Covalently functionalized carbon nanotubes and their electrical properties

Zhang, Kang

2014

Zhang, K. (2014). Covalently functionalized carbon nanotubes and their electrical properties. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/62245>

<https://doi.org/10.32657/10356/62245>

**COVALENTLY FUNCTIONALIZED CARBON
NANOTUBES AND THEIR ELECTRICAL PROPERTIES**

ZHANG KANG

(B.Eng, NTU, MSc., NTU)

A THESIS SUBMITTED

FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

IN ADVANCED MATERIALS FOR MICRO- AND NANO-SYSTEMS

(AMM&NS)

SINGAPORE-MIT ALLIANCE

NANYANG TECHNOLOGICAL UNIVERSITY

2014

DECLARATION

I hereby declare that this thesis is my original work and it has been written by me in its entirety. I have duly acknowledged all the sources of information which have been used in the thesis.

This thesis has also not been submitted for any degree in any university previously.

Zhang Kang

2/10/2014

Acknowledgement

This thesis would not be possible without the founding and support from Advanced Materials for Micro- and Nano-systems (AMM&NS) program of Singapore-MIT Alliance (SMA). I would also like to thank AMM&NS program for offering me the opportunity to take the well-organized courseworks in Massachusetts Institute of Technology and learn from many leading researchers and scientists.

I would like to express my special appreciation and thanks to my supervisor, Professor Zhang Qing from Nanyang Technological University, for his inspiring supervision through my entire PhD candidature. His insightful discussions and scientific advice have been an invaluable treasure for me during my research journey. His enthusiasm and dedication to research have been extremely motivational to me, especially during the tough times in the experiments.

My sincere gratitude goes to my co-supervisor Professor Nicola Marzari from Massachusetts Institute of Technology for his valuable time on the insightful discussion and valuable suggestions from the initial towards the final stage of my thesis project. My special thanks also go to Professor Francesco Stellacci and Assistant Professor Elise Y. Li for their valuable discussions and suggestions during my thesis project.

I would also like to thank all our group members under Professor Zhang Qing for their great helps. In particular, I would like to thank Dr. Li Hong, Dr. Gao Pingqi and Dr. Liu Chao for their detailed advice on device fabrication and chemical functionalization techniques that are essential to the success of all

my experiments. I would also like to thank Dr. Zou Jianping and Mr. Fan Yu for their assistances during my experimental works.

Many thanks and appreciations go to the technicians in Characterization Lab and Nanyang Nano Fabrication Center, Ms. Seet Lye Ping, Mr. Muhd Fauzi bin Abdullah, Mr. Mak Foo Wah and Mr. Mohamad Shamsul bin Mohamad, for their consistent technical assistances.

Finally, I want to thank my parents, my wife, and my brothers for their huge sacrifice to support my work.

Table of Contents

Acknowledgement	i
Abstract	vii
Summary	viii
1 Introduction	1
1.1 Single-Walled Carbon Nanotubes and Their Electronic Properties.....	2
1.1.1 SWCNT Structure.....	3
1.1.2 Electronic Properties of SWCNTs.....	6
1.2 Covalent Functionalizations to the Sidewall of SWCNTs.....	12
1.3 Main Challenges in Covalent Functionalizations on SWCNTs.....	15
1.4 Objectives.....	17
1.5 Major Contributions.....	17
1.6 Thesis Organization.....	18
2 Review of Electrical Properties of SWCNTs Influenced by Sidewall Covalent Functionalizations	19
2.1 Electrical Conductance of SWCNTs Influenced by Sidewall Covalent Functionalizations.....	20
2.1.1 Theoretical Predictions on the Electrical Conductance of SWCNTs Influenced by Sidewall Covalent Functionalizations...	20
2.1.2 Experimental Observations on the Electrical Conductance of SWCNTs Influenced by Sidewall Covalent Functionalizations...	27
2.2 Electronic Band Structure of SWCNTs Influenced by Sidewall Covalent Functionalizations.....	32
2.2.1 Theoretical Predictions on the Influences of Covalent Functionalizations to Electronic Band Structures of SWCNTs...	32
2.2.2 Experimental Observations of the Influence of Covalent Functionalizations on Electronic Band Structures of SWCNTs...	38
2.3 Summary.....	43
3 Diameter Dependent Reactivity of SWCNT on [2+1] Cycloaddition Functionalization	45
3.1 Introduction.....	46
3.2 Experimental.....	48
3.2.1 Sample Preparation.....	48
3.2.2 Characterization of Individual SWCNTs by Raman Scattering...	50

3.2.3 Covalent Functionalization: Addition of Dichlorocarbene to SWCNTs.....	55
3.3 Results and Discussion.....	57
3.3.1 Raman D/G Intensity Ratio Change.....	57
3.3.2 Raman G Intensity Change.....	60
3.3.3 Discussion.....	63
3.4 Summary.....	64
4 Conductance Preservation Effect on [2+1] Cycloaddition Functionalized SWNTs	66
4.1 Introduction.....	67
4.2 Experimental.....	70
4.2.1 Sample Preparation.....	70
4.2.2 Dichlorocarbene Functionalization and Raman Scattering.....	72
4.2.3 Electrical Conductance Measurement of SWCNT FET Platform	73
4.3 Results and Discussion.....	77
4.3.1 Conductance Changes of Metallic SWCNTs.....	77
4.3.2 Discussion.....	79
4.3.3 Conductance Changes of Semiconducting SWCNTs.....	81
4.3.4 Discussion.....	83
4.4 Summary.....	85
5 Metallicity of Covalently Functionalized Metallic SWCNTs Studied by Electrostatic Force Microscopy	86
5.1 Introduction.....	87
5.2 Electrostatic Force Microscopy.....	88
5.3 Experimental.....	90
5.3.1 Experimental Procedure.....	90
5.3.2 Sample Preparation.....	92
5.3.3 Covalent Functionalizations.....	92
5.3.4 Raman Scattering.....	92
5.3.5 EFM Spectroscopy.....	93
5.4 Results and Discussion.....	93
5.4.1 EFM Imaging of Pristine SWCNTs.....	93
5.4.2 EFM Signal of Metallic SWCNT Influenced by the Prato Reaction ([2+3] Cycloaddition).....	95
5.4.3 EFM Signal of Metallic SWCNT Influenced by the Dichlorocarbene Functionalization ([2+1] Cycloaddition).....	97
5.5 Summary.....	99

6 Covalently Functionalized Metallic SWCNTs Studied by Dielectric Force Microscopy	100
6.1 Introduction.....	101
6.2 Experimental.....	108
6.2.1 Experimental Procedure.....	108
6.2.2 Sample Preparation.....	108
6.2.3 Covalent Functionalizations.....	108
6.2.4 Raman Scattering.....	108
6.2.5 DFM Spectroscopy.....	108
6.3 Results and Discussion.....	109
6.3.1 Demonstration of DFM Technique on Pristine SWCNTs.....	109
6.3.2 DFM Image on Covalently Functionalized Metallic SWCNTs....	111
6.3.3 Plots on EFM Signals and DFM Modulation Ratios.....	115
6.3.4 EFM and DFM Image of Partially Functionalized Metallic SWCNTs.....	117
6.3.5 Discussion.....	119
6.4 Summary.....	120
7 [2+1] Cycloaddition Functionalized SWCNTs Networks and Their Potential Applications in Humidity Sensing	122
7.1 Introduction.....	123
7.2 Experimental.....	125
7.2.1 SWCNT Network Device Fabrication.....	125
7.2.2 The Bingel Reaction.....	125
7.2.3 Dichlorocarbene Functionalization.....	125
7.3 Results and Discussion.....	126
7.3.1 Covalent [2+1] Cycloaddition Functionalizations.....	126
7.3.2 Electrical Properties of SWCNT Network Subject to [2+1] Cycloaddition with Periconjugation Effect.....	129
7.3.3 Humidity Response of [2+1] Cycloaddition Functionalized SWCNT Networks.....	131
7.4 Conclusion.....	136
8 Conclusion and Recommendation	137
8.1 Conclusion.....	137
8.2 Recommendation.....	139
Bibliography	141
Appendix	161

A	Diameter Dependent Reactivity Shown on Bulk SWCNTs.....	161
B	Electrical Conductance of Individual SWCNT with Silicon Nitride Passivation.....	163
C	More on DFM Techniques Implementation.....	164
D	DFM of a Semiconducting SWCNT Subject to Dichlorocarbene Functionalization.....	168
E	Raman Spectroscopy Estimation of Degree of Functionalization.....	169
List of Publications		171

Abstract

Single-walled carbon nanotubes (SWCNTs) are promising candidates for nano-electronic applications largely due to their excellent electrical and electronic properties. However, in many of the applications, covalent functionalizations to SWCNTs are inevitable and these covalent modifications generally degrade significantly their electrical conductivities, as well as modify their electronic band structures. In view of this problem, many theorists proposed that a special type of covalent functionalizations, [2+1] cycloaddition, would not have such disadvantages.

In this thesis, the diameter dependent reactivity of the [2+1] cycloaddition to SWCNTs is experimentally demonstrated through dichlorocarbene functionalization. The electrical conductivities of [2+1] cycloaddition functionalized SWCNTs are also tested. Finally, the local electrical properties of covalent functionalized SWCNTs are characterized utilizing contactless electrostatic force microscopy and dielectric force microscopy techniques. Our results suggest that [2+1] cycloaddition is likely an outstanding choice to covalently functionalize SWCNTs, while leaving their electrical and electronic properties largely unaffected.

Summary

This thesis covers the influence of covalent functionalizations on the electrical and electronic properties of single walled carbon nanotubes (SWCNTs). The first chapter introduces the fundamental properties of SWCNTs and covalent functionalizations to SWCNTs. The main challenges, objectives and contributions of this thesis are also given in Chapter 1.

Chapter 2 reviews the influences of covalent functionalizations to the electrical conductivity and electronic band structures of the SWCNTs. The difference between [2+1] cycloaddition functionalization with sp^2 rehybridizations and conventional covalent functionalizations with sidewall sp^3 rehybridizations is highlighted.

In Chapter 3, the diameter dependent reactivity of individual SWCNTs upon dichlorocarbene functionalization ([2+1] cycloaddition) is investigated. Raman spectra D band to G band intensity ratio and G band intensity of the SWCNTs are used to characterize the degree of covalent functionalizations. The results suggest that small diameter SWCNTs are more easily to be functionalized than large diameter SWCNTs, regardless of metallic or semiconducting SWCNTs. This is consistent with relative theoretical predictions and could serve as a strong support of the sidewall C-C bond broken by [2+1] cycloaddition.

Individual SWCNTs with diameter range of 1.2-2.2 nm are investigated on their electrical conductance changes upon dichlorocarbene functionalization in Chapter 4. The electrical measurements are performed with the SWCNTs on conventional field effect transistor (FET) platforms. The findings suggest that both metallic and semiconducting SWCNTs could have their conductance

largely preserved even subject to significant degree of dichlorocarbene functionalizations.

Following the electrical measurements, electrostatic force microscopy (EFM) technique is utilized to characterize the local electronic properties of metallic SWCNTs subject to dichlorocarbene functionalization in Chapter 5. The EFM response of a dichlorocarbene functionalized metallic SWCNT is further compared with a metallic SWCNT subjected to the Prato reaction ([2+3] cycloaddition), and a large metallicity preservation of dichlorocarbene functionalized metallic SWCNTs is observed.

In Chapter 6, a novel dielectric force microscopy (DFM) technique is implemented to inspect the differences between dichlorocarbene and the Prato reaction functionalized metallic SWCNTs. DFM is capable of probing the gate dependent local electrical conductivity and could reflect the band structure, Fermi level and local conductivity of SWCNTs. According to the DFM results, dichlorocarbene functionalized metallic SWCNTs are considered have their electronic band structures largely preserved, while the Prato reaction functionalized metallic SWCNTs are expected to have apparent band gaps presented.

SWCNT networks are also investigated to understand their electrical characteristic changes upon various [2+1] cycloadditions in Chapter 7. It has been found that [2+1] cycloaddition with ring structures could significantly change the electrical behavior of the SWCNT networks even at relatively low degree of the functionalizations. The functionalized SWCNT networks are further subjected to humidity sensing tests, and they show much larger sensitivity to humidity as compared to pristine SWCNT networks.

Finally, Chapter 8 provides conclusive remarks and recommendations for future works on covalent functionalizations and their influences to SWCNTs, especially on [2+1] cycloaddition that has the remarkable conductance preservation effect.

List of Figures

Figure 1.1 Illustration of the structures of a SWCNT (a), DWCNT (b) and MWCNT (c).	3
Figure 1.2 Illustration of the unrolled graphene lattice of a SWCNT with vectors assigned.	4
Figure 1.3 Illustration of the structures of a (8,8) armchair SWCNT (a), a (12,0) zigzag SWCNT (b) and a (10,2) chiral SWCNT (c).	6
Figure 1.4 Quantization of wave states around a graphene cylinder. (a) Wavevectors (k) parallel and perpendicular to the axes of a SWCNT. (b) Contour plot of graphene valence states for a SWCNT with chiral angle $\theta = 0$. The parallel lines indicate the allowed k by the cylindrical boundary condition. (c) Electron states near Fermi Level are defined by the intersection of allowed k with the dispersion cones at the K points. (Figures adapted from Ref. 15)...	7
Figure 1.5 Different alignments between the dispersion cones and the allowed k lines of SWCNTs. (a) If $p=0$, the k line intersection with K point, and this SWCNT is metallic. (b) If $p=1$, the K point and the nearest k line is misaligned, and a band gap is presented. The SWCNT is thus semiconducting. (c) If $p=-1$, the K point and the nearest k line is misaligned, and a band gap is presented. The SWCNT is thus semiconducting. (Figures adapted from Ref.15).	9
Figure 1.6 Band structure, quantum conductance, and density of states of a (5,5) CNT as calculated in the based on Maximally Localized Wannier Functions (solid lines), and compared with the results of a full diagonalization (circles). (Figure adapted from Ref. 16).	11
Figure 1.7 Pd-contacted long (3 μm) and short (0.3 μm) back-gated SWNT devices formed on the same nanotubes on SiO ₂ /Si substrate. (a) SEM (left) and AFM (right) of the device. (b) Transconductance versus gate voltage of the long device at different temperatures. (c) Transconductance versus gate voltage of the short device at different temperatures. (d) On state transconductance of the short device versus temperature. (Figures adapted from Ref. 4).	12

Figure 1.8 Illustration of covalent (a) and non-covalent (b) functionalization to the sidewall of SWCNTs. (Figures adapted from Ref. 19).....	13
Figure 1.9 Different types of sidewall covalent functionalizations to SWCNTs (Figure adapted from Ref. 20).	14
Figure 2.1 Illustration of sp^2 and sp^3 rehybridizations formed on the sidewall of SWCNTs. (a) Sidewall [2+1] cycloaddition with sp^2 rehybridization formed from sidewall carbon bond broken (red dash line). (b) Sidewall [2+3] cycloaddition with sp^3 rehybridization formed.	21
Figure 2.2 Demonstrations of dichlorocarbene attached to the sidewall of a (5,5) armchair SWCNT in skew (a), closed (b) and open (c) configurations and their corresponding quantum conductances (d). (Figures adapted from Ref. 24)	22
Figure 2.3 Quantum conductances of SWCNTs with covalent functionalities. (a) Quantum conductance of 300 nm long (6,6) and (10,10) SWCNTs functionalized with paired phenyl groups (b) Quantum conductance of 1000 nm long (6,6) and (10,10) SWCNTs functionalized with carbene. (Figures adapted from Ref. 25).....	24
Figure 2.4 Quantum conductances at the Fermi level versus covalent functionalization levels for monovalent (-F) and divalent ($>CCl_2$) functionalized (6,6) SWCNT with sidewall opening. (Figure adapted from Ref. 30).	25
Figure 2.5 Quantum conductances of long semiconducting SWCNTs under different degree of CH_2 functionalizations. The (10,0) SWCNT is subject to sidewall carbon bond open upon the functionalization while the (20,0) SWCNT is subject to sidewall carbon bond close upon the functionalization. (Figures adapted from Ref. 31).....	27
Figure 2.6 Electrical conductivity of a metallic SWCNT upon osmylation and after recovery. (a) Illustration of the [2+3] cycloaddition configuration of osmylation functionalized SWCNTs. (b) Resistance change of the metallic SWCNT subject to the osmylation and its recovery. (Figures adapted from Ref. 32)	28
Figure 2.7 Electrical conductance of the metallic SWCNT upon 4-bromobenzene diazonium tetrafluoroborate (4-BBDT) functionalization. (a)	

Raman spectra of the SWCNT upon reaction with 4-BBDT in difference concentration. (b) Electrical conductivity drop of the SWCNT upon reaction with 4-BBDT in difference concentration. (Figures adapted from Ref. 33).....29

Figure 2.8 Conductance recoveries of metallic and semiconducting tubes after thermal annealing removal of the hydroxamic acid functionalities. (Figure adapted from Ref. 34).....30

Figure 2.9 The conductance of a metallic SWCNT upon dichlorocarbene reaction of 5 min, 35 min, and thermal annealing. (Figure adapted from Ref. 26).....31

Figure 2.10 Band gaps of SWCNTs after fully hydrogenations (Figure adapted from Ref. 35).33

Figure 2.11 Band gap of a metallic (8,8) SWCNT at pristine state (a), after PMDE [2+2] cycloaddition functionalization (b) and after PSEPVE [2+2] cycloaddition functionalization (c). (Figures adapted from Ref. 36).34

Figure 2.12 Band structure change of a metallic (4,4) SWCNT subject to [2+3] cycloaddition functionalization. (a) Illustration of type-A and type-B grafting configurations of the [2+3] cycloaddition. (b) Band structure of the metallic tube at pristine state, with type-A attachment and type-B attachment. (Figures adapted from Ref. 37).....35

Figure 2.13 Band structure of a metallic (6,6) SWCNT subject to dichlorocarbene functionalization at low modification ratio. (a) Band structure of the tube at pristine state. (b) Band structure of the tube subject to low degree of dichlorocarbene [2+1] cycloaddition with sidewall carbon bonds open. (c) Band structure of the tube subject to low degree of dichlorocarbene [2+1] cycloaddition with sidewall carbon bonds in closed three-member ring configuration. (Figures adapted from Ref. 28).....36

Figure 2.14 Band structure of metallic (6,6) SWCNT at its pristine state (a), after 12.5% degree of dichlorocarbene functionalization (b) and after 25% degree of dichlorocarbene functionalization. (Figures adapted from Ref. 28).37

Figure 2.15 Change of current versus voltage characteristic of a metallic SWCNT subject to hydrogen plasma treatment at different time (top curve: 0

sec, middle curve: 40 sec, bottom curve: 100 sec). (Figure adapted from Ref. 39).....	39
Figure 2.16 NIR absorption spectrum of [2+3] cycloaddition functionalized SWCNTs. (upper curve: HIPCO, lower curve: HIPCO pyrene) (Figure adapted from Ref. 40).	40
Figure 2.17 Absorption spectra of SWCNTs subject to various degrees of the Bingel reaction. (a) Illustration of the reaction scheme of the Bingel reaction. (b) Absorption spectra of SWCNTs subject to various degrees of the Bingel reaction. Labelling in (b): trace (a) pristine SWCNTs; trace (b) SWCNTs with carboxyl groups; trace (c) SWCNTs with amide groups attached at open ends; trace (d) SWCNTs after Bingel reaction without microwave; trace (e)-(g) SWCNTs after Bingel reaction with microwave power of 40 W, 50 W and 60 W, respectively. (Figures adapted from Ref. 41).....	41
Figure 2.18 Absorption spectra of SWCNTs subject to dichlorocarbene functionalization. (Figure adapted from Ref. 42)	42
Figure 3.1 Binding energy vs. SWCNT diameter (Data used in this graphs is based on the calculation results in Ref. 46).	47
Figure 3.2 SEM image of a typical as-grown SWCNT on Si/SiO ₂ substrate..	49
Figure 3.3 SEM Image of a pair of metal pads deposited on the as-grown SWCNT.....	50
Figure 3.4 Raman shift for a SWCNT on Si/SiO ₂ substrate under 532 nm lasers.....	51
Figure 3.5 Raman D band and G band intensities under different degree of functionalization with G band intensities scaled by a factor of 0.1.....	53
Figure 3.6 SEM (a), Raman mapping (b) and AFM Image (c) of an as fabricated device before the reaction. (Figures adapted from Ref. 68).....	54
Figure 3.7 Reaction scheme for dichlorocarbene functionalization of SWNT.	56
Figure 3.8 Raman scattering of two metallic SWCNTs with various bands. (a) RBM band of SWCNT-1. (b) D band and G band of SWCNT-1. (c) RBM band	

of SWCNT-2. (d) D band and G band of SWCNT-2. (Figures adapted from Ref. 68).	57
Figure 3.9 Raman scattering of two semiconducting SWCNTs with various bands. (a) RBM band of SWCNT-3. (b) D band and G band of SWCNT-3. (c) RBM band of SWCNT-3. (d) D band and G band of SWCNT-3. (Figures adapted from Ref. 68).	59
Figure 3.10 Comparison of Raman G band intensities of SWCNT-1 to -4 (a to d). Raman intensities are normalized to the silicon peak $\sim 520 \text{ cm}^{-1}$. (Figures adapted from Ref. 68).	61
Figure 3.11 Raman G band intensity drops versus SWCNT Diameters.	62
Figure 4.1 Diameter effect on [2+1] cycloaddition induced sidewall C-C opening in armchair SWCNTs. The label "O" refers to orthogonal configuration and the letter "S" refers to skewed configuration (Figures adapted from Ref. 24).	67
Figure 4.2 Carbon bond lengths versus index of zigzag semiconducting SWCNTs. (Figure adapted from Ref. 31).	69
Figure 4.3 SEM Image of as-grown SWCNTs with SiO_2 markers.	70
Figure 4.4 Fabrication process flow of the SWCNT FET device for conductance measurement subject to dichlorocarbene functionalization.	71
Figure 4.5 Illustration of various elements of a SWCNT FET platform.	73
Figure 4.6 Transfer characteristic of SWCNT FET with metallic (a), semi-metallic (b) and semiconducting (c) SWCNTs and their respective band diagram illustrations.	75
Figure 4.7 Raman spectra and electrical response comparisons of two m-SWNTs with different diameters before and after the functionalization. (a) RBM band comparison of SWNT-A. (b) D/G ratio comparison of SWNT-A. (c) Electrical response comparison of SWNT-A. (d) RBM band comparison of SWNT-B. (e) D/G ratio comparison of SWNT-B. (f) Electrical response comparison of SWNT-B. (Figures adapted from Ref. 68).	78

Figure 4.8 Electrical conductivity comparison of a metallic tube before and after [2+3] cycloaddition functionalization. (a) Raman spectra comparison of the SWCNT before and after [2+3] cycloaddition. (b) Electrical conductance comparison before and after [2+3] cycloaddition.....81

Figure 4.9 Raman spectra and electrical response comparisons of two s-SWNTs with different diameter before and after the functionalization. (a) RBM band comparison of SWNT-C. (b) D/G ratio comparison of SWNT-C. (c) Electrical response comparison of SWNT-C. (d) RBM band comparison of SWNT-D. (e) D/G ratio comparison of SWNT-D. (f) Electrical response comparison of SWNT-D. (Figures adapted from Ref. 68).....82

Figure 5.1 Illustration of EFM working principle. As shown in the figure, EFM is conducted in a double pass process. In the first pass, a standard ac-air mode (tapping mode) is implemented to obtain the topographical image of the sample. In the second path, the tip is biased with a constant voltage and lifted at a constant height, z , and then scans over the topographical profile obtained in the first path.....89

Figure 5.2 Experimental procedure of EFM and Raman characterization of the SWCNT before and after functionalization.....91

Figure 5.3 SEM Imaging of pristine SWCNT with different diameters and electronic types. (a) Topographical image. (b) EFM image. (c) EFM signal at the cross section shown in (b). (d) Topographical image. (e) EFM image. (f) EFM signal at the cross section shown in (e).....94

Figure 5.4 EFM signal comparison before and after the Prato reaction. (a) Topographical image of a metallic SWCNT in pristine state. (b) EFM image of the pristine tube. (c) EFM phase values at the cross line shown in (b). (d) Raman spectroscopy of the SWCNT in pristine state. (e) Topographical image of a metallic SWCNT after Prato reaction. (f) EFM image of the SWCNT after Prato reaction. (g) EFM phase values at the cross line shown in (f). (h) Raman spectroscopy of the SWCNT after Prato reaction. (i) EFM phase comparison of the SWCNT before and after Prato reaction with ten sampling point taken at equal distance along the SWCNT.....96

Figure 5.5 EFM signal comparison before and after the dichlorocarbene functionalization. (a) Topographical image of a metallic SWCNT in pristine

state. (b) EFM image of the pristine tube. (c) EFM phase values at the cross line shown in (b). (d) Raman spectroscopy of the SWCNT in pristine state. (e) Topographical image of a metallic SWCNT after dichlorocarbene functionalization. (f) EFM image of the SWCNT after Prato reaction. (g) EFM phase values at the cross line shown in (f). (h) Raman spectroscopy of the SWCNT after dichlorocarbene functionalization. (i) EFM phase comparison of the SWCNT before and after dichlorocarbene functionalization with ten sampling point taken at equal distance along the SWCNT.....98

Figure 6.1 DFM working principle (a) Illustration of DFM setup (b) Band structure influenced by the gate voltage applied. (Figure 6.1b adapted from Ref. 107).103

Figure 6.2 DFM images of a SWCNT (a) topography image (b) phase image (c) ω component of phase image (d) 2ω component of phase image.107

Figure 6.3 Demonstration DFM image of three SWCNTs. (a) topography image of SWCNT-A. (b-d) 2ω component of phase image obtained with DC bias of -1.5V, 0V and +1.5V, respectively. (e) Raman scattering of SWCNT-A. (f) topography image of SWCNT-B. (g-i) 2ω component of phase image obtained with DC bias of -1.5V, 0V and +1.5V, respectively. (j) Raman scattering of SWCNT-B. (k) topography image of SWCNT-C. (l-n) 2ω component of phase image obtained with DC bias of -1.5V, 0V and +1.5V, respectively. (o) Raman scattering of SWCNT-C. (Figures adapted from Ref. 116).....110

Figure 6.4 Comparison of EFM and DFM signals of metallic SWCNT-1 before and after the Prato reaction. (a) Topography image of SWCNT-1 in pristine state. (b) EFM image of SWCNT-1 in pristine state. (c-e) DFM images of pristine SWCNT-1 at gate voltage of -1.5V, 0V and +1.5V, respectively. (f) Raman spectra (normalized to G band) of pristine SWCNT-1. (g) Topography image of SWCNT-1 after the Prato reaction. (h) EFM image of SWCNT-1 after the Prato reaction. (i-k) DFM images of SWCNT-1 functionalized with the Prato reaction at gate voltage of -1.5V, 0V and +1.5V, respectively. (l) Raman spectra (normalized to G band) of the SWCNT-1 functionalized with the Prato reaction. (m) Comparison plot of EFM signals of SWCNT-1 before and after the Prato reaction with 10 data points taken at equal distance of the EFM image shown in (b). (n) Comparison plot of DFM signals of SWCNT-1 before

and after the Prato reaction at different gate voltages. (Figures adapted from Ref. 116).112

Figure 6.5 Comparison of EFM and DFM signals of metallic SWCNT-2 before and after dichlorocarbene functionalization. (a) Topography image of SWCNT-2 in pristine state. (b) EFM image of SWCNT-2 in pristine state. (c-e) DFM images of pristine SWCNT-2 at gate voltage of -1.5V, 0V and +1.5V, respectively. (f) Raman spectra (normalized to G band) of pristine SWCNT-2. (g) Topography image of SWCNT-2 after dichlorocarbene functionalization. (h) EFM image of SWCNT-2 after dichlorocarbene functionalization. (i-k) DFM images of dichlorocarbene functionalized SWCNT-2 at gate voltage of -1.5V, 0V and +1.5V, respectively. (l) Raman spectra (normalized to G band) of dichlorocarbene functionalized SWCNT-2. (m) Comparison plot of EFM signals of SWCNT-2 before and after dichlorocarbene functionalization with 10 data points taken at equal distance of the EFM image shown in (b). (n) Comparison plot of DFM signals of SWCNT-2 before and after dichlorocarbene functionalization at different gate voltages. (Figures adapted from Ref. 116).114

Figure 6.6 EFM and DFM modulation plot of metallic SWCNTs subject to dichlorocarbene functionalization (represented by triangles) and the Prato reaction (represented by squares), respectively. (Figures adapted from Ref. 116).116

Figure 6.7 Statistical Plot of EFM signal preservation and DFM modulation ratios with sampling points taken on all metallic SWCNTs every 1 μm distance. (a) EFM preservation ratio of SWCNTs subject to [2+3] cycloaddition. (b) DFM modulation ratio of SWCNTs subject to [2+3] cycloaddition. (c) EFM preservation ratio of SWCNTs subject to [2+1] cycloaddition. (d) DFM modulation ratio of SWCNTs subject to [2+1] cycloaddition.117

Figure 6.8 EFM and DFM characterization of partially functionalized SWCNT-3 and SWCNT-4. (a) Topography image of SWCNT-3 with the lower portion (separated by the dash line) functionalized with dichlorocarbene functionalization while the upper part intact. (b) EFM image of SWCNT-3. (c-e) DFM images of SWCNT-3 under gate voltage of -1.5V, 0V and +1.5V, respectively. (f) Raman mapping of G band intensity of SWCNT-3 and the typical Raman spectra taken from the pristine (g) and functionalized (h)

portions of SWCNT-3. (i) Topography image of SWCNT-4 with lower portion (separated by the dash line) functionalized by the Prato reaction. (j) EFM image of SWCNT-4. (k-m) DFM images of SWCNT-4 under gate voltage of -1.5V, 0V and +1.5V, respectively. (n) Raman mapping of G band intensity of SWCNT-4 and the typical Raman spectra taken from the pristine (o) and functionalized (p) portions of SWCNT-4. (Figures adapted from Ref. 116). 118

Figure 7.1 Schematic illustrations of the proposed resultant structures of four [2+1] cycloaddition functionalizations.....126

Figure 7.2 Averaged Raman spectra (under 532 nm laser excitation) comparisons of SWCNT network Devices A1, A2, B1 and B2 before and after [2+1] cycloaddition functionalizations.....128

Figure 7.3 Transfer characteristic of SWCNT network FET devices before and after the four [2+1] cycloaddition functionalizations.....129

Figure 7.4 Normalized conductances of SWCNT network samples at different humidity levels.....132

Figure 7.5 Resistive responses of Devices S1, S2 and S5 subjected to humidity switching between RH=10% and RH=30% at 30 s intervals.135

Figure 7.6 Resistive responses of Devices S1, S2 and S5 subjected to humidity switching between RH=30% and RH=65% at 30 s intervals.135

Figure A1 Comparison of RBM before (Red) and after (Blue) reaction under 532 nm laser.....161

Figure A2 Comparison of RBM before (Red) and after (Blue) reaction under 488 nm laser.....162

Figure B1 AFM image of SWCNT FET with only the middle portion of the SWCNT channel exposed.163

Figure B2 Electrical conductance of the SWCNT FET shown in Figure B1 before and after the dichlorocarbene functionalization.....163

Figure C1 Comparison of 2ω component of DFM signal ($V_{dc}=0V$) taken from deflection signal of the cantilever with its resonance turned off and the phase signal with cantilever resonance turned on.164

Figure C2 2ω component of the phase image obtained to calibrate the cantilever.....	165
Figure C3 2ω component of the phase of the substrate at different gate voltages.....	166
Figure C4 Phase image of DFM at $V_g = -3V, -6V, +3V$ and $+6V$	167
Figure D1 EFM comparison of semiconducting SWCNTs before and after dichlorocarbene addition.....	168
Figure D2 DFM comparison of semiconducting SWCNTs before and after dichlorocarbene addition.....	168
Figure E1 Typical Raman spectra of dichlorocarbene functionalized bulk SWCNTs at degree of about 0.1%, 0.5%, 1.5%, 3%, 5% and 10% (calibrated by EDX).....	169
Figure E2 Comparison of the Raman intensities (normalized to silicon peak) of dichlorocarbene functionalized bulk SWCNTs at degree of 0.5%, 3% and 10%, respectively.	170
Figure E3 Raman D-band and G-band intensity versus various different degrees of dichlorocarbene functionalizations.	170

Chapter 1 Introduction

The motivation behind this PhD project is to study the physical phenomena associated with the C-C bond broken on the sidewall of single-walled carbon nanotubes (SWCNTs) upon covalent [2+1] cycloaddition functionalization. It had been predicted that the C-C bond broken could recover the sp^2 hybridizations and thus preserve the remarkable electrical conductivity and electronic band structure of the nanotubes [24]. The basic knowledge of the structural properties and electronic properties of SWCNTs is introduced in this chapter. Covalent sidewall functionalizations to SWCNTs and their influences on the electronic property of SWCNTs are also discussed. The status of the research and the main challenges in this field are then presented. Finally, an overview of each chapter is provided.

1.1 Single-Walled Carbon Nanotubes and Their Electronic Properties

Carbon nanotubes (CNTs) are cylinder like nanomaterials which could be considered as a rolling up of thin graphite sheets, and their sidewalls are hexagon lattices composed by sp^2 hybridized carbon atoms [1]. The diameter of CNTs could vary from sub-nanometer to hundreds of nanometers and their lengths could vary from sub-micron to a few millimeters depending on the synthesis methods and conditions [1]. Over the last decades, CNTs have attracted tremendous attentions of scientists due to their excellent electrical conductance, mechanical strength and etc. [2-4]. In particular, SWCNTs have attracted extraordinary attentions in both fundamental studies and applications due to its unique structural dependent properties [1,3]. CNTs can be easily found to be used in field-effect transistors [4], sensors [5], gas storage material [6], field-emission devices [7], catalyst support [8], probes for scanning probe microscopy [9] and components in high-performance composites [10] etc.

Based on the number of graphene layers to be rolled up, CNTs could be classified into SWCNT (Figure 1.1a), double-walled CNT (DWCNT) (Figure 1.1b), and multiple-walled CNT (MWCNT) (Figure 1.1c).

Figure 1.1 Illustration of the structures of a SWCNT (a), DWCNT (b) and MWCNT (c).

As shown in Figure 1.1a, SWCNTs are the simplest form of CNTs which are considered to be rolled up from a single layer graphene sheet, and their diameters are generally observed between 0.4-3 nm [11,12]. The most attractive feature of SWCNTs lies in their apparent structural dependent properties. For instance, SWCNTs could be purely metallic or apparent semiconducting by just a little difference in their rolling-up angle (or chirality angle) [3]. Tremendous efforts have been undertaken to explore the fundamental properties as well as applications of SWCNTs.

1.1.1 SWCNT Structure

Since SWCNTs could be regarded as rolling up single layer graphene sheets from different angles, a set of vectors could be assigned to identify the SWCNTs formed. Figure 1.2 shows a graphene sheet with directional vectors of the rolling up directions to form SWCNTs.

Figure 1.2 Illustration of the unrolled graphene lattice of a SWCNT with vectors assigned.

As shown in Figure 1.2, a_0 represents the C-C bond length of the unrolled graphene. It is worth noting that the resultant C-C bond length of SWCNT formed is actually slightly larger than a_0 because of the elongation of the C-C bonds by the curvature induced strains in SWCNTs [13]. The primitive lattice vectors of the graphene sheet are shown as $\mathbf{a}_1$ and $\mathbf{a}_2$ in the Figure 1.2, and all SWCNTs could be described by two integer indexes m and n . Therefore, with m and n specified, the SWCNT is conventionally called a (m,n) SWCNT, and all the rest parameters of the SWCNT could thus be defined.

The unit vector length could be expressed as $|\mathbf{a}_1| = |\mathbf{a}_2| = \sqrt{3}a_0$. The chiral vector $\mathbf{OA}$ shows the direction that SWCNT is rolled up, and thus the length

of **OA** equals the circumference of the SWCNT which could be expressed by below equation.

$$|\mathbf{OA}| = \left| \frac{3a_0}{2}(n+m)\mathbf{x} + \frac{\sqrt{3}a_0}{2}(n-m)\mathbf{y} \right| = a_0\sqrt{3(n^2+nm+m^2)} \quad (1.1)$$

Thus the diameter of the SWCNT, D , could be expressed as

$$D = \frac{a_0\sqrt{3(n^2+nm+m^2)}}{\pi} \quad (1.2)$$

The translational vector **T** which is perpendicular to the chiral vector **OA** represents the direction of the SWCNT axis. The translational vector **T** and the chiral vector **OA** thus form the unit cell of the SWCNT. The angle θ between the chiral vector and $\mathbf{a}_1$ or $\mathbf{a}_2$ is generally called chirality angle which could be obtained from the indexes m and n through below expression.

$$\cos \theta = \frac{2n+m}{2\sqrt{n^2+m^2+nm}} \quad (1.3)$$

Although the value of the chirality angle θ could be beyond 30° , it is generally taken to be less than 30° because of the periodic nature of graphene lattice.

Theoretically, there could be infinity number of ways to roll up a graphene sheet. In order to better classify SWCNTs by their structures, it is by convention to name those SWCNTs with $m=n$ as “armchair” SWCNTs, and those SWCNTs with $n=0$ (or $m=0$) as “zigzag” SWCNTs. SWCNTs with all other indexes are classified as “chiral” SWCNTs. Below Figure 1.3 shows the structures of three SWCNTs with the three different types of SWCNTs, respectively.

Figure 1.3 Illustration of the structures of a (8,8) armchair SWCNT (a), a (12,0) zigzag SWCNT (b) and a (10,2) chiral SWCNT (c).

1.1.2 Electronic Properties of SWCNTs

The electronic properties of SWCNTs depend uniquely on their geometry structures. Theoretical calculation suggests that the electronic type of SWCNT could also be classified by their chiral vector indexes m and n . All armchair SWCNTs where $m=n$ are metallic [14] with no energy band gaps, behaving like a piece of metal. For non-armchair SWCNTs, if $m-n$ is an integer multiple of 3, they are called semi-metallic SWCNTs and they have very tiny band gaps. Otherwise, the SWCNTs are semiconducting SWCNTs with apparent energy band gaps [14].

Electronic band structures of SWCNTs can be obtained from the two-dimensional band structure of graphene subject to periodic boundary

conditions. Figure 1.4 shows the quantization of wave states around a graphene cylinder.

Figure 1.4 Quantization of wave states around a graphene cylinder. (a) Wavevectors (k) parallel and perpendicular to the axes of a SWCNT. (b) Contour plot of graphene valence states for a SWCNT with chiral angle $\theta = 0$. The parallel lines indicate the allowed k by the cylindrical boundary condition. (c) Electron states near Fermi Level are defined by the intersection of allowed k with the dispersion cones at the K points. (Figures adapted from Ref. 15).

As SWCNTs have very small diameters, typically less than 3 nm [12], their wave vectors around the nanotube circumference ($k_{\perp}$ in Figure 1.4a) are quantized. Therefore the allowed wavevectors of SWCNT are presented as discrete lines in reciprocal space of a graphene (Figure 1.4b). As a result, for SWCNTs, their one dimensional electronic band structures should be a superposition of all the allowed k lines of graphene electronic bands (see Figure 1.4c).

It is manifested from Figure 1.4c that these allowed k lines of a SWCNT crossing the upper and lower cones in graphene band structure determines the band gap of the SWCNT. Figure 1.5 shows the resultant band structure of SWCNTs with a general index (m,n) .

Figure 1.5 Different alignments between the dispersion cones and the allowed k lines of SWCNTs. (a) If $p=0$, the k line intersection with K point, and this SWCNT is metallic. (b) If $p=1$, the K point and the nearest k line is misaligned, and a band gap is presented. The SWCNT is thus semiconducting. (c) If $p=-1$, the K point and the nearest k line is misaligned, and a band gap is presented. The SWCNT is thus semiconducting. (Figures adapted from Ref.15).

For a given index, m and n , the difference between m and n could always be written as $m-n=3q+p$, where q is an integer, p could have the value of -1, 0 or 1. All the SWCNTs fall into these three families and the number p defines the type of the alignment between the allowed $\mathbf{k}$ lines and the K points as shown in Figure 1.5. If $p=0$ (Figure 1.5a), the $\mathbf{k}$ line intersects with the K point and thus no band gap is presented and the SWCNT is metallic. If $p=-1$ (Figure 1.5b) or $+1$ (Figure 1.5c), the K point and the nearest allowed $\mathbf{k}$ lines are misaligned, and thus the 1-D subbands have a band gap, resulting semiconducting SWCNTs.

The energy band structures shown in Figures 1.4 and 1.5 are calculated based on tight-binding method with linear combination of atomic orbitals [15]. More completed band structures of SWCNTs could be obtained from various kind of simulations. Figure 1.6 shows an example of the band structure, quantum conductance and DOS of a (5,5) armchair SWCNTs by MLWFs (Maximally Localized Wannier Functions) approach.

Figure 1.6 Band structure, quantum conductance, and density of states of a (5,5) CNT as calculated in the based on Maximally Localized Wannier Functions (solid lines), and compared with the results of a full diagonalization (circles). (Figure adapted from Ref. 16).

Another interesting electronic property of SWCNTs, the electrical conductivity, is demonstrated to be much higher than conventional metallic nanowires (with comparable diameters) due to the reduced scattering and extremely large mean free path (ballistic transport) in pristine SWCNTs [4,17-18]. Theoretical calculation by White et al. [17] suggested that the exceptional ballistic transport property and a localization length of over 10 μm could be reached for SWCNTs with diameter typically produced experimentally. Experimental result by Kong et al. [18] showed that the conductance of SWCNTs built on a conventional field-effect transistor (FET) structure could approach the quantum limit $2G_0 = 4e^2/h$. High-performance ballistic nanotube FETs were

also realized by Dai et al. [4] using palladium as the contact as shown in Figure 1.7.

Figure 1.7 Pd-contacted long (3 μm) and short (0.3 μm) back-gated SWNT devices formed on the same nanotubes on SiO₂/Si substrate. (a) SEM (left) and AFM (right) of the device. (b) Transconductance versus gate voltage of the long device at different temperatures. (c) Transconductance versus gate voltage of the short device at different temperatures. (d) On state transconductance of the short device versus temperature. (Figures adapted from Ref. 4).

1.2 Covalent Functionalizations to the Sidewall of SWCNTs

In spite of the interesting electronic properties, SWCNTs are notoriously insoluble and hard to disperse, and thus difficult to be handled and processed

for practical applications. Attaching functional groups to the pristine SWCNT surface would be an important measure to overcome the problem.

Functionalizations to the sidewall of SWCNTs could be classified into two major categories, i.e., covalent functionalization and non-covalent functionalization, according to their different attachment natures [19]. Covalent functionalization refers to the cases where the attached groups have one or more atoms covalently bonded (See Figure 1.8a) to the sp^2 hybridized sidewall carbon atoms, while non-covalent functionalization refers to the cases where the attachment groups are decorated or wrapped (See Figure 1.8b) on the SWCNT sidewalls generally through Van der Waals interactions.

Figure 1.8 Illustration of covalent (a) and non-covalent (b) functionalization to the sidewall of SWCNTs. (Figures adapted from Ref. 19).

Covalent functionalization has remarkable potential to provide a higher degree of tunability of SWCNT properties compared with methods based on non-covalent functionalizations [20]. For SWCNTs to be used as solar energy and biology applications etc., covalent modifications to their sidewalls are generally required to make them more amenable to rational and predictable manipulations [20]. Thus, although SWCNTs are generally considered chemically stable, numerous types of covalent functionalities have been

developed utilizing strong acids, plasmas, and other highly active species [21].

Figure 1.9 briefly summarizes the types of covalent functionalizations that have been developed.

Figure 1.9 Different types of sidewall covalent functionalizations to SWCNTs (Figure adapted from Ref. 20).

As shown in Figure 1.9, most types of sidewall covalent functionalization are either monovalent (here referring to each of the attached molecule is covalently bonded to a single carbon atom on the sidewall of SWCNT) or divalent (here referring to each of the attached molecule is covalently bonded to two adjacent carbon atoms on the sidewall of SWCNT) functionalizations. In divalent functionalizations, SWCNT sidewall carbon atoms participating in the covalent functionalization will normally combine with the attached groups, forming of a cyclic adduct. Depending on the backbone size of the participants forming the covalent ring structure, these divalent functionalizations are commonly referred as the $[m+n]$ cycloadditions. For example, the dichlorocarbene addition shown in Figure 1.9 is regarded as $[2+1]$ cycloaddition because the resultant three-member ring structure contains two carbon atoms from the SWCNT and one carbon atom from the dichlorocarbene group.

1.3 Main Challenges in Covalent Functionalizations on SWCNTs

One of the major drawbacks of covalent functionalization is that the sp^3 rehybridization formed on SWCNT sidewall play a role of scattering centre which significantly degrade the remarkable electrical and electronic properties (conductance, electronic band structure) of SWCNTs. For instance, the electrical conductance drops by most covalent functionalizations were found to be several orders of magnitude [22], which largely limit the applications of covalent chemistry for SWCNTs, especially in the field such as interconnects that utilize the nearly ballistic transport characteristic of SWCNTs. Moreover, the electronic band structures of SWCNTs were also significantly destroyed by the sp^3 rehybridizations formed on their sidewalls [23].

In light of these problems, several theorists [24,25] suggested that a special class of covalent functionalization, [2+1] cycloaddition, to SWCNT sidewalls could break the sidewall C-C bond and recover the pristine sp^2 hybridizations, resulting in a preservation of the SWCNT conductance. Experimental work by Chao Liu et al. [26] demonstrated that the electrical conductance of a metallic SWCNT (with diameter ~ 1.8 nm by AFM measurement) only drop about 50% even upon significant degree of dichlorocarbene functionalization ([2+1] cycloaddition). In contrast, similar degree of hydrogenation (monovalent functionalization) to the metallic SWCNT could cause significant conductance degradation [26].

However, the curvature induced sidewall opening effect was suggested to be largely controlled by the diameter of the SWCNTs and thus only small-diameter tubes were considered to have their sidewall carbon bonds broken up on [2+1] cycloaddition [24]. Thus it would be significant to study if the conductance preservation effect by [2+1] cycloaddition is valid for most experimentally synthesized SWCNTs that have a typical diameter range of ~ 1 -2 nm. Moreover, [2+1] cycloaddition was also expected to be more easily realized on small-diameter tubes as they have larger strain energy release upon the sidewall C-C opening [27]. Thus, observing the diameter dependent reactivity of SWCNTs upon [2+1] cycloaddition become a necessary support to the predicted sidewall C-C bond opening phenomena. In addition, [2+1] cycloaddition to the sidewall of SWCNTs with sp^2 hybridization recovery is expected to also preserve the intrinsic electronic band structures of SWCNTs, while conventional covalent functionalizations with sp^3 hybridizations on the sidewall of SWCNTs significantly perturb their band structures [28]. However, no experimental work had been reported on such comparison.

1.4 Objectives

The main objectives of this thesis are

- To observe the SWCNTs diameter effect on their reactivities upon dichlorocarbene functionalization
- To investigate the influences of dichlorocarbene functionalization on the electrical conductance of individual as-grown SWCNTs with diameter range of 1.2-2.2 nm
- To investigate the electronic structure and local conductivity of SWCNTs affected by dichlorocarbene functionalization ([2+1] cycloaddition) and the Prato reaction ([2+3] cycloaddition)

1.5 Major Contributions

- Experimentally demonstrated the diameter dependent reactivity of SWCNTs upon dichlorocarbene functionalization, regardless metallic or semiconducting SWCNTs. This phenomenon is a further support of the theoretical prediction that the sidewall C-C bond of the SWCNTs could be broken upon [2+1] cycloaddition.
- Experimentally confirmed that SWCNTs with diameter range of 1.2-2.2 nm have their conductance largely preserved upon significant degree of dichlorocarbene functionalizations. This result suggests that [2+1] cycloaddition could be an excellent choice to functionalize and handle SWCNTs over a large diameter range with their electrical conductances largely unaffected.
- Experimentally observed that the electronic property (band structure, longitudinal polarizability) and local conductivity of metallic SWCNTs are largely preserved upon [2+1] cycloaddition, while significantly

degraded upon [2+3] cycloaddition. This result suggests that the resultant covalent configurations (sp^2 or sp^3 rehybridization) on the sidewall of SWCNTs play a fundamental role in the overall electronic properties of the functionalized SWCNTs.

- Dielectric force microscopy (DFM) technique is demonstrated in this work to be a powerful tool to probe the gate dependent local electronic properties of SWCNTs.
- SWCNT networks functionalized by [2+1] cycloaddition with certain chemical groups are shown to have much larger resistive responses to humidity as compared to pristine SWCNT networks.

1.6 Thesis Organization

This thesis is organized in the following way:

Chapter 2 provides a brief literature review on the theoretical and experimental works on the influences of the sidewall covalent configurations on the electrical and electronic properties of SWCNTs. Chapter 3 presents the experimental observations on the influences of the diameter on the reactivity of SWCNTs. Chapter 4 addresses the electrical conductance of individual small-diameter and large-diameter SWCNTs influenced by [2+1] cycloadditions. The local electronic properties of covalently functionalized SWCNTs characterized utilizing electrostatic force microscopy (EFM) and dielectric force microscopy (DFM) are presented in Chapters 5 and 6, respectively. In Chapter 7, electrical characteristics of SWCNT networks are tested upon various [2+1] cycloadditions, and the functionalized SWCNT networks are further tested on their resistive responses to humidity changes. Finally, Chapter 8 summarizes the major findings in this PhD project and provides an outlook of the applications of [2+1] cycloaddition of SWCNTs.

Chapter 2 Review of Electrical Properties of SWCNTs Influenced by Sidewall Covalent Functionalizations

This chapter provides a literature review of the theoretical and experimental works on the electrical conductances and electronic states of SWCNTs influenced by the sidewall C-C bond rehybridizations upon covalent functionalizations.

2.1 Electrical Conductance of SWCNTs Influenced by Sidewall Covalent Functionalizations

2.1.1 Theoretical Predictions on the Electrical Conductance of SWCNTs Influenced by Sidewall Covalent Functionalizations

Covalent functionalizations to SWCNTs are generally considered to saturate their sidewall carbon atoms, resulting in sp^3 rehybridizations. However it has been suggested that, in some special cases like [2+1] cycloaddition, the strain induced sidewall C-C bond broken could recover the sp^2 rehybridizations [29]. Since the extraordinary ballistic transport property of SWCNTs originates from the periodic sp^2 hybridized carbon network, broken or intact sidewall bonds would have a significant influence on the electronic transport properties of SWCNTs [24]. The configurations of a sp^2 and sp^3 rehybridizations formed on the sidewall of SWCNTs are illustrated in Figure 2.1a and Figure 2.1b, respectively.

Figure 2.1 Illustration of sp^2 and sp^3 rehybridizations formed on the sidewall of SWCNTs. (a) Sidewall [2+1] cycloaddition with sp^2 rehybridization formed from sidewall carbon bond broken (red dash line). (b) Sidewall [2+3] cycloaddition with sp^3 rehybridization formed.

Lee and Marzari [24] systematically compared the sidewall C-C bond broken and its influences on the quantum transport properties of metallic SWCNTs upon [2+1] cycloaddition. They firstly studied the grafting stability of different covalent configurations and the results show that [2+1] cycloaddition on armchair SWCNTs always preferentially attached to the orthogonal carbon bonds (as shown in Figure 2.2b), rather than a skew carbon bonds (as shown in Figure 2.2a), with respect to the tube axis. Potential energy versus the C-C bond length (d_{16} in Figure 2.2c) plot shows that, for armchair SWCNTs with diameter small than certain critical value, more stable states were found to be associated with a carbon bond length of about 2.2 Å, which is significantly larger than usual C-C distance (~1.54 Å in diamond and ~1.42 Å in graphite), clearly indicating a sidewall C-C bond broken.

Figure 2.2 Demonstrations of dichlorocarbene attached to the sidewall of a (5,5) armchair SWCNT in skew (a), closed (b) and open (c) configurations and their corresponding quantum conductances (d). (Figures adapted from Ref. 24)

Quantum conductance of a (5,5) armchair SWCNTs was then studied with the sidewall carbon bonds open and close configurations. As shown in Figure 2.2d, the quantum conductance of the (5,5) SWCNT could almost be unaffected by a single CCl_2 group grafted in open configuration, and even after adding 30 groups on the central 43 nm segment of an infinite nanotube the conductance was reduced by only 25% with open configuration (blue line in Figure 2.2d). However, if the sidewall carbon bonds were forced to be configured in closed form, the quantum conductance would drop drastically (red line in Figure 2.2d).

Similar phenomena had been demonstrated by Lopez-Bezanilla et al. [25] in their calculations of quantum transport in covalently functionalized metallic SWCNTs with length reaching micrometre scale and random distributions of functional groups. Their calculation results showed that for a 300 nm long (10,10) metallic SWCNT with only less than 40 phenyl groups (covalently attached with sp^3 rehybridization), the quantum conductance could drop significantly (the quantum conductance even approaches zero at ~ 0.7 eV away from the Fermi level as shown in Figure 2.3a). In sharp contrast, a 1000 nm long (10,10) metallic SWCNT with up to 300 carbene groups (covalently attached in sp^2 rehybridization) only had its quantum conductance decreased modestly near its Fermi level (see Figure 2.3b).

Figure 2.3 Quantum conductances of SWCNTs with covalent functionalities. (a) Quantum conductance of 300 nm long (6,6) and (10,10) SWCNTs functionalized with paired phenyl groups (b) Quantum conductance of 1000 nm long (6,6) and (10,10) SWCNTs functionalized with carbene. (Figures adapted from Ref. 25).

Figure 2.4 shows another work by Park et al. [30] on the quantum conductance change of a (6,6) SWCNTs upon monovalent and divalent functionalization. Their simulation results clearly showed that the quantum conductance of the tube dropped dramatically even at a small degree of monovalent functionalization. In sharp contrast, the quantum conductance of dichlorocarbene functionalized SWCNTs were largely preserved even at high modification ratios.

Figure 2.4 Quantum conductances at the Fermi level versus covalent functionalization levels for monovalent (-F) and divalent (>CCl₂) functionalized (6,6) SWCNT with sidewall opening. (Figure adapted from Ref. 30).

The sidewall C-C broken was also predicted to occur in a general chirality SWCNT provided there were carbon bonds experiencing enough strain.

Calculation results by Lee and Marzari [24] and Lopez et al. [31] suggested that the C-C bonds with largest angle with respect to the tube axis could be more active towards the [2+1] adsorption as they experienced most of the tube curvature. As observed by Lopez et al. [31] in the case of zigzag tubes with [2+1] cycloaddition (:CH_2) on the most orthogonal configuration, there also existed an open to close transition for a (15,0) tube. The quantum conductances of semiconducting SWCNTs with open and close configurations were also compared by Lopez et al. [31]. Figure 2.5 shows the quantum conductance of two covalently functionalized 1 μm long zigzag SWCNTs with chirality (10,0), and (22,0) where the CH_2 groups were expected to be grafted to them in open and close configuration, respectively. The conductance of both SWCNTs with 1, 25, 50 and 100 CH_2 groups randomly grafted on the most orthogonal bonds were calculated. As seen in Figure 2.5, for a single grafted CH_2 group, the scattering could be negligible for the (10,0), but it became significant for the (22,0) tube. This initial difference was then amplified with more CH_2 groups added. For 100 CH_2 groups added, it was noticed that the quantum conductance of the (10,0) tube could be preserved more than 80% near the band edges, while the quantum conductance of the (22,0) tube was shown to be downgraded by more than 80% near the band edges (see blue line in Figure 2.5).

Figure 2.5 Quantum conductances of long semiconducting SWCNTs under different degree of CH₂ functionalizations. The (10,0) SWCNT is subject to sidewall carbon bond open upon the functionalization while the (20,0) SWCNT is subject to sidewall carbon bond close upon the functionalization. (Figures adapted from Ref. 31)

2.1.2 Experimental Observations on the Electrical Conductance of SWCNTs Influenced by Sidewall Covalent Functionalizations

Many experimental findings also confirmed the significant conductance drop of metallic SWCNTs upon covalent functionalizations with sp^3 rehybridizations. In-situ electrical resistivity measurement conducted by Cui et al. [32] revealed that the osmylation reaction of OsO₄ with the sidewall of metallic SWCNTs ([2+3] cycloaddition) decreased their conductance by up to several orders of magnitude. They attributed the resistance increase to the formation of covalent bonds by the cycloaddition that reduce the π electron density. Figure 2.6 illustrates the resistance change of a metallic tube upon activation of the reaction and after removal of the OsO₄ species.

Figure 2.6 Electrical conductivity of a metallic SWCNT upon osmylation and after recovery. (a) Illustration of the [2+3] cycloaddition configuration of osmylation functionalized SWCNTs. (b) Resistance change of the metallic SWCNT subject to the osmylation and its recovery. (Figures adapted from Ref. 32)

Wang et al. [33] performed electrical measurement on a metallic SWCNT built on a conventional FET platform and their results showed that, upon 4-bromobenzene diazonium tetrafluoroborate (4-BBDT) functionalization (monovalent functionalization), the electrical conductance of a metallic tube could be dropped significantly. Figure 2.7a shows the Raman spectra of a SWCNTs at pristine level and after reaction with 4-BBDT at concentration from 1 μM to 10 μM , respectively. The increase in the Raman D band (peaks ~ 1330 cm^{-1}) to G band (peaks ~ 1580 cm^{-1}) intensity ratio indicated an increasing degree of the functionalization. The electrical conductance measurement is shown in Figure 2.7b, and it is observed that the conductance of this tube dropped more than two orders of magnitude at a relative high degree of the functionalization.

Figure 2.7 Electrical conductance of the metallic SWCNT upon 4-bromobenzene diazonium tetrafluoroborate (4-BBDT) functionalization. (a) Raman spectra of the SWCNT upon reaction with 4-BBDT in difference concentration. (b) Electrical conductivity drop of the SWCNT upon reaction with 4-BBDT in difference concentration. (Figures adapted from Ref. 33)

The significant conductance difference between covalent functionalized SWCNTs and pristine SWCNTs had also been demonstrated via thermal removal of the covalent groups attached. Figure 2.8 shows the work by Klinke et al. [34], and it could be seen that the conductance of a metallic SWCNT increased by about five orders of magnitude upon thermally removal of the monovalent attached hydroxamic acid functionalities. Moreover, the on state conductance (at $V_g = -20$ V shown in Figure 2.8) of a semiconducting SWCNT was also shown to be increased by two orders of magnitude after the removal of the covalently functionalized groups.

Figure 2.8 Conductance recoveries of metallic and semiconducting tubes after thermal annealing removal of the hydroxamic acid functionalities. (Figure adapted from Ref. 34).

Experiments had also been performed to investigate the conductance of dichlorocarbene functionalized ([2+1] cycloaddition) SWCNTs where a sidewall C-C bond open configuration was expected. Chao Liu et al. [26] demonstrated that the conductance of a metallic SWCNT (with diameter of ~ 1.8 nm by AFM height measurement) could be preserved up to $\sim 50\%$ even after significant degree of dichlorocarbene functionalization (See Figure 2.9). This experiment was based on the electrical measurement of the metallic SWCNT built on a conventional FET structure and dichlorocarbene functionalization was applied directly on the SWCNT bridging the source and drain of the FET. The conductance of the tube was also shown to be partially recovered after thermal annealing as shown in Figure 2.9.

Figure 2.9 The conductance of a metallic SWCNT upon dichlorocarbene reaction of 5 min, 35 min, and thermal annealing. (Figure adapted from Ref. 26).

In addition, the conductance of a ~ 1.7 nm semiconducting SWCNTs was found to drop significantly upon dichlorocarbene functionalization [26]. The phenomenon was attributed to the prediction that semiconducting SWCNT with diameter larger than 1.2-1.4 nm could have their sidewall C-C bonds in close configuration upon [2+1] cycloaddition [31].

However, since the conductance preservation is largely affected by the diameters of the SWCNTs, or the sidewall C-C broken, it becomes important to observe the conductance variation for [2+1] cycloaddition functionalized SWCNTs with a wide range of diameters.

2.2 Electronic Band Structure of SWCNTs Influenced by Sidewall Covalent Functionalizations

The disruption of the periodic π network on SWCNT sidewall not only affects the transport conductance, but also influences the electronic structures of SWCNTs [35]. Theoretical predictions and experimental works on the influences of covalent functionalizations on the electronic structure of SWCNTs are discussed in the following sections.

2.2.1 Theoretical Predictions on the Influences of Covalent Functionalizations to Electronic Band Structures of SWCNTs

As an extreme case, SWCNTs with all their sidewall carbon atoms saturated with sp^3 rehybridization make their atomic configurations analogue to the diamond structure that has apparent band gap. Actually, T. Yildirim et al. [35] had showed that fully hydrogenations of metallic SWCNTs could induce apparent band gap opening. According to their calculations (shown in Figure 2.10), both zigzag and armchair tubes with fully saturated C-H bonds had band gap opening of about 1.5 eV to 2.5 eV. Moreover, the resultant band gaps showed diameter dependence.

Figure 2.10 Band gaps of SWCNTs after fully hydrogenations (Figure adapted from Ref. 35).

Recent theoretical work by Ogunro et al. [36] showed that [2+2] cycloaddition of fluorinated olefins significantly affected the electronic structure of metallic SWCNTs and opened an apparent band gap. It had also been shown that the band gap opening in the [2+2] cycloaddition functionalized metallic tubes was associated with the sp^2 to sp^3 rehybridization upon the functionalization. Figure 2.11 shows their calculations on the band structure of (8,8) armchair tube at the pristine state and with PMDE and PSEPVE groups covalently attached in [2+2] cycloaddition configuration. Clearly, apparent band gap openings could be observed on the (8,8) SWCNT with the [2+2] cycloaddition functionalizations.

Figure 2.11 Band gap of a metallic (8,8) SWCNT at pristine state (a), after PMDE [2+2] cycloaddition functionalization (b) and after PSEPVE [2+2] cycloaddition functionalization (c). (Figures adapted from Ref. 36).

Simulation work by Cho et al. [37] investigated the influence of [2+3] cycloaddition on the band structure of SWCNTs. A (4,4) SWCNT upon the [2+3] cycloaddition in type-A and type-B grafting configurations (see Figure 2.12a) was shown to have apparent band gap opening (as shown in Figure 2.12b).

Figure 2.12 Band structure change of a metallic (4,4) SWCNT subject to [2+3] cycloaddition functionalization. (a) Illustration of type-A and type-B grafting configurations of the [2+3] cycloaddition. (b) Band structure of the metallic tube at pristine state, with type-A attachment and type-B attachment. (Figures adapted from Ref. 37).

In contrast, for the case of [2+1] cycloaddition with recovered sp^2 hybridizations, it was expected that the electronic band structure could be less perturbed. Theoretical calculations by Zhao et al. [28] showed that the band structure of metallic SWCNTs were almost unaffected upon low degree of dichlorocarbene functionalization ([2+1] cycloaddition) with sidewall C-C broken (shown in Figure 1.12b). However if dichlorocarbene groups were

forced to be configured in a closed three-member ring structure (unstable configuration), significant band structure changes were observed (shown in Figure 2.13c).

Figure 2.13 Band structure of a metallic (6,6) SWCNT subject to dichlorocarbene functionalization at low modification ratio. (a) Band structure of the tube at pristine state. (b) Band structure of the tube subject to low degree of dichlorocarbene [2+1] cycloaddition with sidewall carbon bonds open. (c) Band structure of the tube subject to low degree of dichlorocarbene [2+1] cycloaddition with sidewall carbon bonds in closed three-member ring configuration. (Figures adapted from Ref. 28).

At a high modification ratio, the preservation of the band structure by [2+1] cycloaddition with sidewall opening effect was also shown to be apparent. As shown in Figure 2.14b, with CCl_2 addition at the 12.5% ratio to a (6,6) metallic

SWCNT, which is considered very high experimentally, there could be only minor changes in its band structure, and the band crossing at the Fermi level was still robust and retained its metallic character [28]. Even under an extremely high degree of functionalization of 25%, only a small band ~ 0.34 eV was observed (See Figure 2.14c). This is in sharp contrast with the case of sp^3 hybridized metallic SWCNTs where a low degree of the functionalizations could induce apparent band gap opening.

Figure 2.14 Band structure of metallic (6,6) SWCNT at its pristine state (a), after 12.5% degree of dichlorocarbene functionalization (b) and after 25% degree of dichlorocarbene functionalization. (Figures adapted from Ref. 28).

However, it should be noted that even in the case where the SWCNT sidewall C-C bond open configuration is thermodynamically more stable, there are likely some dichlorocarbene groups attached to the non-orthogonal C-C bonds in experimental synthesis, which probably yield sp^3 rehybridizations. The work by Cho et al. [38] suggested that by considering of the sp^3 grafting configuration on dichlorocarbene functionalized SWCNTs, the energy gap of

the metallic nanotube opened up over the whole range of modification ratio. Therefore, the band gap of [2+1] cycloaddition functionalized SWCNTs were also expected to be affected by the ratio between the sp^2 grafting and sp^3 grafting configurations.

2.2.2 Experimental Observations of the Influence of Covalent Functionalizations on Electronic Band Structures of SWCNTs

The band structure change of SWCNTs upon covalent functionalization had been observed in many experimental works. In SWCNT network FET devices, many groups have selectively attached covalent groups to those metallic SWCNTs and thus increased on/off ratios were generally observed. This could be partially attributed to the band gap opening of metallic SWCNTs upon the functionalizations [22].

The band gap opening of m-SWCNTs was also observed experimentally by Zheng et al. [39] with an in situ electrical measurement on the gate dependent conductivity of metallic SWCNT upon hydrogen plasma treatment. As shown in Figure 2.15, after 100 seconds (lowest curve) of hydrogen plasma treatment, the on/off ratio of this metallic SWCNT increased to about two orders of magnitude, implying a strong semiconducting behaviour. At the same time, the on state conductance (at $V_g = -20$ V) was dropped by more than two orders of magnitude, being consistent with most experimental observations on covalently functionalized SWCNTs.

Figure 2.15 Change of current versus voltage characteristic of a metallic SWCNT subject to hydrogen plasma treatment at different time (top curve: 0 sec, middle curve: 40 sec, bottom curve: 100 sec). (Figure adapted from Ref. 39).

The band structure change of SWCNTs upon covalent functionalizations had also been observed by NIR infrared absorption spectra. Georgakilas et al. [40] studied the NIR absorption spectrum of [2+3] cycloaddition functionalized SWCNTs and found that the absorption peaks of pristine HiPCO SWCNTs (upper curve in Figure 2.16) were largely suppressed by [2+3] cycloaddition with pyrene (lower curve in Figure 2.16), suggesting significant electronic structure changes by the functionalization.

Figure 2.16 NIR absorption spectrum of [2+3] cycloaddition functionalized SWCNTs. (upper curve: HIPCO, lower curve: HIPCO pyrene) (Figure adapted from Ref. 40).

Tomokazu Umeyama et al. [41] investigated the electronic properties of the SWCNTs influenced by the sidewall [2+1] cycloaddition by the microwave assisted Bingel reaction (See Figure 2.17a). Figure 2.17b shows the absorption spectra comparison between the pristine state and subject to the Bingel reaction at different degrees.

Figure 2.17 Absorption spectra of SWCNTs subject to various degrees of the Bingel reaction. (a) Illustration of the reaction scheme of the Bingel reaction. (b) Absorption spectra of SWCNTs subject to various degrees of the Bingel reaction. Labelling in (b): trace (a) pristine SWCNTs; trace (b) SWCNTs with carboxyl groups; trace (c) SWCNTs with amide groups attached at open ends; trace (d) SWCNTs after Bingel reaction without microwave; trace (e)-(g) SWCNTs after Bingel reaction with microwave power of 40 W, 50 W and 60 W, respectively. (Figures adapted from Ref. 41).

The absorption spectra of the [2+1] cycloaddition functionalized SWCNT with increasing degree of the functionalization (controlled by microwave power) are shown in trace (d), (e), (f) and (g), respectively. Trace (a) represents the absorption spectrum of SWCNTs in pristine state. It was observed that all the traces showed similar peaks from the van Hove singularities, implying that the electronic structures of sidewall-functionalized SWNTs using the Bingel reaction could be preserved by up to one diester unit per 75 carbon atoms (estimated degree of functionalization for trace (g)) of the SWCNTs [41]. Their result agreed well with theoretical studies by DFT calculations which indicated

the electronic structures of SWNTs near the Fermi level were only perturbed modestly by functionalization of the sidewall with sp^2 rehybridizations [28].

Hu et al. [42] observed the electronic band structure of SWCNTs modified by dichlorocarbene functionalization. Their results (see Figure 2.18) showed a significant decrease of the absorption peak near FIR (corresponding to M_0 transition of metallic SWCNTs) with 12% and 16% of the functionalizations. Such effect was attributed to the band gap opening of metallic SWCNTs at their Fermi levels [42].

Figure 2.18 Absorption spectra of SWCNTs subject to dichlorocarbene functionalization. (Figure adapted from Ref. 42)

Since the experimental results in Figure 2.18 were obtained on HiPco SWCNTs with diameters between 0.8 nm and 1.2 nm, sidewall opening was expected on most of the tubes upon dichlorocarbene functionalization [24]. However, the results showed significant electronic band structure changes

upon the functionalization, which might be considered to be inconsistent with the electronic band structure preservation effect. One possibility could be that the degree of functionalization on the tubes was too high so that band gap opening could occur even with sidewall C-C bond broken [28]. In addition, there were also likely significant amount of dichlorocarbene groups attached to the non-orthogonal carbon bonds during the kinetic process of the reaction, resulting in sp^3 rehybridizations which could induce apparent band gap opening [38].

2.3 Summary

In summary, both theoretical predictions and experimental observations suggested that covalently functionalization to SWCNTs with sp^3 rehybridization could significantly degrade their excellent electrical conductivities. In contrast, covalently functionalized SWCNTs with sp^2 rehybridizations were shown to have their conductance largely preserved. Since the conductivity preservation effect was attributed to the curvature induced sidewall C-C bond broken, it is meaningful to observe the diameter dependent reactivity of [2+1] cycloaddition to SWCNTs, as well as the conductance preservation effect of [2+1] cycloaddition functionalized SWCNTs over a large diameter range.

Covalently functionalized metallic SWCNTs with sp^3 rehybridizations were also shown to have apparent band gap openings both theoretically and experimentally. In contrast, theoretical calculations suggested that the band gap opening effect of low degree [2+1] cycloaddition functionalized metallic SWCNTs were negligible as the result of the sidewall sp^2 hybridization recovery. However, there still lacks of experimental evidence to address the

significance of the sidewall C-C bond rehybridizations on the electronic structure of SWCNTs.

Chapter 3 Diameter Dependent Reactivity of SWCNT on [2+1] Cycloaddition Functionalization

Diameter dependent reactivity of SWCNTs could serve as a strong support of the relevant theories which predicted that the [2+1] cycloaddition was largely controlled by the strains associated with the sidewall carbon bonds, leading to the sidewall carbon bonds broken effect [29]. In this chapter, individual SWCNTs with a large diameter range are studied on their reactivities subject to dichlorocarbene functionalization.

3.1 Introduction

From the structural property of SWCNTs, it is easy to find that for a specific C-C bond on the sidewall, the strain is determined by the diameter of SWCNT and the C-C bond angle to the circumference axis. Thus, to first approximation, small diameter SWCNTs should have larger strains associated with their C-C bonds and therefore are suggested to be more reactive towards [2+1] cycloaddition. Haddon et al. [43] predicted that the curvature-induced pyramidalization and misalignment of the orbitals of the carbon atoms induced a local strain, and carbon nanotubes were suggested to be more reactive than a flat graphene sheet. Chen et al. [29,44] showed that the π -orbital misalignment and pyramidalization scaled inversely with the SWCNT diameter and thus small diameter SWCNTs were more reactive and even led to sidewall C-C bond broken. Especially, for [2+1] cycloaddition, Lee and Marzari [45] showed that the energy change of armchair SWCNTs upon functionalization nearly scaled linearly with the inverse of the SWCNT diameter. In another work with [2+1] cycloaddition, Li et al. [46] constructed a unique curvature parameter K which was defined as the average curvature of the corresponding arc of a C-C bond in the SWNT. In the works by Li et al. [46], they calculated the variation in the binding energy as a function of bond curvature for a number of SWCNTs with generally chirality. Figure 2-1 shows a plot of the binding energy of the SWCNTs upon [2+1] cycloaddition from their work. The values of the binding energy were taken for the SWCNT C-C bonds that have the largest angle to the tube axis (the most orthogonal C-C bonds).

Figure 3.1 Binding energy vs. SWCNT diameter (Data used in this graphs is based on the calculation results in Ref. 46).

It is noticed from Figure 3.1 that SWCNTs with the same diameter could have different binding energy depending on their chirality. For example, the (6,6) SWCNT has a larger diameter than a (10,0) SWCNT, but the binding energy of a (6,6) SWCNT is much larger than that of the (10,0) SWCNT. This is because there are C-C bonds perpendicular to the tube axis on the sidewall of a (6,6) SWCNT, while no perpendicular C-C bonds on the sidewall of the (10,0) SWCNT. However, due to the periodicity of the SWCNT lattice, there always exist C-C bonds that have their angles to the tube axis larger than or equal to 60° . As a result, by considering only the most orthogonal sidewall C-C bonds on SWCNTs, we should still expect the diameter dependent reactivity of SWCNTs upon [2+1] cycloaddition.

3.2 Experimental

In this study, thermally grown individual SWCNTs on Si/SiO₂ substrate with diameter of 1.2-2.2 nm were used to determine their reactivities upon dichlorocarbene addition. The dichlorocarbene functionalization was directly applied to all the SWCNTs sitting on the substrate and it was assumed that all the SWCNTs were experiencing the same reaction conditions. SWCNTs chosen for investigation were covered with electrodes to limit the functionalizations only to the sidewalls of the tubes, at the same time, the electrodes served as markers to locate the tubes so that characterization of the same SWCNT before and after the functionalization could be realized. Detailed experimental steps are discussed in the following sections.

3.2.1 Sample Preparation

Conventional thermal CVD growth technique [47] of SWCNTs was performed on Si/SiO₂ substrates. Spin coated ferritin that went an oxidation process at 800 °C was used as the precursor of the catalyst. The sample was then under a high temperature (925 °C) growth process in a thermal CVD quartz tube with hydrogen and argon gas as the carrier gas and ethanol as the carbon source. The catalyst density, flow rate and the growth time were adjusted to control the length and density of the produced SWCNTs. Figure 3.2 shows an EFM image of the as grown SWCNTs.

Figure 3.2 SEM image of a typical as-grown SWCNT on Si/SiO₂ substrate.

Electrical pads were randomly deposited to the Si/SiO₂ substrate, covering the SWCNTs as shown in Figure 3.3.

Figure 3.3 SEM Image of a pair of metal pads deposited on the as-grown SWCNT.

These pads (with ~10 μm gap as shown in Figure 3.3) held the SWCNT during the reaction, and at the same time they served as markers to locate the specific SWCNTs. In addition they covered the ends of some SWCNTs so that the chemical functionalization to these SWCNTs was restricted to their sidewalls.

3.2.2 Characterization of Individual SWCNTs by Raman Scattering

Raman spectroscopy was used as a primary tool in this work to characterize the diameter, metallicity type and defects density of individual SWCNTs before and after the functionalizations. The unique optical and spectroscopic properties observed in SWCNTs are largely due to the one dimensional confinement of electronic and phonon states, resulting in the so-called van-Hove singularities (vHSs) in the nanotube density of states (DOS) [49]. Once the phonon energy of a specific incident laser matches a vHS in the joint

density of states (JDOS) of the valence and conduction bands, resonance enhancement would occur. In combination with the unique 1-D electronic structure, the resonantly enhanced Raman scattering intensity allows one to obtain detailed information about the vibrational properties of SWCNTs, even at the isolated individual SWCNT level [50,51]. By interpreting the different vibration modes obtained from the Raman scattering, one could determine the diameter, chirality, defects as well as electronic types of SWCNTs [48-52].

Typical Raman spectrum of SWCNT has three distinct modes, i.e. the radial breathing mode (RBM), D mode and G mode. Figure 3.4 shows a typical Raman spectrum with various modes taken from an individual as-grown SWCNT on Si/SiO₂ substrate with an excitation laser wavelength of 532 nm.

Figure 3.4 Raman shift for a SWCNT on Si/SiO₂ substrate under 532 nm lasers.

As shown in Figure 3.4, the RBM mode is usually in the range of 100–300 cm⁻¹, corresponding to the coherent displacement of all carbon atoms in the

radial direction and therefore usually taken to determine the diameter of SWCNTs [48]. In this thesis, as we used as-grown SWCNTs sitting on Si/SiO₂, the relationship between the diameter of SWCNT and RBM mode peak should be related by $d=\omega/248$ [48], where d represented the tube diameter and ω represented the peak position (in cm⁻¹) of the RBM mode. Moreover, the electronic type of a SWCNT could also be determined by examining the RBM band and the excitation laser wavelength with the aid of Kartura Plot [53].

The G mode normally stays around 1500-1620 cm⁻¹, corresponding to the tangential vibrational modes of SWCNTs. It was generally expected that metallic tubes contains a BWF shape in their G bands, while the detailed BWF shapes was also affected by the diameter of the tubes [49]. Therefore, the BWF shape could also help to identify the metallicity type, or the possible diameter range of metallic tubes with the aid of Kartura plot.

The D mode typically found in 1320-1400 cm⁻¹ refers to the perturbation of the perfect hexagonal lattice of carbon atoms [48]. Raman D band and G band intensities were generally used to provide important information about the defects density of the SWCNT sidewalls [54,55]. It was expected that the D band intensity would increase while the G band intensity would decrease with increasing defects, and therefore D/G intensity ratio was generally taken as an estimation of defects density [54]. However, after the defects density had reached certain degree, the D band intensity also decreased because the SWCNT structure would be significantly perturbed, reducing its resonance with the Raman lasers [54,56,57]. Thus, not only the D/G ratio, but also the intensity values of both D band and G band are important to estimate the degree of functionalizations. In this work, making use of Raman spectroscopy

and EDX measurement on bulk SWCNTs functionalized by dichlorocarbene at various degrees, a “semi-quantitative” relationships between the Raman intensities and the degree of functionalizations was established, which was used to estimate the degree of functionalization on an individual SWCNTs from their Raman spectra. Figure 3.5 shows the D peak and G peak intensity decreases for the SWCNTs subjected to dichlorocarbene functionalizations at different degrees. More data on the correlations between the Raman scattering and the degree of dichlorocarbene functionalization can be found in Appendix E.

Figure 3.5 Raman D band and G band intensities under different degree of functionalization with G band intensities scaled by a factor of 0.1.

In this experiment, Raman spectroscopy was performed with excitation laser lines of 488, 532 and 633 nm, respectively using a confocal Raman system in

air ambient. Figure 3.6 shows a Raman mapping of an as fabricated device with the corresponding SEM image and AFM image.

Figure 3.6 SEM (a), Raman mapping (b) and AFM Image (c) of an as fabricated device before the reaction. (Figures adapted from Ref. 68).

As shown in Figure 3.6a and 3.6b, only two out of the four SWCNT were shown in the Raman mapping image, and this was because not all the SWCNT could have good resonance with a single Raman incident laser (488 nm in Figure 3.6b) [48]. In addition, among these SWCNTs with good resonance, only a fraction of them could have their RBM peaks detected. Therefore, only SWCNTs with good resonance and with RBM peaks appeared were used for the diameter dependent reactivity study in this work. In addition the SWCNTs selected should have their both ends covered by the metal pads, and have a minimum separation of 1 μm (Raman laser size ~0.3-0.8 μm) to their neighbors to avoid crosstalk of the Raman signals.

3.2.3 Covalent Functionalization: Addition of Dichlorocarbene to SWCNTs

The as prepared samples in 3.2.2 were subjected to dichlorocarbene functionalization in solution phase. The reaction was performed in an inert gas environment to avoid highly reactive dichlorocarbene species in reaction with oxygen and water molecules in air ambient.

For a typical reaction, 5 g potassium *tert*-butoxide was added slowly into 20 ml THF in the flask with stirring of 1200 rpm for 3 min to achieve a uniform solution. Subsequently, 5 mg Phase Transfer Catalyst (Dowex[®] 1X2 chloride form, Sigma Aldrich) was added to the solution and another stirring of 3 min was required for a further dispersion. The sample was then dipped into the solution and the system was evacuated and filled with argon gas. Chloroform was then added drop wise to the solution to generate the dichlorocarbene and the reaction time was controlled to be 10 min for all the samples. Figure 3.7 shows a simple reaction scheme of the dichlorocarbene functionalization to SWCNTs.

Figure 3.7 Reaction scheme for dichlorocarbene functionalization of SWNT.

After completion of the chemical reaction, the sample was rinsed thoroughly with acetone, isopropyl alcohol (IPA) and deionized (DI) water in subsequence, and followed by a baking at 100 °C for 5 min in order to remove possible chemical residuals. Raman scattering was then performed again on the same SWCNTs to examine their changes after the functionalization.

3.3 Results and Discussion

3.3.1 Raman D/G Intensity Ratio Change

Figure 3.8 shows the comparison of the Raman scattering results of two SWCNTs named SWCNT-1 and SWCNT-2. The higher wavenumber regions of their Raman scatterings shown in Figure 3.8b and 3.8d were normalized to their G band peaks while the lower wavenumber region in Figure 3.8a and 3.8c were normalized to the silicon peak at $\sim 303 \text{ cm}^{-1}$.

Figure 3.8 Raman scattering of two metallic SWCNTs with various bands. (a) RBM band of SWCNT-1. (b) D band and G band of SWCNT-1. (c) RBM band of SWCNT-2. (d) D band and G band of SWCNT-2. (Figures adapted from Ref. 68).

These two SWCNTs could be classified as metallic tubes from the Kartura plots [53] and also from the BWF shapes [49] of their G peaks. The same

assignment method for electronic types of pristine SWCNTs was used throughout this PhD thesis. The diameters of SWCNT-1 and SWCNT-2 were assigned to be 1.3 nm and 2.2 nm from their respective RBM peaks (see Figure 3.8a and 3.8c). According to Figure 3.8b, SWNT-1 had an increased D/G ratio of ~7% after 10 min of dichlorocarbene functionalization. The degree of the dichlorocarbene functionalization was estimated to be ~3%. However, SWNT-2 had no detectable D band to G band ratio change (see Figure 3.8d) after the same reaction condition.

Figure 3.9 shows the Raman scattering results of two semiconducting tubes, SWCNT-3 and SWCNT-4 with diameter of 1.3 nm and 2.2 nm (see Figure 3.9a and 3.9c), respectively. The normalization of the Raman intensities was exactly the same as used in Figure 3.8.

Figure 3.9 Raman scattering of two semiconducting SWCNTs with various bands. (a) RBM band of SWCNT-3. (b) D band and G band of SWCNT-3. (c) RBM band of SWCNT-3. (d) D band and G band of SWCNT-3. (Figures adapted from Ref. 68).

Similarly, a significant degree of the functionalization was realized on the small diameter semiconducting tube, SWCNT-3, as manifested by its D/G ratio changes upon the functionalization (see Figure 3.9b). In contrast, no detectable Raman D band increase for SWCNT-4 was observed (see Figure 3.9d), suggesting no significant covalent functionalization had been realized on this large diameter tube.

It is clearly seen from above comparison that, regardless of metallic or semiconducting SWCNTs, small diameter tubes always had significant D/G ratio increases while the large diameter SWCNTs had no detectable D/G ratio changes under the same reaction conditions.

Actually, for all samples under investigation, regardless of metallic or semiconducting SWCNTs, significant D/G intensity ratio increases were observed on SWCNTs with diameter $< \sim 1.5$ nm, while no obvious D/G intensity ratio increases were observed on SWCNTs with diameter $> \sim 1.8$ nm under the 10 min reaction. For SWCNTs with diameters in between, some SWCNTs had moderate D/G ratio increase while some had no detectable D/G ratio changes.

3.3.2 Raman G Intensity Change

Although the D/G ratio gives good judgment on the degree of covalent modifications to SWCNTs, it had been noticed that D/G ratio does not always reflect the degree of the functionalizations as the D band intensity of a SWCNT also tends to decrease with increasing functionalizations, as discussed in Section 3.2. However, the G band intensity of a SWCNT was found to continuously decrease as the degree of functionalization increase [58]. Thus, to examine the degree of functionalizations for all SWCNTs, the G band intensity drops of the SWCNTs before and after the dichlorocarbene functionalizations were also compared.

Figure 3.10 shows the Raman scattering results of four SWCNTs with increasing diameters. All the Raman intensities in Figure 3.10 were normalized to the silicon peak ~ 520 cm^{-1} for a reasonable intensity comparison.

Figure 3.10 Comparison of Raman G band intensities of SWCNT-1 to -4 (a to d). Raman intensities are normalized to the silicon peak $\sim 520 \text{ cm}^{-1}$. (Figures adapted from Ref. 68).

The diameters of SWNT-5 to SWNT-8 could be assigned to 1.3 nm, 1.5 nm, 1.7 nm and 2.0 nm, respectively from their RBM peak positions. As shown in Figure 3.10a and 3.10b, small diameter tubes, SWNT-5 and SWCNT-6 had

their G band intensity decrease by more than 50% after 10 min of the dichlorocarbene reaction. However, large diameter SWNT-7 and SWNT-8 had only a slight drop (less than 25%) of their G band intensities. It is worth noting here that the highly reactive tubes, SWCNT-5 and SWCNT-6, were semiconducting while the non-reactive tubes, SWCNT-7 and SWCNT-8, were metallic, which further manifested that the electronic type is less significant in the reactivity of SWCNTs upon dichlorocarbene addition.

In order to have a more statistical observation, Raman G band intensity drops for all the SWCNTs under investigation are plotted in Figure 3.11.

Figure 3.11 Raman G band intensity drops versus SWCNT Diameters.

As seen in Figure 3.11, the Raman G band intensity drop caused by the functionalization tends to decrease with increasing diameter, implying less covalent functionalizations were realized in large diameter SWCNTs. The

trend with diameter was observed regardless of metallic tubes (red dots) or semiconducting tubes (blue triangles), being consistent with the D/G intensity ratio comparisons shown in Figure 3.8, and Figure 3.9.

3.3.3 Discussion

Many evidences above suggest that the reactivity of SWCNTs towards dichlorocarbene addition is dominated by their diameters rather than their electronic types, although electronic dependent reactivity had been observed in many other kinds of covalent functionalizations [22,58-59]. This could be explained by the theory that [2+1] cycloaddition was expected to release much more strain than other types of covalent functionalizations to SWCNTs. As a result, the driving force for such addition is dominated by the strain energy release while not the binding energy for the bond formation. The fact that dichlorocarbene functionalization in this study could be realized in only 10 min while many other types of covalent functionalizations require a few hours or even days to get significant modification also implies the large driving force from the strain release.

It is also noticed that some SWCNTs (e.g. SWCNT-1) in this study had pristine defects prior to the functionalizations, which could possibly contribute to the reactivity of the tubes. However, the contribution of these pristine defects was shown to be insignificant as compared to the diameter effect. To clarify this point, one can compare SWCNT-5 and SWCNT-7 shown in Figure 3.10. As shown in the Raman spectra, the large diameter SWCNT-7 had significant amount of inherent defects but its reactivity was much lower than the small diameter SWCNT-5 which was almost defects free before the reaction.

It is worth noting that the sidewall carbon bonds of SWCNTs are not only determined by the tube diameter, but also by the bond angle with respect to the tube axis. Therefore, SWCNTs with the same diameter are very likely to have a quite different reactivity because of their difference in chirality as shown in the binding energy plot in Figure 3.1. However, as lack of full spectrum laser source, further investigation about chirality effect on the degree of functionalization was not performed in this study.

It should also be noted that although it is thermodynamically favorable for the carbene groups to graft on the more orthogonal bonds (with respect to tube axis), there would be certain groups kinetically attached to the less orthogonal bonds. However, experimental observations on the actually grafting configurations could be very challenging.

Raman scattering results of bulk SWCNTs upon dichlorocarbene functionalization performed in SWCNT suspensions (the same reaction condition as in Section 3.2.3) were included in Appendix to further support the diameter dependence on the reactivity of SWCNTs.

3.4 Summary

In summary, we have investigated the degree of functionalization of individual SWCNTs with various diameters and confirmed that small diameter SWCNTs are more easily to be functionalized with dichlorocarbene than large diameter SWCNTs. This diameter effect is shown to be valid for both metallic and semiconducting SWCNTs. This result supports the theoretical prediction that [2+1] cycloaddition is more pronounced to release the strain of the SWCNTs, and could possibly lead to sidewall C-C cleavage.

The SWCNTs in this work were not assigned with exact chirality numbers as lack of continuously tunable laser sources [50]. Further works with exact (n,m) chirality assignment could enable investigations of chirality dependence on the reactivity as well as the electronic structure contribution to the reactivity of SWCNTs.

Chapter 4 Conductance Preservation Effect on [2+1]

Cycloaddition Functionalized SWNTs

In this chapter, individual SWCNTs with diameter range from 1.2-2.2 nm are investigated on their electrical conductance changes upon dichlorocarbene functionalization. The electrical measurements are performed with SWCNTs built on a conventional field effect transistor (FET) platform.

4.1 Introduction

As the conductance preservation of SWCNTs upon [2+1] cycloaddition was attributed to the strain induced sidewall C-C bond broken [24], such effect should only be observed on small diameter SWCNTs.

Figure 4.1 Diameter effect on [2+1] cycloaddition induced sidewall C-C opening in armchair SWCNTs. The label “O” refers to orthogonal configuration and the letter “S” refers to skewed configuration (Figures adapted from Ref. 24).

Figure 4.1 shows the binding energy and the resultant sidewall C-C bond length of various armchair SWCNTs upon [2+1] cycloadditions calculated by Lee and Marzari [24]. As seen in Figure 4.1a, for CH_2 or NH groups attached to a specific armchair tube through [2+1] cycloaddition, the orthogonal grafting (indicated as “O” in Figure 4.1) configurations would always be more stable (with energy difference as large as ~ 2 eV) than the skewed ones (indicated as “S” in Figure 4.1). In addition, for both orthogonal and skewed

covalent attachment on SWCNT sidewall, the binding energy (with respect to a flat graphene sheet) of attaching CH_2 and NH groups were shown to increase almost linearly with the inverse of the tube radius, suggesting a large driving force of small diameter SWCNTs upon [2+1] cycloadditions.

Figure 4.1b shows the resultant SWCNT sidewall C-C bond lengths (d_{16}) upon CH_2 and NH groups attached through [2+1] cycloaddition. As observed in Figure 4.1b, the resultant orthogonal C-C bond lengths (d_{16}) are always larger than 2 Å for armchair tube with diameter less than 2 nm ($1/r > 0.1 \text{ Å}^{-1}$), suggesting apparent C-C bond broken effect. However, with the diameter of armchair tubes increased beyond ~ 2 nm, the resultant orthogonal C-C bond lengths would decrease sharply to ~ 1.6 Å, implying no significant C-C bond broken effect. In addition, skewed configurations would not induce sidewall C-C bond broken in all armchair SWCNTs studied (refer to Figure 4.1b).

According to the results shown in Figure 4.1b, the sidewall C-C bond broken effect upon [2+1] cycloaddition would disappear as the diameter of armchair SWCNTs increases beyond certain value. Moreover, it is worth noting that the results in Figure 4.1 were calculated based on the perpendicular (with respect to tube axis) C-C bonds in armchair tubes. However, for a non-armchair SWCNT (no perpendicular C-C bonds exist), the critical diameter beyond which sidewall C-C bond broken would disappear should be smaller than 2 nm. Therefore, it is likely that some of the SWCNTs in this work (with SWCNT diameter ~ 1-2 nm) might not have such C-C broken effect when grafted with CH_2 or NH groups through [2+1] cycloadditions.

Figure 4.2 Carbon bond lengths versus index of zigzag semiconducting SWCNTs. (Figure adapted from Ref. 31).

Figure 4.2 shows the work by Lopez et al. [31] on the sidewall carbon bond broken effect of semiconducting tubes upon carbene addition. As shown in their work, the open to close transitions happened at (15,0) and at (19,0) zigzag indexes for small band gap and large band gap tubes, respectively. Therefore, they suggested that carbene functionalized semiconducting tubes with diameter larger than 1.2-1.5 nm might have their sidewall carbon bonds in close configuration [31].

Above results [24,31] clearly showed that the C-C broken effect upon [2+1] cycloaddition should only occur in small diameter SWCNTs. However most experimentally synthesized SWCNTs had a rather large diameter distribution [47], and therefore it becomes important to investigate the conductance preservation effect of SWCNTs in large diameter range.

Electrical conductance measurement in this work was performed on individual tubes built on field effect transistor platform in order to have electrical

conductance measured at different gate voltage modulations [60]. Comparable degree of dichlorocarbene functionalizations to both small diameter and large diameter SWCNTs were realized as manifested by Raman spectroscopy measurements.

4.2 Experimental

4.2.1 Sample Preparation

Well separated individual SWCNTs were grown on Si/SiO₂ substrate with SiO₂ markers that were visible in both SEM and optical microscopy to locate individual SWCNTs. Figure 4.3 shows an SEM image of the as grown SWCNTs on the substrate.

Figure 4.3 SEM Image of as-grown SWCNTs with SiO₂ markers.

SWCNTs with appropriate length (~ 50-100 μm in this experiment), location and good resonant Raman G band and RBM band signals were chosen for

this study. These chosen SWCNTs were then built on FET structures as illustrated in the typical process flow shown in Figure 4.4.

Figure 4.4 Fabrication process flow of the SWCNT FET device for conductance measurement subject to dichlorocarbene functionalization.

As shown in Figure 4.4, the selected SWCNT was covered by a pair of Ti/Au electrodes through a photoresist patterning, metal deposition and lift-off process. The length of the SWCNT in the FET channel was ~10 μm and the

lengths of the SWCNT under both electrodes were adjusted to be more than $\sim 20\ \mu\text{m}$ in order to minimize the contact resistance between the metal and the tube. Moreover, the large portions of the tube under the electrodes should not be affected by the functionalization, so that we can focus on the conductance change of the tubes in the FET channel region. A silicon nitride passivation (refer to Step 6) to the joints between the electrodes and the tube might further protect them from chemical modifications. However, our results showed that SWCNT FET devices with passivation (as shown in Figure 4.5 Step 6) and without passivation (as shown in Figure 4.5 Step 5) had similar electrical characteristic changes after the dichlorocarbene functionalization process, suggesting the electrodes themselves were good enough to prevent the tubes under the electrodes from chemical modifications. Therefore, to avoid possible contaminations/damages during silicon nitride PECVD deposition process, the FET devices in this experiment were not passivated by silicon nitride. (Electrical measurement of a SWCNT FET device with silicon nitride passivation is included in the Appendix B)

4.2.2 Dichlorocarbene Functionalization and Raman Scattering

The as-fabricated samples were subjected to the same dichlorocarbene functionalization process as described in Chapter 3.2.2. However, because of the diameter dependent reactivity of SWCNTs, large diameter tubes were subjected to longer reaction time in order to achieve similar degree of the functionalization as the small diameter tubes. Raman scattering and Raman mapping were performed on the tubes before and after the functionalization with the same condition as described in Chapter 3.2.3.

4.2.3 Electrical Conductance Measurement of SWCNT FET Platform

Electrical measurement of SWCNT was performed on a bottom gate FET (as fabricated following the steps in Figure 4.4) before and after the functionalization to observe the electrical conductance changes at different gate voltages. Figure 4.5 illustrates various components of the FET built in Section 4.2.1. The pair of Ti/Au electrodes served as the source and drain and the heavily doped silicon substrate served as the back gate which is used to provide the field modulations through the SiO₂ dielectric layer.

Figure 4.5 Illustration of various elements of a SWCNT FET platform.

The electrical conductance of the SWCNT FET was expected to be controlled by the contacts between the SWCNT and the source/drain electrodes, as well as the conductance of the SWCNT in the channel [60-66]. SWCNT FET devices with channel length of a few hundreds of nanometers were expected to be a schottky barrier device where most of the current were determined by the gate modulated tunneling efficiency at the metal-nanotube contacts [65,66]. However, in a long SWCNT channel device, it was shown that the gate modulated SWCNT channel conductance seemed to dominant over the schottky contact effect [65,66]. Since the SWCNT FET device in this work had a channel length of ~10 μm , the gate modulation on the conductance of the

SWCNTs channel should have significant contribution to the total conductance of the device [66].

It is worth noting that although the contact resistance between the metal and the SWCNT was generally described by a quantum tunneling effect at the schottky barrier [60-64], systematic study by Chen et al. [64] suggested that, by taking the effect that the real contact between the metal electrode and the nanotube was made over an overlap region that extends for several hundred nanometers, an extended model should be used to take into account of this tunneling barrier phenomenon. Their proposed model described the SWCNT FET as a gated nanotube channel in contact with two reservoirs that were a result of the weak coupling between the metal and the nanotube in the overlap region. Therefore, in our SWCNT FET with $\sim 20\text{ }\mu\text{m}$ portions (much larger than hundreds of nanometers) of the SWCNT under the electrodes, the contact resistance between the metal and the tube might be described by the weak coupling effect [64].

The gate modulated electrical characteristic of the SWCNT FET device had been shown to be largely dependent on the electronic types of the tubes [60-66]. Metallic SWCNTs have no band gaps, and therefore the gate voltage modulation has no effect on the contact barrier and channel conductance. However, for semi-metallic SWCNTs (non-armchair metallic SWCNTs) with tiny band gaps and semiconducting SWCNTs with apparent band gaps, the gate voltage modulates the tunneling barriers between the metal electrodes and the SWCNTs as well as the energy states of SWCNTs in the channel, resulting in different electrical currents under different gate voltages.

Figure 4.6 illustrates the typical transfer characteristic of SWCNT FET devices in this work with SWCNTs of different electronic types and their corresponding band diagrams.

Figure 4.6 Transfer characteristic of SWCNT FET with metallic (a), semi-metallic (b) and semiconducting (c) SWCNTs and their respective band diagram illustrations.

Figure 4.6a shows a typical characteristic of a metallic SWCNT where the current passing through the SWCNT is nearly not affected by the gate voltage. This tube was expected to be an armchair SWCNT with no band gap. However, armchair tubes were seldom found in our experiments, probably due to the low probability of finding tubes with index $n=m$ with random (n,m) distribution. Similar work by Cheung et al. on large amount of experimentally synthesized individual SWCNTs also suggested that nearly all the metallic tube would have tiny band gaps presented [67].

Figure 4.6c shows a typical transfer curve of a semiconducting SWCNT where the current passing through the tube is large affected by the gate voltages. Here we define the on-state current and off-state current to be the

maximum and minimum source to drain current in the entire gate sweep range. The on/off ratio is thus defined as the ratio between the on-state current and off-state current. Therefore, a large on /off ratio of $\sim 10^4$ was observed for the semiconducting SWCNT based FET device. Referring to the band diagram, it could be seen that when the gate voltage is negative, the electronic band of SWCNTs will shift upwards, resulting a smaller tunneling barrier between the electrodes and the valence band of the semiconducting tube and hence a significant tunneling current could flow with bias voltage applied. However, as the gate voltage increases, the tunneling barrier starts to increase and therefore the current passing through the SWCNT decreases exponentially towards the off state. The on/off ratios of individual semiconducting tube based FET devices in this work were found between four orders and six orders.

Figure 4.6b shows a typical transfer characteristic of a semi-metallic SWCNT based FET, where a tiny band gap is expected to be present. Similar to the case of semiconducting SWCNTs, there was a small gate dependence of the current passing through the SWCNT. According to the measurement results in this work, the on/off ratios of pristine semi-metallic tubes were typically less than two.

It is worth noting that the actual physics between the metal electrodes and SWCNTs could be rather complex [64], however, as the contacts between SWCNTs and the electrodes were largely unaffected by the functionalization, it will not be discussed in this work.

4.3 Results and Discussion

4.3.1 Conductance Changes of Metallic SWCNTs

In order to compare the conductance changes of both small and large diameter SWCNTs, similar degree of dichlorocarbene functionalizations were realized in all tubes by controlling their reaction time. Figure 4.7 shows the electrical transfer curves and the Raman scatterings of SWCNT-A and SWCNT-B, with diameters of ~1.3 nm and ~1.9 nm, respectively. Both tubes could be classified as metallic tubes from their respective Raman scattering results at pristine state. SWCNT-B was expected to be less reactive than SWCNT-A because of its large diameter, and thus a longer reaction time (30 min) was used for SWCNT-B to get a significant degree of the functionalization. Therefore, the degrees of functionalization of both tubes were comparable as manifested by their respective Raman scattering shown in Figure 4.7b and Figure 4.7e.

Figure 4.7 Raman spectra and electrical response comparisons of two m-SWNTs with different diameters before and after the functionalization. (a) RBM band comparison of SWNT-A. (b) D/G ratio comparison of SWNT-A. (c) Electrical response comparison of SWNT-A. (d) RBM band comparison of SWNT-B. (e) D/G ratio comparison of SWNT-B. (f) Electrical response comparison of SWNT-B. (Figures adapted from Ref. 68).

Figure 4.7c and 4.7f shows the conductance changes of both tubes subjected to the functionalizations. The electrical conductances of both tubes at their pristine states showed a slightly gate dependence, implying that both tubes were likely semi-metallic SWCNTs with tiny band gaps. However, it is also likely that certain pristine defects (especially in SWCNT-A with obvious D band peak shown in Figure 4.7b) perturbs the electronic structure of the tubes, resulting in additional contribution to the gate dependence of the conductance.

After significant dichlorocarbene functionalizations applied (as manifested by their respective Raman D/G ratios in Figure 4.7b and 4.7e), it was observed

that the conductances of both tubes were only slightly dropped over the whole gate sweeping range (refer to Figure 4.7c and Figure 4.7f). This was in sharp contrast with most covalent functionalizations where few orders of magnitude of SWCNT conductance drops were observed [32-34].

In addition, it was noticed that although the on-state currents of both tubes were preserved more than 50%, the off state currents had much larger drops for both tubes, leading to an increased on/off ratio for both tubes.

4.3.2 Discussion

Since the contacts between the electrodes and the tubes were unaffected, the change of the transfer curve should be caused by the exposed SWCNT portions in the channels. The large preservation of the electrical currents over the entire gate sweep range suggested that the quantum conductances of both tubes were largely preserved. However, the increased on/off ratio for both devices might be caused by a few factors that will be discussed below.

One of the possible origins of such on/off ratio increase could be that there were inhomogeneous quantum conductance drops at different energy levels near the Fermi level of the tubes caused by the attached dichlorocarbene groups. Referring to the theoretical simulation results of the quantum conductances of SWCNTs with random grafting of the dichlorocarbene groups [24] (shown in Figure 2.2, Figure 2.3 and Figure 2.5), it could be seen that there were fluctuations in the quantum conductances at different energy levels near the Fermi level. As a result, at different gate voltages, the conductance drops of the tubes could be very different.

Another possible contribution to the on/off ratio increase could be that there might be contributions from the band structure changes of the SWCNTs upon

the covalent attachments of the dichlorocarbene groups. Although sp^2 rehybridized covalent attachments were expected to only slightly perturb the electronic band structure of metallic SWCNTs, band gap openings of the metallic SWCNTs might occur, especially at high modification ratios [37,38]. In this experiment, both tubes had relative high degree of functionalizations (as manifested by their Raman scatterings), and thus band gap opening by these groups were possible. In addition, although covalent attachments to the orthogonal sidewall C-C bonds was expected to be thermodynamically more stable, there were likely certain dichlorocarbene groups kinetically attached to the non-orthogonal bonds, resulting in sp^3 hybridizations which were more pronounced to open a band gap in metallic SWCNTs [38].

It is worth noting that electronic doping from attached dichlorocarbene groups to the SWCNT could also affect the transfer characteristic of the SWCNT FET devices [60]. However, in this work, such doping effect was shown to be insignificant as manifested by the insignificant Raman G peak shifts for both tubes [48].

In order to further demonstrate the conductance preservation effect, the Prato reaction functionalization ([2+3] cycloaddition) was realized to a metallic SWCNT in a FET platform to examine its conductivity change. As shown in the Raman scattering comparison (Figure 4.8a), the degree of the Prato reaction functionalization was probably lower than that of SWCNT-A and SWCNT-B with dichlorocarbene functionalizations. However, the conductance of this SWCNT was shown to drop by almost two orders after the Prato reaction functionalization (Figure 4.8b).

Figure 4.8 Electrical conductivity comparison of a metallic tube before and after [2+3] cycloaddition functionalization. (a) Raman spectra comparison of the SWCNT before and after [2+3] cycloaddition. (b) Electrical conductance comparison before and after [2+3] cycloaddition.

4.3.3 Conductance Changes of Semiconducting SWCNTs

Semiconducting SWCNTs had been shown to be not reactive towards many organic syntheses as their extremely low electron density near the Fermi level [58]. However, as demonstrated in Chapter 2, semiconducting SWCNTs were shown to be reactive towards dichlorocarbene functionalization. Moreover, semiconducting tubes were also expected to experience the sidewall carbon bond broken effect upon [2+1] cycloaddition [31].

Figure 4.9 shows the electrical transfer curve of two semiconducting SWCNTs, SWCNT-C and SWCNT-D with diameter 1.3 nm and 1.9 nm, respectively.

Figure 4.9 Raman spectra and electrical response comparisons of two s-SWNTs with different diameter before and after the functionalization. (a) RBM band comparison of SWNT-C. (b) D/G ratio comparison of SWNT-C. (c) Electrical response comparison of SWNT-C. (d) RBM band comparison of SWNT-D. (e) D/G ratio comparison of SWNT-D. (f) Electrical response comparison of SWNT-D. (Figures adapted from Ref. 68).

The electrical transfer curves of both tubes in their pristine states confirmed their semiconducting behavior (see Figure 4.9c and 4.9f). The on/off ratio of SWCNT-C was about 10^6 while the on/off ratio of SWCNT-D was about 10^4 . This result was consistent with relevant theories that the band gap of semiconducting SWCNT would decrease with increasing diameter [15,35].

In the dichlorocarbene functionalization process, large diameter tube, SWCNT-D, was subjected to a longer reaction time (30 min) to get a comparable degree of the functionalization to that of SWCNT-C. As shown in Figure 4.9c and 4.9f, the on-state conductances of both tubes were largely

preserved after the functionalizations. The on-state conductance drop of the small diameter tube (SWCNT-C) was ~40%, and the on-state conductance of the large diameter tube (SWCNT-D) was ~60%. As compared to those semiconducting tubes subjected to monovalent functionalizations [33,34], the conductance drops of both SWCNT-C and SWCNT-D upon dichlorocarbene functionalizations were still considered to be much smaller.

Moreover, it was also noticed that, after the functionalizations, the off state conductance of SWCNT-C was shown to be largely increased, while the off state conductance for SWCNT-D showed no noticeable increase. In addition, it could be seen that the degree of functionalization of SWCNT-D was smaller than that of SWCNT-C (refer to Figure 4.9b and 4.9e) although SWCNT-D had been subjected to a longer reaction time. This was probably caused by the low reactivity of SWCNT-D with large diameters, and further increasing the reaction time of SWCNT-D did not produce noticeable changes in its Raman D/G intensity ratio.

4.3.4 Discussion

Theoretical simulation by Lopez et al. [31] showed that [2+1] cycloaddition functionalized semiconducting SWCNTs were more likely to have sp^3 rehybridizations as compared to metallic SWCNTs with similar diameter. According to their results, zigzag semiconducting tubes with diameter larger than 1.5 nm would have their sidewall carbon bonds in close configurations up on [2+1] cycloaddition. As a result, there should be much larger conductance drop of SWCNT-D (diameter ~1.9 nm) than SWCNT-C (diameter ~1.3 nm) caused by the dichlorocarbene functionalization. This was consistent with our observations that the on state conductance of SWCNT-C dropped by ~40%, while the on state conductance of SWCNT-D dropped by

~60%. However, it is worth noting that the conductance of SWCNT-D could still be considered as largely preserved upon dichlorocarbene functionalization as compared to those semiconducting tubes subjected to monovalent functionalizations [33,34]. One possible explanation to such difference could be that [2+1] cycloaddition with sp^3 configuration would form a three-member-ring structure on the sidewall of SWCNTs, so that the two C-C bonds linked to the dichlorocarbene group were very close to each other [29,30]. Therefore, the interactions between the two C-C bonds could create impurity states far away from the Fermi level, so that the scattering effect could be largely reduced [30]. As a result, [2+1] cycloaddition with sp^3 configuration would have less scattering effect than monovalent functionalizations, and consequently the conductance drop of [2+1] cycloaddition functionalized SWCNTs should be always smaller than monovalent functionalizations regardless of the sidewall C-C bond broken effect [30].

The increase of the off state conductance for SWCNT-C was probably due to the quasi-bound states formed within its original band gap as proposed by Cho et al. [38]. It could be seen in Figure 4.9c that although SWCNT-C had its off state current increased, its on/off ratio was still held $\sim 10^4$, comparable to the on/off ratio of SWCNT-D. It is worth noting that electron donating to semiconducting SWCNT-3 could possibly make it towards n-type, resulting in the off-state current increase. However, referring to the Raman scattering in Figure 4.9b, the G peak of SWCNT-3 had an up-shift which was possibly associated with an electron withdrawing rather than electron donation [48]. Thus, the large increase of the off-state current in SWCNT-3 was not likely to be caused by electron donating effect.

4.4 Summary

Electrical measurements on both small diameter and large diameter tubes upon dichlorocarbene functionalizations showed a significant conductance preservation effect which was in sharp contrast with conventional covalent functionalizations where the conductance drop were dropped by a few orders of magnitude. However, certain electronic band structure modifications by the dichlorocarbene groups were reflected in the electrical measurements, where metallic tubes generally had their on/off ratios increased while semiconducting tubes generally had their on/off ratios decreased upon dichlorocarbene functionalizations.

For a more generalized observation, dichlorocarbene functionalization and Bingel reaction functionalization ([2+1] cycloaddition) with various chemical groups were applied to SWCNT network transistors. The results showed that the conductivities of SWCNT networks transistors were also largely preserved. Electrical measurements of SWCNT networks subjected to [2+1] cycloadditions will be discussed in Chapter 7.

In summary, above results suggest that that [2+1] cycloaddition could be an excellent choice of processing, handing SWNTs over a large diameter range with their electronic conductances largely preserved.

Chapter 5 Metallicity of Covalently Functionalized Metallic SWCNTs Studied by Electrostatic Force Microscopy

Electrostatic force microscopy (EFM) technique is a contactless technique to characterize the electronic properties of nanomaterial while eliminates sample contaminations/damages during the analysis process and enables local characterization of the electronic properties of SWCNTs [76]. In this work, utilizing EFM technique, individual SWCNTs are studied on their local electronic property changes upon [2+1] cycloaddition and [2+3] cycloaddition functionalizations.

5.1 Introduction

As discussed in Chapter 2, SWCNTs with [2+1] cycloaddition could have their sidewall C-C bonds broken, recovering their pristine sp^2 hybridizations. Therefore, at small modification ratios, [2+1] cycloadditions to metallic SWCNTs were expected to have little influence to their intrinsic electronic band structures [28]. In contrast, those metallic tubes with sp^3 rehybridized covalent groups on their sidewalls were expected to have apparent band gap openings [35-38].

The band gaps of SWCNTs had been shown to be closely related to their longitudinal polarizabilities, where small band tubes generally had large longitudinal polarizabilities [69]. Metallic tubes were expected to have zero (for armchair tubes) or nearly zero (for non-armchair metallic tubes) band gaps and thus had extremely large longitudinal polarizabilities [69]. Thus, if there were band gap openings in metallic tubes by covalent functionalizations, a suppression of their longitudinal polarizabilities should be expected.

The longitudinal polarizabilities of SWCNTs actually played important roles in manipulating SWCNTs under electrical fields for many applications [70-75]. For example, ac-dielectrophoresis (AC-DEP) technique had been applied to place aligned SWCNTs across desired electrodes utilizing their longitudinal polarizabilities [73-75]. Moreover, if SWCNTs were dispersed in solvents with appropriate dielectric constant, a separation of semiconducting and metallic SWCNTs could be achieved through AC-DEP technique by making use of the distinct longitudinal polarizability differences between semiconducting and metallic SWCNTs [70].

It had been shown in many works that EFM responses of SWCNTs were largely contributed from their longitudinal polarizabilities [76-82]. Thus, EFM could be a useful technique to characterize the longitudinal polarizability changes of individual metallic SWCNTs subject to covalent functionalizations. To demonstrate the influences of sp^2 and sp^3 rehybridized sidewall covalent configurations to the longitudinal polarizabilities of metallic tubes, dichlorocarbene functionalization ([2+1] cycloaddition) and the Prato reaction ([2+3] cycloaddition) were used to modify individual metallic tubes, and EFM scans were performed on these tubes before and after the functionalizations.

5.2 Electrostatic Force Microscopy

Scanning probe microscopy had been demonstrated to be a powerful tool to characterize and manipulate nanomaterial [76-82]. In particular, characterization and manipulation of SWCNTs using SPM technique had attracted many researchers [83]. In the literature, SPM technique had been utilized to measure the transport property of carbon nanotubes [83,84]. Manipulation and assembly of SWCNTs were also realized through the AFM tips, for the purpose of measuring the strain effect of SWCNTs [85-89]. Moreover, SWCNTs had also been used as the probes of the SPM equipment, which combined the fantastic functionality of the SMP technique and the superior properties of SWCNTs [90-93].

EFM is a contactless SPM technique in tapping mode [83], where an oscillating conductive probe scans over the sample surface with voltage applied. During the scanning process, the electrostatic forces arising from the charges and dipoles could be imaged [94-104]. For example, EFM techniques had been implemented to characterize the charge distribution [94], dielectric response [97] and local electronic structures [101] of individual SWCNTs.

Figure 5.1 Illustration of EFM working principle. As shown in the figure, EFM is conducted in a double pass process. In the first pass, a standard ac-air mode (tapping mode) is implemented to obtain the topographical image of the sample. In the second path, the tip is biased with a constant voltage and lifted at a constant height, z , and then scans over the topographical profile obtained in the first path.

As illustrated in Figure 5.1, EFM measurement was conducted based on a double pass process. In the first pass, a standard ac-air mode (tapping mode) scan was performed to obtain the topographical morphology. In the second scan pass, the cantilever was lifted to a constant height over the topographical profile obtained in the first scan. In all the scans, the cantilever was mechanically driven at its resonance frequency. However, only in the second scan path, a constant voltage was applied to the conductive tip. Therefore, during the second scan path, the induced charges and dipoles in SWCNTs interacted with the AFM tip, affecting the resonant vibration of the cantilever and caused a slight phase shift of the cantilever which was recorded as the EFM signal. The EFM signals at each sampling points were recorded and output as a pixel of the final EFM image. It had been demonstrated that, for a small vibration amplitude of the cantilever, a linear relationship between the electrostatic force gradient normal to the substrate

and the cantilever phase shift could be established, i.e., $\Delta\phi \propto \partial F / \partial z$, where z is the distance from the tip to the substrate [103,104]. The electrostatic force between the sample and the EFM tip could be expressed as $F_{dc} = \frac{1}{2} dC/dz \left[(V_{dc} + V_{cp} + V_Q)^2 \right]$, where C represents the tip to substrate capacitance, V_{dc} represents the DC voltage applied to the tip, V_{cp} represents the contact potential difference between the tip and the sample and V_Q represents the response originates from the charges in the samples [108]. Thus, the EFM signal of SWCNT is comprised of the transverse dielectric of the SWCNT and induced charges in the SWCNT.

It is worth noting that the EFM signal strength was also influenced by the diameter of the tube (transverse dielectric of SWCNT is controlled by its diameter) [105-107]. Thus, EFM comparisons in this work were made on the same tube in its pristine and functionalized states so that the diameter effect could be safely excluded. Moreover, EFM signals were shown to be sensitive to the tips used [105-107], and thus the same tip was used to characterize each tube.

5.3 Experimental

5.3.1 Experimental Procedure

A brief experimental procedure is illustrated in below Figure 5.2.

Figure 5.2 Experimental procedure of EFM and Raman characterization of the SWCNT before and after functionalization.

As illustrated in Figure 5.2, the as grown individual pristine SWCNT was located and characterized by Raman spectroscopy and EFM probing in sequence. Following that, the SWCNT laying on the substrate was subjected

to the chemical functionalization process. Upon completion of the functionalization and sample cleaning process, Raman spectroscopy was implemented again on this tube to estimate its degree of the functionalization. Finally, the functionalized tube was subjected to EFM characterization again using the same AFM tip and set up.

5.3.2 Sample Preparation

As-grown individual SWCNTs as shown in Chapter 4 were used in this work. The positions of each individual SWCNTs could be located by the markers created on the substrate prior to the SWCNT growth process.

5.3.3 Covalent Functionalizations

Dichlorocarbene Functionalization ([2+1] cycloaddition): refer to Section 3.2.2

Prato Reaction ([2+3] cycloaddition): In a typical Prato reaction [109,110], 10 mg Sarcosine (N-methylglycine) was dissolved in 20 ml toluene with 10 ml formaldehyde (37%) solution added. The mixture was then stirred at 1000 rpm for 5 min. The as prepared sample with SWCNT sitting on Si/SiO₂ substrate was then dipped into the solution at the solution was heated at 130°C in nitrogen environment. Upon completion of the reaction, the sample was washed thoroughly with acetone, IPA and DI water in sequence and then baked on a hot plate at 120°C for 3 min to remove possible chemical residues.

5.3.4 Raman Scattering

Raman scattering (refer to Section 3.2.2) was performed to examine the degree of the functionalizations as illustrated in Figure 5.2.

5.3.5 EFM Spectroscopy

Cypher Atomic Force Microscopy (AFM) MF3D (Asylum Research) was used for EFM scanning. Conductive tips with a resonance frequency of ~ 75 kHz and a spring constant of about 2.8 N/m were used. As illustrated in Figure 5.1, EFM measurement was conducted based on a double pass process. In the first scan, a standard AC air mode was performed to obtain the topographical morphology. In the second pass, the cantilever was lifted at a constant height of 30 nm over the topographical baseline obtained in the first pass. A constant DC voltage of 3 V with an offset voltage (typically ~ 0.1 V) was applied to the conductive tip only in the second scan. The applied offset voltage was used to offset the contact potential difference between the tip and the SWCNT. During the second scan path, the induced charges and dipoles in SWCNTs would interact with the cantilever so that the resonant vibration of the cantilever was affected, and the phase shift of the cantilever deflection signal was recorded as the EFM signal.

5.4 Results and Discussion

5.4.1 EFM Imaging of Pristine SWCNTs

In order to calibrate our system, a few pristine SWCNTs with different diameters and electronic types were tested under our EFM setup. Figure 5.3 compares the EFM signals of metallic and semiconducting tubes with different diameters in the same scan.

Figure 5.3 SEM Imaging of pristine SWCNT with different diameters and electronic types. (a) Topographical image. (b) EFM image. (c) EFM signal at the cross section shown in (b). (d) Topographical image. (e) EFM image. (f) EFM signal at the cross section shown in (e).

As discussed in the EFM working principle (Section 5.2), the EFM signal of SWCNT is dependent on their diameters and electronic types. Therefore, a large diameter metallic tube was expected to have significantly stronger single than a small diameter semiconducting tube, and this was consistent with our EFM signal of pristine tubes. As seen in Figure 5.3c, the peak EFM signal value of the large diameter (~ 2 nm) metallic SWCNT was more than twice of that of the small diameter (~ 1.3 nm) semiconducting tube. Figure 5.3d and 5.3e shows another EFM scan with a small diameter (~ 1.3 nm) metallic tube and a large diameter (~ 2.1 nm) semiconducting tube. As shown in Figure 5.3f, both tubes had a comparable EFM signal with the signal of the metallic slightly larger. This result suggested that the electronic type of SWCNTs played a more significant role than the diameter of SWCNT in our

EFM implementation. This result was also consistent with the general expectation that, if there were charges present, semiconducting material would have its dielectric response dominated by the charges rather than the dipoles [107].

5.4.2 EFM Signal of Metallic SWCNT Influenced by the Prato Reaction ([2+3] Cycloaddition)

Figure 5.4 shows the EFM image comparison of a metallic SWCNT before and after the Prato reaction.

Figure 5.4 EFM signal comparison before and after the Prato reaction. (a) Topographical image of a metallic SWCNT in pristine state. (b) EFM image of the pristine tube. (c) EFM phase values at the cross line shown in (b). (d) Raman spectroscopy of the SWCNT in pristine state. (e) Topographical image of a metallic SWCNT after Prato reaction. (f) EFM image of the SWCNT after Prato reaction. (g) EFM phase values at the cross line shown in (f). (h) Raman spectroscopy of the SWCNT after Prato reaction. (i) EFM phase comparison of the SWCNT before and after Prato reaction with ten sampling point taken at equal distance along the SWCNT.

The Raman scattering of the pristine tube (see Figure 5.4d) had a BWF shape of its G⁺ band, implying its metallic behavior [47-49]. As the Raman laser wavelength of 532 nm was used, this metallic tube should have its diameter either ~1.2 nm or ~1.8 nm according to the Kartura plot [53]. Further characterization by AFM measurement showed that this tube had a diameter of ~1.7 nm.

The Raman D band increase (Figure 5.4h) after the Prato reaction suggested that the tube had been successfully covalently functionalized. It was also noticed that the BWF shape of its G band had changed to a more distinct two separate peaks, which could be caused by the electron density drop near the Fermi level and/or electronic band structure changes [49].

As seen in Figure 5.4b and 5.4f (plotted with same color scale), the brightness of EFM image of this tube was significantly dropped, suggesting a significant drop of the EFM signal strength. Cross section EFM signal plot in Figure 5.4c and 5.4g showed an EFM signal drop of more than 50%. Figure 5.4i shows the comparison of ten sampling points selected at equal distance along the tube, where all the data points showed a drop of more than 50% of the EFM signals after the functionalization.

5.4.3 EFM Signal of Metallic SWCNT Influenced by the Dichlorocarbene Functionalization ([2+1] Cycloaddition)

The effect of dichlorocarbene functionalization on the EFM signal of metallic SWCNT is demonstrated in Figure 5.5.

Figure 5.5 EFM signal comparison before and after the dichlorocarbene functionalization. (a) Topographical image of a metallic SWCNT in pristine state. (b) EFM image of the pristine tube. (c) EFM phase values at the cross line shown in (b). (d) Raman spectroscopy of the SWCNT in pristine state. (e) Topographical image of a metallic SWCNT after dichlorocarbene functionalization. (f) EFM image of the SWCNT after Prato reaction. (g) EFM phase values at the cross line shown in (f). (h) Raman spectroscopy of the SWCNT after dichlorocarbene functionalization. (i) EFM phase comparison of the SWCNT before and after dichlorocarbene functionalization with ten sampling point taken at equal distance along the SWCNT.

As seen from the Raman scattering results in Figure 5.5h, the degree of the functionalization to this tube was comparable to that of the Prato reaction. By comparing the EFM signal before (Figure 5.5b) and after (Figure 5.5f) the functionalization, it could be seen that the EFM was largely unaffected by the functionalization. Cross sectional data in Figure 5.5c and 5.5g showed a drop of EFM signal less than 20%. The EFM signal comparison of sampling points

taken at equal distance along the tube (Figure 5.5i) showed the largest EFM signal drop was only ~23% along the tube.

As discussed in Section 5.2, EFM signal originates from both the diameter dependent transverse dielectric and the longitudinal polarizability of the SWCNTs. However, since the comparisons were made on the same tube before and after the functionalization, the contribution from the transverse polarizability could be ignored. Therefore, the changed of the EFM signal was mainly contributed by the metallicity (i.e. longitudinal polarizability) change of the tubes.

5.5 Summary

In summary, the EFM signals of two individual metallic SWCNTs before and after dichlorocarbene functionalization and the Prato reaction functionalization were compared. The result showed that metallic SWCNT with the Prato reaction functionalized metallic tube had its EFM signal largely dropped, while the dichlorocarbene functionalization functionalized metallic tube had its EFM signal largely preserved. This result further supports the theoretical prediction that the electronic property of SWCNTs could be largely preserved after [2+1] cycloaddition (dichlorocarbene functionalization) with sidewall C-C bond broken effect.

Chapter 6 Covalently Functionalized Metallic SWCNTs Studied by Dielectric Force Microscopy

Dielectric Force Microscopy (DFM) had been demonstrated to be a powerful tool to characterize the gate dependent electrical and electronic properties of SWCNTs [107]. In this chapter, utilizing our DFM technique, metallic SWCNTs subjected to dichlorocarbene functionalization and the Prato reaction were characterized in order to investigate the difference in the electronic structure and local conductivity changes.

6.1 Introduction

As discussed in Chapter 2, apparent band gaps opening could be realized on metallic SWCNTs upon covalent functionalizations. Theoretical predictions suggested that covalent functionalization with sidewall sp^3 hybridization could open apparent band gap on metallic SWCNTs even at a small degree of the functionalization [35-38]. In contrast, [2+1] cycloaddition with sidewall carbon bond opening effect was not expected to perturb much the electronic structure of metallic tubes, even at relative high degree of functionalizations [28,29]. Thus, the comparison of the influences of sp^2 and sp^3 sidewall rehybridizations to the electronic band structure of metallic tube could be an important measure to validate such theory [28,29].

In Chapter 5, the metallicity drops of metallic tubes after dichlorocarbene functionalization and the Prato reaction were compared using conventional EFM technique. However, EFM technique is not capable to probe further information about the electronic property such as local conductivity and gate dependent carrier responses of the SWCNTs. In literature, the local conductivity and transport properties of nanomaterial were generally measured using contact mode AFM [112,113]. However, contact mode AFM was generally considered to be destructive where damages and contaminations to the samples were generally observed [113]. Scanning gate microscopy (SGM) technique was also developed to resolve the gate dependent local conductivity of the SWCNTs through a contactless scan over the entire tubes [114]. However, in SGM, the quality of the electrical contacts made to the tubes would also contribute to the total current so that the conductivity obtained was subject to the influence of contact resistance [115]. Moreover, both conductive AFM and scanning gate microscopy techniques

required fabrication of electrodes, resulting in process complexity and possible sample contaminations/damages. Therefore, in this Chapter, a contactless Dielectric Force Microscopy (DFM) technique [107] was implemented to determine the local conductivity and gate modulated carrier response of SWCNTs. The DFM technique utilized contactless scan technique so that the local conductivity of the tubes could be imaged without physically touching the tubes. In addition, the DFM technique requires no fabrication of electrodes to the tubes so that contaminations and damages to the tubes could be minimized.

DFM imaging setup was developed from EFM working principle and the basic principle of DFM technique is illustrated in Figure 6.1a.

Figure 6.1 DFM working principle (a) Illustration of DFM setup (b) Band structure influenced by the gate voltage applied. (Figure 6.1b adapted from Ref. 107).

In the second scan pass of the DFM technique, the resonant oscillation of the cantilever was turned off [107]. In addition, an AC voltage, a gate voltage and an offset voltage were applied to the tip and the 2ω component of the cantilever deflection signal was recorded as the DFM signal [107].

To understand the information obtained from the DFM signal, it is important to interpret the different electrostatic force terms between the tip and the sample with ac and dc voltages applied on the tip.

In the second scan with a dc+ac voltage ($V_{dc} + V_{ac} \sin \omega t$) applied on the tip, the electrostatic forces between the tip and the sample could be decomposed into three terms [108].

Firstly, the DC component could be expressed as

$$F_{dc} = -\frac{1}{2} \frac{dC}{dz} \left[(V_{dc} + V_{cp} + V_Q)^2 + \frac{1}{2} V_{ac}^2 \right] \quad 6.1$$

where C is the tip to sample capacitance, V_{dc} is the dc voltage applied to AFM tip, V_{cp} is the contact potential difference between the AFM tip and the sample and V_Q represents the response originating from the charges in the samples.

This zero order force would continuously bend the cantilever, but it was hard to get useful information from this force component [108].

The second component could be expressed as

$$F(\omega) = \frac{dC}{dz} (V_{dc} + V_{cp} + V_Q) V_{ac} \sin \omega t \quad 6.2$$

This term had a linear dependence on the capacitive coupling dC/dz and sample voltages V_{dc} , V_{cp} and V_Q . Thus this term could represent the static dipoles as well as static charges in the tube, which was similar to conventional EFM image with dc voltage applied [103].

The third component could be expressed as

$$F(2\omega) = -\frac{1}{4} \frac{dC}{dz} V_{ac}^2 \cos 2\omega t \quad 6.3$$

It is worth noting that, from equation 6.3, the 2ω component of the electrostatic force, $F(2\omega)$, is independent of the dc voltages applied and the strength of this component is only determined by the ac amplitude of the applied voltages. This 2ω component of the electrostatic force should originate from the induced oscillations at ω frequency in the material under test [103]. In SWCNTs, such induced oscillations were expected to be the induced dipole oscillations and the induced charge oscillations by the applied ac voltage on the tip [107]. Therefore, in DFM, the applied gate voltage (dc voltage) did not contribute directly to the electrostatic force. Instead, it modulated the local carrier density and thus affected the strength of the local charge oscillation, contributing to the 2ω components of the electrostatic force.

In semiconductors, the carrier density modified by static electrical field was expected to be dependent on its band gap and Fermi level [2], and therefore these electronic properties of the material could be indirectly imaged by DFM. As illustrated in Figure 6.1b, a p-type semiconducting tube was expected to have a higher carrier density at negative gate voltage applied than at positive gate voltage, and therefore this tube should have a higher DFM signal (2ω component) at negative gate voltage applied on the tip. However, it is important to take note that the charge oscillation strength in SWCNTs does not only depend on the carrier density, but also depend on the carrier mobility. Therefore, the 2ω component of the electrostatic force could also provide the information of the gate dependent local carrier conductivity of the tube.

Although the induced dipoles were also expected to contribute to the 2ω component of the DFM signal, the contribution was considered to be much smaller than the carrier response in SWCNTs [107]. Moreover, the induced dipole oscillation was considered not dependent on the gate voltage applied,

and therefore the gate modulated 2ω component of the electrostatic force could be interpreted as the gate dependent local conductivity of the tubes [111].

In order to obtain useful information from DFM scan, a necessary step was to extract the 2ω component of the electrostatic force from the signals obtained. In Ref. 71, the second scan path was performed with the mechanical resonant oscillation of the tip turned off, and the cantilever was purely driven by the applied voltages. Therefore, the 2ω component of the cantilever deflection signal was used as their DFM signal to represent the 2ω component of the electrostatic forces. However, in the second scan path, if the resonant oscillation of the cantilever was turned on, the 2ω component of the phase shift could also be used to represent the 2ω component of the electrostatic force because of the linear relationship between the phase shift and the force gradient at small oscillation amplitude [72,73]. These two setups had been compared using our DFM setup, and the phase imaging method (with the resonant oscillation of the cantilever turned on) was selected for our DFM experiments as it showed lower noise and better linearity probably because of the nature of cantilevers used (Detailed comparison is attached in Appendix C). Figure 6.2 demonstrates a typical dc component (zero order), ω component and 2ω component of the DFM phase image of a SWCNT.

Figure 6.2 DFM images of a SWCNT (a) topography image (b) phase image (c) ω component of phase image (d) 2ω component of phase image.

In the DFM experiments, the low frequency dielectric responses from the Si/SiO₂ substrate were considered to be consistent over the whole dc voltage range and thus the 2ω phase differences between the substrate and the SWCNTs were taken as the DFM values of the SWCNTs. However, there was a possibility that the dc voltage was too high so that there were changes in the DFM response from the Si/SiO₂ substrate probably due to the electronic structure changes in the heavily doped Si and/or the SiO₂ dielectric. Moreover, large dc voltage might also drive the cantilever beyond its linear regime, resulting in inaccurate measurement results. Therefore, for each cantilever and substrate, it was necessary to check the DFM response from the Si/SiO₂ substrate at different dc voltages in order to validate the DFM

results of the SWCNTs obtained. (A typical test of a SWCNT under large dc voltage range is included in Appendix C)

6.2 Experimental

6.2.1 Experimental Procedure

Refer to Chapter 5.3.1.

6.2.2 Sample Preparation

Refer to Chapter 5.3.2.

6.2.3 Covalent Functionalizations

Refer to Chapter 5.3.3.

6.2.4 Raman Scattering

Refer to Chapter 2.2.

6.2.5 DFM Spectroscopy

EFM imaging: Refer to Chapter 5.3.4

DFM imaging: Atomic Force Microscopy (AFM) MF3D (Asylum Research) was used for all EFM and DFM experiments. Conductive tips with a resonance frequency of about 75 kHz and a spring constant of about 2.8 N/m were used. As illustrated in Figure 6.1, DFM measurements were conducted with a double pass process. In the first pass of a scan line, a standard AC air mode (tapping mode) scan was performed to obtain the topographical morphology. In the second pass, the cantilever was lifted at a constant height of 30 nm over the topographical baseline obtained in the first pass. An ac voltage (3V amplitude, $\omega=500\text{Hz}$), a gate voltage (-3V to +3V) and the offset

voltage were applied to the tip and the 2ω component of the phase shift of the cantilever deflection signal was used as the DFM signal. The DFM images were extracted from the offline phase images through a low pass filter (lock-in filter). The low pass filter used had a cutoff frequency of $\omega/2$ with an attenuation of 77 dB at ω and 161 dB at 2ω .

6.3 Results and Discussion

6.3.1 Demonstration of DFM Technique on Pristine SWCNTs

The first experiment was performed on pristine SWCNTs to demonstrate that our DFM setup was able to detect their gate dependent electronic properties. Three typical pristine SWCNTs were selected to examine the influences of the gate voltages on their DFM signals. Figure 6.3 shows the AFM morphologies (Figures 6.3a, 3f, 3k), DFM images (Figures 3b-d, 3g-i and 3l-n) and Raman spectra (Figures 6.3i, 6.3j, 3o) of the three SWCNTs.

Figure 6.3 Demonstration DFM image of three SWCNTs. (a) topography image of SWCNT-A. (b-d) 2w component of phase image obtained with DC bias of -1.5V, 0V and +1.5V, respectively. (e) Raman scattering of SWCNT-A. (f) topography image of SWCNT-B. (g-i) 2w component of phase image obtained with DC bias of -1.5V, 0V and +1.5V, respectively. (j) Raman scattering of SWCNT-B. (k) topography image of SWCNT-C. (l-n) 2w component of phase image obtained with DC bias of -1.5V, 0V and +1.5V, respectively. (o) Raman scattering of SWCNT-C. (Figures adapted from Ref. 116).

Raman scattering results suggested that SWCNT-A and SWCNT-C were semiconducting, while SWCNT-B is metallic [48,49]. As seen from Figures 6.3g, 6.3h and 6.3i, the DFM response of SWCNT-B at different gate voltages (from -1.5 to +1.5 volts) were almost identical, indicating no detectable gate effect which was consistent with its expected metallic behavior from its Raman scattering. In contrast, the DFM signals of both SWCNT-A and SWCNT-C were largely modulated by the gate voltages applied from -1.5 to +1.5 volts, suggesting the large gate dependence on their local conductivities, i.e., apparent band gap should present in the tubes which was also consistent with their Raman scattering results.

If the DFM signal ratio between $V_G = -1.5\text{V}$ and $V_G = +1.5\text{V}$ was taken as the “modulation ratio” (similar definition was used in Ref. 71), SWCNT-B showed a modulation ratio of $\sim 0.8\text{-}1.2$, while SWCNT-A and -C had modulation ratios of $\sim 1.8\text{-}5$. Since the dielectric/dipole response of the DFM signal (2ω component) was insensitive to gate voltages [71], the modulation ratio should be attributed to the charge carrier density variation induced by the gate voltages.

It should be pointed out that although the DFM signal of a SWCNT partially depended on the SWCNT diameter (which determines its polarizability in transverse direction), the modulation ratios here were obtained from the same SWCNT in its pristine state and functionalized state so that the variations caused by diameter variations could be excluded in this work.

6.3.2 DFM Image on Covalently Functionalized Metallic SWCNTs

SWCNT-1 was analyzed using AFM, EFM, DFM and Raman spectra before (see Figure 6.4a-f) and after [2+3] cycloaddition functionalization (See Figures 6.4g-l).

Figure 6.4 Comparison of EFM and DFM signals of metallic SWCNT-1 before and after the Prato reaction. (a) Topography image of SWCNT-1 in pristine state. (b) EFM image of SWCNT-1 in pristine state. (c-e) DFM images of pristine SWCNT-1 at gate voltage of -1.5V, 0V and +1.5V, respectively. (f) Raman spectra (normalized to G band) of pristine SWCNT-1. (g) Topography image of SWCNT-1 after the Prato reaction. (h) EFM image of SWCNT-1 after the Prato reaction. (i-k) DFM images of SWCNT-1 functionalized with the Prato reaction at gate voltage of -1.5V, 0V and +1.5V, respectively. (l) Raman spectra (normalized to G band) of the SWCNT-1 functionalized with the Prato reaction. (m) Comparison plot of EFM signals of SWCNT-1 before and after the Prato reaction with 10 data points taken at equal distance of the EFM image shown in (b). (n) Comparison plot of DFM signals of SWCNT-1 before and after the Prato reaction at different gate voltages. (Figures adapted from Ref. 116).

Pristine SWCNT-1 could be classified as a metallic tube from its Raman scattering result in Figure 6.4f [48,49]. The gate independent DFM signals

shown in Figures 6.3c-e also suggested its metallic behavior. As compared to Figure 6.4f, Figure 6.4l shows a significant Raman D band increase, suggesting that [2+3] cycloaddition had been successfully realized. The degree of the functionalization was estimated to be ~1.5% by comparing their Raman spectroscopy results before and after the functionalization. From the comparison between Figure 6.4h and 6.4b, the EFM signal of SWCNT-1 was significantly weakened after the functionalization. With ten sampling points picked along SWCNT-1 from its pristine and functionalized state, the normalized EFM signal plot shown in Figure 6.3m clearly shows that the signal drop was more than 50% upon the Prato reaction, indicating a significant drop of the metallicity upon the functionalization.

As seen in Figures 6.3i-k, the DFM images of the tube were also significantly influenced by the functionalization. The gate independent DFM signal at the pristine stage became strongly gate dependent upon the functionalization (See Figures 6.4i-k). The modulation ratio of the functionalized tube between $V_g = -1.5\text{V}$ and $V_g = +1.5\text{V}$ was approximately five, falling in the modulation ratio range of pristine semiconducting SWCNTs.

Since the DFM signal of SWCNT-1 was determined by its local conductivity [11], the strong gate dependent DFM signals suggested that apparent band gap opening should have been realized by the [2+3] cycloaddition. The weakening of the DFM signal could be caused by the reduction of the local conductivity induced as highly scattering sp^3 rehybridizations were expected on the sidewall of the tube [110].

As a comparison, the effect of dichlorocarbene functionalization ([2+1] cycloaddition) on the DFM is illustrated in Figure 6.5.

Figure 6.5 Comparison of EFM and DFM signals of metallic SWCNT-2 before and after dichlorocarbene functionalization. (a) Topography image of SWCNT-2 in pristine state. (b) EFM image of SWCNT-2 in pristine state. (c-e) DFM images of pristine SWCNT-2 at gate voltage of -1.5V, 0V and +1.5V, respectively. (f) Raman spectra (normalized to G band) of pristine SWCNT-2. (g) Topography image of SWCNT-2 after dichlorocarbene functionalization. (h) EFM image of SWCNT-2 after dichlorocarbene functionalization. (i-k) DFM images of dichlorocarbene functionalized SWCNT-2 at gate voltage of -1.5V, 0V and +1.5V, respectively. (l) Raman spectra (normalized to G band) of dichlorocarbene functionalized SWCNT-2. (m) Comparison plot of EFM signals of SWCNT-2 before and after dichlorocarbene functionalization with 10 data points taken at equal distance of the EFM image shown in (b). (n) Comparison plot of DFM signals of SWCNT-2 before and after dichlorocarbene functionalization at different gate voltages. (Figures adapted from Ref. 116).

Raman scattering of SWCNT-2 at its pristine state shows its metallic characteristic (Figure 6.5f). The gate independent DFM signals (Figures 6.5c-e) also suggested its metallic behavior. Raman scattering results of SWCNT-2 shown in Figure 6.5l showed a significant D peak increase, suggesting the successful of the dichlorocarbene functionalization. Comparison of its EFM and DFM signals before (Figures 6.5b-e) and after (Figures 6.5h-k) the functionalization showed that both signals were largely unaffected by the reaction. With ten sampling points taken along SWCNT-2 from its pristine and functionalized state, the normalized EFM signal plot shown in Figure 6.5m clearly shows that the EFM signal was preserved up to 80%, indicating significant metallicity preservation upon the functionalization.

As seen in Figures 6.5i-k, the DFM images of the tube were also almost unaffected by the functionalization. Moreover, the DFM signal at functionalized state remained almost gate independent (See Figures 6.4i-k). The modulation ratio of the functionalized tube between $V_g = -1.5\text{V}$ and $V_g = +1.5\text{V}$ was approximately 1.1, similar to the modulation ratio of a pristine metallic SWCNTs.

6.3.3 Plots on EFM Signals and DFM Modulation Ratios

For a more statistical observation, six metallic SWCNTs were studied on dichlorocarbene functionalization, while another six metallic SWCNTs were studied on the Prato reaction. The degrees of the functionalizations to all the SWCNTs were estimated to be ~0.5-3% according to their Raman scattering results. The EFM and DFM signal strength for a particular tube was averaged by taking ten sampling points from each tube. The averaged EFM signal strength and modulation ratio changes before and after the functionalizations are shown in Figure 6.6.

Figure 6.6 EFM and DFM modulation plot of metallic SWCNTs subject to dichlorocarbene functionalization (represented by triangles) and the Prato reaction (represented by squares), respectively. (Figures adapted from Ref. 116).

As seen from the plot, the EFM signals of dichlorocarbene functionalized metallic SWCNTs was preserved up to 80% as compared to their pristine states, while the Prato reaction functionalized metallic SWCNTs showed a EFM signal drop of more than 50% from their pristine states. Moreover, dichlorocarbene functionalized metallic SWCNTs showed relatively unchanged modulation ratios (0.9~1.1), while these Prato reaction functionalized metallic SWCNTs had modulation ratios beyond 1.5.

The distribution of all the sampling points taken was also plotted in Figure 6.7. The statistical plots clearly shows that dichlorocarbene functionalized metallic tubes had typical EFM preservations of more than 80% (Figure 6.7c) and DFM modulation ratios less than 1.5 (Figure 6.7d). In contrast, the Prato

reaction functionalized metallic tubes had typical EFM preservation of less than 50% (Figure 6.7a) and DFM modulation ratio more than 1.5 (Figure 6.7b).

Figure 6.7 Statistical Plot of EFM signal preservation and DFM modulation ratios with sampling points taken on all metallic SWCNTs every 1 μm distance. (a) EFM preservation ratio of SWCNTs subject to [2+3] cycloaddition. (b) DFM modulation ratio of SWCNTs subject to [2+3] cycloaddition. (c) EFM preservation ratio of SWCNTs subject to [2+1] cycloaddition. (d) DFM modulation ratio of SWCNTs subject to [2+1] cycloaddition.

6.3.4 EFM and DFM Image of Partially Functionalized Metallic SWCNTs

To compare the effect of the covalent functionalizations in one scan, the functionalizations were also realized on half-length of metallic SWCNTs, with the other half-length of the tube covered with silicon nitride (~ 200 nm by PECVD) prior to the functionalizations. The silicon nitride was etched away using dilute HF ($\text{HF}:\text{H}_2\text{O} = 1:100$) upon successful functionalizations. Two metallic SWCNTs were selected for the experiments and they were named as

SWCNT-3 (see Figure 6.8a for its AFM image) and SWCNT-4 (See Figure 6.8i).

Figure 6.8 EFM and DFM characterization of partially functionalized SWCNT-3 and SWCNT-4. (a) Topography image of SWCNT-3 with the lower portion (separated by the dash line) functionalized with dichlorocarbene functionalization while the upper part intact. (b) EFM image of SWCNT-3. (c-e) DFM images of SWCNT-3 under gate voltage of -1.5V, 0V and +1.5V, respectively. (f) Raman mapping of G band intensity of SWCNT-3 and the typical Raman spectra taken from the pristine (g) and functionalized (h) portions of SWCNT-3. (i) Topography image of SWCNT-4 with lower portion (separated by the dash line) functionalized by the Prato reaction. (j) EFM image of SWCNT-4. (k-m) DFM images of SWCNT-4 under gate voltage of -1.5V, 0V and +1.5V, respectively. (n) Raman mapping of G band intensity of SWCNT-4 and the typical Raman spectra taken from the pristine (o) and functionalized (p) portions of SWCNT-4. (Figures adapted from Ref. 116).

Figures 6.8b-e shows the EFM and DFM image of SWCNT-3 whose lower portion was successfully functionalized with [2+1] cycloaddition while the rest part remained intact. The degree of the functionalization was estimated to be ~2% (estimated from the Raman scattering in Figure 6.8f-h). These EFM and DFM images suggested that both portions were almost identical, indicating that the electronic property of the functionalized portion of SWCNT-3 was almost identical to the tube at its pristine state.

Figures 6.8j-m show the EFM and DFM images of a partially [2+3] cycloaddition functionalized SWCNT-4. The Raman scattering comparison shown in Figures 6.8n and 6.8p indicated the successful of the functionalization. The degree of functionalization was ~1.5% which was comparable to that of [2+1] cycloaddition of SWCNT-3. However, Figure 6.8j shows a sharp contrast of the EFM signal between the functionalized and pristine portions. In addition, the DFM images in Figures 6.8k-m shows that the functionalized portion of the SWCNT had gate dependence, while the pristine portion remained gate independent.

6.3.5 Discussion

Clear evidences presented above suggested that, at a low degree of functionalizations, metallic SWCNTs could preserve their metallicity after dichlorocarbene functionalization ([2+1] cycloaddition). In contrast, they could lose their metallicity upon Prato reaction ([2+3] cycloaddition). These can be interpreted through C-C reconfigurations where [2+1] cycloaddition with sp^2 rehybridization could preserve the intrinsic electronic property of metallic SWCNTs while [2+3] cycloaddition could result in sp^3 rehybridizations that would largely degrade the electronic property of the functionalized metallic SWCNTs [30,36-38].

It is worth noting that the sidewall C-C bond broken was largely dependent on the diameter of the SWCNTs as well as the orthogonal angles of the C-C bond with respect to the tube axis [24,31]. For example, only armchair metallic SWCNTs with diameter less than 2.4 nm could have their sidewall C-C broken on the orthogonal C-C bonds [24]. In this work, the diameters of the metallic SWCNTs were ~1.7-1.9 nm (manifested by Raman scattering and

AFM height measurement) and therefore the more stable sidewall C-C broken configuration should be dominated in our samples.

Another point needs to be take note is that the covalently functional groups might also contribute to the DFM and EFM signals through electronic doping. However, the fact that the Raman G^+ park positions did not shift upon the functionalizations suggested the insignificance of the doping effect. Furthermore, relatively unchanged contact potential between the AFM tip and the SWCNTs after the functionalizations also indicated that the electron Fermi level should not be largely affected by the covalent groups.

6.4 Summary

It had been demonstrated that DFM could be a powerful tool to characterize the electronic properties of SWCNTs. EFM and DFM signals of metallic SWCNTs were almost unaffected upon dichlorocarbene functionalizations, while were largely suppressed after the Prato reaction functionalizations. The results imply that the electronic property of metallic SWCNT could be largely preserved upon [2+1] cycloaddition while largely degraded after [2+3] cycloaddition. In addition, the DFM modulation ratio of the Prato reaction functionalized metallic tube was shown to be largely increased which could be explained by a band gap opening effect. In contrast, such band gap opening effect was not observed on dichlorocarbene functionalized tube under similar degree of the functionalizations. Semiconducting SWCNTs were also characterized before and after dichlorocarbene functionalizations, however, no significant changes in their EFM and DFM signals were observed. The comparison of EFM and DFM images of a semiconducting SWCNT before and after dichlorocarbene functionalization is included in Appendix D.

The results demonstrated the large influence of the sidewall bond configurations on the electronic property of metallic SWCNTs and could serve as a strong support to relative theories that the sp^2 hybridization recovery on the sidewall of SWCNTs by [2+1] cycloaddition was the key to the metallicity preservation in metallic SWCNTs [27,28].

Chapter 7 [2+1] Cycloaddition Functionalized SWCNTs Networks and Their Potential Applications in Humidity Sensing

In this chapter, various [2+1] cycloaddition functionalizations were applied to SWCNT networks to observe their electrical characteristic changes on a FET platform. It was found that those [2+1] cycloaddition functionalizations with ring structured chemical groups (which were expected to have strong periconjugation effect [128]) had significant different influences to the electrical characteristics of SWCNT network based FET devices as compared to other [2+1] cycloaddition functionalizations. The [2+1] cycloaddition functionalizations were then introduced to as grown SWCNT networks for resistive humidity sensing test and a large sensitivity increase was observed.

7.1 Introduction

As grown random SWCNT networks are excellent choices for gas and biological sensing for their low cost, high surface to volume ratio and the stability of the carbon materials [117,118]. The conductance of a SWCNT network is dependent on the conductivity through tube-tube connection as well as the conductance of the tubes themselves [119]. In as grown SWCNT network at low concentration (below metallicity percolation limit), the resistance would be predominated by semiconducting tubes while the inter-tube junction resistance is less significant [119,126,127]. Since the conductivity of semiconducting tube was very sensitive to doping effect, many sensing applications made use of low density as-grown SWCNT networks [117,118,127].

In order to increase the sensitivity and selectivity of as grown SWCNT network based sensors, many functionalizations had been applied directly to the as grown tube networks [117,118]. However, most of those functionalizations were based on non-covalent functionalization [120] or metal nanoparticle functionalization [121,122], while covalent functionalizations were seldom applied. It has been noticed that, in the literature, covalently functionalized as grown SWCNT network sensors were only based on esterification or amidation of carboxylic acid groups that could be introduced onto defect sites of the tubes during acid treatment [117,123]. The reason that many covalent functionalizations were not applied to SWCNT network based sensors is probably that they could largely degrade the conductivity of the SWCNT networks so that the signal to noise ratios of the sensors is largely reduced [22,124]. Since [2+1] cycloaddition has been shown to be able to largely preserve the conductivity of both metallic and semiconducting

SWCNTs, it might be useful to functionalize as grown SWCNT networks to improve the performances of the SWCNT based sensors [68].

As grown SWCNT network device subject to dichlorocarbene functionalization has been demonstrated by Liu et al. [26] on a FET platform, and the results showed a large preservation of the conductivity at a low degree of the functionalization. While at an extremely high degree of the functionalization, the 'on' state conductivity could drop significantly so that the on/off ratio was large reduced [26], unlike of most type of covalent functionalizations where increased on/off ratios were observed [21,22]. However, in order to make use of [2+1] cycloaddition for sensing applications, chemical groups with various functionalities might be required to be attached. In the literature, the most popular [2+1] cycloaddition were realized through carbene addition (as well as nitrene addition) [20]. For carbene addition, beside the dichlorocarbene addition that has been discussed in earlier chapters, Bingel reaction is another very important synthesis mechanism to functionalize fullerene materials [125]. In this work, [2+1] cycloaddition functionalizations with different chemical groups were successfully realized to as grown SWCNT networks through the Bingel reaction.

It is worth noting that the sidewall C-C bond opening effect of SWCNTs subject to [2+1] cycloaddition functionalizations was also expected to be affected by attached chemical groups [24,128]. For example, in armchair tubes, [2+1] cycloaddition with "five-member-ring" groups was expected to have the sidewall C-C bond broken with SWCNT diameter less than ~1.3 nm [128], while dichlorocarbene functionalization was expected to have the sidewall C-C bond broken effect with SWCNT diameter less than 2.4 nm [24]. Therefore, in a SWCNT network with large diameter distribution and random

chirality, the actual grafting configuration of [2+1] cycloaddition functionalization could be largely dependent of the individual SWCNTs in the network.

7.2 Experimental

7.2.1 SWCNT Network Device Fabrication

The growth method of SWCNT network was exactly the same as shown in Chapter 2.2. For SWCNT field effect transistor fabrication, Ti/Au electrodes were formed using standard photolithography and metallization processes. The contact area between the electrodes and SWCNT network were passivated by 200 nm silicon nitride through PECVD.

7.2.2 The Bingel Reaction

The Bingel reaction was performed directly to as grown SWCNT network on a Si/SiO₂ substrate. In a typical reaction, 1.8 mmol of diethyl bromomalonate (i.e., 2-Bromo-1,3-indandione and 2-Bromo-1,3-cyclohexanedione were used for the other two [2+1] cycloaddition functionalizations) was added into 25 ml dry *ortho*-dichlorobenzene (*o*-DCB). The solution was then stirred at 1200 rpm for 10 min. The Si/SiO₂ sample with as grown SWCNT networks exposed was then immersed into the solution and the stirring speed was reduced to 800 rpm. The sample was then evacuated to a nitrogen environment and 3.3 mmol of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) was added to the solution. The reaction was controlled for 2 hours.

7.2.3 Dichlorocarbene Functionalization

Refer to Chapter 3.2.3

7.3 Results and Discussion

7.3.1 Covalent [2+1] Cycloaddition Functionalizations

Four different [2+1] cycloaddition functionalizations were performed to four SWCNT network samples. The corresponding resultant structures upon successful functionalization are illustrated in Figure 7.1.

Figure 7.1 Schematic illustrations of the proposed resultant structures of four [2+1] cycloaddition functionalizations.

As shown in Figure 7.1a and 7.1b, Device A1 and A2 were functionalized by dichlorocarbene and diethyl bromomalonate, respectively. In contrast, Device B1 (Figure 7.1c) and B2 (Figure 7.1d) were attached with chemical groups with ring structures. It had been shown that the addend π bonds by nature preferred the flat orientation if they were free to rotate, but they could be

“locked” in place by a ring structure [128]. The ring structures formed on the sidewall of SWCNTs were suggested to have a “periconjugation” effect and, as a result, the SWCNT C-C bond close configuration could be more favorable [128]. “Periconjugation” refers to the through-space π - π interaction between the tubes and the attached groups (C=O) [130]. As a result, a strong charge transfer between the addend group and the fullerene could occur [128,130]. Therefore, it is reasonable to assume that [2+1] cycloaddition with periconjugation effect could result in larger band structure modifications as well as stronger charge transfer to SWCNTs as compared to those [2+1] cycloaddition functionalizations without periconjugation effect. Detailed discussions about the periconjugation effect of [2+1] cycloaddition functionalizations to SWCNTs were given in Ref. 128.

Raman spectroscopy was used to characterize SWCNT networks upon the functionalizations. Since SWCNT network contained many SWCNTs, collective Raman scattering taken at random locations were used to show the overall effect of the functionalizations. Figure 7.2 shows the Raman results of all the SWCNT network samples before and after the functionalizations.

Figure 7.2 Averaged Raman spectra (under 532 nm laser excitation) comparisons of SWCNT network Devices A1, A2, B1 and B2 before and after [2+1] cycloaddition functionalizations.

Raman spectra in Figure 7.2 were obtained based on the average Raman mapping with 50x50 points on a 10 μm x 10 μm area in the SWCNT network devices before and after the functionalizations. All the SWCNT networks show noticeable increases of their D peaks, suggesting the successful of the functionalizations. No obvious G^+ peak shifts were observed in all the Raman spectra, indicating no strong doping effect by covalent groups [48]. For Devices A2, B1 and B2 subjected to the Bingel reaction, further increasing the reaction time did not cause noticeable change to their Raman spectra. This was probably due to the inefficient Bingel reaction scheme as the organic synthesis could only be realized at the solid liquid interface. It is worth noting that the diameter and chirality of SWCNTs could affect their reactivities and, therefore, individual tubes in the SWCNT network samples might not be functionalized to the same degree.

7.3.2 Electrical Properties of SWCNT Network Subject to [2+1] Cycloaddition with Periconjugation Effect

Figure 7.3 shows the electrical characteristic comparisons of all SWCNT network devices before and after the functionalizations.

Figure 7.3 Transfer characteristic of SWCNT network FET devices before and after the four [2+1] cycloaddition functionalizations.

As illustrated in Figure 7.3, all the pristine SWCNT network FET devices showed p-type with the on/off ratios about one order of magnitude. The gate dependence of the transfer curves were determined by the electronic band alignment between the electrodes and SWCNT network, as well as the field induced modulation of the conductance in the SWCNT network channel region. Since the contacts between the electrodes and the SWCNT network were well passivated in all devices, their transfer curves changes upon the

functionalizations should result from the influences of the functionalizations to the tubes in the channel region.

Figures 7.3a and 7.3b show the electrical transfer curve of Devices A1 and A2 that were subjected to a low degree of dichlorocarbene functionalization and diethyl bromomalonate functionalization, respectively. It is noticed that both curves have only slight downward shifts, probably a signature of conductance preservation effect. In contrast, Devices B1 (Figure 7.3c) and B2 (Figure 7.3d) had their transfer curves largely affected. At negative gate voltages, the current drops were slightly larger than Devices A1 and A2. However, the conductance were still considered to be largely preserved (~50%) as compared to other types of covalent functionalizations [32,33]. All devices subject to [2+1] cycloaddition with ring structures showed a bit ambipolar characteristic. This might suggest that the Fermi level of the SWCNT network in the channel is slightly shifted towards the conduction band due to electron doping from attached groups. However, as the electrical characteristic was a collective behavior of all the SWCNTs, possible electronic structure changes of the tubes upon the functionalizations might also contribute to the electrical characteristic changes. This finding was consistent with the theoretical prediction mentioned above [128,130], i.e., [2+1] cycloaddition functionalizations with ring structures and "C=O" were likely to cause strong charge transfer and/or electronic band structure modifications to the SWCNTs as compared to other [2+1] cycloaddition functionalizations at a similar degree of functionalizations. However, the doping effect was not strong enough to cause significant Raman G^+ peak shift in the averaged Raman spectra shown in Figure 7.3.

7.3.3 Humidity Response of [2+1] Cycloaddition Functionalized SWCNT Networks

In this work, SWCNT network based humidity sensors were fabricated with SWCNT networks grown on large area quartz substrates. Metals electrodes were deposited through a shadow mask in order to minimize contaminations. Three types of SWCNT samples were prepared for the sensing tests, i.e., (1) as grown pristine SWCNT network, (2) the SWCNT networks functionalized by several [2+1] cycloaddition functionalizations and (3) SWCNT network subject to acid treatment (to make SWCNTs more hydrophilic) [124,129]. In all samples, the contact areas between Ti/Au electrodes and SWCNT networks were covered with 200 nm thick silicon nitride to ensure the sensing response would originate from the SWCNT networks, rather than the metallic contacts.

Humidity level in the test chamber was adjusted through humid air to dry air flow ratio. The resistance changes of the SWCNT networks at different humidity levels at room temperature were tested and compared.

Figure 7.4 Normalized conductances of SWCNT network samples at different humidity levels.

Figure 7.4 shows normalized conductance versus humidity for six SWCNT network samples. Devices S1 and S2 represented pristine and acid treated SWCNT network samples, respectively. Devices S3, S4, S5 and S6 represented SWCNT network sensors functionalized by dichlorocarbene, diethyl bromomalonate, 2-Bromo-1,3-indandione and 2-Bromo-1,3-cyclohexanedione, respectively. From Figure 7.4, one can see that the conductance changes of S1-S4 were relatively small as humidity increases. In sharp contrast, Devices S5 and S6 show much larger responses, especially for the humidity level above RH=40%.

Up to now, there is still controversy whether the resistive response of individual SWCNTs to humidity originates from electronic donation from water molecule to the tubes [127,129], hydrogen bonding with oxygen defect sites on SWCNTs [131], or the introduction of charge-trapping sites on the SWCNTs through direct H₂O adsorption and/or interaction with the substrate [132]. However, recent reports [127,129] suggested that electron donation from to semiconducting SWCNT could cause significant increase in the electron conductivities in semiconducting SWCNTs, especially for humidity level above RH= $\sim$ 70%.

In this work, the conductances of as grown SWCNT networks were largely controlled by the semiconducting tubes so that such electron doping from water molecules to semiconducting tubes should have significant influence to the conductivity of the SWCNT networks. Pristine semiconducting SWCNTs were generally considered being slightly p-doped by ambient oxygen molecules [133], while with environmental humidity increase, electron donations from water molecules would compensate the hole hopping, resulting in a decrease of the hole conductivities of semiconducting tubes [127]. However, at higher humidity, significant electron doping from water molecules to semiconducting tubes could enhance their electron conductivity [127]. Therefore, if we treat the conductance increase with humidity in all the devices (refer to Figure 7.4) to be caused by the enhancement of electron conductance of the SWCNT networks originating from electron donation by water molecules, it becomes reasonable to assume that SWCNT networks functionalized by [2+1] cycloadditions with ring structure (Devices S5 and S6) had larger electron conduction enhancement upon electron doping from water molecules. However, it is worth noting that hole conductance suppression

induced SWCNT network conductance drops were not observed in our samples at low humidity levels (such effects were observed in Ref. 127 and Ref. 129), implying that the doping mechanism alone might not be sufficient to explain the resistive humidity response of the SWCNTs networks in our samples. In addition, the humidity responses of Devices S5 and S6 were also much larger than that of Device S2 (with acid treatment to make SWCNTs more hydrophilic), suggesting the large humidity responses of S5 and S6 as compared to pristine SWCNT network, S1, were not likely caused by the hydrophilicity increase of the tubes.

The SWCNT network devices were also tested under a humidity level switched between a low humidity (between RH=10% and RH=30%) for 30 s and a high humidity (between RH=30% and RH=65%) for 30s. From Figure 7.4, Device S1 had the lowest sensitivity subject to such humidity variations. Devices S2, S3 and S4 showed slightly higher sensitivity, while Devices S5 and S6 were of the largest sensitivity. Figure 7.5 and Figure 7.6 show the humidity response of Devices S1, S2 and S5 for comparisons in the low and higher humidity region, respectively.

Figure 7.5 Resistive responses of Devices S1, S2 and S5 subjected to humidity switching between RH=10% and RH=30% at 30 s intervals.

Figure 7.6 Resistive responses of Devices S1, S2 and S5 subjected to humidity switching between RH=30% and RH=65% at 30 s intervals.

As shown in Figures 7.5 and 7.6, the response time for Device S1 was larger than that for Device S2. This was probably caused by the more hydrophilic SWCNTs in Device S2 (subjected to acid treatment) than those pristine SWCNTs in Device S1. In sharp contrast, the large resistive response of Device S5, especially in Figure 7.6 at high humidity levels, was attributed to its large electron conducting enhancement upon water molecule doping as discussed above.

7.4 Conclusion

In this work, we have shown that various [2+1] cycloaddition could largely preserve the conductance of the functionalized SWCNT networks. Especially [2+1] cycloaddition functionalization with ring structured chemical groups (2-Bromo-1,3-indandione and 2-Bromo-1,3-cyclohexanedione) could change the transfer characteristic from p-type to ambipolar type. This finding implies that possible electron doping and/or electronic band structure change by the special arrangement of 'periconjugation' effect [130]. Finally, the SWCNT networks functionalized by [2+1] cycloaddition with ring structures were shown to have a large response to humidity variation. The results suggest that [2+1] cycloaddition with different chemical groups could possibly make SWCNT network in favor of humidity detection.

Chapter 8 Conclusion and Recommendation

8.1 Conclusion

This thesis focuses on the electrical conductance and electronic property of SWCNTs upon covalent functionalizations. Electrical measurements showed that the conductance of individual SWCNTs with diameters of 1.2~2.2 nm can be largely preserved upon [2+1] cycloaddition functionalization. Utilizing EFM and DFM techniques, we confirmed that the electronic properties of metallic SWCNT could be largely preserved upon [2+1] cycloaddition functionalization, while largely degraded upon the Prato reaction. These results support the theoretical predictions that [2+1] cycloaddition functionalization could break the sidewall carbon bonds and recover the sp^2 rehybridization on SWCNT sidewalls, and thus preserve the intrinsic electronic property of SWCNTs.

For most experiments in this thesis, well separated individual as-grown SWCNTs were used. These as-grown tubes were considered free from chemical contaminations and thus suitable to be used to examine the influences of the covalent functionalizations. Micrometer scale markers were generally used to identify the locations of individual SWCNTs so that comparisons of the same SWCNT before and after the functionalizations can be obtained. Raman spectroscopy technique was used in all experiments to determine the structural and electronic property of the SWCNTs, as well as to examine the covalent modifications to these tubes.

First of all, we presented an analysis of the reactivity of individual as-grown SWCNTs upon dichlorocarbene functionalization. The result showed that there was significant degree of covalent functionalization realized on small diameter (~1.3 nm) tubes, while no detectable covalent functionalization on

large diameter (~2.0 nm) tubes. To first approximation, the degree of the functionalization decreases as SWCNT diameter increases. The results imply that the curvature induced strain release could be the driving force for such diameter dependent reactivity, and thus it is likely for the tubes to have sidewall carbon bond broken effect upon [2+1] cycloaddition functionalizations.

The electrical measurement on individual SWCNTs (with diameter range ~1.2-2.2 nm) showed a significant conductance preservation effect; in sharp contrast with most conventional covalent functionalizations in the literature where the conductance drops could be several orders of magnitude. Possible electronic band structure modifications by the dichlorocarbene groups were reflected in the electrical measurement, where metallic tubes generally had their on/off ratios increased while semiconducting tubes generally had their on/off ratios decreased upon the functionalization.

The local electrical and electronic properties of SWCNTs were firstly characterized with a conventional EFM technique before and after dichlorocarbene functionalization and the Prato reaction. The EFM signal of the metallic tube were largely unaffected by dichlorocarbene functionalization, indicating a strong metallicity preservation effect. In contrast, after the Prato reaction, the EFM signal of the functionalized metallic tube was largely suppressed, indicating that the metallicity of the tube was largely degraded.

Utilizing a novel DFM technique, we had successfully investigated the band gap and local conductivity of metallic tubes affected by the covalent functionalizations. The results showed that DFM signals of metallic SWCNTs was almost unaffected upon dichlorocarbene functionalization, while largely suppressed after the Prato reaction functionalization. This further

demonstrates the local conductivity preservation effect of [2+1] cycloaddition to SWCNTs. In addition, the DFM modulation ratios of the Prato reaction functionalized metallic tubes became largely gate dependent, suggesting that a significant band gap opening is caused upon the functionalization. This band gap opening effect (modulation ratio increase) was not observed on dichlorocarbene functionalized metallic tubes with similar degree of the functionalization, serving as an additional support to the theories on the electronic structure preservation effect of [2+1] cycloaddition functionalized SWCNTs.

Last, various [2+1] cycloaddition functionalizations applied to SWCNT networks showed that, at a low degree of the functionalization, [2+1] cycloadditions with ring structure could largely modify the electrical behavior of the SWCNT network transistors. Such [2+1] cycloaddition functionalized SWCNT networks were implemented as the sensing elements for humidity detection. A much larger sensitivity of the [2+1] cycloaddition (with ring structure) functionalized SWCNT network was achieved as compared to pristine SWCNT network and acid treated (more hydrophilic) SWCNT network.

8.2 Recommendation

In this thesis, through the reactivity, conductivity and scanning probe characterization, the influences of [2+1] cycloaddition on the electrical properties of functionalized SWCNTs were clearly demonstrated. However, the research should be carry on to gain a deep understanding.

First of all, the diameter dependence, together with the chirality dependence on the reactivity is worth studying in order to have a full physical picture how

carbon-carbon bonds of SWCNTs and the electronic properties are adjusted upon the functionalizations.

Secondly, although dichlorocarbene functionalized SWCNTs with diameter range of 1.2-2.2 nm show significant conductance and electronic property preservation, [2+1] cycloaddition functionalization with other chemical groups to SWCNTs might not be guaranteed to have such conductance preservation effect. This is because the interactions between different covalent groups to the sidewall of SWCNTs could be quite different, and the 'critical diameter' for open to close transition could also be largely different. Therefore, for a specific or specific type of covalent groups, much smaller diameter SWCNTs might be needed to have the sidewall C-C bond broken induced electrical property preservation effect. Moreover, it could be interesting to find individual SWCNTs with much larger diameter (>2.4 nm) to investigate the effect of [2+1] cycloadditions.

In addition, it has been predicted that the sidewall carbon bond broken effect could be reversible upon changing the chemical structure of the covalent groups attached [128]. Thus, possible sensing elements could be realized based on such switchable conductance effect by using SWCNT with appropriate diameters.

Lastly, [2+1] cycloaddition functionalized SWCNT networks with various chemical groups may find useful applications in gas sensing.

Bibliography

- [1] T. W. Odom, J. L. Huang, P. Kim *et al.*, "Atomic structure and electronic properties of single-walled carbon nanotubes," *Nature*, vol. 391, no. 6662, pp. 62-64, Jan 1, 1998.
- [2] T. W. Ebbesen, H. J. Lezec, H. Hiura *et al.*, "Electrical conductivity of individual carbon nanotubes," *Nature*, vol. 382, no. 6586, pp. 54-56, Jul 4, 1996.
- [3] P. C. Eklund, B. K. Pradhan, U. J. Kim *et al.*, "Large-scale production of single-walled carbon nanotubes using ultrafast pulses from a free electron laser," *Nano Letters*, vol. 2, no. 6, pp. 561-566, Jun, 2002.
- [4] A. Javey, J. Guo, Q. Wang *et al.*, "Ballistic carbon nanotube field-effect transistors," *Nature*, vol. 424, no. 6949, pp. 654-657, Aug 7, 2003.
- [5] S. Liu, Q. Shen, Y. Cao *et al.*, "Chemical functionalization of single-walled carbon nanotube field-effect transistors as switches and sensors," *Coordination Chemistry Reviews*, vol. 254, no. 9-10, pp. 1101-1116, May, 2010.
- [6] Y. C. Ma, Y. Y. Xia, M. W. Zhao *et al.*, "Effective hydrogen storage in single-wall carbon nanotubes," *Physical Review B*, vol. 63, no. 11, pp. 115422-115422, Mar 15, 2001.
- [7] W. A. Deheer, A. Chatelain, and D. Ugarte, "A Carbon Nanotube Field-Emission Electron Source," *Science*, vol. 270, no. 5239, pp. 1179-1180, Nov 17, 1995.

- [8] X. Wang, W. Z. Li, Z. W. Chen *et al.*, "Durability investigation of carbon nanotube as catalyst support for proton exchange membrane fuel cell," *Journal of Power Sources*, vol. 158, no. 1, pp. 154-159, Jul 14, 2006.
- [9] H. Nishijima, S. Kamo, S. Akita *et al.*, "Carbon-nanotube tips for scanning probe microscopy: Preparation by a controlled process and observation of deoxyribonucleic acid," *Applied Physics Letters*, vol. 74, no. 26, pp. 4061-4063, Jun 28, 1999.
- [10] A. B. Dalton, S. Collins, E. Munoz *et al.*, "Super-tough carbon-nanotube fibres - These extraordinary composite fibres can be woven into electronic textiles.," *Nature*, vol. 423, no. 6941, pp. 703-703, Jun 12, 2003.
- [11] H. W. Zhu, C. L. Xu, D. H. Wu *et al.*, "Direct synthesis of long single-walled carbon nanotube strands," *Science*, vol. 296, no. 5569, pp. 884-886, May 3, 2002.
- [12] C. Journet, W. K. Maser, P. Bernier *et al.*, "Large-scale production of single-walled carbon nanotubes by the electric-arc technique," *Nature*, vol. 388, no. 6644, pp. 756-758, Aug 21, 1997.
- [13] L. A. Girifalco, M. Hodak, and R. S. Lee, "Carbon nanotubes, buckyballs, ropes, and a universal graphitic potential," *Physical Review B*, vol. 62, no. 19, pp. 13104-13110, Nov 15, 2000.
- [14] S. Iijima, "Carbon nanotubes: past, present, and future," *Physica B-Condensed Matter*, vol. 323, no. 1-4, pp. 1-5, Oct, 2002.

-
- [15] Minot, Ethan Davis. "Tuning the band structure of carbon nanotubes." PhD thesis, Cornell University, 2004.
- [16] Y. S. Lee, M. B. Nardelli, and N. Marzari, "Band structure and quantum conductance of nanostructures from maximally localized wannier functions: The case of functionalized carbon nanotubes," *Physical Review Letters*, vol. 95, no. 7, pp. 076804-076804, Aug 12, 2005.
- [17] C. T. White, and T. N. Todorov, "Carbon nanotubes as long ballistic conductors," *Nature*, vol. 393, no. 6682, pp. 240-242, May 21, 1998.
- [18] J. Kong, E. Yenilmez, T. W. Tombler *et al.*, "Quantum interference and ballistic transmission in nanotube electron waveguides," *Physical Review Letters*, vol. 87, no. 10, pp. 106801-106801, Sep 3, 2001.
- [19] A. Hirsch, "Functionalization of single-walled carbon nanotubes," *Angewandte Chemie-International Edition*, vol. 41, no. 11, pp. 1853-1859, 2002.
- [20] S. Banerjee, T. Hemraj-Benny, and S. S. Wong, "Covalent surface chemistry of single-walled carbon nanotubes," *Advanced Materials*, vol. 17, no. 1, pp. 17-29, Jan 18, 2005.
- [21] S. Banerjee, M. G. C. Kahn, and S. S. Wong, "Rational chemical strategies for carbon nanotube functionalization," *Chemistry-a European Journal*, vol. 9, no. 9, pp. 1899-1908, May 9, 2003.
- [22] H. M. So, B. K. Kim, D. W. Park *et al.*, "Selective suppression of conductance in metallic carbon nanotubes," *Journal of the American Chemical Society*, vol. 129, no. 16, pp. 4866-4867, Apr 25, 2007.

-
- [23] T. Yildirim, O. Gulseren, and S. Ciraci, "Exohydrogenated single-wall carbon nanotubes," *Physical Review B*, vol. 64, no. 7, pp. 075404-075404, Aug 15, 2001.
- [24] Y.-S. Lee, and N. Marzari, "Cycloaddition Functionalizations to Preserve or Control the Conductance of Carbon Nanotubes," *Physical Review Letters*, vol. 97, no. 11, pp. 116801-116801, 2006.
- [25] A. Lopez-Bezanilla, F. Triozon, S. Latil *et al.*, "Effect of the Chemical Functionalization on Charge Transport in Carbon Nanotubes at the Mesoscopic Scale," *Nano Letters*, vol. 9, no. 3, pp. 940-944, Mar, 2009.
- [26] C. Liu, Q. Zhang, F. Stellacci *et al.*, "Carbene-Functionalized Single-Walled Carbon Nanotubes and Their Electrical Properties," *Small*, vol. 7, no. 9, pp. 1257-1263, May 9, 2011.
- [27] L. M. Peng, Z. L. Zhang, Z. Q. Xue *et al.*, "Stability of carbon nanotubes: How small can they be?," *Physical Review Letters*, vol. 85, no. 15, pp. 3249-3252, Oct 9, 2000.
- [28] J. J. Zhao, Z. F. Chen, Z. Zhou *et al.*, "Engineering the electronic structure of single-walled carbon nanotubes by chemical functionalization," *Chemphyschem*, vol. 6, no. 4, pp. 598-601, Apr, 2005.
- [29] Z. F. Chen, S. Nagase, A. Hirsch *et al.*, "Side-wall opening of single-walled carbon nanotubes (SWCNTs) by chemical modification: A critical theoretical study," *Angewandte Chemie-International Edition*, vol. 43, no. 12, pp. 1552-1554, 2004.

-
- [30] H. Park, J. J. Zhao, and J. P. Lu, "Effects of sidewall functionalization on conducting properties of single wall carbon nanotubes," *Nano Letters*, vol. 6, no. 5, pp. 916-919, May, 2006.
- [31] A. Lopez-Bezanilla, X. Blase, and S. Roche, "Quantum Transport Properties of Chemically Functionalized Long Semiconducting Carbon Nanotubes," *Nano Research*, vol. 3, no. 4, pp. 288-295, Apr, 2010.
- [32] J. B. Cui, M. Burghard, and K. Kern, "Reversible sidewall osmylation of individual carbon nanotubes," *Nano Letters*, vol. 3, no. 5, pp. 613-615, May, 2003.
- [33] C. J. Wang, Q. Cao, T. Ozel *et al.*, "Electronically selective chemical functionalization of carbon nanotubes: Correlation between Raman spectral and electrical responses," *Journal of the American Chemical Society*, vol. 127, no. 32, pp. 11460-11468, Aug 17, 2005.
- [34] C. Klinke, J. B. Hannon, A. Afzali *et al.*, "Field-effect transistors assembled from functionalized carbon nanotubes," *Nano Letters*, vol. 6, no. 5, pp. 906-910, May, 2006.
- [35] J. J. Zhao, H. K. Park, J. Han *et al.*, "Electronic properties of carbon nanotubes with covalent sidewall functionalization," *Journal of Physical Chemistry B*, vol. 108, no. 14, pp. 4227-4230, Apr 8, 2004.
- [36] O. O. Ogunro, C. I. Nicolas, E. A. Mintz *et al.*, "Band Gap Opening in the Cycloaddition Functionalization of Carbon Nanotubes," *Acs Macro Letters*, vol. 1, no. 4, pp. 524-528, Apr, 2012.

-
- [37] E. Cho, S. Shin, and Y. G. Yoon, "First-principles studies on carbon nanotubes functionalized with azomethine ylides," *Journal of Physical Chemistry C*, vol. 112, no. 31, pp. 11667-11672, Aug 7, 2008.
- [38] E. Cho, H. Kim, C. Kim *et al.*, "Ab initio study on the carbon nanotube with various degrees of functionalization," *Chemical Physics Letters*, vol. 419, no. 1-3, pp. 134-138, Feb 15, 2006.
- [39] G. Zheng, Q. Q. Li, K. L. Jiang *et al.*, "Transition of single-walled carbon nanotubes from metallic to semiconducting in field-effect transistors by hydrogen plasma treatment," *Nano Letters*, vol. 7, no. 6, pp. 1622-1625, Jun, 2007.
- [40] V. Georgakilas, K. Kordatos, M. Prato *et al.*, "Organic functionalization of carbon nanotubes," *Journal of the American Chemical Society*, vol. 124, no. 5, pp. 760-761, Feb 6, 2002.
- [41] T. Umeyama, N. Tezuka, M. Fujita *et al.*, "Retention of intrinsic electronic properties of soluble single-walled carbon nanotubes after a significant degree of sidewall functionalization by the bingel reaction," *Journal of Physical Chemistry C*, vol. 111, no. 27, pp. 9734-9741, Jul 12, 2007.
- [42] H. Hu, B. Zhao, M. A. Hamon *et al.*, "Sidewall functionalization of single-walled carbon nanotubes by addition of dichlorocarbene," *Journal of the American Chemical Society*, vol. 125, no. 48, pp. 14893-14900, Dec 3, 2003.
- [43] M. A. Hamon, M. E. Itkis, S. Niyogi *et al.*, "Effect of rehybridization on the electronic structure of single-walled carbon nanotubes," *Journal of*

- the American Chemical Society*, vol. 123, no. 45, pp. 11292-11293, Nov 14, 2001.
- [44] Z. F. Chen, W. Thiel, and A. Hirsch, "Reactivity of the convex and concave surfaces of single-walled carbon nanotubes (SWCNTs) towards addition reactions: Dependence on the carbon-atom pyramidalization," *Chemphyschem*, vol. 4, no. 1, pp. 93-97, Jan 13, 2003.
- [45] Y. S. Lee, and N. Marzari, "Cycloadditions to control bond breaking in naphthalenes, fullerenes, and carbon nanotubes: A first-principles study," *Journal of Physical Chemistry C*, vol. 112, no. 12, pp. 4480-4485, Mar 27, 2008.
- [46] J. Q. Li, G. X. Jia, Y. F. Zhang *et al.*, "Bond-curvature effect of sidewall [2+1] cycloadditions of single-walled carbon nanotubes: A new criterion to the adduct structures," *Chemistry of Materials*, vol. 18, no. 15, pp. 3579-3584, Jul 25, 2006.
- [47] J. Kong, H. T. Soh, A. M. Cassell *et al.*, "Synthesis of individual single-walled carbon nanotubes on patterned silicon wafers," *Nature*, vol. 395, no. 6705, pp. 878-881, Oct 29, 1998.
- [48] M. S. Dresselhaus, G. Dresselhaus, and A. Jorio, "Raman spectroscopy of carbon nanotubes in 1997 and 2007," *Journal of Physical Chemistry C*, vol. 111, no. 48, pp. 17887-17893, Dec 6, 2007.
- [49] S. D. M. Brown, A. Jorio, P. Corio *et al.*, "Origin of the Breit-Wigner-Fano lineshape of the tangential G-band feature of metallic carbon nanotubes," *Physical Review B*, vol. 63, no. 15, pp. 155414-155414, Apr 15, 2001.

- [50] A. Jorio, R. Saito, J. H. Hafner *et al.*, "Structural (n, m) determination of isolated single-wall carbon nanotubes by resonant Raman scattering," *Physical Review Letters*, vol. 86, no. 6, pp. 1118-1121, Feb 5, 2001.
- [51] A. Jorio, C. Fantini, M. A. Pimenta *et al.*, "Resonance Raman spectroscopy (n,m)-dependent effects in small-diameter single-wall carbon nanotubes," *Physical Review B*, vol. 71, no. 7, pp. 075401-075401, Feb, 2005.
- [52] A. Jorio, M. A. Pimenta, A. G. Souza *et al.*, "Characterizing carbon nanotube samples with resonance Raman scattering," *New Journal of Physics*, vol. 5, pp. 139.1-139.17, Oct 16, 2003.
- [53] H. Kataura, Y. Kumazawa, Y. Maniwa *et al.*, "Optical properties of single-wall carbon nanotubes," *Synthetic Metals*, vol. 103, no. 1-3, pp. 2555-2558, Jun, 1999.
- [54] R. Graupner, "Raman spectroscopy of covalently functionalized single-wall carbon nanotubes," *Journal of Raman Spectroscopy*, vol. 38, no. 6, pp. 673-683, Jun, 2007.
- [55] M. S. Dresselhaus, A. Jorio, A. G. Souza *et al.*, "Defect characterization in graphene and carbon nanotubes using Raman spectroscopy," *Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences*, vol. 368, no. 1932, pp. 5355-5377, Dec 13, 2010.
- [56] A. C. Ferrari, and J. Robertson, "Interpretation of Raman spectra of disordered and amorphous carbon," *Physical Review B*, vol. 61, no. 20, pp. 14095-14107, May 15, 2000.

-
- [57] C. Casiraghi, A. C. Ferrari, and J. Robertson, "Raman spectroscopy of hydrogenated amorphous carbons," *Physical Review B*, vol. 72, no. 8, pp. 085401-085401, Aug, 2005.
- [58] M. S. Strano, C. A. Dyke, M. L. Usrey *et al.*, "Electronic structure control of single-walled carbon nanotube functionalization," *Science*, vol. 301, no. 5639, pp. 1519-1522, Sep 12, 2003.
- [59] M. Kanungo, H. Lu, G. G. Malliaras *et al.*, "Suppression of Metallic Conductivity of Single-Walled Carbon Nanotubes by Cycloaddition Reactions," *Science*, vol. 323, no. 5911, pp. 234-237, Jan 9, 2009.
- [60] J. Appenzeller, J. Knoch, V. Derycke *et al.*, "Field-modulated carrier transport in carbon nanotube transistors," *Physical Review Letters*, vol. 89, no. 12, pp. 126801-126801, Sep 16, 2002.
- [61] C. X. Chen, W. Zhang, B. Zhao *et al.*, "Investigation of Schottky-Barrier carbon nanotube field-effect transistor by an efficient semi-classical numerical modeling," *Physics Letters A*, vol. 374, no. 2, pp. 309-312, Dec 28, 2009.
- [62] J. Appenzeller, J. Knoch, M. Radosavljevic *et al.*, "Multimode transport in Schottky-barrier carbon-nanotube field-effect transistors," *Physical Review Letters*, vol. 92, no. 22, pp. 226802-226802, Jun 4, 2004.
- [63] S. Heinze, M. Radosavljevic, J. Tersoff *et al.*, "Unexpected scaling of the performance of carbon nanotube Schottky-barrier transistors," *Physical Review B*, vol. 68, no. 23, pp. 235418-235418, Dec, 2003.

-
- [64] Z. H. Chen, J. Appenzeller, J. Knoch *et al.*, "The role of metal-nanotube contact in the performance of carbon nanotube field-effect transistors," *Nano Letters*, vol. 5, no. 7, pp. 1497-1502, Jul, 2005.
- [65] S. D. Li, Z. Yu, C. Rutherglen *et al.*, "Electrical properties of 0.4 cm long single-walled carbon nanotubes," *Nano Letters*, vol. 4, no. 10, pp. 2003-2007, Oct, 2004.
- [66] T. Durkop, S. A. Getty, E. Cobas *et al.*, "Extraordinary mobility in semiconducting carbon nanotubes," *Nano Letters*, vol. 4, no. 1, pp. 35-39, Jan, 2004.
- [67] M. Ouyang, J. L. Huang, C. L. Cheung *et al.*, "Energy gaps in "metallic" single-walled carbon nanotubes," *Science*, vol. 292, no. 5517, pp. 702-705, Apr 27, 2001.
- [68] K. Zhang, Q. Zhang, C. Liu *et al.*, "Diameter Effect on the Sidewall Functionalization of Single-Walled Carbon Nanotubes by Addition of Dichlorocarbene," *Advanced Functional Materials*, vol. 22, no. 24, pp. 5216-5223, Dec 19, 2012.
- [69] B. Kozinsky, and N. Marzari, "Static dielectric properties of carbon nanotubes from first principles," *Physical Review Letters*, vol. 96, no. 16, pp. 166801-166801, Apr 28, 2006.
- [70] R. Krupke, F. Hennrich, H. von Lohneysen *et al.*, "Separation of metallic from semiconducting single-walled carbon nanotubes," *Science*, vol. 301, no. 5631, pp. 344-347, Jul 18, 2003.

-
- [71] C. A. Martin, J. K. W. Sandler, A. H. Windle *et al.*, "Electric field-induced aligned multi-wall carbon nanotube networks in epoxy composites," *Polymer*, vol. 46, no. 3, pp. 877-886, Jan 26, 2005.
- [72] N. Peng, Q. Zhang, J. Q. Li *et al.*, "Influences of ac electric field on the spatial distribution of carbon nanotubes formed between electrodes," *Journal of Applied Physics*, vol. 100, no. 2, pp. 024309-024309, Jul 15, 2006.
- [73] J. Q. Li, Q. Zhang, D. J. Yang *et al.*, "Fabrication of carbon nanotube field effect transistors by AC dielectrophoresis method," *Carbon*, vol. 42, no. 11, pp. 2263-2267, 2004.
- [74] A. Vijayaraghavan, S. Blatt, D. Weissenberger *et al.*, "Ultra-large-scale directed assembly of single-walled carbon nanotube devices," *Nano Letters*, vol. 7, no. 6, pp. 1556-1560, Jun, 2007.
- [75] S. Shekhar, P. Stokes, and S. I. Khondaker, "Ultrahigh Density Alignment of Carbon Nanotube Arrays by Dielectrophoresis," *Acs Nano*, vol. 5, no. 3, pp. 1739-1746, Mar, 2011.
- [76] S. V. Kalinin, and N. Balke, "Local Electrochemical Functionality in Energy Storage Materials and Devices by Scanning Probe Microscopies: Status and Perspectives," *Advanced Materials*, vol. 22, no. 35, pp. E193-E209, Sep 15, 2010.
- [77] T. Melin, H. Diesinger, D. Deresmes *et al.*, "Probing nanoscale dipole-dipole interactions by electric force microscopy," *Physical Review Letters*, vol. 92, no. 16, pp. 166101-166101, Apr 23, 2004.

- [78] O. Cherniavskaya, L. W. Chen, V. Weng *et al.*, "Quantitative noncontact electrostatic force Imaging of nanocrystal polarizability," *Journal of Physical Chemistry B*, vol. 107, no. 7, pp. 1525-1531, Feb 20, 2003.
- [79] N. Balke, S. Jesse, Y. Kim *et al.*, "Real Space Mapping of Li-Ion Transport in Amorphous Si Anodes with Nanometer Resolution," *Nano Letters*, vol. 10, no. 9, pp. 3420-3425, Sep, 2010.
- [80] T. S. Jespersen, and J. Nygard, "Mapping of individual carbon nanotubes in polymer/nanotube composites using electrostatic force microscopy," *Applied Physics Letters*, vol. 90, no. 18, pp. 183108-183108, Apr 30, 2007.
- [81] J. F. Campbell, I. Tessmer, H. H. Thorp *et al.*, "Atomic force microscopy studies of DNA-wrapped carbon nanotube structure and binding to quantum dots," *Journal of the American Chemical Society*, vol. 130, no. 32, pp. 10648-10655, Aug 13, 2008.
- [82] S. S. Wong, J. D. Harper, P. T. Lansbury *et al.*, "Carbon nanotube tips: High-resolution probes for imaging biological systems," *Journal of the American Chemical Society*, vol. 120, no. 3, pp. 603-604, Jan 28, 1998.
- [83] A. Bachtold, M. S. Fuhrer, S. Plyasunov *et al.*, "Scanned probe microscopy of electronic transport in carbon nanotubes," *Physical Review Letters*, vol. 84, no. 26, pp. 6082-6085, Jun 26, 2000.
- [84] H. W. C. Postma, M. de Jonge, Z. Yao *et al.*, "Electrical transport through carbon nanotube junctions created by mechanical

- manipulation," *Physical Review B*, vol. 62, no. 16, pp. 10653-10656, Oct 15, 2000.
- [85] J. Lefebvre, J. F. Lynch, M. Llaguno *et al.*, "Single-wall carbon nanotube circuits assembled with an atomic force microscope," *Applied Physics Letters*, vol. 75, no. 19, pp. 3014-3016, Nov 8, 1999.
- [86] H. W. C. Postma, A. Sellmeijer, and C. Dekker, "Manipulation and imaging of individual single-walled carbon nanotubes with an atomic force microscope," *Advanced Materials*, vol. 12, no. 17, pp. 1299-1302, Sep 1, 2000.
- [87] D. Bozovic, M. Bockrath, J. H. Hafner *et al.*, "Plastic deformations in mechanically strained single-walled carbon nanotubes," *Physical Review B*, vol. 67, no. 3, pp. 033407-033407, Jan 15, 2003.
- [88] M. R. Falvo, G. J. Clary, R. M. Taylor *et al.*, "Bending and buckling of carbon nanotubes under large strain," *Nature*, vol. 389, no. 6651, pp. 582-584, Oct 9, 1997.
- [89] E. D. Minot, Y. Yaish, V. Sazonova *et al.*, "Tuning carbon nanotube band gaps with strain," *Physical Review Letters*, vol. 90, no. 15, pp. 156401-156401, Apr 18, 2003.
- [90] S. S. Wong, A. T. Woolley, E. Joselevich *et al.*, "Covalently-functionalized single-walled carbon nanotube probe tips for chemical force microscopy," *Journal of the American Chemical Society*, vol. 120, no. 33, pp. 8557-8558, Aug 26, 1998.

- [91] C. L. Cheung, J. H. Hafner, T. W. Odom *et al.*, "Growth and fabrication with single-walled carbon nanotube probe microscopy tips," *Applied Physics Letters*, vol. 76, no. 21, pp. 3136-3138, May 22, 2000.
- [92] Q. Ye, A. M. Cassell, H. B. Liu *et al.*, "Large-scale fabrication of carbon nanotube probe tips for atomic force microscopy critical dimension Imaging applications," *Nano Letters*, vol. 4, no. 7, pp. 1301-1308, Jul, 2004.
- [93] H. J. Dai, J. H. Hafner, A. G. Rinzler *et al.*, "Nanotubes as nanoprobe in scanning probe microscopy," *Nature*, vol. 384, no. 6605, pp. 147-150, Nov 14, 1996.
- [94] P. Keblinski, S. K. Nayak, P. Zapol *et al.*, "Charge distribution and stability of charged carbon nanotubes," *Physical Review Letters*, vol. 89, no. 25, pp. 255503-255503, Dec 16, 2002.
- [95] T. S. Jespersen, and J. Nygard, "Charge trapping in carbon nanotube loops demonstrated by electrostatic force microscopy," *Nano Letters*, vol. 5, no. 9, pp. 1838-1841, Sep, 2005.
- [96] W. Lu, D. Wang, and L. W. Chen, "Near-static dielectric polarization of individual carbon nanotubes," *Nano Letters*, vol. 7, no. 9, pp. 2729-2733, Sep, 2007.
- [97] J. A. Fagan, J. R. Simpson, B. J. Landi *et al.*, "Dielectric response of aligned semiconducting single-wall nanotubes," *Physical Review Letters*, vol. 98, no. 14, pp. 147402-147402, Apr 6, 2007.
- [98] W. Lu, Y. Xiong, and L. W. Chen, "Length-Dependent Dielectric Polarization in Metallic Single-Walled Carbon Nanotubes," *Journal of*

- Physical Chemistry C*, vol. 113, no. 24, pp. 10337-10340, Jun 18, 2009.
- [99] M. Paillet, P. Poncharal, and A. Zahab, "Electrostatics of individual single-walled carbon nanotubes investigated by electrostatic force microscopy," *Physical Review Letters*, vol. 94, no. 18, pp. 186801-186801, May 13, 2005.
- [100] P. Poncharal, Z. L. Wang, D. Ugarte *et al.*, "Electrostatic deflections and electromechanical resonances of carbon nanotubes," *Science*, vol. 283, no. 5407, pp. 1513-1516, Mar 5, 1999.
- [101] J. S. Heo, and M. Bockrath, "Local electronic structure of single-walled carbon nanotubes from electrostatic force microscopy," *Nano Letters*, vol. 5, no. 5, pp. 853-857, May, 2005.
- [102] S. R. Hunt, E. J. Fuller, B. L. Corso *et al.*, "Distinguishing carbon nanotube defect chemistry using scanning gate spectroscopy," *Physical Review B*, vol. 85, no. 23, pp. 235418-235418, Jun 7, 2012.
- [103] T. D. Krauss, and L. E. Brus, "Charge, polarizability, and photoionization of single semiconductor nanocrystals (vol 83, pg 4840, 1999)," *Physical Review Letters*, vol. 84, no. 7, pp. 1638-1638, Feb 14, 2000.
- [104] T. Melin, H. Diesinger, D. Deresmes *et al.*, "Electric force microscopy of individually charged nanoparticles on conductors: An analytical model for quantitative charge imaging," *Physical Review B*, vol. 69, no. 3, pp. 035321-035321, Jan, 2004.

-
- [105] W. Lu, Y. Xiong, A. Hassanien *et al.*, "A Scanning Probe Microscopy Based Assay for Single-Walled Carbon Nanotube Metallicity," *Nano Letters*, vol. 9, no. 4, pp. 1668-1672, Apr, 2009.
- [106] A. P. M. Barboza, A. P. Gomes, H. Chacham *et al.*, "Probing electric characteristics and sorting out metallic from semiconducting carbon nanotubes," *Carbon*, vol. 48, no. 11, pp. 3287-3292, Sep, 2010.
- [107] W. Lu, J. Zhang, Y. S. Li *et al.*, "Contactless Characterization of Electronic Properties of Nanomaterials Using Dielectric Force Microscopy," *Journal of Physical Chemistry C*, vol. 116, no. 12, pp. 7158-7163, Mar 29, 2012.
- [108] P. Girard, "Electrostatic force microscopy: principles and some applications to semiconductors," *Nanotechnology*, vol. 12, no. 4, pp. 485-490, Dec, 2001.
- [109] M. Prato, and M. Maggini, "Fulleropyrrolidines: A family of full-fledged fullerene derivatives," *Accounts of Chemical Research*, vol. 31, no. 9, pp. 519-526, Sep, 1998.
- [110] N. Tagmatarchis, and M. Prato, "Functionalization of carbon nanotubes via 1,3-dipolar cycloadditions," *Journal of Materials Chemistry*, vol. 14, no. 4, pp. 437-439, Feb 21, 2004.
- [111] J. Zhang, W. Lu, Y. S. Li *et al.*, "Probing Electronic Doping of Single-Walled Carbon Nanotubes by Gaseous Ammonia with Dielectric Force Microscopy," *Journal of Physical Chemistry Letters*, vol. 3, no. 23, pp. 3509-3512, Dec 6, 2012.

- [112] A. Bietsch, and B. Michel, "Size and grain-boundary effects of a gold nanowire measured by conducting atomic force microscopy," *Applied Physics Letters*, vol. 80, no. 18, pp. 3346-3348, May 6, 2002.
- [113] G. Reguera, K. D. McCarthy, T. Mehta *et al.*, "Extracellular electron transfer via microbial nanowires," *Nature*, vol. 435, no. 7045, pp. 1098-1101, Jun 23, 2005.
- [114] R. Decker, Y. Wang, V. W. Brar *et al.*, "Local Electronic Properties of Graphene on a BN Substrate via Scanning Tunneling Microscopy," *Nano Letters*, vol. 11, no. 6, pp. 2291-2295, Jun, 2011.
- [115] R. A. Jalabert, W. Szewc, S. Tomsovic *et al.*, "What Is Measured in the Scanning Gate Microscopy of a Quantum Point Contact?," *Physical Review Letters*, vol. 105, no. 16, pp. 166802-166802, Oct 11, 2010.
- [116] K. Zhang, N. Marzari, and Q. Zhang, "Covalently Functionalized Metallic Single-Walled Carbon Nanotubes Studied Using Electrostatic Force Microscopy and Dielectric Force Microscopy," *Journal of Physical Chemistry C*, vol. 117, no. 46, pp. 24570–24578, Nov 21, 2013.
- [117] T. Zhang, S. Mubeen, N. V. Myung *et al.*, "Recent progress in carbon nanotube-based gas sensors," *Nanotechnology*, vol. 19, no. 33, pp. 332001-332001, Aug 20, 2008.
- [118] D. R. Kauffman, and A. Star, "Carbon nanotube gas and vapor sensors," *Angewandte Chemie-International Edition*, vol. 47, no. 35, pp. 6550-6570, 2008.

-
- [119] A. Salehi-Khojin, F. Khalili-Araghi, M. A. Kuroda *et al.*, "On the Sensing Mechanism in Carbon Nanotube Chemiresistors," *Acs Nano*, vol. 5, no. 1, pp. 153-158, Jan, 2011.
- [120] R. J. Chen, S. Bangsaruntip, K. A. Drouvalakis *et al.*, "Noncovalent functionalization of carbon nanotubes for highly specific electronic biosensors," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 100, no. 9, pp. 4984-4989, Apr 29, 2003.
- [121] G. H. Jeong, "Surface functionalization of single-walled carbon nanotubes using metal nanoparticles," *Transactions of Nonferrous Metals Society of China*, vol. 19, no. 4, pp. 1009-1012, Aug, 2009.
- [122] S. Mubeen, T. Zhang, B. Yoo *et al.*, "Palladium nanoparticles decorated single-walled carbon nanotube hydrogen sensor," *Journal of Physical Chemistry C*, vol. 111, no. 17, pp. 6321-6327, May 3, 2007.
- [123] P. G. He, and L. M. Dai, "Aligned carbon nanotube-DNA electrochemical sensors," *Chemical Communications*, no. 3, pp. 348-349, Feb 7, 2004.
- [124] I. Dumitrescu, N. R. Wilson, and J. V. Macpherson, "Functionalizing single-walled carbon nanotube networks: Effect on electrical and electrochemical properties," *Journal of Physical Chemistry C*, vol. 111, no. 35, pp. 12944-12953, Sep 6, 2007.
- [125] K. S. Coleman, S. R. Bailey, S. Fogden *et al.*, "Functionalization of single-walled carbon nanotubes via the Bingel reaction," *Journal of the American Chemical Society*, vol. 125, no. 29, pp. 8722-8723, Jul 23, 2003.

- [126] V. K. Sangwan, A. Behnam, V. W. Ballarotto *et al.*, "Optimizing transistor performance of percolating carbon nanotube networks," *Applied Physics Letters*, vol. 97, no. 4, pp. 043111-043111, Jul 26, 2010.
- [127] P. S. Na, H. J. Kim, H. M. So *et al.*, "Investigation of the humidity effect on the electrical properties of single-walled carbon nanotube transistors," *Applied Physics Letters*, vol. 87, no. 9, pp. 093101-093101, Aug 29, 2005.
- [128] E. Y. Li, N. Poilvert, and N. Marzari, "Switchable Conductance in Functionalized Carbon Nanotubes via Reversible Sidewall Bond Cleavage," *Acs Nano*, vol. 5, no. 6, pp. 4455-4465, Jun, 2011.
- [129] J. W. Han, B. Kim, J. Li *et al.*, "Carbon Nanotube Based Humidity Sensor on Cellulose Paper," *Journal of Physical Chemistry C*, vol. 116, no. 41, pp. 22094-22097, Oct 18, 2012.
- [130] M. Eiermann, R. C. Haddon, B. Knight *et al.*, "Electrochemical Evidence for through-Space Orbital Interactions in Spiromethanofullerenes," *Angewandte Chemie-International Edition in English*, vol. 34, no. 15, pp. 1591-1594, Aug 18, 1995.
- [131] P. C. P. Watts, N. Mureau, Z. N. Tang *et al.*, "The importance of oxygen-containing defects on carbon nanotubes for the detection of polar and non-polar vapours through hydrogen bond formation," *Nanotechnology*, vol. 18, no. 17, pp. 175701-175701, May 2, 2007.
- [132] W. Kim, A. Javey, O. Vermesh *et al.*, "Hysteresis caused by water molecules in carbon nanotube field-effect transistors," *Nano Letters*, vol. 3, no. 2, pp. 193-198, Feb, 2003.

- [133] D. Kang, N. Park, J. H. Ko et al., "Oxygen-induced p-type doping of a long individual single-walled carbon nanotube," *Nanotechnology*, vol. 16, no. 8, pp. 1048-1052, Aug, 2005.

Appendix A Diameter Dependent Reactivity Shown on Bulk SWCNTs

A highly packed network of SWCNTs with diameter range of 0.9-1.6 nm is treated under the same chemical reaction conditions for 10 min as described in the experimental section. The Raman scattering with excitation lasers of 488, 532 nm are performed to characterize the network before and after the functionalization.

The comparison spectra (normalized to G peak) are shown in the following Figures a1 and a2.

Figure A1 Comparison of RBM before (Red) and after (Blue) reaction under 532 nm laser.

Figure A2 Comparison of RBM before (Red) and after (Blue) reaction under 488 nm laser.

In both Figures a1 and a2, the D bands increase significantly after the functionalization, this further confirms the success of the functionalization as described in the article.

As seen from Figure a, the RBM intensity of SWNTs with diameter ~ 0.9 nm (RBM ~ 270 cm $^{-1}$) dropped significantly after the functionalization as compared to SWNTs with diameter ~ 1.6 nm (RBM ~ 155 cm $^{-1}$). This further confirmed that the smaller the diameters of SWNTs, the more reactive they are.

In Figure b, the RBM intensity of SWNTs with ~ 1.1 nm (RBM ~ 220 cm $^{-1}$) and ~ 1.5 nm (RBM ~ 165 cm $^{-1}$) are comparable before the functionalization. However, after the functionalization, the RBM ~ 220 cm $^{-1}$ almost completely disappeared, and the RBM ~ 165 cm $^{-1}$ become dominant. This further confirms the diameter dependent reactivity.

Appendix B: Electrical Conductance of Individual SWCNT with Silicon Nitride Passivation

Figure B1 AFM image of SWCNT FET with only the middle portion of the SWCNT channel exposed.

Figure B2 Electrical conductance of the SWCNT FET shown in Figure B1 before and after the dichlorocarbene functionalization.

Appendix C: More on DFM Techniques Implementation

1. Comparison of DFM with resonant oscillation on and off in the second scan path

Figure C1 Comparison of 2ω component of DFM signal ($V_{dc}=0V$) taken from deflection signal of the cantilever with its resonance turned off and the phase signal with cantilever resonance turned on.

Figure C1a shows the 2ω component of the deflection signal of the cantilever in the second scan path of DFM with the resonant oscillation of the cantilever turned off. Figure C1b shows the 2ω component of the phase of the cantilever resonant oscillation in the second scan path of DFM. In our experimental setup, the deflection signal is always much more noisy than the phase images, and therefore our DFM scan are conducted with the resonant oscillation of the cantilever turned on, and the phase image of the cantilever are used as our DFM signal.

C2. Obtaining DC Voltage Range Applicable in DFM Setup

Figure C2 2ω component of the phase image obtained to calibrate the cantilever

As shown in Figure C2, it is the 2ω component of the DFM phase of the Silicon substrate suddenly drops significantly at $V_g = -7\text{V}$ and $V_g = +7\text{V}$. With calibrating results at different voltage levels, we are able to determine the range of applied voltage so that the DFM data is valid for comparison. Figure C3 Plot of 2ω phase of SiO_2 versus gate voltage applied to the cantilever in the second scan path of DFM experiment.

Figure C3 2ω component of the phase of the substrate at different gate voltages.

It could be seen from Figure C3 that at gate voltage larger than 6 volts, the 2ω phase image on SiO_2 starts to drop significantly, suggesting that the DFM signal from the substrate has been changed. The possibility might be that at a larger bias, the low frequency dielectric response of the $\text{p}^+\text{Si}/\text{SiO}_2$ structure starts to change at large vertical DC field. As the DFM signal of the tubes are calculated with respect to the SiO_2 substrate, data taken beyond above critical value are considered not valid. Therefore, in this thesis, the DFM measurement are constrained from $V_g = -3 \text{ V}$ to $V_g = +3 \text{ V}$ so that the DFM results of the tubes are valid for comparison. Below Figure C4 shows the phase image obtained in the scan at various gate voltages.

Figure C4 Phase image of DFM at $V_g = -3V$, $-6V$, $+3V$ and $+6V$.

Appendix D: DFM of a Semiconducting SWCNT Subject to Dichlorocarbene Functionalization

1. EFM Comparison of Semiconducting SWCNT

Figure D1 EFM comparison of semiconducting SWCNTs before and after dichlorocarbene addition.

2. DFM Comparison of Semiconducting SWCNT

Figure D2 DFM comparison of semiconducting SWCNTs before and after dichlorocarbene addition.

Appendix E: Raman Spectroscopy Estimation of Degree of Functionalization

Figure E1 Typical Raman spectra of dichlorocarbene functionalized bulk SWCNTs at degree of about 0.1%, 0.5%, 1.5%, 3%, 5% and 10% (calibrated by EDX).

Figure E2 Comparison of the Raman intensities (normalized to silicon peak) of dichlorocarbene functionalized bulk SWCNTs at degree of 0.5%, 3% and 10%, respectively.

Figure E3 Raman D-band and G-band intensity versus various different degrees of dichlorocarbene functionalizations.

List of Publications

- [1] Zhang, K.; Zhang, Q.; Liu, C.; Marzari, N.; Stellacci, F., Diameter Effect on the Sidewall Functionalization of Single-Walled Carbon Nanotubes by Addition of Dichlorocarbene. *Adv. Funct. Mater.* **2012**, 22 (24), 5216-5223.
- [2] Zhang, K.; Marzari, N.; Zhang, Q., Covalently Functionalized Metallic Single-Walled Carbon Nanotubes Studied Using Electrostatic Force Microscopy and Dielectric Force Microscopy. *J. Phys. Chem. C* **2013**, 117 (46), 24570-24578.
- [3] Gao, P. Q.; Zou, J. P.; Li, H.; Zhang, K.; Zhang, Q., Complementary Logic Gate Arrays Based on Carbon Nanotube Network Transistors. *Small* **2013**, 9 (6), 813-819.