in Figure 7.3.3 (d).

Moreover, since in Case B the highest occupied minority-spin band bends below E_F near K point, the total magnetic moment is a little smaller than that in Case A. In Figure 7.3.4 (a) and (b), the spin density evidently exhibit that three atoms in the middle of the graphene [atom C-2, C-4 and C-5 labeled in Figure 7.2.1 (c)] resulting in more unpaired spins than others, while atom C-1, C-3 and C-6 gain fewer magnetic moments due to π - σ hybridization effect of the six nearby atoms[136]. The projected DOS of atoms C2-C4-C5 and atoms C1-C3-C6 in Figure 7.3.2 (a) and (b) also present the same phenomenon. The formation of the chemical bond can be also explained by examining the relevant bond lengths for the carbon atoms involved (see Figure 7.3.5). Obviously, each green carbon atom labeled as C1-C6 in Figure 7.2.1 (c) has two sp^3 bonds and one sp^2 bond, which gains nearly one unpaired electron in agreement with

the analysis in Figure 7.3.3(d). The pink carbon atoms (see Figure 7.2.1) are denoted as associated positions with C_{54} . The measured bond lengths for each pink atoms show that they are all sp^3 bonding (see Figure 7.3.5) and have no unpaired electrons. Therefore, the unpaired spin are localized on green colored atoms in Case A and B, while Case C and D are nonmagnetic. In a word, the different binding positions demonstrate whether the magnetism could be generated.

Figure 7.3.4. Isosurfaces of (a) [or (b)] spin density ($0.2 e / \text{\AA}^3$) for Case A [or Case B] denoted by red lobes. In (a) and (b), the C_{54} structures are shown in olive.

Figure 7.3.5. The bond lengths (Å) in Case A-D are marked in (a)-(d), respectively. The pink carbon atoms are denoted as associated positions. The green carbon atoms in (a) and (b) are presented the spin positions.

7.3.5 Comparing CNT-based with graphene-based nanobuds

To deeply discuss the mechanism of nanobuds, it is necessary to discuss other factors such as negative Gaussian curvature[137-138] and charity effects comparing the results of our cases with CNT-fullerene nanobuds[77]. We examnin the total magnetic moment by VASP package [139-140] with a value of $6 \mu_B$ [141] in two magnetic

graphene-based nanobuds, while $5.95 \mu_B$ of 9-6 (10,10), $5.27 \mu_B$ of 9-6 (8,8), $6 \mu_B$ for 8-7 (10,10) and $4 \mu_B$ for 8-7 (17,0) CNT nanobuds[77].

9-6 or 8-7 connection in (10,10) CNT nanobuds has almost the same magnetic moments, as well as that in graphene nanobuds (9-6/8-7 connection in Case A/B). It is obvious that the different effect of 9-6 or 8-7 connection is very small and it is the least factor to affect the magnetic moments of nanobuds.

In different diameter CNTs nanobuds, negative Gaussian curvature could affect[77]. The smaller diameter of CNT with the larger curvature causes a larger angle of two adjacent π bonds. Then, a strong spin coupling strength happens, resulting in a smaller magnetic moment. The angles in 9-6 (10,10) and 9-6 (8,8) CNT nanobuds are 13.9° and 24.2° respectively[77]. Therefore, the magnetic moment of 9-6 (10,10) nanobuds is about $0.23 \mu_B$ larger than 9-6 (8,8) CNT nanobud[77]. The curvature of flat graphene could be estimated as 0. The angle between two π bonds of Case A and B is smaller than 14° , correspondingly, leading to a much smaller exchange coupling and resulting in a value of $\sim 6 \mu_B$ for these two graphene-based nanobuds. We also observe that (10,10) CNT nanobud has nearly the same angle as that in Case A and B, thus in large diameters of CNTs or graphene, the negative Gaussian curvature does not significantly affect the magnetic moments. Meanwhile, we notice that the angle in Case C is around 40° due to the lift of the associated six atoms, and that in Case D is smaller than 2° since new bonds are almost perpendicular to graphene. Thus, this effect could not affect nonmagnetic structures.

Another difference between graphene- and CNT-based nanobuds is the charity effect. The 8-7 (17,0) CNT nanobud can only possess a value of $4 \mu_B$ magnetic moment comparing with $6 \mu_B$ in 8-7 (10,10) structure[77]. Since no charity exists in graphene, both Case A and B can result in magnetic moments of nearly $6 \mu_B$. So charity is somehow more important in CNT-based nanobuds.

It is worthy of a note that Zhu et al[77] has proposed magnetism in CNT nanobuds but not reported relation with the bonding positions of carbons in the nanobuds. This work reveals that the effect order of various configuration parameters on the magnetism is binding positions (see Figure 7.3.3) > charity effect > negative Gaussian curvature > 8-7 or 9-6 connection. In particular, only the binding position has effect on the magnetism of graphene nanobuds. Contradictorily, the first three factors can influence the magnetic moments of the CNT nanobuds in terms of our studies. It is also found by us that the graphene nanobuds can generally produce stronger magnetism. Apparently, it is more applicable to have graphene-based nanobuds' spintronics to get rid of these effects.

7.4 Conclusion

In summary, the magnetic properties of proposed all-carbon graphene-fullerene nanobuds have been investigated. Case A and B are ferromagnetic at their ground states, while Case C and D are nonmagnetic. The analysis of the positions of new chemical bonds reveals that the connections of two atoms in different sublattices of graphene cannot generate

unpaired spins, thus resulting in non-magnetic states in Case C and D. Case A and B possess nearly magnetic moments of $6 \mu_B$, originating from unpaired spins, due to the chemical bond formation from two next-nearest atoms in graphene. Comparing with CNT-fullerene nanobuds, graphene-based nanobuds have no chirality and few negative Gaussian curvature effects, consequently obtaining nearly $6 \mu_B$, while (17, 0) CNT-based nanobud only possesses $4 \mu_B$. The spin densities of nanobuds (Case A and B) mainly locate around the connection region of graphene and fullerene. Due to these detailed electronic analysis, this kind of nanobuds hold good promise in the field of spintronics. The controllable experimental process is needed to achieve with desired geometries for future applications. It is worthy of a note that the graphene nanostructures discussed above are feasible to synthesize experimentally but it has not been done up to date and needs further efforts.

Chapter 8 General Conclusion and Outlook

8.1 General conclusion

Due to current limitations of engineering and technology, new materials and devices at nanoscale are required to meet these new needs. Recently, it has been found that carbon materials possess unique optical, electronic, mechanical and dynamic properties. In particular, a very new allotrope of carbon - graphene - first reported in 2004 and awarded the 2010 Nobel Prize in Physics, has attracted extensive experimental and theoretical interests. However, the originations and determined factors of recently reported experimental results are still not clear. Theoretical investigations can help researchers to understand and predict new properties and designs for future applications.

Based on the unclear structures of the reported magnetic phenomenon of oxidized graphene experimentally, three oxidized graphene structures with hydroxyl groups have been investigated through spin-polarized density functional theory. The results reveal that only in a graphene hexagonal ring structure chemical bond formation by two non-neighbored hydroxyl-bonded carbon atoms but with one carbon atom between can cause unpaired spins to produce a magnetic moment of $1.2 \mu_B$. This work provides fundamentals to controllably synthesize and/or oxidized graphene with hydroxyl groups at specific carbon positions for magnetic properties. The magnetic oxidized graphenes have great promise for new spintronics.

During fabrications and modifications of graphene, epoxy groups always functionalize graphene. A series of structures with an epoxy-pair chain at various positions on zigzag graphene nanoribbons are considered. The results show that this kind of graphene oxide is ferromagnetic at ground state, providing great promise in the field of spintronics. In comparison to zigzag graphene nanoribbons of the same width, this graphene oxide is metallic and its spin density distribution is modified by epoxy pairs at different locations, rendering some fundamental insights into graphene-based materials.

Moreover, a theoretical study of electronic transport property in the structure of an epoxy-pair chain on zigzag graphene nanoribbons is performed. The results indicate that this graphene oxide can have a negative differential resistance (NDR) phenomenon, supported by bias dependent transmission curves of different orientation spins. Applying non-zero bias voltages makes the density of states (DOS) of the right electrodes shift down. Due to an energy gap between LUMO and LUMO+1 in ZGOs, with a certain bias, the conduction band of the right electrode cannot match the LUMO of the scattering region, and then NDR occurs. With a larger bias, NDR ends when the second conduction band of the right electrode's DOS covers the LUMO of the scattering region. As most of proposed ZGO systems possess such a gap between LUMO and LUMO+1, NDR can be widely observed. This discovery may provide great potential for applications in NDR-based nanoelectronics by using modified graphene materials.

Based on experimental evidence of carbon composite nanostructure - CNT-fullerene nanobuds - the proposed all-carbon graphene-fullerene nanobuds have been investigated through spin-polarized density functional theory. Four structures (A, B, C and D) are

proposed in terms of the geometry, and analysis of formation of new chemical bonds in nanobuds is conducted. Cases A and B possess nearly magnetic moments of $6 \mu_B$, originating from unpaired spins due to the chemical bond formation from two next-nearest atoms in graphene. In Cases C and D, the connections of two atoms in different sublattices of graphene cannot generate unpaired spins, resulting in non-magnetic states. The magnetic nanobuds have gain great promise for new spintronics and guide the controllable experimental synthesis for desired geometries.

These accomplishments firstly explain recent magnetism in oxidized graphene and secondly provide new approaches to designing carbon materials, including graphene nanobuds and graphene oxygen in spintronics. Moreover, the NDR phenomenon has been predicted for promising nanoelectronic devices.

8.2 Outlook

The change between sp^2 and sp^3 hybridizations in carbon systems is one of the most important reactions to produce new structures and devices. The ratios of modifications and the strengths of sp^2 and sp^3 hybridizations determine the electronic properties of carbon systems. The functional groups including hydroxyl and epoxy groups on the surface of graphene and zigzag graphene nanoribbon can introduce ferromagnetism. With the different ratios of the functional groups may affect the magnitude of the magnetism and the transport, and lastly improve performance again.

The vacancies and adatoms of carbons could be two important approaches to prepare new

materials in experiments, which can also introduce changes between sp^2 and sp^3 hybridizations. P- and N-type materials could be feasible and useful for field emission transistors (FETs) and solar cell devices (see Figure 2.6.5). Carbon nanotube and fullerene have been used and synthesis in these devices experimentally, providing impressive perspectives. Recently, graphene materials have also begun to investigate their own P- and N-type ones. Without an atomic understanding, it is not clear that the mechanism and the morphology effects of interface to improve the devices.

Moreover, graphene is predicted to have a large adsorption area. The adsorptions of different gases on graphene surfaces can provide potential applications of gas sensors, such as NO_2 and NH_3 sensors. Determining how to extend adsorption, sensitivity and selectivity is one of the greatest challenges. Through the first-principle investigations of the modifications of functional groups, better carbon structures can be designed. The covalent and non-covalent adsorptions could provide different transport properties, which could serve as new FET devices as well (see Figure 8.2.1).

Figure 8.2.1. Diagram of a FET working as a gas sensor. The pink dots are presented as

the functionalized groups on the P/N materials.

Additionally, other properties including optics and classical mechanics attract researchers' interests as well. To extend the optical property, the issue of how to control band gaps for appropriate light adsorption, emission, and photoluminescence is an interesting one for carbons. With theoretical investigations, optical carbon structures can be well designed for controllable experimental synthesis to enlarge the optoelectronics. On the other hand, graphene and CNT belong to the strongest materials. Molecular dynamics and first-principle investigations can develop the technological requirement for potential industrial applications. Meanwhile, the reduction of the materials' size leads to nanoscale mechanical and dynamic instruments, such as giga- or even tera-Hz oscillators to approach special requirements. These are definitely exciting and challenging directions for the future.

Abbreviations

CNT: carbon nanotube

DFT: density functional theory

FM: ferromagnetic / ferromagnetism

AFM: antiferromagnetic / antiferromagnetism

NM: nonmagnetic / nonmagnetism

E_F : Fermi level

HOMO: highest occupied molecular orbital

LUMO: lowest unoccupied molecular orbital

DOS: density of states

PDOS: projected density of states

GNR: graphene nanoribbon

AGNR: armchair graphene nanoribbon

ZGNR: zigzag graphene nanoribbon

GO: graphene oxide / oxidized graphene

ZGO: an epoxy-pair chain on zigzag graphene nanoribbons

NDR: negative differential resistance

FET: field emission transistor

Publications

1. M. Wang and C. M. Li, *Nanoscale*, 2011, **3**, 2324.
2. M. Wang and C. M. Li, *Phys. Chem. Chem. Phys.*, 2011, **13**, 5945.
3. M. Wang, W. Huang, M. B. Chan-Park and C. M. Li, *Nanotechnology*, 2011, **22**, 105702.
4. M. Wang and C. M. Li, *Phys. Chem. Chem. Phys.*, 2011, **13**, 1413.
5. M. Wang and C. M. Li, *New Journal of Physics*, 2010, **12**, 083040.
6. M. Wang and C. M. Li, *Nanotechnology*, 2010, **21**, 035704.
7. M. Wang and C. M. Li, *Nanoscale*, submitted.

References

- [1] D. J. Frank, R. H. Dennard, E. Nowak, P. M. Solomon, Y. Taur and H. S. P. Wong, *Proceedings of the Ieee*, 2001, **89**, 259.
- [2] K. P. C. Vollhardt and N. E. Schore, *Organic Chemistry* W. H. Freeman, 2009.
- [3] L. Pauling, *J. Am. Chem. Soc.*, 1932, **54**, 3570.
- [4] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162.
- [5] S. Iijima, *Nature*, 1991, **354**, 56.
- [6] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666.
- [7] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos and A. A. Firsov, *Nature*, 2005, **438**, 197.
- [8] Y. B. Zhang, Y. W. Tan, H. L. Stormer and P. Kim, *Nature*, 2005, **438**, 201.
- [9] Z. H. Chen, Y. M. Lin, M. J. Rooks and P. Avouris, *Physica E-Low-Dimensional Systems & Nanostructures*, 2007, **40**, 228.
- [10] M. Y. Han, B. Ozyilmaz, Y. B. Zhang and P. Kim, *Phys. Rev. Lett.*, 2007, **98**, 206805.
- [11] M. I. Katsnelson, K. S. Novoselov and A. K. Geim, *Nature Physics*, 2006, **2**, 620.
- [12] Y. M. Lin, K. A. Jenkins, A. Valdes-Garcia, J. P. Small, D. B. Farmer and P. Avouris, *Nano Lett.*, 2009, **9**, 422.
- [13] X. L. Feng, N. Chandrasekhar, H. B. Su and K. Mullen, *Nano Lett.*, 2008, **8**, 4259.
- [14] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, J. H. Ahn, P. Kim, J. Y. Choi and B. H. Hong, *Nature*, 2009, **457**, 706.
- [15] G. Eda, G. Fanchini and M. Chhowalla, *Nat. Nanotechnol.*, 2008, **3**, 270.
- [16] C. X. Guo, H. B. Yang, Z. M. Sheng, Z. S. Lu, Q. L. Song and C. M. Li, *Angewandte Chemie-International Edition*, 2010, **49**, 3014.
- [17] V. P. Gusynin, S. G. Sharapov and J. P. Carbotte, *New Journal of Physics*, 2009, **11**, 095013.
- [18] T. Hasan, Z. P. Sun, F. Q. Wang, F. Bonaccorso, P. H. Tan, A. G. Rozhin and A. C. Ferrari, *Advanced Materials*, 2009, **21**, 3874.
- [19] F. N. Xia, T. Mueller, Y. M. Lin, A. Valdes-Garcia and P. Avouris, *Nat. Nanotechnol.*, 2009, **4**, 839.
- [20] A. N. Khlobystov, D. A. Britz, A. Ardavan and G. A. D. Briggs, *Phys. Rev. Lett.*, 2004, **92**, 245507.
- [21] B. W. Smith, M. Monthieux and D. E. Luzzi, *Nature*, 1998, **396**, 323.
- [22] B. W. Smith, R. M. Russo, S. B. Chikkannanavar and D. E. Luzzi, *J. Appl. Phys.*, 2002, **91**, 9333.
- [23] M. Wang and C. M. Li, *Nanotechnology*, 2010, **21**, 035704.
- [24] H. B. Su, W. A. Goddard and Y. Zhao, *Nanotechnology*, 2006, **17**, 5691.
- [25] B. Corzilius, K. P. Dinse and K. Hata, *Phys. Chem. Chem. Phys.*, 2007, **9**, 6063.

- [26] J. A. Rodriguez-Manzo, F. Lopez-Urias, M. Terrones and H. Terrones, *Nano Lett.*, 2004, **4**, 2179.
- [27] H. B. Su, R. J. Nielsen, A. C. T. van Duin and W. A. Goddard, *Physical Review B*, 2007, **75**, 134107.
- [28] A. G. Nasibulin, P. V. Pikhitsa, H. Jiang, D. P. Brown, A. V. Krashenninnikov, A. S. Anisimov, P. Queipo, A. Moisala, D. Gonzalez, G. Lientschnig, A. Hassanien, S. D. Shandakov, G. Lolli, D. E. Resasco, M. Choi, D. Tomanek and E. I. Kauppinen, *Nat. Nanotechnol.*, 2007, **2**, 156.
- [29] B. Biel, X. Blase, F. Triozon and S. Roche, *Phys. Rev. Lett.*, 2009, **102**, 096803.
- [30] P. V. Kamat, *J. Phys. Chem. Lett.*, 2010, **1**, 520.
- [31] E. J. Kan, Z. Y. Li, J. L. Yang and J. G. Hou, *J. Am. Chem. Soc.*, 2008, **130**, 4224.
- [32] X. L. Li, X. R. Wang, L. Zhang, S. W. Lee and H. J. Dai, *Science*, 2008, **319**, 1229.
- [33] O. V. Yazyev and L. Helm, *Phys. Rev. B*, 2007, **75**, 125408.
- [34] S. Okada, S. Saito and A. Oshiyama, *Physical Review Letters*, 2001, **86**, 3835.
- [35] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen and R. S. Ruoff, *Nature*, 2006, **442**, 282.
- [36] S. S. Rao, A. Stesmans, D. V. Kosynkin, A. Higginbotham and J. M. Tour, *arXiv:1006.4942v1*, 2010.
- [37] Y. Wang, Y. Huang, Y. Song, X. Y. Zhang, Y. F. Ma, J. J. Liang and Y. S. Chen, *Nano Lett.*, 2009, **9**, 220.
- [38] S. S. Rao, A. Stesmans, Y. Wang and Y. Chen, *arXiv:1006.4840v1*, 2010.
- [39] G. Cicero, J. C. Grossman, E. Schwegler, F. Gygi and G. Galli, *Journal of the American Chemical Society*, 2008, **130**, 1871.
- [40] X. Y. Yang, X. Dou, A. Rouhanipour, L. J. Zhi, H. J. Rader and K. Mullen, *Journal of the American Chemical Society*, 2008, **130**, 4216.
- [41] Z. F. Wang, Q. X. Li, H. X. Zheng, H. Ren, H. B. Su, Q. W. Shi and J. Chen, *Physical Review B*, 2007, **75**, 113406.
- [42] S. D. Wu, L. Jing, Q. X. Li, Q. W. Shi, J. Chen, H. B. Su, X. P. Wang and J. L. Yang, *Physical Review B*, 2008, **77**, 195411.
- [43] L. A. Agapito and H. P. Cheng, *Journal of Physical Chemistry C*, 2007, **111**, 14266.
- [44] W. Y. Kim, Y. C. Choi, S. K. Min, Y. Cho and K. S. Kim, *Chemical Society Reviews*, 2009, **38**, 2319.
- [45] Y. Xu, G. Zhang and B. W. Li, *Journal of Physical Chemistry B*, 2008, **112**, 16891.
- [46] K. H. Khoo, J. B. Neaton, Y. W. Son, M. L. Cohen and S. G. Louie, *Nano Lett.*, 2008, **8**, 2900.
- [47] W. Y. Kim, S. K. Kwon and K. S. Kim, *Physical Review B*, 2007, **76**, 033415.
- [48] A. Iyengar, T. Luo, H. A. Fertig and L. Brey, *Physical Review B*, 2008, **78**, 235411.
- [49] S. U. Lee, M. Khazaei, F. Pichierri and Y. Kawazoe, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5225.
- [50] P. C. P. Watts, W. K. Hsu, D. P. Randall, H. W. Kroto and D. R. M. Walton, *Phys. Chem. Chem. Phys.*, 2002, **4**, 5655.
- [51] L. A. Agapito, E. J. Bautista and J. M. Seminario, *Physical Review B*, 2007, **76**,

115316.

- [52] J. Taylor, H. Guo and J. Wang, *Physical Review B*, 2001, **63**, 245407.
- [53] Y. P. An, C. L. Yang, M. S. Wang, X. G. Ma and D. H. Wang, *Journal of Physical Chemistry C*, 2009, **113**, 15756.
- [54] W. Haiss, S. Martin, L. E. Scullion, L. Bouffier, S. J. Higgins and R. J. Nichols, *Phys. Chem. Chem. Phys.*, 2009, **11**, 10831.
- [55] C. K. Wang, Y. Fu and Y. Luo, *Phys. Chem. Chem. Phys.*, 2001, **3**, 5017.
- [56] P. R. Wallace, *Physical Review*, 1947, **71**, 622.
- [57] A. K. Geim and K. S. Novoselov, *Nature Materials*, 2007, **6**, 183.
- [58] Y. W. Son, M. L. Cohen and S. G. Louie, *Phys. Rev. Lett.*, 2006, **97**, 216803.
- [59] Y. W. Son, M. L. Cohen and S. G. Louie, *Nature*, 2006, **444**, 347.
- [60] Y. C. Huang, C. P. Chang and M. F. Lin, *Nanotechnology*, 2007, **18**, 495401.
- [61] L. Y. Jiao, L. Zhang, X. R. Wang, G. Diankov and H. J. Dai, *Nature*, 2009, **458**, 877.
- [62] D. V. Kosynkin, A. L. Higginbotham, A. Sinitskii, J. R. Lomeda, A. Dimiev, B. K. Price and J. M. Tour, *Nature*, 2009, **458**, 872.
- [63] L. A. Ponomarenko, F. Schedin, M. I. Katsnelson, R. Yang, E. W. Hill, K. S. Novoselov and A. K. Geim, *Science*, 2008, **320**, 356.
- [64] B. Trauzettel, D. V. Bulaev, D. Loss and G. Burkard, *Nature Physics*, 2007, **3**, 192.
- [65] T. Gokus, R. R. Nair, A. Bonetti, M. Bohmler, A. Lombardo, K. S. Novoselov, A. K. Geim, A. C. Ferrari and A. Hartschuh, *ACS Nano*, 2009, **3**, 3963.
- [66] J.-L. Li, K. N. Kudin, M. J. McAllister, R. K. Prud'homme, I. A. Aksay and R. Car, *Phys. Rev. Lett.*, 2006, **96**, 176101.
- [67] Z. Y. Li, W. H. Zhang, Y. Luo, J. L. Yang and J. G. Hou, *Journal of the American Chemical Society*, 2009, **131**, 6320.
- [68] Z. S. Wu, W. C. Ren, L. B. Gao, B. L. Liu, J. P. Zhao and H. M. Cheng, *Nano Research*, 2010, **3**, 16.
- [69] S. M. Bachilo, M. S. Strano, C. Kittrell, R. H. Hauge, R. E. Smalley and R. B. Weisman, *Science*, 2002, **298**, 2361.
- [70] M. J. O'Connell, S. M. Bachilo, C. B. Huffman, V. C. Moore, M. S. Strano, E. H. Haroz, K. L. Rialon, P. J. Boul, W. H. Noon, C. Kittrell, J. P. Ma, R. H. Hauge, R. B. Weisman and R. E. Smalley, *Science*, 2002, **297**, 593.
- [71] Y. Tian, D. Chassaing, A. G. Nasibulin, P. Ayala, H. Jiang, A. S. Anisimov, A. Hassanien and E. I. Kauppinen, *Physica Status Solidi B-Basic Solid State Physics*, 2008, **245**, 2047.
- [72] Y. Tian, D. Chassaing, A. G. Nasibulin, P. Ayala, H. Jiang, A. S. Anisimov and E. I. Kauppinen, *J. Am. Chem. Soc.*, 2008, **130**, 7188.
- [73] X. X. Wang, C. G. Ma, K. Chen, H. N. A. Li and P. Wang, *Physics Letters A*, 2009, **374**, 87.
- [74] T. Z. Meng, C. Y. Wang and S. Y. Wang, *Phys. Rev. B*, 2008, **77**, 033415.
- [75] X. J. Wu and X. C. Zeng, *ACS Nano*, 2008, **2**, 1459.
- [76] J. A. Fürst, J. Hashemi, T. Markussen, M. Brandbyge, A. P. Jauho and R. M. Nieminen, *Phys. Rev. B*, 2009, **80**, 035427.
- [77] X. Zhu and H. B. Su, *Phys. Rev. B*, 2009, **79**, 165401.
- [78] X. J. Wu and X. C. Zeng, *Nano Lett.*, 2009, **9**, 250.

- [79] S. M. M. Dubois, Z. Zanolli, X. Declerck and J. C. Charlier, *Eur. Phys. J. B*, 2009, **72**, 1.
- [80] A. A. Farajian, K. Esfarjani and Y. Kawazoe, *Phys. Rev. Lett.*, 1999, **82**, 5084.
- [81] C.-C. Kaun, B. Larade, H. Mehrez, J. Taylor and H. Guo, *Physical Review B*, 2002, **65**, 205416.
- [82] Z. F. Wang, Q. X. Li, Q. W. Shi, X. P. Wang, J. L. Yang, J. G. Hou and J. Chen, *Appl. Phys. Lett.*, 2008, **92**, 133114.
- [83] H. Ren, Q. X. Li, Y. Luo and J. L. Yang, *Appl. Phys. Lett.*, 2009, **94**, 173110.
- [84] W. Y. Kim and K. S. Kim, *Nat. Nanotechnol.*, 2008, **3**, 408.
- [85] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov and A. K. Geim, *Proc. Natl Acad. Sci. USA*, 2005, **102**, 10451.
- [86] B. C. Brodie, *Ann. Chim. Phys.*, 1860, **59**, 466.
- [87] L. Staudenmaier, *Ber. Deut. Chem. Ges*, 1898, **37**, 1481.
- [88] W. S. Hummers and R. E. Offeman, *Journal of the American Chemical Society*, 1958, **80**, 1339.
- [89] H. He, J. Klinowski, M. Forster and A. Lerf, *Chemical Physics Letters*, 1998, **287**, 53.
- [90] X. Li, C. Y. Li, H. W. Zhu, K. L. Wang, J. Q. Wei, X. M. Li, E. Y. Xu, Z. Li, S. Luo, Y. Lei and D. H. Wu, *Chem. Commun.*, 2010, **46**, 3502.
- [91] S. S. Li, K. H. Tu, C. C. Lin, C. W. Chen and M. Chhowalla, *ACS Nano*, 2010, **4**, 3169.
- [92] J. Cumings and A. Zettl, *Science*, 2000, **289**, 602.
- [93] Q. S. Zheng and Q. Jiang, *Physical Review Letters*, 2002, **88**, 045503.
- [94] S. B. Legoas, V. R. Coluci, S. F. Braga, P. Z. Coura, S. O. Dantas and D. S. Galvao, *Physical Review Letters*, 2003, **90**, 055504.
- [95] P. Liu, Y. W. Zhang and C. Lu, *J. Appl. Phys.*, 2005, **97**, 4.
- [96] S. B. Legoas, V. R. Coluci, S. F. Braga, P. Z. Coura, S. Dantas and D. S. Galvao, *Nanotechnology*, 2004, **15**, S184.
- [97] P. Liu, Y. W. Zhang and C. Lu, *Journal of Applied Physics*, 2005, **97**, 094313.
- [98] M. Born and R. Oppenheimer, *Annalen der Physik*, 1927, **389**, 457.
- [99] P. Hohenberg and W. Kohn, *Physical Review B*, 1964, **136**, B864.
- [100] W. Kohn and L. J. Sham, *Physical Review*, 1965, **140**, 1133.
- [101] N. Troullier and J. L. Martins, *Phys. Rev. B*, 1991, **43**, 1993.
- [102] J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejon and D. Sanchez-Portal, *Journal of Physics-Condensed Matter*, 2002, **14**, 2745.
- [103] M. Brandbyge, J. L. Mozos, P. Ordejon, J. Taylor and K. Stokbro, *Physical Review B*, 2002, **65**, 165401.
- [104] M. Büttiker, Y. Imry, R. Landauer and S. Pinhas, *Physical Review B*, 1985, **31**, 6207.
- [105] Z. Y. Yin, S. Y. Sun, T. Salim, S. X. Wu, X. A. Huang, Q. Y. He, Y. M. Lam and H. Zhang, *ACS Nano*, 2010, **4**, 5263.
- [106] M. Wang and C. M. Li, *Phys. Chem. Chem. Phys.*, 2010, DOI:10.1039/C0CP00828A.
- [107] Z. S. Lu, C. X. Guo, H. B. Yang, Y. Qiao, J. Guo and C. M. Li, *Journal of Colloid and Interface Science*, 2010, **353**, 588.

- [108] M. Z. S. Flores, P. A. S. Autreto, S. B. Legoas and D. S. Galvao, *Nanotechnology*, 2009, **20**, 465704.
- [109] T. L. Makarova, B. Sundqvist, R. Hohne, P. Esquinazi, Y. Kopelevich, P. Scharff, V. A. Davydov, L. S. Kashevarova and A. V. Rakhmanina, *Nature*, 2001, **413**, 716.
- [110] R. Hohne and P. Esquinazi, *Advanced Materials*, 2002, **14**, 753.
- [111] S. Sahoo, T. Kontos, J. Furer, C. Hoffmann, M. Graber, A. Cottet and C. Schonenberger, *Nature Physics*, 2005, **1**, 99.
- [112] N. Tombros, S. J. van der Molen and B. J. van Wees, *Physical Review B*, 2006, **73**, 233403.
- [113] T. L. Makarova and F. Palacio, *Carbon-Based Magnetism*, Elsevier, Amsterdam, 2006.
- [114] D. W. Boukhvalov, M. I. Katsnelson and A. I. Lichtenstein, *Physical Review B*, 2008, **77**, 035427.
- [115] D. W. Boukhvalov and M. I. Katsnelson, *Nano Lett.*, 2008, **8**, 4373.
- [116] M. Wang and C. M. Li, *New Journal of Physics*, 2010, **12**, 083040.
- [117] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, *Carbon*, 2007, **45**, 1558.
- [118] D. Pandey, R. Reifengerger and R. Piner, *Surface Science*, 2008, **602**, 1607.
- [119] D. W. Lee, J. M. Cole, J. W. Seo, S. S. Saxena, C. H. W. Barnes, E. E. M. Chia and C. Panagopoulos, *arXiv:1005.5580v1*, 2010.
- [120] S. S. Alexandre, M. S. C. Mazzoni and H. Chacham, *Phys. Rev. Lett.*, 2008, **100**, 146801.
- [121] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova and D. M. Treger, *Science*, 2001, **294**, 1488.
- [122] I. Zutic, J. Fabian and S. Das Sarma, *Rev. Mod. Phys.*, 2004, **76**, 323.
- [123] C. L. Kane and E. J. Mele, *Phys. Rev. Lett.*, 2005, **95**, 226801.
- [124] C. L. Kane and E. J. Mele, *Phys. Rev. Lett.*, 2005, **95**, 146802.
- [125] M. Topsakal, V. M. K. Bagci and S. Ciraci, *Physical Review B*, 2010, **81**, 205437.
- [126] A. Sinitskii and J. M. Tour, *ACS Nano*, 2009, **3**, 2760.
- [127] P. O. Lehtinen, A. S. Foster, Y. C. Ma, A. V. Krashennnikov and R. M. Nieminen, *Phys. Rev. Lett.*, 2004, **93**, 187202.
- [128] Y. Zhang, S. Talapatra, S. Kar, R. Vajtai, S. K. Nayak and P. M. Ajayan, *Phys. Rev. Lett.*, 2007, **99**, 107201.
- [129] P. O. Lehtinen, A. S. Foster, A. Ayuela, A. Krashennnikov, K. Nordlund and R. M. Nieminen, *Phys. Rev. Lett.*, 2003, **91**, 017202.
- [130] N. Park, M. Yoon, S. Berber, J. Ihm, E. Osawa and D. Tomanek, *Phys. Rev. Lett.*, 2003, **91**, 237204.
- [131] J. Cervenka, M. I. Katsnelson and C. F. J. Flipse, *Nature Physics*, 2009, **5**, 840.
- [132] M. M. Ugeda, I. Brihuega, F. Guinea, oacute, R. mez, iacute and J. M. guez, *Physical Review Letters*, 2010, **104**, 096804.
- [133] M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, *Journal of Materials Research*, 1993, **8**, 2054.
- [134] A. D. Becke, *Journal of Chemical Physics*, 1993, **98**, 5648.
- [135] G. Fitzgerald and J. Andzelm, *Journal of Physical Chemistry*, 1991, **95**, 10531.
- [136] X. Blase, L. X. Benedict, E. L. Shirley and S. G. Louie, *Phys. Rev. Lett.*, 1994, **72**,

1878.

- [137] T. Lenosky, X. Gonze, M. Teter and V. Elser, *Nature*, 1992, **355**, 333.
- [138] G. E. Scuseria, *Chem. Phys. Lett.*, 1992, **195**, 534.
- [139] G. Kresse and J. Furthmuller, *Comput. Mater. Sci.*, 1996, **6**, 15.
- [140] G. Kresse and J. Hafner, *Phys. Rev. B*, 1994, **49**, 14251.
- [141] Because of the limitations of computational resources, we cannot use VASP packages to get the band structures of nanobuds. Here we have to choose SIESTA package to investigate the system and use VASP package to study the magnetic moments to compare with CNT-based nanobuds' values. In the calculations by VASP, the energy cut-off is 400 eV. The frozen-core projector augmented wave (PAW) approach is used to treat the interaction between ions and electrons.