Chirally selective synthesis of single walled carbon nanotubes on novel catalysts

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**CHIRALLY SELECTIVE SYNTHESIS OF SINGLE
WALLED CARBON NANOTUBES ON NOVEL
CATALYSTS**

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**SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING
NANYANG TECHNOLOGICAL UNIVERSITY**

2013

Chirally Selective Synthesis of Single-Walled Carbon Nanotubes on Novel Catalysts

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Table of Contents

Table of Contents.....	1
Abstract.....	5
List of Abbreviations.....	7
List of Figures.....	9
List of Tables.....	15
Chapter 1 Introduction.....	18
1.1 SWCNT.....	19
1.2 SWCNT synthesis methods.....	20
1.3 Effective catalysts for chirally selective synthesis of SWCNTs.....	22
1.4 Growth parameters influencing (n,m) selectivity	29
1.4.1 Temperature	30
1.4.2 Carbon precursors.....	31
1.4.3 Catalyst substrates	32
1.4.4 Additives.....	33
1.5 Mechanism of SWCNT (n,m) selectivity	34
1.6 Motivation and scope	37
Chapter 2 General Experimental Methods.....	39
2.1 Catalyst preparation.....	39
2.2 Catalyst characterization	39
2.2.1 X-ray diffraction	39
2.2.2 Nitrogen physisorption	40
2.2.3 H ₂ -temperature programmed reduction	40
2.2.4 UV-vis diffuse reflectance spectroscopy	41

2.2.5 Elemental analysis	41
2.2.6 Scanning electron microscope	41
2.2.7 X-ray absorption spectroscopy	42
2.3 SWCNT synthesis	43
2.4 SWCNT purification	43
2.5 SWCNT characterization	44
2.5.1 Raman spectroscopy	44
2.5.2 PL spectroscopy	45
2.5.3 UV-vis-NIR absorption spectroscopy	46
2.5.4 Thermogravimetric analysis	47
2.5.5 Transmission electron microscopy	47
2.5.6 Atomic force microscopy	48
Chapter 3 Selective Synthesis of (9,8) SWCNTs on Cobalt Incorporated TUD-1 Catalysts	49
3.1 Co-TUD-1 catalyst preparation	49
3.2 Physicochemical properties of Co-TUD-1 catalyst	50
3.3 SWCNT synthesis and purification	53
3.4 SWCNT (<i>n,m</i>) analysis	53
3.5 Mechanism	57
3.6 Conclusion	58
Chapter 4 Chiral-Selective CoSO₄/SiO₂ Catalyst for (9,8) SWCNT Growth	59
4.1 CoSO ₄ /SiO ₂ catalyst preparation	60
4.2 SWCNT synthesis and purification	60
4.3 SWCNT (<i>n,m</i>) analysis	61
4.3.1 Raman spectroscopy	61
4.3.2 PL spectroscopy	67

4.3.3 UV-vis-NIR absorbance spectroscopy	69
4.4 Carbon yield	78
4.5 Morphology	80
4.6 Physicochemical properties of CoSO ₄ /SiO ₂ catalyst.....	83
4.7 Correlation between (9,8) SWCNT and Co cluster size.....	84
4.7.1 XAS spectra analysis	84
4.7.2 Spin-polarized density functional study	87
4.8 The role of sulfur	89
4.9 Conclusion.....	93
Chapter 5 CoSO₄/SiO₂ Catalyst for Selective Synthesis of (9,8) SWCNTs: Effect of Catalyst Calcination.....	95
5.1 CoSO ₄ /SiO ₂ catalyst preparation.....	95
5.2 SWCNT synthesis and purification	95
5.3 SWCNT (<i>n,m</i>) analysis	96
5.3.1 Raman spectroscopy	96
5.3.2 PL spectroscopy	98
5.3.3 UV-vis-NIR absorption spectroscopy	104
5.4 Carbon yield	106
5.5 Morphology of carbon deposits.....	107
5.6 Characterization of the CoSO ₄ /SiO ₂ catalyst	108
5.6.1 Catalyst morphology.....	108
5.6.2 Structure by XRD and physisorption.....	109
5.6.3 H ₂ -TPR	111
5.6.4 UV-vis diffuse reflectance spectroscopy	112
5.6.5 XANES spectra at Co K-edge	113
5.7 Sulfur in the CoSO ₄ /SiO ₂ catalyst	117

5.8 Effect of catalyst calcination	118
5.9 Conclusion.....	121
Chapter 6 Sulfur Doped Co/SiO₂ Catalysts for Chirally Selective Synthesis of SWCNTs	122
6.1 Sulfur doped Co/SiO ₂ catalyst preparation	122
6.2 SWCNT synthesis and purification	123
6.3 SWCNT (<i>n,m</i>) analysis	123
6.4 Catalyst characterization	128
6.5 Mechanism	130
6.6 (NH ₄) ₂ SO ₄ doped Co/SiO ₂ catalyst	132
6.6.1 Doping method	132
6.6.2 PL and abundance of (<i>n,m</i>) species	132
6.6.3 Absorption spectra	133
6.6.4 H ₂ -TPR and UV-vis diffuse reflectance spectroscopy	134
6.7 Conclusion.....	135
Chapter 7 Application of (9,8) SWCNTs in Field Effect Transistors.....	136
7.1 Fabrication of SWCNT thin film FETs	136
7.2 Electronic performances of SWCNT thin film FETs	137
7.3 Conclusion.....	141
Chapter 8 Summary and Future Research.....	142
Reference.....	147
Appendix.....	158

Abstract

Single-walled carbon nanotubes (SWCNTs) have excellent electronic, thermal, optical, and magnetic properties, which depend on their specific (n,m) structure; therefore precise control of SWCNT (n,m) structure is crucial to realize their potential applications. So far, a few catalysts can achieve selective synthesis of SWCNTs with a narrow (n,m) distribution; however, most of the chiral-selective growth is restricted to one or two small diameter SWCNTs, such as (6,5) and (7,5) nanotubes ($d < 0.9\text{nm}$). The development of novel catalysts is suggested as the premier target to realize chirally selective synthesis of SWCNTs, especially large diameter SWCNTs.

Co incorporated mesoporous TUD-1 catalyst (Co-TUD-1) and $\text{CoSO}_4/\text{SiO}_2$ catalyst were developed for SWCNT synthesis. Both catalysts are highly selective towards a large diameter (9,8) SWCNTs ($d = 1.17\text{nm}$) which account for more than 50% of semiconducting nanotubes under optimal growth conditions. The uniqueness of Co-TUD-1 catalyst lies in its low reduction temperature ($483\text{ }^\circ\text{C}$), large surface area ($740\text{ m}^2/\text{g}$), and strong metal-support interaction, which stabilizes Co clusters responsible for the growth of (9,8) nanotubes. While the specificity of the $\text{CoSO}_4/\text{SiO}_2$ catalyst is the presence of chelating bidentate SO_4^{2-} bonded with cobalt on the silica surface. The coexistence of sulfur atoms near Co atoms may limit the aggregation of Co atoms and/or form various Co-S compounds during the SWCNT growth, which contributes to the formation of Co clusters for (9,8) nanotube growth. Both XAS results and theoretical study confirm the close matching between the size of stable Co clusters and the diameter of (9,8) nanotubes. Compared to Co-TUD-1 catalyst, $\text{CoSO}_4/\text{SiO}_2$ catalyst has more

advantages: lower cost, shorter synthesis time, easier preparation, and higher carbon yields (3.8wt% vs. 1.5wt%). Therefore, $\text{CoSO}_4/\text{SiO}_2$ catalyst is more promising for scaling up the production of (9,8) SWCNTs. The $\text{CoSO}_4/\text{SiO}_2$ catalyst also shows tunable nanotube chiral selectivity from large diameter (9,8) nanotubes to small diameter nanotubes by changing catalyst calcination temperature from 400 °C to 800 °C. At low calcination temperature ($\leq 400^\circ\text{C}$), it has excellent single chiral selectivity towards (9,8) nanotubes, while the removal of sulfur at higher calcination temperatures forms surface cobalt oxides and silicates that shift the chiral selectivity towards small diameter nanotubes.

Since the presence of sulfur affects the formation of stable Co clusters with an appropriate size for (9,8) SWCNT growth, a sulfur doping method was developed to prepare catalysts. Three types of Co/SiO_2 catalysts, which are either inactive for the SWCNT growth or only selective towards small diameter nanotubes, can be converted into chirally selective catalysts to grow SWCNTs enriched with large diameter (9,8) tubes. Last, SWCNT thin film field effect transistors were fabricated using (9,8) nanotubes from the synthesis process, which demonstrated better electronic performances than those using (6,5) nanotubes.

Overall, work in this thesis has made progresses on the development of novel catalysts for chirally selective synthesis of SWCNTs: (1) growth of a large diameter (9,8) SWCNTs with a narrow (n,m) distribution using Co-TUD-1 catalyst and $\text{CoSO}_4/\text{SiO}_2$ catalyst; (2) shifting the (n,m) distribution by sulfur removal (calcination) in catalysts; and (3) converting non-selective Co/SiO_2 catalysts for the (9,8) SWCNT growth by sulfur doping.

List of Abbreviations

AFM	Atomic Force Microscopy
BET	Brunauer-Emmett-Teller
BJH	Barret-Joyner-Halenda
CNT	Carbon Nanotube
CVD	Chemical Vapor Deposition
DTG	Differential Thermogravimetric
EXAFS	Extended X-ray absorption fine structure
FET	Field Effect Transistors
HiPCo	High Pressure Co
MCM-41	Mobil Composition of Matter 41
MWCNTs	Multi-Walled Carbon Nanotubes
OD	Optical Density
PL	Photoluminescence
RBM	Radial Breathing Mode
SDBS	Sodium Dodecyl Benzene Sulfonate
SEM	Scanning Electron Microscope
SWCNT	Single-Walled Carbon Nanotube
TCD	Thermal Conductivity
TEA	Triethanolamine
TEAOH	Tetraethyl Ammonium Hydroxide

TEM	Transmission Electron Microscopy
TEOS	Tetraethyl Orthosilicate
TGA	Thermogravimetric Analysis
TPR	Temperature Programmed Reduction
TUD-1	Technische Universiteit Delft 1
UV-vis-NIR	Ultraviolet-visible-Near Infrared
XANES	X-ray Absorption Near Edge Structure
XAS	X-Ray Absorption
XRD	X-Ray Diffraction

List of Figures

Figure 1-1 Schematic representation of SWCNT structure: zigzag type nanotube, chiral type nanotube and armchair type nanotube. ¹⁸	19
Figure 1-2 Schematic illustration of the CVD system. ³³	21
Figure 1-3 Two general growth modes of nanotubes in CVD: base growth mode (left) and tip growth mode (right)	35
Figure 3-1 (a) XRD pattern of Co-TUD-1. (b) Nitrogen physisorption isotherm of Co-TUD-1. The insert shows the pore size distribution determined by the BJH method. ¹¹³	51
Figure 3-2 (a) UV-vis reflectance spectra of Co-TUD-1 and the Co ₃ O ₄ reference. (b) H ₂ -TPR profile of Co-TUD-1.	52
Figure 3-3 PL maps of SDBS-dispersed SWCNTs produced from Co-TUD-1 after prereduction under H ₂ at different temperatures: (a) 400 °C, (b) 500 °C and (c) 600 °C. (d) UV-vis-NIR spectra of SWCNTs. (e) Raman spectra of as-synthesized SWCNTs grown after 500 °C prereduction using the excitation laser wavelengths of 633 and 785 nm. The inset panel shows the enlarged RMB area... ..	53
Figure 3-4 Chirality maps of SWCNTs grown from Co-TUD-1.....	57
Figure 4-1 (a–b) Raman spectra of SWCNTs under three excitation wavelengths for catalyst reduction at 540 and 780 °C respectively. The regions on the left between 100 and 350 cm ⁻¹ correspond to RBM peaks, while the regions on the right correspond to D and G bands. (c–d) PL contour plots as a function of excitation and emission energies from SDBS-dispersed SWCNTs grown after catalyst reduction at 540 and 780 °C, respectively. Major chiral tubes identified in PL are marked with their (n,m) indexes.	61
Figure 4-2 Optical transition energies versus RBM frequencies for SWCNTs. RBM frequencies from peaks identified in Raman analysis of SWCNT samples (red dots) are plotted against theoretical and experimental transition energies. The three horizontal lines correspond to the laser excitation used for SWCNT characterization. The solid circles in navy color are E ₁₁ and E ₂₂ van Hove transitions of semiconducting SWCNTs from an empirical Kataura plot. ¹²⁰ The open and solid circles in black color are E ₁₁ transitions of	

metallic SWCNTs, E_{33} transitions of semiconducting SWCNTs, and other higher order transitions of SWCNTs from Kataura plots computed using a tight-binding model.¹¹⁹ . 63

Figure 4-3 Transition energies versus nanotube diameter and RBM frequency. Expanded view of the Kataura plots show in Figure 4-2 near to the laser energy at 514 nm. The dotted horizontal lines correspond to the upper and lower limits of the resonance window of approximate 100 meV. The vertical dashed lines around the experimental data points indicate $\pm 4 \text{ cm}^{-1}$ variability in measurement of RBM frequencies because of different environments or instruments as suggested by previous researchers.¹⁰⁹ 63

Figure 4-4 Transition energies versus nanotube diameter and RBM frequency. Expanded view of the Kataura plots shown in Figure 4-2 near to the laser energy at 633 nm..... 64

Figure 4-5 Transition energies versus nanotube diameter and RBM frequency. Expanded view of the Kataura plots shown in Figure 4-2 near to the laser energy at 785 nm..... 65

Figure 4-6 (a) Relative abundance (based on RA (n,m) (%) (semi+met) listed in Table 4-4 and 4-6) of (n,m) SWCNTs produced from the $\text{CoSO}_4/\text{SiO}_2$ catalyst after catalyst reduction at 540 °C. They are main (n,m) species identified by the three characterization techniques. Blue: PL; red Raman; and yellow: absorption. (b) Two dimensional projected chirality map of SWCNTs. Most of (n,m) species produced in the work are at larger diameter around 1.17 nm, as compared to previous chiral selectivity synthesis studies usually at around 0.76 nm. 69

Figure 4-7 (a) UV–vis-NIR absorption spectra of SDBS-dispersed SWCNTs grown after catalyst reduction at 540 °C before and after baseline subtraction. (b) E_{11}^S spectral reconstruction by the summation of the contribution from each (n,m) semiconducting SWCNT (Lorentzian peaks in black). (c) E_{11}^M and E_{22}^S spectral reconstruction by the summation of the contribution from both semiconducting (black) and metallic (blue) SWCNTs. The (n,m) indexes, thick solid line and red circles represent the same as in (b). (d) Relative abundance of both semiconducting (black) and metallic (blue) (n,m) SWCNTs obtained from the reconstruction of absorption spectra..... 77

Figure 4-8 TGA and DTG profiles of carbon deposits synthesized on the $\text{CoSO}_4/\text{SiO}_2$ catalyst. (a) Catalyst reduction at 540 °C, and then SWCNT growth at 780 °C, (b) reduction at 780 °C for 30 min, and then SWCNT growth. The samples were oxidized in air. The total

carbon yield is calculated from the weight loss between 200 and 1000 °C.	78
Figure 4-9 SEM (a–d) and TEM (e–g) images of catalysts and SWCNTs. (a) fresh catalyst; (b) catalyst after reduction in H ₂ at 540 °C, and then cooled to room temperature under He; (c) as-synthesized SWCNTs on catalyst; (d) SWCNT films after SiO ₂ removal; (e) The same sample as (b); (f) and (g) as-synthesized SWCNTs on catalyst; (h) the diameter distribution of nanotubes obtained by measuring ~100 nanotubes in TEM images. The scale bars in (a–c) are at 1 μm, and is 100 nm in (d).	82
Figure 4-10 Physicochemical properties of the CoSO ₄ /SiO ₂ catalyst. (a) XRD pattern of the calcined CoSO ₄ /SiO ₂ catalyst. (b) Nitrogen physisorption isotherms and pore size distribution (insert) of the catalyst. (c) UV–vis absorption spectra of the catalyst and several references (Co ₃ O ₄ , CoSO ₄ powders and fumed SiO ₂). (d) H ₂ -TPR profiles of the catalyst and several Co references (Co ₃ O ₄ , CoO and CoSO ₄).	83
Figure 4-11 XAS spectra of the CoSO ₄ /SiO ₂ catalysts and model of Co clusters. (a) Near-edge spectra at the Co-K edge (E ₀ = 7709 eV) of fresh catalyst, catalyst after reduction at 540 °C and SWCNT growth, and Co foil. (b) Fourier transform of EXAFS spectra at the Co-K edge for samples in (a). (c) The average diameter of Co metal clusters in catalysts determined by the first shell coordination number from XAS spectra. (d) The optimized structures of Co _n (n=13, 55, and 147) clusters from theoretical simulation and their likely matching carbon caps.....	86
Figure 4-12 Sulfur content in CoSO ₄ /SiO ₂ catalyst. (a) XANES spectra at sulfur K-edge of fresh and treated catalysts at different reduction conditions. CoSO ₄ · 7H ₂ O and CoS are references. Four samples include (1) fresh catalyst; (2) catalyst reduced in H ₂ at 540 °C, and then cooled to room temperature under He; (3) catalyst reduced in H ₂ at 540 °C, and then increased temperature to 700 °C under He before cooled to room temperature; and (4) catalyst reduced in H ₂ at 700 °C, and then cooled to room temperature under He. The dashed line indicates the location of CoS peak. (b) Sulfur content in catalyst determined by elemental analysis and integrated sulfur peak area of XANES spectra. Four samples are the same as (a) and one more sample after reduction in H ₂ at 780 °C.	92
Figure 5-1 Raman spectra of SWCNTs grown from catalysts calcined at different conditions marked on the right side of figures. (a) under the excitation of 514 nm laser, (b) under the	

785 nm laser. The region on the left of each graph between 100 and 350 cm^{-1} correspond to RBM peaks, while the region on the right corresponds to D and G bands.	96
Figure 5-2 PL contour plots as a function of excitation and emission energies of SDBS-dispersed SWCNTs grown from catalysts calcined at different conditions. (a) uncalcined, (b) 400, (c) 500, (d) 600, (e) 700, and (f) 800 $^{\circ}\text{C}$. Major chiral species identified in PL are marked with their (n,m) indices.	98
Figure 5-3 (a) The change of relative abundance of semiconducting (n,m) tubes at different catalyst calcination temperatures. The relative abundance is calculated from the intensity of PL peaks of various (n,m) species. (b) A chiral map of (n,m) species identified in PL plots. The few major species shown in (a) are highlighted in different colors.	103
Figure 5-4 UV–vis-NIR absorption spectra of SDBS-dispersed SWCNTs grown from catalysts calcined at different conditions. The label E_{11}^{S} (shaded purple) marks the absorption bands of the first one-dimensional van Hove singularities from semiconducting SWCNTs; the E_{22}^{S} and E_{11}^{M} (shaded yellow) correspond to the overlapping absorption bands of the first van Hove singularities from metallic SWCNTs and the second van Hove singularities from semiconducting SWCNTs. All spectra were normalized at 1420 nm for easy comparison.....	105
Figure 5-5 TG and DTG profiles of carbon deposits grown on the $\text{CoSO}_4/\text{SiO}_2$ catalysts (with ~1 wt% Co) calcined at three different temperatures. (a) 400 $^{\circ}\text{C}$, (b) 700 $^{\circ}\text{C}$, and (c) 900 $^{\circ}\text{C}$	106
Figure 5-6 TEM images of SWCNTs and other carbon species grown from the $\text{CoSO}_4/\text{SiO}_2$ catalyst. (a–b) the catalyst calcined at 400 $^{\circ}\text{C}$. (d–f) the catalyst calcined at 800 $^{\circ}\text{C}$. (c) AFM image of purified SWCNTs deposited on silicon wafer and the height profile of nanotubes along the red line.	107
Figure 5-7 SEM of the $\text{CoSO}_4/\text{SiO}_2$ catalyst calcined at (a) 400 $^{\circ}\text{C}$ and (b) 900 $^{\circ}\text{C}$	109
Figure 5-8 XRD patterns of the $\text{CoSO}_4/\text{SiO}_2$ catalyst calcined at different conditions. $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ is a reference.....	109
Figure 5-9 Nitrogen physisorption isotherms and pore size distributions (insert) of the $\text{CoSO}_4/\text{SiO}_2$ catalyst calcined at 400 and 800 $^{\circ}\text{C}$	110
Figure 5-10 H_2 -TPR profiles of the $\text{CoSO}_4/\text{SiO}_2$ catalyst calcined at different conditions and	

several Co references (Co_3O_4 , CoO , $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and CoSiO_3).....	111
Figure 5-11 UV–vis diffuse reflectance spectra of the $\text{CoSO}_4/\text{SiO}_2$ catalyst calcined at different conditions and references (Co_3O_4 , CoO , CoSO_4 , CoSiO_3 and fumed SiO_2)..	113
Figure 5-12 XAS spectra of $\text{CoSO}_4/\text{SiO}_2$ catalysts calcined at different conditions and several references ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, CoSiO_3 , CoO , Co_3O_4 and Co foil). (a) XANES spectra near the Co K-edge. The inset shows the enlarged spectra near the Co K-edge. (b) Fourier transforms of EXAFS spectra in r -space at the Co K-edge for samples in (a).	113
Figure 5-13 The weight fraction of sulfur in $\text{CoSO}_4/\text{SiO}_2$ catalysts calcined at different temperatures and after reduction in H_2 at 540°C during SWCNT growth.	117
Figure 5-14 Schematic illustration of catalyst transitions at different calcination temperatures. Silica particles are around 20 nm in diameter, thus a curved surface is used to represent the surface of silica particles.....	118
Figure 6-1 PL maps and UV–vis-NIR absorption spectra of SDBS-dispersed SWCNTs grown on undoped and sulfur doped Co/SiO ₂ catalysts. PL maps: (a) CoACAC/SiO ₂ , (b) CoCl/SiO ₂ , (c) CoN/SiO ₂ , (d) CoACAC/SiO ₂ /S, (e) CoCl/SiO ₂ /S, and (f) CoN/SiO ₂ /S. Some major (n,m) species identified on PL maps are marked. Absorption spectra: undoped (g) and sulfur doped (h). The shaded pink indicates the E_{11}^S absorption band and the shaded blue shows the overlapping E_{22}^S and E_{11}^M bands.	124
Figure 6-2 Raman spectra of SWCNTs grown on undoped Co/SiO ₂ catalysts (a and c) and sulfur doped Co/SiO ₂ (b and d) under 785 and 514 nm laser excitations, respectively. The regions on the left correspond to RBM peaks, while the regions on the right correspond to D and G bands.....	126
Figure 6-3 H_2 -TPR profiles of undoped and sulfur doped Co/SiO ₂ catalysts and several Co references (CoO , Co_3O_4 , CoSiO_3 , CoCl_2 and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$).	129
Figure 6-4 UV–vis diffuse reflectance spectra: (a) Co/SiO ₂ catalysts and references (Co_3O_4 , CoO and CoSiO_3), (b) sulfur doped Co/SiO ₂ catalysts as well as the reference CoCl and CoSO_4	130
Figure 6-5 Schematic illustration of changes in Co species on Co/SiO ₂ catalysts caused by sulfur doping.....	130

Figure 6-6 PL map of SDBS-dispersed SWCNTs grown on the CoN/SiO ₂ /AS catalyst.	132
Figure 6-7 UV–vis–NIR absorption spectra of SDBS-dispersed SWCNTs grown on CoN/SiO ₂ /AS catalyst.....	133
Figure 6-8 H ₂ –TPR profile (a) and UV–vis diffuse reflectance spectrum (b) of CoN/SiO ₂ /AS catalyst.	134
Figure 7-1 A schematic drawing of the device composed of SWCNT thin films bridging a pair of Au source and drain electrodes.....	137
Figure 7-2 (a) PL map and (b) UV–vis–NIR spectrum of (6,5) SWCNTs produced on Co-Mo catalysts.....	138
Figure 7-3 Typical AFM images of SWCNT networks in FET device channels. (a) (9,8) enriched SWCNTs produced on Co-TUD-1, (b) (6,5) enriched SWCNTs produced on Co-Mo catalysts.	138
Figure 7-4 Current–voltage characteristics (I_d – V_d) of devices at different V_g from -100 to 100 V with the step of 10 V from bottom to top. (a) A typical device fabricated by (9,8) nanotubes from Co–TUD-1 catalysts. (b) A typical device fabricated by (6,5) nanotubes from Co-MO catalysts.	139
Figure 7-5 (a) Typical drain current–gate voltage curves of the thin film FETs from (9,8) and (6,5) SWCNTs. (b) Percentage histogram of FET on-off ratios from the two types of SWCNTs.	140
Figure 7-6 Percentage histogram of FET device mobilities from (9,8) and (6,5) SWCNTs.	140

List of Tables

Table 3-1 Tabulated values of PL intensities and relative abundances of (n,m) species in SWCNTs produced on Co–TUD-1 after prereduction at 400 °C.....	54
Table 3-2 Tabulated values of PL intensities and relative abundances of (n,m) species in SWCNTs produced on Co–TUD-1 after prereduction at 500 °C.....	55
Table 3-3 Tabulated values of PL intensities and relative abundances of (n,m) species in SWCNTs produced on Co–TUD-1 after prereduction at 600 °C.....	56
Table 4-1 Summary of chirality assignment for RBM peaks identified in Raman analysis of SWCNT samples.....	66
Table 4-2 PL intensities for (n,m) nanotubes identified in SWCNTs produced on $\text{CoSO}_4/\text{SiO}_2$ catalyst after catalyst reduction at 540 °C. The relative abundance is calculated based on the PL intensity of different (n,m) tubes.	67
Table 4-3 PL intensities for (n,m) nanotubes identified in SWCNTs produced on $\text{CoSO}_4/\text{SiO}_2$ catalyst after catalyst reduction at 780 °C for 30 min. The relative abundance is calculated based on the PL intensity of different (n,m) nanotubes.....	68
Table 4-4 Parameters used to reconstruct E_{11}^S absorption spectra of semiconducting SWCNTs. The relative abundance (semi) is calculated based on the reconstructed absorbance E_{11}^S peak area of each semiconducting (n,m) tube only. The relative abundance (semi+met) is calculated based on the reconstructed absorbance E_{11}^S peak area of each (n,m) tube, including both semiconducting and metallic SWCNTs.	71
Table 4-5 Parameters used to reconstruct E_{22}^S absorption spectra of semiconducting SWCNTs. The relative abundance (semi) is calculated based on the reconstructed absorbance E_{22}^S peak area of each semiconducting (n,m) tube. For all semiconducting SWCNTs E_{22}^S reconstruction, $C_1 = 22$ and $C_2 = 120$	74
Table 4-6 Parameters used to reconstruct E_{11}^M absorption spectra of metallic SWCNTs. The relative abundance (semi+met) is calculated based on the reconstructed absorbance E_{11}^S peak area of each semiconducting (n,m) tube and E_{11}^M peak area of each metallic (n,m) tube. For all metallic SWCNTs E_{11}^M reconstruction, fitting factors $C_1 = 8.2$ and $C_2 = 160$.	

.....	76
Table 4-7 Comparison of (<i>n,m</i>) selectivity and carbon yield among several reported chiral selective growth studies.	80
Table 4-8 Structure parameters of the first Co–Co coordination shell in catalysts determined from the EXAFS data (Figure 4-11b) at Co K edge by fitting using FEFF 9.	86
Table 4-9 Calculated results of the average binding energy E_b (eV), bond lengths from the central Co atom $R_{\text{Co-Cen}}$ (Å), and surface bond lengths $R_{\text{Co-Co}}$ (in Å) for pure Co_n clusters (with $n=2, 3, 5, 13, 55$, and 147), respectively.	88
Table 5-1 Summary of RBM peaks identified in Figure 5-1 from SWCNT samples synthesized from the $\text{CoSO}_4/\text{SiO}_2$ catalysts uncalcined and calcined at different temperatures.	97
Table 5-2 Tabulated values of PL peak intensity and the relative abundance of (<i>n,m</i>) species in SWCNTs grown on the uncalcined $\text{CoSO}_4/\text{SiO}_2$ catalyst.	99
Table 5-3 Tabulated values of PL peak intensity and the relative abundance of (<i>n,m</i>) species in SWCNTs grown on the $\text{CoSO}_4/\text{SiO}_2$ catalyst calcined at 400 °C.	99
Table 5-4 Tabulated values of PL peak intensity and the relative abundance of (<i>n,m</i>) species in SWCNTs grown on the $\text{CoSO}_4/\text{SiO}_2$ catalyst calcined at 500 °C.	99
Table 5-5 Tabulated values of PL peak intensity and the relative abundance of (<i>n,m</i>) species in SWCNTs grown on the $\text{CoSO}_4/\text{SiO}_2$ catalyst calcined at 600 °C.	100
Table 5-6 Tabulated values of PL peak intensity and the relative abundance of (<i>n,m</i>) species in SWCNTs grown on the $\text{CoSO}_4/\text{SiO}_2$ catalyst calcined at 700 °C.	100
Table 5-7 Tabulated values of PL peak intensity and the relative abundance of (<i>n,m</i>) species in SWCNTs grown on the $\text{CoSO}_4/\text{SiO}_2$ catalyst calcined at 800 °C.	101
Table 5-8 Tabulated values of PL peak intensity and the relative abundance of (<i>n,m</i>) species in SWCNTs grown on the $\text{CoSO}_4/\text{SiO}_2$ catalyst calcined at 900 °C.	101
Table 5-9 Structure parameters of the first Co–O coordination shell in catalysts determined from the EXAFS data (Figure 5-12b) at the Co K-edge by fitting using FEFF 9.	115
Table 6-1 Tabulated values of PL intensities and relative abundances of (<i>n,m</i>) species in SWCNTs produced on the $\text{CoACAC}/\text{SiO}_2/\text{S}$ catalyst.	125
Table 6-2 Tabulated values of PL intensities and relative abundances of (<i>n,m</i>) species in SWCNTs produced on the $\text{CoCl}/\text{SiO}_2/\text{S}$ catalyst.	125

Table 6-3 Tabulated values of PL intensities and relative abundances of (n,m) species in SWCNTs produced on the CoN/SiO ₂ /S catalyst.....	126
Table 6-4 Tabulated values of PL intensities and relative abundances of (n,m) species in SWCNTs produced on the CoN/SiO ₂ /AS catalyst.....	132
Table 7-1 Average electronic characteristics of semiconducting FETs (with $I_{on}/I_{off} > 10^3$) fabricated with (9,8) and (6,5) nanotubes.	141

Chapter 1 Introduction

Carbon is one of the most important elements on earth. Carbon has a number of allotropes, including amorphous carbon, diamond, graphite, fullerene, carbon nanotubes (CNTs), and graphene. Among them, fullerenes, CNTs, and graphene have the same structural unit: a single-layer graphene sheet. Fullerenes and CNTs are formed by wrapping and rolling of the graphene sheet into sphere or tube. Intensive research on CNTs started from the discovery by Iijima in 1991,¹ although other researchers previously reported the structure of CNT.^{2,3} Iijima observed multi-walled carbon nanotubes (MWCNTs), whose walls have multiple layers of graphene sheets. Two years later since then, single-walled carbon nanotubes (SWCNTs) with one atomic-layer thick wall were synthesized independently by Iijima and Bethune.^{4,5} Quickly, SWCNTs were synthesized by many research groups using different methods, such as laser vaporization, arc discharge, and chemical vapor deposition (CVD).^{6,7} For more than 20 years' research, much progress has been made in SWCNT synthesis, understanding its growth mechanism, purification and sorting, and applications.⁶⁻¹⁰ CNTs have been synthesized in large-scale industrial production.^{6,11} However, there are still many obstacles needed to be overcome for its practical applications. One major challenge is the selective synthesis of SWCNTs with specific chiral structures. Each chiral structure of the SWCNTs is a distinct molecule with structure-dependent properties; it is therefore essential to grow chirally pure SWCNTs and extend chirality control to various chiral species for various applications. Experimental and theoretical studies show that catalysts play a crucial role to achieve this goal.^{6,12,13}

Therefore, my PhD thesis work was focusing on chirally selective synthesis of SWCNTs on novel catalysts. This thesis begins with introduction, followed by the development of novel catalysts and chirally selective synthesis of SWCNTs on those catalysts as well as the preliminary application of synthesized SWCNTs.

1.1 SWCNT

Since the discovery of SWCNTs in 1993,¹ they have attracted intense efforts because of their applications in various fields, such as electronics, mechanics, energy, catalysis and bio-applications.^{9,14-17} Their extraordinary electronic, thermal, optical and mechanical properties rely on their special atomic chiral structures.¹⁵ Chiral structures of SWCNTs are described by the chiral index (n,m) depending on the rolling direction of graphene sheet.

Figure 1-1 Schematic representation of SWCNT structure: zigzag type nanotube, chiral type nanotube and armchair type nanotube.¹⁸

As illustrated in Figure 1-1, related to an origin point, a unique SWCNT can be formed by rolling the graphene sheet from the origin point toward any other (n,m) point (where a carbon atom locates. n and m are integers, $0 \leq |m| \leq n$). The rolling direction can be defined by a

chiral vector, $\mathbf{R} = n\mathbf{a}_1 + m\mathbf{a}_2$, where $\mathbf{a}_1$ and $\mathbf{a}_2$ are lattice unit vectors of the graphene sheet. Each (n,m) SWCNT corresponds to a certain diameter and chiral angle (θ). The diameter can be determined by (n,m) using the equation $d = 0.0783\sqrt{(n^2 + m^2 + nm)}$ nm, and the chiral angle θ could be also calculated by using $\theta = \tan^{-1}[\sqrt{3}m/(2n + m)]$ ($0 \leq \theta \leq 30^\circ$). Nanotubes are called zigzag nanotubes when $m = 0$, and armchair nanotubes when $n = m$. SWCNTs can also be divided into two groups: metallic and semiconducting nanotubes. A SWCNT is considered metallic if the value of $n-m$ can be divisible by three; otherwise, it is semiconducting. Therefore, by random selection, the ratio of metallic and semiconducting SWCNTs should be 1:2. The total number of SWCNT chiral indexes (n,m) is limited because SWCNTs with extreme small or large diameters are unstable. In general, there are more than 200 different (n,m) species if considering SWCNTs with diameter from 0.6–3nm.

SWCNTs of different (n,m) structures have distinct properties; hence it is highly desirable to precisely control their (n,m) structures for potential applications ranging from nanoelectronics to nanomedicine.¹⁹ However, current synthesis methods generally produce SWCNTs with random (n,m) distributions. Although single-chirality nanotubes can be separated from SWCNT mixtures through different techniques, such as density-gradient ultracentrifugation²⁰ and chromatography separation,^{21,22} the yield, scalability and cost of such separation, as well as the properties (length and functionality) of the resulting SWCNTs depend on the initial chirality distribution in SWCNT mixtures determined during growth.

1.2 SWCNT synthesis methods

Currently, CNTs can be synthesized by three different techniques: (1). arc discharge between two high-purity graphite electrodes.⁴ During arcing, carbon vapor is created by

consuming solid carbon electrodes and CNTs are formed by carbon vapor condensation. SWCNTs have also been produced using the arc discharge method by adding different metals in the electrodes such as Co,²³ Co-Ru,²⁴ Rh-Pt,²⁵ Ni-Y,²⁶ and Co-Ni-Fe-Ce.²⁷ (2). laser evaporation of carbon targets.^{28,29} This method has a similar mechanism as that of the arc discharge method, but it uses a laser instead of current to vaporize carbon. (3). CVD through the catalytic decomposition of carbon-bearing gases.³⁰⁻³² The first two methods can yield high-quality SWCNTs. For example, SWCNTs have been produced by using a Ni-Y catalyst in arc discharge²⁶ and using a Co/Ni contained graphite composite in laser ablation.²⁸ However, there is little control over SWCNT structures (chirality, diameter and length) and alignment by these two techniques. CVD method has the advantages of controllable synthesis and mild operating conditions. Thus, CVD method holds the most promise in achieving large-scale production of SWCNTs with a more controllable chirality distribution.⁷ As such, CVD method was used in this thesis. Figure 1-2 depicts the typical CVD system which contains a quartz tube, a furnace, mass flow controllers and gas lines for delivering various gases to the quartz tube.

Figure 1-2 Schematic illustration of the CVD system³³

The CVD growth process usually starts with heating a catalyst to high temperatures in

hydrogen or inert gas atmosphere, and then carbon precursors decompose on the catalyst in the quartz tube over a period of time. The gas flow rate and pressure can be controlled during heating and carbon precursor decomposition. Finally, SWCNTs grown on the catalyst can be collected after the system is cooled to room temperature. The general principle of SWCNT CVD suggests that carbon precursors, such as carbon monoxide (CO), methane, and other hydrocarbons,^{32,34} decompose on nanosized metal catalysts at high temperature, and carbon atoms may dissolve and saturate metal nanoparticles, and then precipitate from the saturated metal nanoparticles, resulting in the formation of tubular carbon solids in sp^2 structure.³⁵

1.3 Effective catalysts for chirally selective synthesis of SWCNTs

Nowadays, SWCNT can be successfully grown on various types of catalysts, including metal thin films,³⁶ unsupported and supported metallic catalyst nanoparticles,³⁶ and even semiconductor particles (Si, Ge, SiC),³⁷ insulator particles (SiO_2)³⁸ and diamond.³⁹ However, metal catalysts are more efficient for SWCNT growth. Various metals or their combinations can be employed to prepare catalysts, such as, Fe, Co, Ni, Au, Ag, Pt, Pd, Cu, Mo, Mn, Cr, Sn, Al, and Mg^{34,40-43} using various catalyst preparation methods, such as impregnation, co-precipitation, atomic layer deposition, sol-gel process and many others.^{44,45} However, most catalysts have relatively low selectivity toward a specific chiral SWCNT. The difficulty in the synthesis of highly selective catalysts lies in the fact that the catalysts should provide small nanoparticles (1–2 nm) well-dispersed and stabilized at high reaction temperatures in order to initiate the SWCNT growth and to control its structure.

Three approaches have been studied to design chirally selective catalysts for SWCNT synthesis. The first approach uses bimetallic catalysts supported on porous supports.⁴⁶⁻⁵⁰ The

second metal influences the size or crystal structure of catalytic nanoparticle or forms alloys with the catalytic nanoparticle, yielding the chiral selectivity of catalysts. CoMoCAT is the first effective (n,m) selective bimetallic catalyst reported by Resasco *et al.*⁴⁶ This catalyst was prepared by impregnating cobalt nitrate and ammonium heptamolybdate on silica particles (6 nm pore size and surface area of 480 m²/g). The total metal loading in this catalyst was 2 wt%, in which the Co:Mo molar ratio was 1:3. During the SWCNT growth, this catalyst was first reduced to 500 °C in a H₂ flow. The CO disproportionation reaction was carried out in a fluidized bed reactor under pure CO at 5 atm and 750 °C to produce SWCNTs.⁴⁶ Photoluminescence (PL) spectroscopy results demonstrated that (6,5) and (7,5) accounted for 57% of the semiconducting tubes assuming that tube abundance is proportional to its PL intensity.⁴⁶ The success of CoMoCAT comes from a synergistic effect between Co and Mo.^{51,52} Co²⁺ ions are stabilized by interaction with molybdenum oxide, and when exposed to CO, those Co²⁺ ions convert into well spread small Co clusters, resulting in SWCNTs with a narrow (n,m) distribution centered at (6,5) and (7,5).⁴⁶

Subsequently, Fe/Co catalyst supported on zeolite was synthesized by Maruyama *et al.*, which demonstrated a similar narrow (n,m) distribution using alcohol catalytic CVD method. This catalyst was prepared by impregnation of iron acetate and cobalt acetate on a Y-type zeolite (HSZ-390HUA). The concentration of Fe and Co were 2.5 wt% each. The SWCNT growth was carried out in ethanol (5 Torr) without catalyst prereduction. PL spectroscopy results indicated a narrower (n,m) distribution at growth temperature of 650 °C compared to 750 and 850 °C, and a high selectivity towards the higher chiral angle tubes close to armchair

tubes existed. This tendency was more pronounced for smaller diameter tubes.⁴⁷ Maruyama *et al.* did not report detailed information of the physicochemical properties of this Fe/Co catalyst.

FeRu catalyst developed by Dai *et al.* is another bimetallic catalyst supported on silica, which can afford SWCNT growth with narrow diameter and (n,m) distribution in methane CVD.⁴⁸ The FeRu catalyst was prepared by sonicating a mixture of silica support (7 nm average particle size and surface area of $380 \pm 30 \text{ m}^2/\text{g}$) and iron nitrate and ruthenium chloride hydrate in methanol for 1h. The catalyst was prereduced in H_2 for 10 min and heated to the growth temperature in 200 sccm of H_2 , and then maintained at this temperature in 200 sccm CH_4 for 8mins. According to absorption and PL characterization, FeRu catalyst produced the narrowest (n,m) distribution with a dominant (6,5) nanotubes at 600 °C, and the enrichment of (6,5) SWCNT relative to other (n,m) tubes is similar to that produced by CoMoCAT. Higher growth temperature led to larger diameter tubes and wider (n,m) distribution of semiconducting tubes. The uniqueness of FeRu catalyst is the formation of small FeRu alloy particles in the 1-2 nm range. These FeRu nanoclusters are stable at lower growth temperature of 600 °C, which is responsible for the good selectivity.⁴⁸

Considering the cost and removal of supports, He *et al.* developed a cheaper FeCu catalyst supported on magnesia (MgO) to provide a selective growth of (n,m) SWCNTs.⁴⁹ The FeCu catalyst was deposited on a porous MgO support using the atomic layer deposition technique. The SWCNT growth was carried out in a cold-wall CVD micro-reactor (Linkam CCR1000) using CO as the carbon precursor at ambient pressure. The catalyst was first heated in Ar to desired temperature, and then exposed to CO for 15min. Absorption spectra and PL spectra were used to evaluate the relative abundance of different (n,m) species, which shows a higher

selectivity towards (6,5) tubes relative to other (n,m) tubes in the 600 °C growth process compared to CoMoCAT and Fe-Ru catalyst. They also observed an increase in the SWCNT diameter and a broadening of the diameter distribution at higher growth temperatures. The role of Cu is to enhance the reducibility of Fe and stabilize reduced metallic Fe clusters, which leads to favorable SWCNT growth at low temperature and the greatly enhanced SWCNT yield.

The above catalysts demonstrated some common phenomena: selective growth of SWCNTs with a small diameter and narrow chirality distribution was achieved under low growth temperature, while high temperature would lead to the growth of SWCNTs with relatively large diameters with a broad chirality distribution. However, this is not always true. Liu *et al.* performed the selective growth of narrow chirality distributed SWCNTs at a high reaction temperature using atmospheric pressure alcohol CVD on a silica-supported CoPt catalysts.⁵⁰ Different from the previously developed catalysts, the (6,5)-dominated SWCNTs with high quality can be selectively grown at 800 °C by the CoPt catalyst. The abundance of (6,5) nanotubes is approximately 30% in the semiconducting tubes quantified by PL spectra. They also suggested that the formation of a CoPt alloy and its improved stability are responsible for the selective growth of SWCNTs with small diameters and narrow chiralities at high temperature.

Apart from the particle size, the elemental composition of catalytic nanoparticles is also linked to the nanotube chirality. Chiang *et al.* employed a two-step, continuous gas-phase process consisting of an atmospheric-pressure microplasma reactor for $\text{Ni}_x\text{Fe}_{1-x}$ (with $0 \leq x \leq 1$) catalyst preparation.⁵³ By precisely tuning the composition of $\text{Ni}_x\text{Fe}_{1-x}$ particles while keeping

the diameter constant at around 2 nm, they found that it is possible to change the chirality distributions of SWCNTs. Eventually, they managed to synthesize a dominant (8,4) nanotubes with smaller fraction of (7,5), (6,5), (7,6) and (8,3) nanotubes using the $\text{Ni}_{0.27}\text{Fe}_{0.73}$ clusters. They believed that the perturbations in the crystal structure of the nanocatalysts caused by compositional tuning lead to the observed shifts in the chirality distributions.⁵³

For supported catalysts prepared by impregnation and atomic layer deposition, and the metal species always stay on the surface of the supports. If metal species can be located in the structure of the support, it would enhance the interaction between the metal and the support. Therefore, the other approach is to incorporate metal species in high surface area mesoporous substrates.⁵⁴⁻⁵⁹ Incorporation means to replace ions in the substrate with desired metal during substrate formation. Catalysts synthesized by incorporation method, have a very high homogeneity in metal dispersion and large surface area,⁶⁰ so that the size of resulting metal particles can be precisely tuned under different process parameters. Co incorporated MCM-41 (Mobil Composition of Matter 41) (Co-MCM-41) is a typical example, in which isolated Co ions staying in the amorphous mesoporous MCM-41 structure (surface area > 1000 m²/g). This catalyst shows high selectivity toward (7,5) tubes.^{54,61} The mechanism was investigated by in situ X-ray absorption on Co-MCM-41 during prereduction and SWCNT growth.^{54,62} Co species in MCM-41 can nucleate in two steps. First, Co^{2+} ions are partially reduced to Co^{1+} intermediate species during prereduction in H_2 at 500°C. These Co species, however, are still dispersed isolatedly in tetrahedral environment of the MCM-41 silica framework. After exposure to CO, the Co^{1+} species likely form Co carbonyl-like compounds with a high mobility. Increasing Co mobility allows fast migration and formation of small metal clusters

capable of dissociating CO and initiating the growth of SWCNTs.⁵⁴ The efficient control of Co species using MCM-41 template has produced as-synthesized SWCNTs with the narrow (*n,m*) distribution around (7,5) nanotubes. Based on Co-MCM-41, bimetallic CoCr-MCM-41, CoMn-MCM-41 and CoMo-MCM-41 were also developed by incorporation of a second metal such as Cr, Mn or Mo into the structures of MCM-41 catalyst.⁵⁷⁻⁵⁹ All of these three catalysts show a high selectivity towards small diameter SWCNTs. For Co-Mn-MCM-41 and Co-Cr-MCM-41 catalysts under optimal SWCNT growth conditions, carbon yields (per % Co loading) of these catalysts are 11.7% and 6.3%, and the abundance of (6,5) nanotube in semiconducting nanotubes is 47.4% and 30.9% respectively according to the quantification by PL spectra. In these catalysts, only Co is responsible for SWCNT growth, while Cr, Mn and Mo are not involved in the nucleation of SWCNT. Instead, they act as an anchoring site for Co particles formed during the synthesis process.

In addition, there is another approach in designing catalysts, in which metal thin film is deposited on flat substrates (e.g. SiO₂/Si wafer, sapphire). Examples of such catalysts include Co-Mo-sapphire catalyst,⁶³ Au catalyst,⁶⁴ and Co-Si catalyst.⁶⁵ Compared to the former two approaches, this one is more difficult to control the chirality of SWCNT, but it is useful for the fabrication of electronic nanotube-based devices.

Ishigami *et al.* utilized a Co-Mo catalyst by dip coating on sapphire to grow SWCNTs in CVD. Their work showed that the crystal plane of sapphire influenced the orientation, diameter and chirality of SWCNTs. The catalyst was heated in Ar flow under atmospheric pressure, and when the temperature (750-900 °C) was reached, the catalyst was reduced in H₂ flow for 10 mins before exposure to a CH₄/H₂ gas mixture at 1000 sccm. PL results revealed

that SWCNTs on the A-plane were near-zigzag tubes with narrow chirality distribution whereas SWCNTs observed on the R-plane showed dominant near-armchair tubes with relatively wider chirality distribution. This crystal plane-dependent selectivity was explained that dissimilar sapphire surface atomic structures induce the different particle morphology and orientation as well as the epitaxial relationship, resulting in the formation of specific cap structures during the initial SWCNT growth.⁶³ Au catalyst reported by Kato *et al.* was prepared by vacuum evaporation and sputtering thin films of Au(~ 0.2 nm)/Al₂O₃(20nm) on a SiO₂/Si substrate. The narrow-chirality distributed (6,5) nanotubes was synthesized by diffusion plasma chemical vapor deposition under the appropriate H₂ concentration (7 sccm H₂ flow rate). They attributed the chiral selectivity to the stability of the (6,5) cap structure and hydrogen-assisted Au catalyzation which suppressed the growth of large diameter nanotubes.⁶⁴ Recently, Fouquet *et al.* obtained a narrow chiral distribution using an ultrathin Co film (nominal 0.1 nm thickness) on SiO₂ (200 nm)-coated Si wafers in a low-pressure CVD chamber. The Co film was first treated by vacuum annealing at 600 or 700 °C followed by SWCNT growth in pure C₂H₂ (10⁻³ mbar), and the results showed that the growth at 600 °C resulted in dominant (6,5), (6,6) and (7,4) nanotubes with abundance of 27%, 19% and 19% respectively quantified by Raman spectroscopy, while increasing to 700 °C would synthesize SWCNTs with a broader chiral distribution. They proposed a two-step mechanism to explain the chiral-selective growth, including the formation of correct particle size and energy-dependent selective SWCNT cap nucleation.⁶⁵

Since the first report of narrow-chirality distributed (6,5) nanotubes produced on CoMoCAT in 2003, much effort has been put into the selective synthesis of specific (*n,m*)

species on novel catalysts; however, those chiral-selective catalysts can only produce small diameter (n,m) nanotubes around (6,5), (7,5), (7,6) and (8,4) tubes ($d < 0.9\text{nm}$). Furthermore, from the point of economical nanotube mass production, these catalysts have obvious drawbacks. Bimetallic catalysts (such as catalysts containing Mo, Cr, Ru and Pt) are usually more difficult to be removed compared to mono-metallic catalysts using routine chemical reagents in the SWCNT purification process, while the preparation of mono-metallic Co-MCM-41 catalysts needs various expensive surfactants and long synthesis time (6 days in the autoclave),⁶⁶ which greatly increases the cost of SWCNTs, let alone the expensive Au catalyst and Co-Mo-sapphire catalyst. Therefore, it is desirable to obtain novel mono-metallic catalysts, which can retain a good selectivity towards narrow (n,m) distributed SWCNTs with large diameter and high productivity, and at the same time can be synthesized at a lower cost and shorter time.

1.4 Growth parameters influencing (n,m) selectivity

According to the above literature review, selective growth of SWCNTs with a narrow (n,m) distribution can be only achieved by highly specific catalysts in combination with empirically optimized SWCNT growth conditions. SWCNT synthesis is a sensitive catalytic reaction affected by many parameters, such as temperature,^{49,59,67} catalyst supports,^{67,68} carbon precursors³² and additives.⁴⁴ Research studies suggest that a narrow SWCNT synthesis window may exist, in which those growth parameters can be manipulated to achieve a right balance^{32,56} to produce SWCNTs with narrow (n,m) distribution. Here, several parameters are summarized, which should be considered for the (n,m) selective growth of SWCNTs.

1.4.1 Temperature

For most catalysts used in CVD system, metallic ions are normally present in the form of metal oxide or incorporated into the framework of substrates after the calcination in air at high temperature. Therefore, catalysts should be reduced to catalytically active metal nanoparticles to catalyze the decomposition of carbon precursors. Both prereduction and growth temperatures greatly influence SWCNTs yield, selectivity, and diameter uniformity. Increasing prereduction temperature may increase carbon yield, because more metal ions can be reduced, and it makes more metallic nanoparticles accessible to carbon precursors during SWCNTs synthesis. However, if the prereduction temperature is too high, excessive reduction of metal oxides may lead to the formation of large metal clusters which have poor selectivity to SWCNTs.⁵⁴ Resasco and Chen *et al.* have reported such phenomena on Co-Mo catalyst^{52,69} and Co-MCM-41 catalysts.⁵⁴ On the other hand, the dependence of SWCNT selectivity on growth temperature has been widely addressed by many researchers on various catalysts.^{49,70,71} Although a high growth temperature is usually more favorable for carbon precursor decomposition, it can also lead to a faster nucleation of nanoparticles, resulting in SWCNTs with a broader (n,m) distribution.

In general, prereduction and growth temperatures can change the size of metal nanoparticles, while growth temperature also affects carbon precursor decomposition. Therefore, temperature should be finely tuned in order to control the (n,m) distribution of SWCNTs.

1.4.2 Carbon precursors

Carbon precursors have also been found to have strong impacts on the (n,m) selectivity in SWCNT growth. Many different carbon precursors have been utilized in SWCNT growth, including CO, hydrocarbons such as methane (CH_4), ethanol ($\text{C}_2\text{H}_5\text{OH}$), methanol (CH_3OH), ethylene (C_2H_2) and many others. These carbon precursors have distinct decomposition rates and chemical compositions.

Comparisons of different carbon sources have been made by researchers to synthesize SWCNTs in the CVD system. Resasco *et al.* compared the (n,m) distribution of SWCNTs produced by using CO and CH_4 under the same growth condition, and found that CH_4 is less (n,m) selective than CO. The difference has been attributed to their different decomposition kinetics and byproducts. The byproduct of CO disproportionation is an oxidant (CO_2), while CH_4 decomposition produces a reducing agent (H_2) which not only facilitate the aggregation of Co nanoclusters, but also hinder carbon species from nucleating on the cluster surface by lowering the carbon surface fugacity.⁶⁷ He *et al.* also studied the influence of CO and CH_4 on SWCNT on Fe-containing catalysts, and observed the same phenomena that large diameter SWCNTs with a wider diameter distribution were synthesized using CH_4 as the carbon precursor.⁷² Our group³² has investigated the (n,m) selectivity of four different carbon precursors including CO, CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ and C_2H_2 on Co-Mo catalyst. SWCNTs with narrow (n,m) distribution can only be synthesized under high-pressure CO or vacuumed $\text{C}_2\text{H}_5\text{OH}$ and CH_3OH . $\text{C}_2\text{H}_5\text{OH}$ and CH_3OH have been suggested to provide oxygen-containing species, like OH radicals, which may facilitate the oxidation of amorphous carbon and selectively etch metallic SWCNTs.^{73,74} They may also provide an optimal C and H

ratio in the reaction condition, which favors SWCNT growth and results in the narrower (n,m) distribution. The broader (n,m) distribution of SWCNTs is produced by C_2H_2 , because H_2 is also the byproduct of C_2H_2 decomposition.³² Compared to other carbon precursors, CO disproportionation reaction often requires a temperature range of 600-900 °C, and because it is kinetically slow at low temperature (<600 °C) and thermodynamically limited at high temperature, high pressures are employed to regulate the equilibrium and to control the quality and structures of SWCNTs.^{6,54,75} However, for different catalyst systems, e.g. FeRu catalyst,⁴⁸ CoPt catalyst,⁵⁰ and Co-Si catalyst,⁶⁵ various carbon precursors may behave in different way. Therefore, it is necessary to evaluate carbon precursors with specific catalysts together.

1.4.3 Catalyst substrates

Catalysts are usually composed of active metal species and substrates. The same metal species may have distinct activities in SWCNT synthesis, if they are dispersed on different substrates.⁷⁶ Catalyst substrates also play a very important role in (n,m) selectivity of SWCNTs. There are two types of substrates commonly applied in catalysts for SWCNT growth, *i.e.* structural and flat substrates. Structural substrates for SWCNT synthesis possess high thermal stability, large surface area to disperse metal particles at high loading, and strong metal-support interactions to minimize nanoparticle aggregation. Furthermore, this type of substrates is desired to be dissolved in acid or alkaline solutions, so that SWCNTs can be easily recovered from catalysts if necessary. Most widely used structural substrates include SiO_2 , Al_2O_3 , MgO, zeolites and MCM-41.^{44,68} Resasco *et al.* compared SWCNT growth from Co-Mo supported on SiO_2 and MgO under the same growth condition.⁶⁷ They found that SWCNTs produced on the MgO support have more (7,5), (8,4), and (6,6) nanotubes, while SWCNTs produced on SiO_2

have more (6,5) nanotubes. They claimed that the difference in surface morphology caused by metal-support interactions leads to the growth of different (n,m) SWCNTs. Our group⁶⁸ evaluated the (n,m) selectivity of Co-Mo on four representative catalyst supports, including SiO₂, MgO, Al₂O₃ and TiO₂. Both SiO₂ and MgO can provide Co species well dispersed on Mo oxides, resulting in SWCNTs with a narrow (n,m) distribution around the (7,5) nanotube. On the contrary, catalysts supported on TiO₂ and Al₂O₃ are not selective for SWCNT growth, because very strong interactions between supports (TiO₂ and Al₂O₃) and Co/Mo disrupts the synergistic effect between Co and Mo.

Compared to structural substrates, flat substrates usually do not possess large surface areas, thus the loading of metal species on flat substrates is lower. When SWCNTs are grown on flat substrates such as SiO₂/Si wafer,⁷⁷ quartz^{74,78} or sapphire,⁷⁹ their alignments (either vertically⁷⁴ or horizontally⁸⁰) and positions⁸¹ can be easily controlled. Hence, catalysts supported on flat substrates have unique advantages in fabricating SWCNT-based electronic devices. It has also been suggested that it may be possible to influence the (n,m) selection through the epitaxial interaction between metal nanoparticles and single-crystal substrates.⁶³

Generally, the above three representative parameters, in combination with others, such as carbon feed pressure⁷⁵ and flow rate⁶⁴ can be further finely tuned to change the SWCNT (n,m) distribution.

1.4.4 Additives

Additives are commonly used in the form of vapor during the SWCNT growth process, which can significantly improve catalyst activity and also affect SWCNT structures (diameter and chirality). Common additives include sulfur and sulfur-containing compounds, oxidative

gases (H_2O , CO_2 , and O_2) and NH_3 .^{44,82,83}

Sulfur and sulfur-containing compounds (thiophene,^{84,85} H_2S ^{86,87} and CS_2 ⁸⁸) have been widely used in the CNTs growth in CVD.⁸⁹ Appropriate amount of sulfur not only promotes the growth rate and the yield of CNTs but also strongly affects the shell number and diameter of CNTs.⁹⁰⁻⁹² The addition of sulfur is found to lower the melting point and induce localized liquid areas where SWCNT can be nucleated, and the diameters and chirality of SWCNTs can be changed by the sulfur amount.^{84,93}

A controlled amount of H_2O is usually used to remove the amorphous carbon during SWCNT growth and thus high-purity SWCNT can be obtained,⁹⁴ and the amount of H_2O can also tune the chirality and diameter distribution of SWCNTs.⁹⁵ Appropriate amounts of CO_2 can act as an etching agent and selectively etch small diameter tubes, and the mean diameters of SWCNTs can be shifted from 1.2 to 1.9 nm with the increase of CO_2 concentration.⁹⁶ Oxygen can also be applied to selectively etch metallic SWCNTs.⁹³ In addition, a small amount of ammonia (NH_3) was reported as an additive in the SWCNT growth, producing high-quality SWCNTs with narrow chiralities around the (13,12) nanotube.⁹⁷ Therefore, beyond the above parameters, appropriate amounts of additives can be considered to not only improve the quality and yields of SWCNT but also tune its (n,m) selectivity.

1.5 Mechanism of SWCNT (n,m) selectivity

A thorough understanding on the growth mechanism of SWCNTs is crucial to design appropriate synthesis conditions for controlling their (n,m) selectivity. For SWCNT growth in the CVD system, growth mechanisms are generally classified into root growth or tip growth as shown in Figure 1-3.³⁵ These two different growth modes result from the distinct interaction

strengths between metallic nanoparticles and substrates. It has also been suggested that the size of metallic clusters determines whether SWCNTs, MWCNTs or carbon filaments are to be formed, and it is also closely related to the diameter of SWCNTs.⁹⁸

Figure 1-3 Two general growth modes of nanotubes in CVD: base growth mode (left) and tip growth mode (right)

Based on experiments and numerical simulations, it is commonly suggested that the carbon atoms which result from decomposition of carbon containing precursors on the catalytic surface may follow this sequence of steps: (1) carbon atoms dissolve into the metal cluster, (2) carbon chains form on the metal cluster surface, (3) cap structures form by carbon chains interacting with each other and lift off the metal surface, and (4) nanotube grows. Selective growth of a specific (n,m) nanotube may happen either in step 3 or 4. In step 3, the formation of certain caps would be thermodynamically or kinetically preferred.⁹⁹ Maruyama *et al.* suggested to interpret (n,m) selectivity by considering the stability and the number of possible cap structures.⁴⁷ Dai *et al.* conducted density functional theory calculations to investigate the stability and energetics of various nanotubes, and found that semiconducting

SWCNTs show the lowest energies and are the most stable compared to metallic and quasi-metallic SWCNTs, and this could lead to the preferential growth of semiconducting nanotubes.¹⁰⁰ Balbuena *et al.* has shown that the armchair and near-armchair caps facilitate nanotube growth thermodynamically and kinetically as compared to near-zigzag caps.¹⁰¹ They further studied the interactions between carbon caps and small metal clusters, indicating that the (n,m) selectivity of nanotubes could be determined by the cap/catalyst nanoparticle interactions.¹⁰² Reich *et al.*¹⁰³ proposed a mechanism that particular caps would be favored by their epitaxial relation to the catalyst surface, resulting in corresponding selectivity toward specific chiral tubes. They claimed that the (n,m) selectivity of nanotubes is determined during the cap nucleation stage, and sequentially grow into the specific SWCNT with the corresponding (n,m) structure. However, this argument may be not correct, because recent studies demonstrated that chirality can be further changed during the SWCNT growth.^{104,105}

If the selective growth proceeds in step 4, then it could be determined by an overall effect of several factors including but not limited to growth conditions, the substrate and catalyst, physical and chemical properties of different nanotubes, and the interaction between the nanotube and the metal cluster.⁹⁹ Neyts *et al.* have demonstrated that the evolution of the nanotube chirality from (11,0) over (9,3) to (7,7) during the growth process due to the metal-mediated restructuring process.¹⁰⁶ The growth rate of SWCNTs is also found related to the possible SWCNT chirality.¹⁰⁷ Ding *et al.* proposed that growth rates of SWCNTs are proportional to their chiral angles,¹⁰⁸ which has been validated by measurements of individual SWCNT growth rate using in situ Raman spectroscopy.¹⁰⁹ Ding *et al.* also noticed that strong adhesion between SWCNTs and metal clusters is necessary for SWCNT growth, and the

adhesion energy is (n,m) dependent. This result implies that chirality-controlled growth can be reached by careful selection of metal catalysts.¹¹⁰ However, metal catalyst is not necessarily required for SWCNT growth based on recent experimental studies. The growth of SWCNT is also feasible on non-metal catalysts according to experimental results.³⁸ Our group demonstrated that SWCNT growth and chirality changes are both thermodynamically and kinetically feasible under catalyst-free growth conditions based on abounding density function calculations.¹¹¹

So far, although there are still no reliable mechanisms available to provide a clear path towards achieving the (n,m) selectivity in SWCNT growth, understanding on (n,m) selective SWCNT growth can provide useful information to help design more selective catalysts and choose appropriate growth conditions in order to improve SWCNT chirality control.

1.6 Motivation and scope

Obtaining SWCNTs with specific chirality is essential for their advanced applications. Currently, there are a few catalysts which can synthesize SWCNTs with narrow (n,m) distribution. Despite the noticeable selectivity reported on these catalysts, their applicability in achieving selective synthesis of desired (n,m) SWCNTs is still limited. All catalysts show similar selectivity toward higher chiral angle tubes, in particular small tubes such as (6,5), (7,5), (7,6) and (8,4). Their diameters are less than 0.9 nm. These catalysts lose their (n,m) selectivity when the SWCNT diameter increases. So far, no effective selectivity towards other chiral tubes has been reported, especially larger diameter tubes, while SWCNTs with large diameter have smaller bandgaps which would be more promising to construct high performance transistors.¹¹² Therefore, the overall objective of my research is development of

new catalysts to obtain the narrowly (n,m) distributed large diameter SWCNTs.

This thesis will be presented in the following structure. Firstly, the basic experimental methods and techniques used for the synthesis and characterization of the catalysts and SWCNTs are described in Chapter 2. Chapter 3 presents selective synthesis of (9,8) SWCNTs on Co-TUD-1 catalysts. Chapter 4 illustrates the chiral-selective $\text{CoSO}_4/\text{SiO}_2$ catalyst for (9,8) SWCNT growth. Chapter 5 investigates the effect of catalyst calcination temperature on selective synthesis of (9,8) SWCNTs. Chapter 6 discusses sulfur doped Co/SiO_2 catalysts for chirally selective growth of (9,8) SWCNTs. Chapter 7 demonstrates the preliminary application of (9,8) SWCNTs in field effect transistors. Lastly, Chapter 8 summarizes the thesis and proposes the future work.

Chapter 2 General Experimental Methods

This thesis focuses on novel catalyst development for chirally selective growth of SWCNTs. Two novel catalysts were developed and applied into the synthesis of SWCNTs. In this chapter, a wide range of experimental methods and techniques for the synthesis and characterization of catalysts and SWCNTs were described in detail.

2.1 Catalyst preparation

Impregnation and hydrothermal methods are extensively used for catalyst preparation. Impregnation method is to directly mix substrates with desired metal ions in solutions, followed by drying and calcination. Metal atoms are randomly distributed on substrate surface, and /or in the pores of substrates. Impregnation method is relatively simple. For hydrothermal method, metal atoms can be incorporated into the substrate during the formation of substrates in order to produce catalysts with well-dispersed stable metal particles and strong metal-substrate interaction. In this thesis, these two methods were employed to prepare catalysts.

2.2 Catalyst characterization

The physiochemical properties of catalysts were characterized by X-ray diffraction, nitrogen physisorption, H₂-temperature programmed reduction, UV-vis diffuse reflectance spectroscopy, elemental analysis, scanning electron microscope, and X-ray absorption spectroscopy.

2.2.1 X-ray diffraction

X-ray diffraction (XRD) is commonly used to reveal the crystallographic structure of

catalysts. In this thesis, XRD measurements of catalysts were carried out on a Bruker Axs D8 X-ray diffractometer (Cu K α , λ = 0.154 nm, 40 kV, 30 mA).

2.2.2 Nitrogen physisorption

Nitrogen physisorption is utilized to measure the surface area and pore size distribution of catalysts. In this study, nitrogen adsorption-desorption isotherms of catalysts were measured at 77 K using a Quantachrome Autosorb-6b static volumetric instrument. The catalyst samples were first degassed at 250 °C under high vacuum (< 0.01 mbar). The specific surface area of catalysts was calculated by the Brunauer-Emmet-Teller (BET) method, while the pore size and pore size distribution were calculated by the Barrett-Joyner-Halenda (BJH) method using the desorption branch of the isotherms.¹¹³

2.2.3 H₂-temperature programmed reduction

H₂-temperature programmed reduction (H₂-TPR) is very useful in investigating the metal support interaction and providing surface chemical information, such as stability, metal species, and metal distribution.¹¹⁴ In this thesis, the reducibility of catalysts was investigated by TPR system equipped with a thermal conductivity (TCD) detector of a gas chromatography (Techcomp 7900). 200 mg of the catalyst or reference samples with equivalent Co loadings were loaded into a quartz cell. CoO (99.99%, Aldrich), Co₃O₄ (99.8%, Aldrich), CoSiO₃ (ICN215905, MP Biomedicals), CoSO₄ · 7H₂O (99%, Sigma-Aldrich) and CoCl₂ (Alfa Aesar, 97%) were used as reference samples in TPR analysis. H₂ (5%) in Ar was introduced to the quartz cell at a flow rate of 30 sccm. Pure Ar gas was used as a reference for the TCD. After the TCD baseline was stable, the temperature of the quartz cell was increased to 950 °C at 5

°C/min, and then held at 950 °C for 30 min. An acetone–liquid N₂ trap was installed between the quartz cell and the TCD to condense water or H₂S produced during catalyst reduction.

2.2.4 UV-vis diffuse reflectance spectroscopy

UV-vis diffuse reflectance spectroscopy is employed to investigate the local environment of cobalt in the solid catalyst. UV-vis diffuse reflectance spectra of the solid catalyst samples and references, such as CoO, Co₃O₄, CoSO₄, CoSiO₃, CoCl₂ and fumed silica, were recorded on a Varian Cary 5000 spectrophotometer with an integrating sphere for solid-phase characterization. The samples were first dried at 100 °C for 3 h, and then UV-vis spectra were recorded in the range of 200–800 nm with BaSO₄ as a reference.

2.2.5 Elemental analysis

Elemental analysis can be used to analyze materials quantitatively for the elemental composition. In this thesis, the weight fraction of sulfur in catalysts was measured by an Elementarvario CHN elemental analyzer. Before each test, all samples were dried at 100 °C overnight. About 5 mg sample was used in each test, and each catalyst sample was tested three times to obtain the average and standard errors.

2.2.6 Scanning electron microscope

Scanning electron microscope (SEM) is widely applied for providing microscale information about surface morphology. In this thesis, SEM images of catalysts were obtained by using JEOL field-emission SEM (JSM–6701F) at 5 kV.

2.2.7 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) is a widely used for determining the local geometric and/or electronic structure of matters. XAS was used in this thesis to provide information on the local environments of Co atoms in catalysts and as-synthesized SWCNT samples, such as the bond lengths and coordination numbers, which can be used to determine chemical structures and cluster sizes. XAS was also utilized to study the states of sulfur species in the catalysts. The X-ray Absorption Near Edge Structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra at the Co K-edge (7709eV) were collected at the beamline X18B, National Synchrotron Light Source at Brookhaven National Laboratory, USA. The monochromator of this beamline is a double-crystal Si (111). Catalysts were pressed into round self-supporting wafers (1.5 cm in diameter) using a hydraulic pellet press under ~ 2 tons forces. The thickness of wafers was made near the optimum absorption thickness, where $\Delta\mu x \approx 1.0$ ($\Delta\mu$ is the absorption edge, and x is the thickness of catalyst wafers). XAS spectra were collected in a fluorescence mode at room temperature by scanning from 200 below to 1000 eV above the Co-K edge using gas-filled ionization chamber detectors.

The XAS data at the Co K-edge were analyzed using the IFEFFIT program.¹¹⁵ First, the XAS function (χ) was obtained by background subtraction and step-edge normalization. Next, the normalized $\chi(E)$ was transformed to photoelectron wave vector k -space, and the k^2 -weighted $\chi(k)$ data in a k -range from 2 to 12.5 $\text{\AA}^{-1}$ (or 2 to 10 $\text{\AA}^{-1}$) for the Co K-edge were then Fourier transformed to r -space to separate the contribution from different coordination shells. Last, the spectra in the r -space between 1.1 and 3.35 $\text{\AA}$ (or 0.8 and 2.0 $\text{\AA}$) were fitted using theoretical paths of metallic Co (or Co_3O_4 and CoSO_4) generated by the FEFF 9 program

to obtain parameters, including the first shell coordination number ($N_{\text{Co-Co}}$ or $N_{\text{Co-O}}$), the bond distance (R) and the Debye–Waller factor ($\Delta\sigma^2$).

The sulfur K-edge XANES spectra of catalysts were recorded at the beamline X15B at Brookhaven National Laboratory. The sample powder was brushed onto a thin strip of sulfur-free kapton tape, uncovered, facing the beam at 45°. The XANES spectra were collected in a fluorescence mode at room temperature with the energy range of 2450–2600 eV. $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and cobalt sulfide were used as reference compounds. Pure sulfur was used to calibrate the Si (111) monochromator.

2.3 SWCNT synthesis

To catalyze SWCNT growth, 200 mg of catalyst was loaded in a ceramic boat at the centre of a horizontal CVD reactor. The catalyst was first reduced under pure H_2 (1 bar, 50 sccm, 99.99% from Alphagaz, Soxal), during which the reactor temperature was increased from room temperature to an elevated temperature at 20 °C/min. After reduction, the reactor was purged by Ar (99.99% from Alphagaz, Soxal), while its temperature was further increased to growth temperature. And then, pressured CO (6 bar, 99.9% from Alphagaz, Soxal) was introduced into the reactor at 200 sccm flow rate to initiate SWCNT growth, and the growth time was 1 h. Carbonyl residues in CO gas were removed by a purifier (Nanochem, Matheson Gas Products) before CO entering the reactor.

2.4 SWCNT purification

As-synthesized SWCNTs were refluxed in NaOH aqueous solution (1.5 mol/L) to dissolve the catalyst support, and then filtered on a nylon membrane (0.2 μm pore). To obtain SWCNT

suspension, carbon deposits on filter membranes were further dispersed in 2 wt% sodium dodecyl benzene sulfonate (SDBS) (Aldrich) D₂O (99.9 atom % D, Sigma-Aldrich) solution by sonication in a cup-horn ultrasonicator (SONICS, VCX-130) at 20 W for 1 h. Subsequently, the SWCNT suspension was centrifuged for 1 h at 50,000 *g*. SWCNT supernatant obtained after centrifugation was further characterized by several spectroscopies.

2.5 SWCNT characterization

There are six characterization techniques: Raman spectroscopy, photoluminescence (PL) spectroscopy, ultraviolet–visible–near-infrared (UV-vis-NIR) absorption spectroscopy, thermogravimetric analysis, transmission electron microscopy and atomic force microscopy, which have been utilized to characterize SWCNTs in order to analyze carbon species existing in a sample, the quality and purity of SWCNTs in a sample, the diameter and (*n,m*) distribution of a SWCNT sample.

2.5.1 Raman spectroscopy

Raman spectroscopy is a noncontact and nondestructive technique, which is commonly used to characterize SWCNT. There are mainly three features corresponding to SWCNT structures: the Radial Breathing Mode (RBM), the Disorder-induced band (D band) and the Graphite-like band (G band).¹¹⁶ RBM always locates at the low frequency range (100–400cm⁻¹), which can be applied to identify the existence of SWCNTs in a sample, and it is also employed to estimate SWCNT diameters. The band observed between 1500 and 1600cm⁻¹ is denoted by the G band which comes from the graphite tangential vibration mode. The D band at ~1300cm⁻¹ is induced by defects in SWCNTs and amorphous carbon.¹¹⁷ Most

Raman system with single laser excitation can only show certain species of the whole SWCNT ensemble, multiple laser excitations are required to perform a more complete analysis of (n,m) distribution.

Raman spectroscopy was used in this thesis for the following purposes: (1) to identify the existence of SWCNTs in samples, (2) to determine the diameter distribution of SWCNT samples, and (3) to evaluate the SWCNT quality by D/G ratio. Raman spectra were obtained by a Renishaw Ramanscope in the backscattering configuration over a few random spots on samples using three different lasers 514 nm (2.41 eV), 633 nm (1.96 eV), and 785 nm (1.58 eV). The integration time is 10s, and laser energies of 2.5-5 mW were used to prevent sample damages during the measurement.

2.5.2 PL spectroscopy

Photoluminescence (PL) studies of SWCNT focus on electronic transitions of semiconducting tubes, because metallic tubes don't show light emission due to the available electronic states between their valence and conduction bands. The relation between electronic transitions and all possible (n,m) SWCNTs can be described in a Kataura plot based on calculation using a tight binding model.¹¹⁸ New empirically-based Kataura plots were developed to obtain more reliable predictions of (n,m) structures using measured SWCNT optical transitions (E_{11} , E_{22}).¹¹⁹

PL spectroscopy can provide a quick identification for the (n,m) distribution of semiconducting SWCNTs. The abundance of each (n,m) species can also be easily related to their PL intensity. Early studies directly applied the PL intensity of individual (n,m) species to determine their relative abundance.^{46,120} Some theoretical studies later suggested that (n,m)

species may have significantly different photoluminescence quantum efficiencies, which could introduce errors in their relative abundances calculated by the PL intensity alone.^{121,122} However, experiments indicate that the quantum efficiency difference among various (n,m) SWCNT species may not be as large as theoretical predictions.¹²³ In our previous studies, we have compared the abundance values calculated with or without considering (n,m) photoluminescence quantum efficiency coefficients.^{75,124} No significant differences were observed. These findings support the direct use of measured PL intensity in determining the SWCNT (n,m) abundance. Thus, in this study, the relative abundance of (n,m) species was calculated by dividing the PL intensity of individual (n,m) species by the sum of intensities of all (n,m) species. PL spectra were measured by a Jobin-Yvon Nanolog-3 spectrofluorometer with the excitation scanned from 450 to 950 nm and the emission collected from 900 to 1600 nm.

2.5.3 UV-vis-NIR absorption spectroscopy

Absorption spectroscopy is a technique measuring the optical absorption of a sample in a particular wavelength range. The application of UV-vis-NIR absorption spectroscopy in SWCNT characterization is based on electronic transitions between energy bands of SWCNT caused by incoming photons. Both semiconducting and metallic SWCNTs can be detected. Because transition energies of different SWCNTs could be very close, each peak in an absorption spectrum may represent the combination of several (n,m) SWCNT species. In order to identify different (n,m) species in an absorption spectrum, several spectrum deconvolution scenario (Lorentz, Gauss or Voigt) have been used.¹²⁵ However, the absorption spectrum deconvolution of a bulk SWCNT sample into distinct (n,m) contributions is very difficult,

especially for samples having a broad (n,m) distribution.

In this thesis, UV–vis–NIR absorption spectroscopy was mainly used to analyze the (n,m) distribution of SWCNT samples. UV–vis–NIR absorption spectra were measured from 500 to 1600 nm on the Varian Cary 5000 spectrophotometer.

2.5.4 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was used to analyze the carbon yield on catalysts and different carbon species of carbon deposits. The total carbon yield was determined by analyzing weight loss of as-synthesized carbon deposits with catalysts. Carbon deposits contain not only SWCNTs but also other impurities like amorphous carbon, MWCNTs and graphite, which can be determined based on DTG (derivative thermogravimetry) patterns obtained by taking the derivative of TGA profiles. TGA was conducted on a PerkinElmer Diamond TG instrument. For a typical test, about 2 mg as-synthesized catalyst was placed in an alumina pan. The sample was heated to 200 °C, and held for 10 min under airflow (200 sccm) to remove moisture. Subsequently, its temperature was continuously raised from 200 to 1000 °C at a 10 °C /min rate. The weight loss was monitored and recorded as a function of the temperature. The same procedure was repeated after the sample was cooled to room temperature to get the second weight–temperature curve for baseline correction. The differential thermogravimetric (DTG) analysis was performed on the baseline corrected TG profiles.

2.5.5 Transmission electron microscopy

Transmission electron microscopy (TEM) is the most powerful tool to image nanoscale

materials with atomic scale resolution. TEM images of catalysts were recorded on a Philips Tecnai 12 microscope. The solid samples were first dispersed in anhydrous ethanol by bath sonication for 30 min, and then one drop of the suspension was applied to a TEM grid covered with holey carbon film.

2.5.6 Atomic force microscopy

Atomic force microscopy (AFM) was employed to estimate the diameter and length distributions of SWCNTs. SWCNTs were first deposited on wafer surfaces. AFM images were captured using an MFP3D microscope (Asylum Research, Santa Barbara, CA). The scan rate was set to 1 Hz with the data resolution of 512 pixels $\times$ 512 lines. The first-order flattening was applied to AFM amplitude profiles to remove the Z offset between scan lines.

Chapter 3 Selective Synthesis of (9,8) SWCNTs on Cobalt Incorporated TUD-1 Catalysts

As discussed in Chapter 1, a major obstacle for SWCNT applications is that the current synthesis methods produce SWCNTs with different (n,m) structures, leading to mixtures with distinct electronic properties ranging from metal to semiconductors with different band gaps.¹²⁶ Although a few catalysts have shown chiral-specific growth, current chirality control growth has only achieved at small diameter (6,5) and (7,5) nanotubes.^{46,48-50,54,58,73} Considering that there are more than 100 different chiral SWCNTs with diameters just between 0.6 and 1.5 nm, novel catalysts with specific single chirality selectivity are highly pursued. Co has been used in a few chirally selective catalysts,^{46,49,65,73,127} therefore Co is chosen as the catalytic metal catalyst in this study. Since supported catalysts have more advantages, structural supports are preferred to well disperse and stabilize the Co atoms. TUD-1 is a mesoporous silica matrix with large surface area and high thermal stability. Moreover, various metal ions can be incorporated in the silica matrix, which makes TUD-1 a good catalyst candidate.¹²⁸ A cobalt incorporated TUD-1 catalyst (Co-TUD-1) has been used in the oxidation reactions.^{129,130} However, Co-TUD-1 has yet been applied for SWCNT growth. Therefore, in this study, Co-TUD-1 catalyst was developed for SWCNT growth.

3.1 Co-TUD-1 catalyst preparation

Co-TUD-1 with 1 wt% cobalt was synthesized using a hydrothermal method modified from the previous work of Hamdy *et al.*¹²⁹ In a typical synthesis, 0.28 g of cobalt (II) sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, > 99%, Sigma-Aldrich) was dissolved in deionized water, and

then the CoSO_4 solution was added dropwise into 10 g of tetraethyl orthosilicate (TEOS, > 98%, Sigma-Aldrich) under vigorous stirring. After stirring for 0.5 hour, 7.2 g of triethanolamine (TEA, > 98.5%, Fluka) and 1.8 g of deionized water were added dropwise into the TEOS solution, and further stirred for 2 h. Subsequently, 6.1 g of tetraethyl ammonium hydroxide (TEAOH, 35%, Sigma-Aldrich) was added to the mixed solution, and then the solution was aged for 24 h at room temperature. After aging, the mixture was dried at 100 °C for 24 hours, followed by hydrothermal treatment in a Teflon-lined stainless steel autoclave for 8 hours at 180 °C. The final solid product was calcined at 600 °C for 10 hours under a steady airflow to remove sulfate ions and organic templates. The total synthesis takes about 3 days.

3.2 Physicochemical properties of Co-TUD-1 catalyst

Physicochemical properties of Co-TUD-1 catalyst were characterized by XRD, nitrogen physisorption, UV-vis spectroscopy, and H_2 -TPR. XRD was applied to characterize the physical structure of Co-TUD-1. Figure 3-1a illustrates the low angle XRD pattern of the 1 wt% Co-TUD-1. An intense diffraction peak at the vicinity of $2\theta = 0.8^\circ$ to 1.0° indicates that Co-TUD-1 is a mesostructured material, which agrees with previous publications.¹²⁹⁻¹³¹ Nitrogen physisorption was used to provide more detailed physical structures. The adsorption/desorption isotherm in Figure 3-1b has a step increase in nitrogen uptake at the relative pressure (P/P_0) of 0.5 – 0.8, suggesting that Co-TUD-1 has a typical mesoporous structure. The isotherm also demonstrates a hysteresis shape belonging to a type IV isotherm. The insert of Figure 3-1b indicates that the Co-TUD-1 sample possesses well defined pores, having an average diameter of 7.4 nm with a narrow pore size distribution. Data extracted from the physisorption isotherm also confirm that the sample possesses a surface area of 740 m^2/g

and a large pore volume of 1.42 mL/g.

Figure 3-1 (a) XRD pattern of Co-TUD-1. (b) Nitrogen physisorption isotherm of Co-TUD-1.

The insert shows the pore size distribution determined by the BJH method.¹¹³

Chemical properties of Co-TUD-1 were characterized by UV-vis spectroscopy and TPR. UV-vis spectra in Figure 3-2a designate the local environment of Co ions in the TUD-1 silica matrix. Co-TUD-1 exhibits a minor peak shoulder at 660 nm and two broad peaks at 410 and 710 nm, respectively. The peak at 660 nm has been assigned to $v_2 \text{ } ^4A_2 \rightarrow \text{ } ^4T_1(P)$ transition, indicating the presence of tetrahedral Co^{2+} .¹³² The absorption peaks at 410 and 710 nm are similar to those detected on the Co_3O_4 reference, which can be assigned to $v_1 \text{ } ^4A_{1g} \rightarrow \text{ } ^1T_{1g}$ and $v_2 \text{ } ^1A_{1g} \rightarrow \text{ } ^1T_{2g}$ transitions, respectively. They point to the existence of octahedral Co^{3+} ions.¹³² The absorption peak of Co-TUD-1 at 410 nm is much broader compared to that of the Co_3O_4 reference. This may be caused by the masking or overlapping between the 410 nm peak and additional peaks associated with tetrahedral Co^{2+} ions, which are typically observed in the range of 500 to 600 nm.¹³² In addition, no absorption peaks from octahedral Co^{2+} ions were observed, which can be contributed to the fact that extinction coefficients of tetrahedral Co^{2+}

ions are usually much stronger than those of Co^{2+} octahedral ions.

Figure 3-2 (a) UV-vis reflectance spectra of Co-TUD-1 and the Co_3O_4 reference. (b) H_2 -TPR profile of Co-TUD-1.

Figure 3-2b shows the TPR profile of Co-TUD-1. It illustrates the stability of Co ions in the TUD-1 matrix. A distinct and narrow reduction peak is centered at 483 $^{\circ}\text{C}$. This reduction temperature is higher than that of impregnated cobalt catalysts supported on silica particles,⁶⁸ while is much lower than that of Co-MCM-41 catalyst.¹³³ Two peak shoulders exist at 439 and 383 $^{\circ}\text{C}$, respectively. They correspond to the reduction process of $\text{Co}_3\text{O}_4 \rightarrow \text{CoO} \rightarrow \text{Co}$.⁶⁸ Therefore, the peak at 483 $^{\circ}\text{C}$ can be ascribed to the reduction of Co ions incorporated in the TUD-1 matrix.

Overall, physical and chemical characterization results show that Co-TUD-1 catalyst possesses highly ordered mesoporous structure, large surface area, narrowly distributed pore size, and stable incorporated Co species in its silica matrix. These properties are considered to be crucial for the production of high quality SWCNTs.^{54,133}

3.3 SWCNT synthesis and purification

SWCNTs were synthesized in a pressured CO chemical vapor deposition reactor. Co-TUD-1 catalysts were initially prereduced at a certain temperature in H₂ for 0.5 hour. Subsequently, the reactor temperature was increased to 800 °C under Ar flow, and eventually CO (6 bar, 100sccm) was introduced at 800 °C for 1 hour. Prereduction temperature under H₂ was adjusted from 400 to 600 °C, while keeping other reaction parameters the same. The detailed SWCNT synthesis and purification of as-synthesized SWCNTs were described in Chapter 2.

3.4 SWCNT (*n,m*) analysis

Figure 3-3 PL maps of SDBS-dispersed SWCNTs produced from Co-TUD-1 after prereduction under H₂ at different temperatures: (a) 400 °C, (b) 500 °C and (c) 600 °C. (d) UV-vis-NIR spectra of SWCNTs. (e) Raman spectra of as-synthesized SWCNTs grown after 500 °C prereduction using the excitation wavelengths of 633 and 785 nm. The inset panel

shows the enlarged RMB area.

Figures 3-3a to 3-3c show PL maps of SWCNTs produced on Co-TUD-1. The resonance behaviors of excitation and emission yield peaks corresponding to transition pairs from individual semiconducting (n,m) species.¹³⁴ The relative abundance of every species was calculated based on their PL peak intensities and the findings are listed in Table 3-1 to 3-3.

Figure 3-3b shows a high selectivity toward (9,8) nanotubes after prereduction at 500 °C, in which 59.1% of semiconducting nanotubes are (9,8) (Table 3-2). At prereduction temperature of 400 °C, (6,5) have the highest PL intensity with 32.6% abundance (Figure 3-3a and Table 3-1). In contrast, (10,9), (9,8), (9,7), and (6,5) were produced after prereduction at 600 °C with the abundances of 7.4, 43.5, 12.3 and 8.9%, respectively (Table 3-3). UV-vis-NIR spectra were examined to corroborate the PL results. Figure 3-3d confirms that (9,8) is the dominant (n,m) species in producing SWCNTs after prereduction at 500 °C. For two other prereduction conditions, absorption spectra also agree with the PL results. Furthermore, an intense and narrow RBM peak is observed at close to 209 cm^{-1} under 785 and 633 nm excitation in Raman spectra (Figure 3-3e), which corresponds to (9,8) nanotubes.¹³⁵

Table 3-1 Tabulated values of PL intensities and relative abundances of (n,m) species in SWCNTs produced on Co-TUD-1 after prereduction at 400 °C.

(n,m) index	Diameter d_t (nm)	Chiral angle θ (°)	E_{11} (nm)	E_{22} (nm)	PL intensity (counts)	Relative abundance, (%)
(6,5)	0.76	27.00	978	570	4376.5	32.6
(7,3)	0.71	17.00	991	510	1547.4	11.5

(7,5)	0.83	24.50	1029	644	994.5	7.4
(7,6)	0.90	27.46	1120	646	1507.0	11.2
(8,3)	0.78	15.30	956	666	254.5	1.9
(8,4)	0.84	19.11	1116	578	909.6	6.8
(8,6)	0.97	25.28	1170	718	449.8	3.4
(8,7)	1.03	27.80	1271	730	840.2	6.3
(9,7)	1.10	25.87	1319	794	666.2	5.0
(9,8)	1.17	28.05	1416	822	1301.4	9.7
(10,8)	1.24	26.30	1477	870	300.8	2.2
(10,9)	1.31	28.30	1565	890	273.3	2.0

Table 3-2 Tabulated values of PL intensities and relative abundances of (n,m) species in SWCNTs produced on Co-TUD-1 after prereduction at 500 °C.

(n,m) index	Diameter d_t (nm)	Chiral angle θ (°)	E_{11} (nm)	E_{22} (nm)	PL intensity (counts)	Relative abundance, (%)
(6,5)	0.76	27.00	978	570	109.4	2.5
(7,3)	0.71	17.00	992	498	98.4	2.3
(7,5)	0.83	24.50	1023	646	58.6	1.3
(7,6)	0.90	27.46	1111	638	68.2	1.6
(8,3)	0.78	15.30	953	666	49.8	1.1
(8,4)	0.84	19.11	1109	586	67.5	1.6
(8,6)	0.97	25.28	1173	714	58.2	1.3

(8,7)	1.03	27.80	1264	726	162.1	3.7
(9,7)	1.10	25.87	1321	790	583.7	13.4
(9,8)	1.17	28.05	1416	822	2568.9	59.1
(10,8)	1.24	26.30	1469	870	170.4	3.9
(10,9)	1.31	28.30	1562	890	354.0	8.1

Table 3-3 Tabulated values of PL intensities and relative abundances of (n,m) species in SWCNTs produced on Co-TUD-1 after prereduction at 600 °C.

(n,m) index	Diameter d_t (nm)	Chiral angle θ (°)	E_{11} (nm)	E_{22} (nm)	PL intensity (counts)	Relative abundance, (%)
(6,5)	0.76	27.00	981	566	883.1	8.9
(7,3)	0.71	17.00	987	510	395.0	4.0
(7,5)	0.83	24.50	1022	638	176.7	1.8
(7,6)	0.90	27.46	1113	638	395.0	4.0
(8,3)	0.78	15.30	951	666	55.2	0.6
(8,4)	0.84	19.11	1110	578	375.6	3.8
(8,6)	0.97	25.28	1167	714	170.6	1.7
(8,7)	1.03	27.80	1263	726	725.8	7.3
(9,7)	1.10	25.87	1321	790	1227.0	12.3
(9,8)	1.17	28.05	1414	818	4324.4	43.5
(10,8)	1.24	26.30	1469	866	470.3	4.7
(10,9)	1.31	28.30	1561	886	740.0	7.4

Figure 3-4 Chirality maps of SWCNTs grown from Co-TUD-1.

Prereduction temperature is a critical factor for achieving high selectivity toward (9,8) nanotubes. As illustrated in Figure 3-4, when Co-TUD-1 is reduced to 400 °C, major (*n,m*) species are at 0.757 nm. When the prereduction temperature is increased to 500 °C, (9,8) is 1.17 nm. Conversely, the catalyst lose its (*n,m*) selectivity when the prereduction temperature is further raised to 600 °C. The optimal prereduction temperature at 500 °C has strongly correlated with the TPR reduction temperature at 483 °C, as evidenced in Figure 3-2b. SWCNT growth temperature was varied under CO from 600 to 900 °C. The growth temperature between 600 to 800 °C only affected carbon yield other than (*n,m*) selectivity. When the growth temperature was higher than 850 °C, SWCNTs show a broad (*n,m*) distribution similar to that of HiPco nanotubes, regardless of the prereduction temperature.

3.5 Mechanism

Analogous to Co-MCM-41 catalyst,^{54,62} Co species on TUD-1 can nucleate in two steps. First, Co²⁺ ions are partially reduced in H₂ during prereduction, but they are still dispersed isolatedly on the large surface of TUD-1. Second, Co atoms aggregate quickly into clusters

under CO to initiate SWCNT growth. The uniqueness of Co–TUD-1 relies on its low reduction temperature (483 °C vs. 700–900 °C of Co–MCM-41), which increases the amount of reduced Co atoms available for forming Co clusters when CO is introduced. At the same time, its large surface area and the strong metal–support interaction are sufficient in stabilizing these clusters with a narrow diameter distribution at around 1.2 nm, responsible for the growth of (9,8) nanotubes. If prereduction temperature is too low, less reduced Co atoms are available, causing slightly smaller Co clusters to grow smaller diameter nanotubes, such as (6,5). On the other hand, if the prereduction temperature is too high, TUD-1 cannot stabilize the large amount of reduced Co atoms, and Co clusters with various sizes could form, which leads to the loss of (*n,m*) selectivity. The overall high selectivity toward large chiral angle nanotubes is also noticeable. Although some theoretical studies have tried to explain this,^{103,108,110} more studies are required to provide a comprehensive explanation.

3.6 Conclusion

In conclusion, (9,8) nanotubes can be selectively grown on Co–TUD-1 catalyst. Prereduction in H₂ at 500 °C results in 59.1% of semiconducting nanotubes having the (9,8) structure. The uniqueness of Co–TUD-1 relies on its low reduction temperature (483 °C), large surface area, and strong metal–support interaction, which stabilizes Co clusters responsible for the growth of (9,8) nanotubes.

Chapter 4 Chiral-Selective $\text{CoSO}_4/\text{SiO}_2$ Catalyst for (9,8) SWCNT Growth

In Chapter 3, a novel Co-TUD-1 catalyst was prepared and demonstrated a good selectivity towards (9,8) SWCNT; however, the total carbon yield of Co-TUD-1 is low, and it would take 3 days to prepare the catalyst by aging, drying and hydrothermal treatment, which results in the difficulty in achieving scalable production of desired SWCNTs. It is worth developing more efficient catalysts for selective growth of large diameter SWCNTs.

Many catalysts used for SWCNT synthesis are prepared by the conventional incipient wetness impregnation method, and different Co salts supported on silica have been evaluated for synthesis of SWCNTs, including Co (II) nitrate, Co (II) acetate, Co (II) acetylacetonate, and Co (III) acetylacetonate.^{124,127,136,137} After solvent drying and catalyst calcination, different Co species are formed on the substrates, such as Co oxides or Co silicates. Nevertheless, none of above Co precursors results in catalysts with good selectivity towards large diameter SWCNTs. Several previous studies have showed that suitable amounts of sulfur species added in the gas phase with carbon precursors can promote the growth rate and the yield of carbon nanotubes; in addition, sulfur in the gas phase also strongly affects nanotube structures (such as shell number and diameter of MWCNTs).⁹⁰⁻⁹² It is hypothesized that if sulfur compounds can be incorporated directly in catalysts, the resulting catalysts may have interesting chiral selectivity. CoSO_4 is a soluble sulfur-containing cobalt salt, and catalyst supports can be impregnated with CoSO_4 solution. Therefore, a new sulfate-promoted $\text{CoSO}_4/\text{SiO}_2$ catalyst was developed for SWCNT growth.

4.1 CoSO₄/SiO₂ catalyst preparation

The CoSO₄/SiO₂ catalyst was prepared by the incipient wetness impregnation method, in which metal salt dissolved in deionized water was added to the catalyst support materials. Cobalt(II) sulfate heptahydrate (Sigma-Aldrich, ≥99% purity) was first dissolved in deionized water, and then added to CAB-O-SIL[®] M-5 fumed silica with a surface area of 254 m²/g and a pore volume of 0.89 mL/g. The total Co weight loading in the catalyst is ~1.0 wt% (based on the starting materials used). The mixture was first aged at room temperature for 1 h, and dried in an oven at 100 °C for 2 h. The dried catalyst was ground into fine powders, and further calcined under a dry airflow of 20 sccm per gram of catalyst from room temperature to 400 °C at 1 °C/min ramping rate, and then kept at 400 °C for 1 h before cooling to room temperature.

4.2 SWCNT synthesis and purification

The catalyst was used to catalyze SWCNT growth in a continuous-flow tubular CVD reactor. It was reduced in H₂ at 540 °C before exposed to 6 bar CO at 780 °C. In another experiment, the catalyst was reduced in H₂ from room temperature to 780 °C, and further reduced for 30 min at 780 °C and then exposed to CO. The detailed SWCNT synthesis and purification of as-synthesized SWCNTs were described in Chapter 2.

4.3 SWCNT (n,m) analysis

Figure 4-1 (a–b) Raman spectra of SWCNTs under three excitation wavelengths for catalyst reduction at 540 and 780 °C respectively. The regions on the left between 100 and 350 cm⁻¹ correspond to RBM peaks, while the regions on the right correspond to D and G bands. (c–d) PL contour plots as a function of excitation and emission energies from SDBS-dispersed SWCNTs grown after catalyst reduction at 540 and 780 °C, respectively. Major chiral tubes identified in PL are marked with their (n,m) indexes.

4.3.1 Raman spectroscopy

The collected solid carbon products were first characterized by Raman spectroscopy at three excitation wavelengths (785, 633 and 514 nm) shown in Figure 4-1a and 4-1b. The

presence of the RBM peaks between 100 and 350 cm^{-1} and the low ratio of the D-to-G band intensities indicated that samples consist primarily of SWCNTs. The sample produced after reduction at 540 $^{\circ}\text{C}$ consists of fewer RBM peaks centered around 202–215 cm^{-1} compared with the sample produced after 780 $^{\circ}\text{C}$ reduction. The chiral indexes (n,m) of RBM peaks are assigned based on empirical and theoretical Kataura plots (Figures 4-2 to 4-5, Table 4-1). A combination of empirical and theoretical Kataura plots are used because for E_{11} and E_{22} van Hove transitions of semiconducting SWCNTs, the available empirical Kataura plots¹¹⁹ are more accurate, while no empirical Kataura plots are currently available for metallic SWCNTs and higher order transitions of semiconducting SWCNTs. According to the literature,¹¹⁹ RBM frequencies are related to SWCNT diameters using the formula $\omega_{\text{RBM}} = (223.5 \text{ cm}^{-1}/d_t) + 12.5 \text{ cm}^{-1}$ in this thesis. There is no obvious difference among the diameters of SWCNTs calculated by several relations ($\omega_{\text{RBM}} = A/d_t + B$) considering the state of SWCNTs reported in literatures.^{119,138,139}

Figure 4-2 Optical transition energies versus RBM frequencies for SWCNTs. RBM frequencies from peaks identified in Raman analysis of SWCNT samples (red dots) are plotted against theoretical and experimental transition energies. The three horizontal lines correspond to the laser excitation used for SWCNT characterization. The solid circles in navy color are E_{11} and E_{22} van Hove transitions of semiconducting SWCNTs from an empirical Kataura plot.¹¹⁹ The open and solid circles in black color are E_{11} transitions of metallic SWCNTs, E_{33} transitions of semiconducting SWCNTs, and other higher order transitions of SWCNTs from Kataura plots computed using a tight-binding model.¹¹⁸

Figure 4-3 Transition energies versus nanotube diameter and RBM frequency. Expanded view of the Kataura plots show in Figure 4-2 near to the laser energy at 514 nm. The dotted horizontal lines correspond to the upper and lower limits of the resonance window of approximate 100 meV. The vertical dashed lines around the experimental data points indicate $\pm 4 \text{ cm}^{-1}$ variability in measurement of RBM frequencies because of different environments or

instruments as suggested by previous researchers.¹⁰⁹

Five RBM peaks are identified under the 514 nm laser in the Raman analysis of SWCNT samples (Figure 4-1 and 4-3) at 193, 213, 246, 293, and 312 cm^{-1} respectively. The peak at 193 cm^{-1} may be contributed by two types of chiral nanotubes: (16,0) and (15,2), as they are both close to the resonance window. Similarly, the peak at 213 cm^{-1} is from (12,3), and the peak at 246 cm^{-1} is assigned to (11,2) and (12,0). There are no chiral nanotubes in the resonance windows of 293 and 312 cm^{-1} peaks, and they are assigned to the nearest (10,0) and (7,3). Figure 4-1a and 4-1b show that the peak at 213 cm^{-1} is much more intense compared to other three peaks. The diameter of (12,3) nanotube at 1.11 nm is similar to that of (9,8) nanotube at 1.17 nm, which would be one of the main chiral nanotubes in the SWCNT samples.

Figure 4-4 Transition energies versus nanotube diameter and RBM frequency. Expanded view of the Kataura plots shown in Figure 4-2 near to the laser energy at 633 nm.

Five RBM peaks are observed under the 633 nm laser (Figure 4-1 and 4-4) at 177, 197, 252, 262, and 282 cm^{-1} , respectively. As shown in Figure 4-4, 177 and 197 cm^{-1} peaks come from metallic nanotubes, which cannot be detected in PL spectroscopy. They are assigned to E_{11} transitions of (15,3), (9,9), (13,4), (14,2) and (15,0) metallic nanotubes based on Kataura plots computed using a tight-binding model. The other three peaks at 252, 262, and 282 cm^{-1} are from E_{22} transitions of semiconducting (10,3), (7,6) and (7,5) nanotubes, respectively. The peak at 197 cm^{-1} is much more intense compared to others, thus, (9,9), (13,4), (14,2) and (15,0) nanotubes would have higher abundance.

Figure 4-5 Transition energies versus nanotube diameter and RBM frequency. Expanded view of the Kataura plots shown in Figure 4-2 near to the laser energy at 785 nm.

There are five RBM peaks identified under the 785 nm laser (Figure 4-1 and Figure 4-5) at 183, 202, 215, 236, and 280 cm^{-1} , respectively. No chiral nanotubes are found in the resonance

windows of the peaks at 183 and 280 cm^{-1} . Thus, they are assigned to (16,0) and (11,0) respectively, which are the chiral structures closest to their resonance windows. On the other hand, several chiral nanotubes fall within the resonance windows of the peaks at 202, 215, and 236 cm^{-1} . The peak at 202 cm^{-1} can be attributed to (12,5), (13,3) and (9,8). The peak at 215 cm^{-1} is from (9,7). (11,3) and (12,1) contribute to the peak at 236 cm^{-1} . The major peaks are at 202 and 215 cm^{-1} , thus (12, 5), (13, 3), (9, 8) and (9, 7) would be among the main chiral nanotubes in the SWCNT samples.

Table 4-1 Summary of chirality assignment for RBM peaks identified in Raman analysis of SWCNT samples

Excitation Laser (nm)	RBM frequency (cm^{-1})	d_t (nm)	Chirality
514	193	1.24	(16,0), (15,2)
	213	1.11	(12,3)
	246	0.96	(12,0), (11,2)
	293	0.80	(10,0)
	312	0.75	(7,3)
633	177	1.36	(15,3)
	197	1.20	(9,9), (15,0), (14,2), (13,4)
	252	0.93	(10,3)
	262	0.90	(7,6)
785	282	0.83	(7,5)
	183	1.30	(16,0)
	202	1.18	(12,5), (13,3), (9,8)
	215	1.10	(9,7)
	236	1.00	(11,3), (12,1)
	280	0.84	(11,0)

*Major Raman peaks and their corresponding (*n,m*) tubes are highlighted in bold.

In summary, according to Raman analysis, the most intense RBM peaks belong to (12,3), (9,9), (15,0), (14,2), (13,4), (12,5), (13,3), (9,8) and (9,7) tubes, which are highlighted as red bars and hexagons ((9,8) and (9,7) are shown in blue) in Figure 4-6. This result suggests

diameter selectivity around 1.17 nm in SWCNT growth.

4.3.2 PL spectroscopy

Next, PL spectroscopy was employed to assign the (n,m) structure of semiconducting tubes. Figure 4-1c and 4-1d show PL contour plots collected from SDBS-dispersed SWCNTs as a function of excitation and emission. The relative abundance of semiconducting (n,m) tubes identified in Figure 4-1c and 4-1d is determined by their PL intensities. Results are listed on Table 4-2 and 4-3. Figure 4-1c and Table 4-2 show that the catalyst is highly selective to the single chiral (9,8) tube (51.7%) after 540 °C reduction. Several other (n,m) tubes (with relative abundance >3%) are also detectable in Figure 4-1c, *i.e.* (9,7), (10,6), (10,8), (8,7), (10,9) and (6,5). These main species are also highlighted as blue bars and hexagons ((6,5) is shown in purple) in Figure 4-6. Similar to previous studies,^{46,48,73} the existence of those species suggests a strong selectivity towards high chiral angle tubes in SWCNT growth. In contrast, the sample grown after 780 °C reduction comprises of numbers of (n,m) tubes centered around (6,5) (16.3%) and (9,8) (17.5%).

Table 4-2 PL intensities for (n,m) nanotubes identified in SWCNTs produced on CoSO₄/SiO₂ catalyst after catalyst reduction at 540 °C. The relative abundance is calculated based on the PL intensity of different (n,m) tubes.

(<i>n,m</i>) index	Diameter <i>d_t</i> (nm)	Chiral angle <i>θ</i> (°)	E ₁₁ (nm)	E ₂₂ (nm)	PL intensity (counts)	Relative abundance* (%)
(6,5)	0.76	27.00	983	570	209.4	3.6%
(7,3)	0.71	17.00	993	502	168.9	2.9%
(7,5)	0.83	24.50	1022	638	79.0	1.4%
(7,6)	0.90	27.46	1113	642	82.0	1.4%
(8,4)	0.84	19.11	1102	578	124.7	2.1%
(8,6)	0.97	25.28	1165	718	44.2	0.8%
(8,7)	1.03	27.80	1263	726	209.8	3.6%
(9,7)	1.10	25.87	1321	790	861.8	14.8%
(9,8)	1.17	28.05	1414	818	3007.6	51.7%
(10,6)	1.11	21.79	1384	754	447.7	7.7%
(10,8)	1.24	26.30	1467	870	188.7	3.2%
(10,9)	1.31	28.30	1559	886	395.2	6.8%

Major (*n,m*) tubes (with relative abundance > 3%), including (9,8), (9,7), (10,6), (8,7), (10,8), (10,9), and (6,5) are highlighted in bold.

Table 4-3 PL intensities for (*n,m*) nanotubes identified in SWCNTs produced on CoSO₄/SiO₂ catalyst after catalyst reduction at 780 °C for 30 min. The relative abundance is calculated based on the PL intensity of different (*n,m*) nanotubes.

(<i>n,m</i>) index	Diameter <i>d_t</i> (nm)	Chiral angle <i>θ</i> (°)	E ₁₁ (nm)	E ₂₂ (nm)	PL intensity (counts)	Relative abundance* (%)
(6,5)	0.76	27.00	983	570	2754.9	16.3%
(7,3)	0.71	17.00	991	514	1144.8	6.7%
(7,5)	0.83	24.50	1022	638	788.9	4.7%
(7,6)	0.90	27.46	1114	642	1537.8	9.1%
(8,4)	0.84	19.11	1110	574	1330.3	7.8%
(8,6)	0.97	25.28	1166	710	620.3	3.7%
(8,7)	1.03	27.80	1263	726	1663.0	9.8%
(9,7)	1.10	25.87	1321	790	1596.0	9.4%
(9,8)	1.17	28.05	1415	822	2972.5	17.5%
(10,6)	1.11	21.79	1380	754	1045.5	6.2%
(10,8)	1.24	26.30	1470	870	624.2	3.7%
(10,9)	1.31	28.30	1559	890	872.3	5.1%

*Relative abundance (*RA* (*n,m*)) in Table 4-2 and 4-3 was calculated using the equation (1):

$$RA(n, m) = \frac{I(n,m)_{PL}^{exp}}{\sum I(n,m)_{PL}^{exp}} \times 100\% \quad (1)$$

Figure 4-6 (a) Relative abundance (based on RA (n,m) (%)) (semi+met) listed in Table 4-4 and 4-6) of (n,m) SWCNTs produced from the $\text{CoSO}_4/\text{SiO}_2$ catalyst after catalyst reduction at 540 °C. They are main (n,m) species identified by the three characterization techniques. Blue: PL; red Raman; and yellow: absorption. (b) Two-dimensional projected chirality map of SWCNTs. Most of (n,m) species produced in the work are at larger diameter around 1.17 nm, as compared to previous chiral selectivity synthesis studies usually around 0.76 nm.

4.3.3 UV-vis-NIR absorbance spectroscopy

To further evaluate the abundance of metallic tubes which cannot be observed in PL analysis, UV-vis-NIR absorbance spectrum of the sample produced after catalyst reduction at

540 °C is shown in Figure 4-7. The label E_{11}^S (shaded yellow) indicates the absorption bands of the first one-dimensional van Hove singularities from semiconducting SWCNTs; the E_{11}^M and E_{22}^S (shaded purple) correspond to the overlapping absorption bands of the first van Hove singularities from metallic SWCNTs and the second van Hove singularities from semiconducting SWCNTs. Intense absorption peaks at 1416 and 816 nm correspond to the first and second one-dimensional van Hove singularity transitions of (9,8) tubes. Additional absorption peaks below 700 nm may be assigned to either the E_{11}^M transition of metallic tubes or E_{22}^S transition of semiconducting tubes.

A modified method was used based on the electron-phonon interaction model to reconstruct the UV–vis–NIR absorbance spectrum (see Table 4-4 to 4-6).^{122,125} A baseline based on the power law (that is $A\lambda^{-b}$) curve was subtracted from the experimental spectrum as shown in Figure 4-7a. The NIR portion of absorption spectra belonging to the E_{11}^S transition of semiconducting SWCNTs between 935 and 1590 nm was reconstructed firstly. The equation (2) was used to calculate the overall contribution of all (n,m) SWCNTs to the expected optical density (OD) at a specific optical energy E , where C is the normalization factor introduced to account for sampling conditions and the collection geometries. The relative contribution ($A(n,m)$) of individual (n,m) tubes to the OD was calculated using the equation (3). $I(n,m)_{PL}^{exp}$ is the experimental PL intensity of individual (n,m) tubes extracted from Figure 4-1c and Table 4-2. $I(n,m)_{PL}^{cal}$ and $W_{cal}^{abs}(n,m)$ are the calculated corresponding PL and absorption intensity based on an electron-phonon interaction model.¹²² γ_e is the width of optical transitions, and it is related to the lifetime of excited states, and γ_e is approximated by the equation (4) with C_1 and C_2 as adjustable parameters. $E(n,m)$ values were obtained from

PL measurement in Table 4-2 or from theoretical Kataura plots.

$$OD(E) = C \sum_{n,m} A(n, m) \frac{\gamma_e}{4(E - E(n, m))^2 + \gamma_e^2} \quad (2)$$

$$A(n, m) = \frac{I(n, m)_{PL}^{exp}}{I(n, m)_{PL}^{cal}} W_{cal}^{abs}(n, m) \quad (3)$$

$$\gamma_e = C_1 + C_2/W_{cal}^{abs} \quad (4)$$

Following an analysis routine used in our previous publication,¹²⁴ the contribution from (n, m) tubes identified in PL analysis was considered firstly. Their contribution ($A(n, m)$) to OD was directly calculated using experimental PL intensity from Table 4-2. However, (n, m) tubes identified in PL analysis alone cannot reconstruct the absorption spectra well. Thus, additional semiconducting tubes identified in Raman analysis from Table 4-1, as well as other tubes with similar diameters, were added. The fitting result was significantly improved, as presented in Figure 4-7b. The thin Lorentzian peaks (black) in Figure 4-7b are from the contribution of individual semiconducting tubes, calculated by using the electron-phonon interaction model. Tubes with major contributions are marked with their (n, m) indexes. The thick solid line depicts the sum of all Lorentzian lines, and red circles are experimental data points. All data used in the reconstruction of E_{11}^S transition of semiconducting SWCNTs are listed in Table 4-4. The relative abundance of individual semiconducting (n, m) tubes was recalculated by the equation (5) using the reconstructed absorption E_{11}^S peak area from each (n, m) tube, and results are also listed in Table 4-4.

$$RA(n, m) = \frac{Area(n, m)_{Abs}^{Fitted}}{\sum Area(n, m)_{Abs}^{Fitted}} \times 100\% \quad (5)$$

Table 4-4 Parameters used to reconstruct E_{11}^S absorption spectra of semiconducting SWCNTs.

The relative abundance (semi) is calculated based on the reconstructed absorbance E_{11}^S peak area of each semiconducting (n, m) tube only. The relative abundance (semi+met) is calculated

based on the reconstructed absorbance E_{11}^S peak area of each (n,m) tube, including both semiconducting and metallic SWCNTs.

(n,m) index	Diameter d_t (nm)	$E(n,m)$ (nm)	I_{PL}^{exp}	I_{PL}^{cal}	W_{abs}^{cal}	$A(n,m)$	$Area(n,m)_{Abs}^{Fitted}$	RA (n,m) (%) (semi)	RA (n,m) (%) (semi+met)
(n,m) tubes identified in PL ($C_1 = 25, C_2 = 1$)									
(7,3)	0.706	992	168.9	0.61	1.65	456.86	0.309	0.508	0.417
(6,5)	0.757	975	209.4	0.67	1.85	578.19	0.370	0.609	0.499
(7,5)	0.829	1018	79.0	0.71	2.04	226.99	0.159	0.261	0.214
(8,4)	0.84	1110	124.7	0.46	1.77	479.82	0.349	0.574	0.471
(7,6)	0.895	1120	82.0	0.47	1.98	345.45	0.253	0.416	0.341
(8,6)	0.966	1176	44.2	0.49	2.18	196.64	0.145	0.238	0.196
(8,7)	1.032	1262	209.8	0.3	2.06	1440.63	1.067	1.755	1.439
(9,7)	1.103	1320	861.8	0.27	2.22	7085.91	5.254	8.641	7.085
(10,6)	1.111	1370	447.7	0.21	2.03	4327.77	3.496	5.749	4.714
(9,8)	1.17	1416	3007.6	0.19	2.14	33875.07	24.855	40.881	33.516
(10,8)	1.24	1467	188.7	0.18	2.16	2264.40	1.633	2.687	2.202
(10,9)	1.307	1555	395.2	0.14	2.22	6266.74	2.917	4.798	3.933
(n,m) tubes identified in Raman ($C_1 = 25, C_2 = 1$)									
(10,0)	0.794	1156				1445.27	0.793	1.304	1.069
(11,0)	0.873	1037				1953.44	1.756	2.888	2.368
(10,3)	0.936	1247				937.10	0.579	0.952	0.781
(12,1)	0.995	1330				937.47	0.786	1.292	1.060
(11,3)	1.014	1197				601.84	0.527	0.867	0.711
Other possible (n,m) tubes ($C_1 = 25, C_2 = 1$)									
(8,3)	0.782	950				937.10	0.563	0.926	0.759
(10,2)	0.884	1053				1275.88	1.145	1.883	1.544
(11,1)	0.916	1265				40.69	0.000	0.000	0.000
(9,4)	0.916	1102				598.32	0.466	0.766	0.628
(9,5)	0.976	1244				3.66	0.000	0.000	0.000
(13,0)	1.032	1395				349.25	0.223	0.367	0.301
(12,2)	1.041	1377				4.88	0.003	0.005	0.004
(10,5)	1.050	1256				3.49	0.000	0.000	0.000
(14,0)	1.111	1295				261.47	0.248	0.409	0.334
(13,2)	1.12	1307				500.24	0.437	0.719	0.589
(12,4)	1.145	1458				4240.89	3.692	6.073	4.979
(14,1)	1.153	1502				1268.02	0.881	1.449	1.188
(13,3)	1.17	1498				1980.51	1.299	2.136	1.752
(12,5)	1.201	1499				1421.39	1.002	1.648	1.351
(15,1)	1.232	1426				3880.16	2.786	4.583	3.757
(14,3)	1.248	1447				5554.95	2.806	4.615	3.784

Semiconducting (n,m) tubes with relative abundance more than 3% are marked in bold,

including (9,7), (10,6), (9,8), (10,9), (12,4), (15,1) and (14,3).

Next step is to reconstruct the absorbance spectra belonging to the E_{22}^S transition of semiconducting SWCNTs and E_{11}^M transition of metallic SWCNTs between 500 and 935 nm. There are two issues related to the reconstruction. First, the theoretical absorption intensity $W_{cal}^{abs}(n,m)$ for E_{22}^S transition is currently unavailable. Second, the E_{11}^M transition of metallic SWCNTs overlaps with the E_{22}^S transition of semiconducting SWCNTs in the same spectra range. In order to obtain an estimation of abundance for all (n,m) tubes in the SWCNT sample, the following protocol was proposed to address these two issues. First, from the study of Popov *et al.*,¹⁴⁰ the absorption matrix element patterns for the E_{11}^S and E_{22}^S transitions are similar, thus the theoretical absorption intensity $W_{cal}^{abs}(n,m)$ of E_{11}^S was directly used to approximate the theoretical absorption intensity of E_{22}^S . Second, a two-step reconstruction procedure was used to separate the contribution of semiconducting SWCNTs from metallic SWCNTs.

Firstly, assuming that the relative contribution to OD among each semiconducting (n,m) tubes was similar in both E_{11}^S and E_{22}^S transitions, thus the $A(n,m)$ values from E_{11}^S transitions in Table 4-4 were used to reconstruct major E_{22}^S peaks. As shown in Figure 4-7c, the reconstructed spectrum matches well with the experimental data, especially for larger diameter tubes with E_{22}^S absorption above 800 nm. There is some overestimation for smaller diameter tubes between 700 and 800 nm, suggesting the abundance of small diameter tubes could be less than what predicts by PL analysis. The relative abundance of individual semiconducting (n,m) tubes was calculated again by the equation (5) using their reconstructed absorption E_{22}^S peak area, and results are listed in Table 4-5.

Table 4-5 Parameters used to reconstruct E_{22}^S absorption spectra of semiconducting SWCNTs.

The relative abundance (semi) is calculated based on the reconstructed absorbance E_{22}^S peak area of each semiconducting (n,m) tube. For all semiconducting SWCNTs E_{22}^S reconstruction, $C_1 = 22$ and $C_2 = 120$.

(n,m) index	Diameter d_t (nm)	$E(n,m)$ (nm)	W_{abs}^{cal}	$A(n,m)$	Area	RA (n,m) (%) (semi)
(7,3)	0.706	505	1.65	456.86	0.082	0.336
(6,5)	0.757	565	1.85	578.19	0.162	0.663
(7,5)	0.829	645	2.04	226.99	0.068	0.278
(8,4)	0.84	594	1.77	479.82	0.139	0.569
(7,6)	0.895	648	1.98	345.45	0.104	0.426
(8,6)	0.966	718	2.18	196.64	0.059	0.241
(8,7)	1.032	728	2.06	1440.63	0.436	1.784
(9,7)	1.103	799	2.22	7085.91	2.126	8.700
(10,6)	1.111	754	2.03	4327.77	1.434	5.868
(9,8)	1.17	816	2.14	33875.07	10.094	41.305
(10,8)	1.24	865	2.16	2264.40	0.646	2.643
(10,9)	1.307	878	2.22	6266.74	1.101	4.505
(8,3)	0.782	665	2.43	937.10	0.319	1.305
(10,0)	0.794	537	1.59	1445.27	0.28	1.146
(11,0)	0.873	745	2.69	1953.44	0.744	3.044
(10,2)	0.884	740	2.67	1275.88	0.481	1.968
(11,1)	0.916	610	1.73	40.69	0	0.000
(9,4)	0.916	722	2.27	598.32	0.193	0.790
(10,3)	0.936	632	1.80	937.10	0.233	0.953
(9,5)	0.976	672	1.88	3.66	0	0.000
(12,1)	0.995	799	2.42	937.47	0.318	1.301
(11,3)	1.014	793	2.53	601.84	0.214	0.876
(13,0)	1.032	677	1.86	349.25	0.092	0.376
(12,2)	1.041	686	1.87	4.88	0.001	0.004
(10,5)	1.050	788	2.33	3.49	0	0.000
(14,0)	1.111	859	2.74	261.47	0.097	0.397
(13,2)	1.12	858	2.52	500.24	0.17	0.696
(12,4)	1.145	855	2.57	4240.89	1.476	6.040
(14,1)	1.153	753	2.10	1268.02	0.377	1.543
(13,3)	1.17	764	1.98	1980.51	0.554	2.267
(12,5)	1.201	793	2.13	1421.39	0.425	1.739
(15,1)	1.232	920	2.10	3880.16	0.828	3.388
(14,3)	1.248	920	2.10	5554.95	1.185	4.849

Comparing the relative abundance of individual semiconducting tubes obtained from E_{11}^S and E_{22}^S reconstruction, no significant differences are observed. This supports the approach of using $A(n,m)$ values from E_{11}^S transitions to reconstruct major E_{22}^S peaks first.

Secondly, the contribution of semiconducting tubes (the spectrum reconstructed by semiconducting SWCNTs only) was subtracted from the overall $E_{11}^M + E_{22}^S$ absorbance spectrum. Then, the remaining peaks of the absorbance spectrum (mostly between 500 and 800 nm) were reconstructed with possible metallic tubes. The metallic tubes are either identified in Raman analysis or tubes with similar diameters of major semiconducting tubes. All metallic tubes identified are listed in Table 4-6. The $E(n,m)$ values of metallic tubes were obtained from the study by Maultzsch *et al.*¹⁴¹ Their theoretical absorption intensity $W_{cal}^{abs}(n,m)$ is currently not available. The average value (2.155) of all semiconducting tubes identified in this study was used as an approximation for all metallic tubes. Similar to the reconstruction of E_{11}^S spectrum, the relative contribution ($A(n,m)$) of individual metallic tubes to the OD was then calculated using the equation (2). The reconstructed spectrum is shown in Figure 4-7c. The reconstructed E_{11}^M absorbance peak area of each metallic (n,m) tube is listed in Table 4-6.

Finally, the relative abundance of both semiconducting and metallic tubes together was calculated using their respective E_{11}^S and E_{11}^M peak areas. The results are listed in Table 4-4 and 4-6. Those main species (with relative abundance more than 3%) are also highlighted as yellow bars and hexagons in Figure 4-6 ((9,7), (10,6), (9,8), (10,9) are shown in blue).

Table 4-6 Parameters used to reconstruct E_{11}^M absorption spectra of metallic SWCNTs. The relative abundance (semi+met) is calculated based on the reconstructed absorbance E_{11}^S peak area of each semiconducting (n,m) tube and E_{11}^M peak area of each metallic (n,m) tube. For all metallic SWCNTs E_{11}^M reconstruction, fitting factors $C_1 = 8.2$ and $C_2 = 160$.

(n,m) index	Diameter d_t (nm)	$E(n,m)$ (nm)	W_{abs}^{cal}	A (n,m)	Area	RA (n,m) (%) (semi+met)
(10,1)	0.825	527.7	2.155	762.26	0.9303	1.254
(12,0)	0.940	568.8	2.155	245.62	0.32161	0.434
(11,2)	0.950	558.6	2.155	680.95	0.88426	1.192
(10,4)	0.978	553.6	2.155	594.22	0.76762	1.035
(9,6)	1.024	551.1	2.155	1928.00	2.48327	3.349
(13,1)	1.060	602.8	2.155	337.76	0.44907	0.606
(12,3)	1.077	599.0	2.155	601.34	0.79858	1.077
(8,8)	1.085	556.1	2.155	941.81	1.21995	1.645
(11,5)	1.111	596.2	2.155	245.62	0.32588	0.439
(10,7)	1.159	599.9	2.155	372.66	0.49503	0.668
(15,0)	1.175	649.9	2.155	1317.86	1.76728	2.383
(14,2)	1.183	641.2	2.155	37.27	0.04992	0.067
(13,4)	1.206	639.2	2.155	37.27	0.04991	0.067
(9,9)	1.221	613.9	2.155	37.27	0.04969	0.067
(12,6)	1.244	642.5	2.155	40.65	0.05447	0.073
(11,8)	1.294	646.8	2.155	308.29	0.41328	0.557
(10,10)	1.357	659.6	2.155	1712.88	2.29919	3.100

Metallic (n,m) tubes with relative abundance more than 3% are marked in bold, including (9,6) and (10,10).

Other than (n,m) tubes identified in Raman and PL, Figure 4-7b and 4-7c show a few additional peaks identified in absorption spectra, including semiconducting (12,4), (14,3) and (15,1) and metallic (9,6) and (10,10). Using the contribution from each (n,m) tubes obtained in reconstructing the absorbance spectrum, their relative abundance of (n,m) tubes is shown in Figure 4-7d. It indicates that the dominant semiconducting tubes identified in PL have much higher abundance as compared to additional metallic tubes identified in absorption

spectroscopy. Overall, the abundance of (9,8) tubes is 33.5%, followed by (9,7) at 7.1%. This further corroborates that the $\text{CoSO}_4/\text{SiO}_2$ catalyst is highly selective towards the (9,8) tube.

Figure 4-7 (a) UV-vis-NIR absorption spectra of SDBS-dispersed SWCNTs grown after catalyst reduction at 540 °C before and after baseline subtraction. (b) E_{11}^S spectral reconstruction by the summation of the contribution from each (n,m) semiconducting SWCNT (Lorentzian peaks in black). (c) E_{11}^M and E_{22}^S spectral reconstruction by the summation of the contribution from both semiconducting (black) and metallic (blue) SWCNTs. The (n,m) indexes, thick solid line and red circles represent the same as in (b). (d) Relative abundance of both semiconducting (black) and metallic (blue) (n,m) SWCNTs obtained from the

reconstruction of absorption spectra.

4.4 Carbon yield

Figure 4-8 TGA and DTG profiles of carbon deposits synthesized on the $\text{CoSO}_4/\text{SiO}_2$ catalyst.

(a) Catalyst reduction at 540 °C, and then SWCNT growth at 780 °C, (b) reduction at 780 °C for 30 min, and then SWCNT growth. The samples were oxidized in air. The total carbon yield is calculated from the weight loss between 200 and 1000 °C.

The carbon yield is an important criterion for evaluating catalysts used in SWCNT growth. It is necessary to achieve not only good chiral selectivity but also adequate nanotube yield so

that scalable production process can be further developed. TGA was used to determine the yield of carbon species. Figure 4-8 shows the TG and DTG profiles of carbon deposits on catalysts after two reduction conditions. The total carbon yields (the weight loss between 200 and 1000 °C) are 3.8 and 3.5 wt% for the 540 °C and 780 °C reduction, respectively. The Co loading on the SiO₂ substrate is ~1 wt%, thus the CoSO₄/SiO₂ catalyst has the carbon/metal ratio of 3.8. Based on the Raman spectroscopy results shown in Figure 4-1a, the dominant DTG peak at 560 °C on Figure 4-8a can be attributed to the oxidation of SWCNTs, which counts for more than 90% of the total carbon deposits based on the integrated peak areas. There are multiple DTG peaks of different carbon species in Figure 4-8b. The peak around 300 °C can be credited to the oxidation of amorphous carbon. The peak at 520 °C is contributed by SWCNTs. The peak above 800 °C may come from the oxidation of graphite layers covering large Co particles.

The result in this work was compared with a number of previous SWCNT chiral selectivity growth studies, as listed in Table 4-7. Especially, compared to the Co-TUD-1 catalyst, which has similar chiral selectivity towards (9, 8) tubes, the carbon yield of the CoSO₄/SiO₂ catalyst is more than twice that of the Co-TUD-1 catalyst (1.5 wt%). Moreover, it would take 3 days to synthesize the Co-TUD-1 catalyst through aging, drying and hydrothermal treatments, while the CoSO₄/SiO₂ catalyst can be produced by impregnation within 12 h. Overall, the CoSO₄/SiO₂ catalyst shows several advantages: first, it provides a unique single chiral selectivity toward a large diameter tube; second, this catalyst has an adequate SWCNT yield, which is important for scalable production of SWCNTs; and third, it is easy to synthesize, as compared to many mesoporous catalysts.

Table 4-7 Comparison of (*n,m*) selectivity and carbon yield among several reported chiral selective growth studies.

Catalysts	Dominant (<i>n,m</i>) species	Reported chiral selectivity (characterization methods used)	Carbon yields (over the total catalyst weight including catalyst substrates)
Co-MCM-41 ^{54,133}	(7,5)	45% (PL)	4 wt%
Co-Mo CAT ⁴⁶	(6,5), (7,5)	two together 62% (PL)	didn't report
Fe/Co-zeolite ⁴⁷	(6,5), (7,5)	no quantitative data	didn't report
Fe-Ni ⁵³	(8,4)	no quantitative data	didn't report
Fe-Ru ⁴⁸	(6,5)	similar to Co-Mo CAT	didn't report
Au catalysts ⁶⁴	(6,5)	no quantitative data	didn't report
Fe-Cu ⁴⁹	(6,5)	no quantitative data	didn't report
Co/Pt ⁵⁰	(6,5)	30% (PL)	didn't report
Co-Mn-MCM41 ⁵⁸	(6,5)	47.4% (PL)	11 wt%
Co-Cr-MCM-41 ⁵⁷	(6,5)	30.9% (PL)	6.3 wt%
Ferrocene+NH ₃ ⁹⁷	(13,12),(12,11),(13,11)	30%	didn't report
Co-TUD-1 ¹⁴²	(9,8)	59.1% (PL)	1.5 wt%
This work	(9,8)	51.7% (PL)	3.8 wt%

4.5 Morphology

To better understand the CoSO₄/SiO₂ catalyst, its morphology was first characterized by SEM and TEM. Figure 4-9a shows that fresh catalyst is comprised of small SiO₂ particles. Figure 4-9e indicates that the size of SiO₂ particles is around 20 nm. They aggregate together to form a porous composite. After catalyst reduction at 540 °C and SWCNT growth, the catalyst shows no noticeable morphological changes (see Figure 4-9b and 4-9c). This is because the fumed SiO₂ particles are produced by the flame hydrolysis of chlorosilanes at high temperature, and they are usually stable after high-temperature treatments. Figure 4-9c shows a

large amount of SWCNTs on the surface of aggregated SiO₂ particles. Figure 4-9f and 4-9g indicates that SWCNTs grow from Co particles on/in SiO₂ particles and aggregate together into small bundles of 10–20 nm in diameter. The diameter of produced SWCNTs was also analyzed by TEM. As shown in Figure 4-9h, the diameter of 45% tubes among ~100 measured ones is between 1.15 and 1.20 nm, which agrees with the above spectroscopic results. Very few Co particles can be easily observed in TEM analysis of the catalysts after reduced at 540 °C or after SWCNT growth, because Co particles could be embedded under or near the surface of SiO₂ particles. This also suggests that Co species are well dispersed on SiO₂ particles. After SWCNT growth, SiO₂ particles can be easily dissolved by refluxing in NaOH aqueous solution. Figure 4-9d shows dense SWCNT networks on filter paper after SiO₂ removal.

Figure 4-9 SEM (a–d) and TEM (e–g) images of catalysts and SWCNTs. (a) fresh catalyst; (b) catalyst after reduction in H₂ at 540 °C, and then cooled to room temperature under He; (c) as-synthesized SWCNTs on catalyst; (d) SWCNT films after SiO₂ removal; (e) the same sample as (b); (f) and (g) as-synthesized SWCNTs on catalyst; (h) the diameter distribution of nanotubes obtained by measuring ~100 nanotubes in TEM images. The scale bars in (a–c) are

at 1 μm , and is 100 nm in (d).

4.6 Physicochemical properties of $\text{CoSO}_4/\text{SiO}_2$ catalyst

Figure 4-10 Physicochemical properties of the $\text{CoSO}_4/\text{SiO}_2$ catalyst. (a) XRD pattern of the calcined $\text{CoSO}_4/\text{SiO}_2$ catalyst. (b) Nitrogen physisorption isotherms and pore size distribution (insert) of the catalyst. (c) UV-vis reflectance spectra of the catalyst and several references (Co_3O_4 , CoSO_4 powders and fumed SiO_2). (d) H_2 -TPR profiles of the catalyst and several Co references (Co_3O_4 , CoO and CoSO_4).

Physicochemical properties of the $\text{CoSO}_4/\text{SiO}_2$ catalyst were further characterized by XRD, nitrogen physisorption, UV-vis spectroscopy and H_2 -TPR. Figure 4-10a shows a broad diffraction peak near $2\theta = 21^\circ$ originated from SiO_2 supports, suggesting the absence of Co

oxides (CoO_x) or bulk Co silicates. Figure 4-10b shows the catalyst is a porous material with pore size around 32 nm. The pores are likely the gaps among SiO_2 particles in the catalyst aggregate. It has a surface area of 208 m^2/g , and a large pore volume of 1.54 mL/g . UV-vis spectra in Figure 4-10c designate the local environment of Co species on SiO_2 . Similar to the pure CoSO_4 , the catalyst shows a broad peak ascribed to the ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ transition of octahedral Co^{2+} ions.¹³² In contrast to Co_3O_4 , the catalyst doesn't have absorption peaks at 410 and 710 nm. This is also different from the UV-vis spectrum of the Co-TUD-1 catalyst, which displays a minor peak shoulder at 660 nm and two broad peaks at 410 and 710 nm, pointing to the existence of tetrahedral Co^{2+} and octahedral Co^{3+} ions.^{132,142} The H_2 -TPR profile of the catalyst in Figure 4-10d shows a sharp reduction peak centered at 470 °C. This is significantly different from common CoO_x catalysts, which are usually reduced below 400 °C, as sketched by the two CoO_x references (CoO and Co_3O_4). In comparison, pure CoSO_4 powder is reduced at 584 °C, suggesting the reduction peak at 470 °C is credited to the reductive decomposition of highly dispersed CoSO_4 . These results show the $\text{CoSO}_4/\text{SiO}_2$ catalyst has unique physicochemical properties, as compared with other Co catalysts,^{46,56} with a very narrow Co reduction window.

4.7 Correlation between (9,8) SWCNT and Co cluster size

4.7.1 XAS spectra analysis

The narrow reduction window suggests that Co particles with a narrow size distribution may have been formed. Previous experimental and theoretical studies predict a linear correlation between catalyst particle size and SWCNT diameter¹⁴³⁻¹⁴⁶ with their ratio ranging

from 1.1 to 1.6.¹⁴⁷ The (9,8) tubes at 1.17 nm produced after catalyst reduction at 540 °C suggest catalytic particles have a narrow diameter distribution around 1.29–1.87 nm.¹⁴⁷ To verify this hypothesis, catalysts were investigated using XAS. XAS was used here, because most of small Co particles are under the surface of SiO₂ particles, and it is difficult to quantify their diameters by TEM. The XANES at the Co K-edge in Figure 4-11a shows that Co atoms in the fresh catalyst are oxidized with a strong white line peak. After H₂ reduction and SWCNT growth, the white line is reduced together with the appearance of a strong pre-edge peak, showing the formation of metal Co particles. The EXAFS of catalysts was Fourier transformed to *r*-space to separate the contribution from different coordination shells of Co atoms. Figure 4-11b shows that the fresh catalyst has a strong Co–O peak, while the reduced catalyst after SWCNT growth has an intense Co–Co peak. The spectrum in the *r*-space was fitted using paths of metallic Co generated by the FEFF 9 program¹¹⁵ to obtain the first shell coordination number (N_{Co-Co}), listed in Table 4-8. The catalyst reduced at 540 °C after SWCNT growth has a N_{Co-Co} of 7.04. The difference in bond distances with respect to the theoretical references (dR) is -0.016. The Debye–Waller factor ($\Delta\sigma^2$) is 0.007, indicating that the fit is within acceptable limits. The first shell coordination number of nanoparticles is a nonlinear function of particle size, which has been used to quantify the nanoparticle size. Using a (111)-truncated hemispherical cubic octahedron model,¹⁴⁸ Figure 4-11c shows the average size of Co particles produced after catalyst reduction at 540 °C is 1.23 nm, which matches with the diameter of (9, 8) tubes.

Table 4-8 Structure parameters of the first Co–Co coordination shell in catalyst determined from the EXAFS data (Figure 4-11b) at Co K-edge by fitting using FEFF 9.

Catalyst	Co-Co first shell fitting results		
	$N_{\text{Co-Co}}$	$dR(\text{\AA})$	$\Delta\sigma^2$
540 °C	7.04 ± 0.86	-0.016 ± 0.007	0.007

Figure 4-11 XAS spectra of the CoSO₄/SiO₂ catalysts and model of Co clusters. (a) Near-edge spectra at the Co K-edge ($E_0 = 7709$ eV) of fresh catalyst, catalyst after reduction at 540 °C and SWCNT growth, and Co foil. (b) Fourier transform of EXAFS spectra at the Co K-edge for samples in (a). (c) The average diameter of Co metal clusters in catalysts determined by the first shell coordination number from XAS spectra. (d) The optimized structures of Co_n ($n=13$, 55, and 147) clusters from theoretical simulation and their likely matching carbon caps.

4.7.2 Spin-polarized density functional study

An intriguing question is why the selectivity of the $\text{CoSO}_4/\text{SiO}_2$ catalyst is towards (9, 8) tubes rather than some other chiral species? I emphasized the tentative nature of the following explanation on the chiral selectivity towards (9, 8) tubes in the spirit of stimulating further exploration in understanding the chiral selection mechanism in SWCNT growth. Previous theoretical studies on the structure stability of Ni_{2-55} ¹⁴⁹ and the electric dipole polarizability experimental study of Ni_{12-58} ¹⁵⁰ and Pt_n ($n=13, 38$ and 55)¹⁵¹ showed that some nanoparticles with optimized structures are more stable than others. Using the method of previous studies,^{152,153} the structures of a series of Co_n ($n = 2, 3, 5, 13, 55$, and 147) particles were investigated. Co particles with icosahedral structures are lower in energy than other structures. Co_{13} , Co_{55} , and Co_{147} adopt the icosahedral geometry. Co_{13} has one atom at the center of its structure and the other 12 identical atoms on the spherical shell surface with a coordination number of 6. From the Co_{13} icosahedral structure, the Co_{55} was built by adding 30 atoms on the edge atoms of Co_{13} with a coordination of 8, and additional 12 atoms on the vertex atoms of Co_{13} with a coordination number of 6. Using the same methodology, Co_{147} was built by adding 80 atoms on the edge atoms of Co_{55} with a coordination of 8, and additional 12 atoms on the vertex atoms of Co_{55} with a coordination number of 6. Their diameters successively increase from ~ 0.46 to ~ 0.93 and 1.22 nm, respectively. The geometrical structure of these three clusters is illustrated in Figure 4-11d. Co_2 , Co_3 , Co_5 clusters, and Co-bulk have also been calculated as references. The detailed calculated results, including the average binding energy E_b , bond lengths from the central Co atom $R_{\text{Co-Cen}}$, and surface bond lengths $R_{\text{Co-Co}}$, are listed in Table 4-9.

Table 4-9 Calculated results of the average binding energy E_b (eV), bond lengths from the central Co atom $R_{\text{Co-Cen}}$ (Å), and surface bond lengths $R_{\text{Co-Co}}$ (in Å) for pure Co_n clusters (with $n=2, 3, 5, 13, 55$, and 147), respectively.

	Co_2	Co_3	Co_5	Co_{13}	Co_{55}	Co_{147}	Co-bulk
E_b	1.88	2.24	2.99	3.67	4.54	4.81	5.57
$R_{\text{Co-Cen}}$		1.38	3.06	2.31	2.38, 4.03, 4.71	6.08, 6.21, 7.09	
$R_{\text{Co-Co}}$	1.97	2.08, 2.42	2.19, 2.65	2.43	2.48, 2.49	2.47, 2.51	2.51

As sketched in Figure 4-11d, the stable Co_{13} and Co_{55} particles are comparable with carbon caps (cap 20 and cap (6,5)) at diameter of 6.2 and 8.3 Å, respectively. Very small SWCNTs extended from the “cap 20” are unstable. Thus, they are seldom found in SWCNT products. The (6,5) tube matching with the Co_{55} is the most common species found in a number of (n,m) selective synthesis studies.^{46,48,49,56,73} By adding one complete atomic layer of Co atoms on the surface of Co_{55} , the Co_{147} particle is more stable than other clusters in its diameter range. The cap (9,8) with diameter of 11.55 Å fits well with the Co_{147} . There is a clear match between the most abundant (n,m) species (*i.e.* (6,5) and (9,8)) and the stable Co particles (*i.e.* Co_{55} and Co_{147}). The shift of (n,m) selectivity from the small diameter (6,5) tube to the larger diameter (9,8) tube found in this study could be credited to the jump in the diameter of Co particles with optimized structures. Although many previous chirality selective growth studies managed to tune (n,m) selectivity to some extent,^{47,63,67,68,75,124} none can achieve continuous changes of (n,m) selectivity over a wider diameter range. This suggests that matching with stable catalytic particles may be a fundamental requirement governing the growth of SWCNTs. It highlights that the efforts in achieving chiral-selective synthesis of SWCNTs should focus on growing

chiral tubes with diameters similar to the most stable particles in their size range under growth conditions, other than seeking selectivity to random chiral structures. It should also be noted that adsorption and diffusion of carbon species or the formation of carbide during SWCNT growth can cause the reconstruction of catalytic particles,¹⁵⁴⁻¹⁵⁶ which may also change the (n,m) selectivity to some extent. This may explain why tubes, such as (9,7), (10,6) and (10,9) near the main (9,8), are also produced. Moreover, the chiral angle dependent growth rate^{108,109} could also be the reason of growing the large chiral angle (9,8) tubes, rather than other (n,m) species at the same diameter with smaller chiral angles.

4.8 The role of sulfur

From the catalyst design perspective, a key task is to find out what components in the $\text{CoSO}_4/\text{SiO}_2$ catalyst are responsible for stabilizing Co particles which lead to the growth (9,8) tubes. Cobalt oxides (CoO_x) are usually reduced below 400 °C leading to large Co particles, which are easily covered by graphite layers during SWCNT synthesis. On the other hand, Co incorporated in some mesoporous SiO_2 templates, such as MCM-41, or in Co silicates, is reduced at temperature above 700 °C.^{60,157} They would form smaller Co particles, which are selective to smaller diameter tubes, such as (6,5) and (7,5). In the previous study of Co–TUD-1 catalyst,¹⁴² it was proposed that Co species on the mesoporous TUD-1 can nucleate in two steps. First, Co^{2+} ions are partially reduced in H_2 during prereduction, but they are still dispersed in an isolated manner on the large surface of TUD-1. Second, Co atoms aggregate quickly into clusters under CO to initiate SWCNT growth. Co ions are incorporated into the amorphous silica walls of TUD-1, and the large surface area of TUD-1 and the strong metal-support interaction are sufficient in stabilizing these clusters with a narrow diameter

distribution at around 1.2 nm, responsible for the growth of (9,8) nanotubes. However, the structure of the $\text{CoSO}_4/\text{SiO}_2$ catalyst is very different from the Co–TUD-1: first, Co ions cannot be incorporated into solid SiO_2 particles by the impregnation method; second, the surface area of the $\text{CoSO}_4/\text{SiO}_2$ catalyst is much smaller ($208 \text{ m}^2/\text{g}$) as compared to TUD-1 ($740 \text{ m}^2/\text{g}$). Thus, the way the $\text{CoSO}_4/\text{SiO}_2$ catalyst controls the formation of Co particles is expected to be different from that of the Co–TUD-1. Different Co precursors were further tested in catalyst synthesis, including cobalt (II) nitrate, cobalt (II) acetate, cobalt (II) acetylacetonate, and cobalt (III) acetylacetonate. None of the above Co precursors deposited on SiO_2 particles showed good selectivity towards (9, 8) tubes. Thus, it is proposed that the narrow reduction peak of the $\text{CoSO}_4/\text{SiO}_2$ catalyst at 470°C can be credited to the reduction of highly dispersed CoSO_4 , following the chemical reaction equations (1) and (2). The reduction of Co_3O_4 and CoO (chemical reaction equations (3) and (4)) was used as references to quantify the H_2 consumption in CoSO_4 reduction on the $\text{CoSO}_4/\text{SiO}_2$ catalyst. Stoichiometric ratio of H_2 needed for reducing the same amount of Co ions in CoSO_4 over those in Co_3O_4 or CoO is 3.75–3 or 5–4, respectively. The integrated reduction peak area ratio between CoSO_4 and Co_3O_4 in Figure 4-10d is 3.68; and the ratio between CoSO_4 and CoO is 4.12. It is consistent with the proposed chemical reaction equations. Moreover, the existence of reaction equation (2) suggests that the presence of sulfur or SO_4^{2-} ions is a contributing factor to stabilize Co particles on the $\text{CoSO}_4/\text{SiO}_2$ catalyst.

Next, the existence of sulfur compounds in the catalyst during SWCNT synthesis was

verified by XAS and elemental analysis. Figure 4-12a shows the XANES spectra at sulfur K-edge of catalysts after different treatments. The peak belonging to SO_4^{2-} ions decreases with the increase of reduction temperature, and a small CoS peak can be observed. Sulfur contents in catalysts were quantified by integrating sulfur peak area of XANES spectra. Figure 4-12b shows that sulfur content decreases with increasing reduction temperature. This is further corroborated by elemental analysis of sulfur. The sulfur content in fresh catalyst is 0.65 wt%. After reduction at 540 °C, it drops to 0.36 wt%. In contrast, after reduction at 780 °C, catalyst only contains 0.11 wt% of sulfur. Figure 4-12, combining with the above SWCNT analysis suggests that the sulfur content correlates with the (n,m) selectivity changes of the $\text{CoSO}_4/\text{SiO}_2$ catalyst. From the TPR result in Figure 4-10d, the reduction of Co species under H_2 starts at 435 °C, and completes at 530 °C. When catalyst is reduced at 540 °C, the existence of sulfur compounds may stabilize reduced Co atoms for forming Co particles with suitable diameter and composition under CO. Such particles lead to the selective growth of (9,8) tubes. In contrast, if the reduction temperature is further increased to 780 °C, sulfur compounds (*e.g.* SO_4^{2-} ions) are removed from the catalysts, and reduced Co atoms nucleate into Co particles with various diameters, leading to SWCNTs with a broader (n,m) distribution. The TGA result in Figure 4-8b shows the formation of amorphous carbon and graphite, resulting from Co particles of random sizes.

Figure 4-12 Sulfur content in CoSO₄/SiO₂ catalyst. (a) XANES spectra at sulfur K-edge of fresh and treated catalysts at different reduction conditions. CoSO₄·7H₂O and CoS are references. Four samples include (1) fresh catalyst; (2) catalyst reduced in H₂ at 540 °C, and then cooled to room temperature under He; (3) catalyst reduced in H₂ at 540 °C, and then increased temperature to 700 °C under He before cooled to room temperature; and (4) catalyst reduced in H₂ at 700 °C, and then cooled to room temperature under He. The dashed line indicates the location of CoS peak. (b) Sulfur content in catalyst determined by elemental analysis and integrated sulfur peak area of XANES spectra. Four samples are the same as (a) and one more sample after reduction in H₂ at 780 °C.

Previous studies showed that when suitable amounts of sulfur are added in carbon precursors, it not only promotes the growth rate and the yield of carbon nanotubes, but also

strongly affects nanotube structures (such as shell number and diameter).⁹⁰⁻⁹³ One study proposed a mechanism that sulfur (from thiophene or carbon disulfide added in gas phase) would restrict the growth of Fe particles at ~1.6 nm for chiral selective growth of metallic (9,9) and (12,12) tubes.¹⁵⁸ They also suggested that sulfur may form C–S bonds at the edge steps of nanotube growth front, which lowers the activation energy of Stone-Thrower-Wales dislocation motion for SWCNT growth.¹⁵⁸ In this study, sulfur compounds are directly impregnated on catalyst instead, and the growth temperature at 780 °C is much lower than the previous study at 1200 °C.¹⁵⁸ Thus, the Co particles would not be in liquid state during SWCNT growth. It is proposed that sulfur could play two roles: first, the coexistence of sulfur atoms near Co atoms may limit the aggregation of Co atoms, which does not happen on catalysts prepared using other Co precursors without sulfur. Second, sulfur atoms may also form various Co–S compounds on Co particles, as indicated by the small CoS peak in XAS results (Figure 4-12a). The Co–S compounds could enable the specific chiral selectivity different from pure Co particles. More studies are still on-going in our lab to better understand the detailed roles of sulfur on stabilizing Co particles and the exact size, morphology and composition of chirally selective Co particles.

4.9 Conclusion

Sulfate-promoted CoSO₄/SiO₂ catalyst is highly selective in growing large diameter (9, 8) SWCNTs. In contrast, the chiral selectivity reported by most previous studies is restricted to small diameter (6,5) and (7,5) SWCNTs. After the catalyst is reduced in H₂ at 540 °C, it grows 51.7% (by PL, 33.5% by absorption) of (9,8) tubes. The total carbon yield over all catalyst materials used is 3.8 wt%, in which at least 90% is SWCNTs. The selectivity towards (9,8)

tubes disappears if the catalyst is reduced at 780 °C. The uniqueness of the CoSO₄/SiO₂ catalyst is that the highly dispersed CoSO₄ is reduced in a narrow window near 470 °C. XAS results indicate the formation of Co particles with average size of 1.23 nm, matching the diameter of (9, 8) tubes. Experimental and theoretical results suggest a correlation between the most abundant (*n,m*) species and the stable Co particles of scattered sizes. This suggests that growing chiral tubes with diameters matching the most stable particles in their size range could be much easier than seeking selectivity to random chiral structures. Furthermore, XAS results show that the sulfur content in the catalyst changes after catalyst reduction at different conditions, which correlates with the (*n,m*) selectivity change observed. Sulfur compounds incorporated in catalyst preparation may help to limit the aggregation of Co atoms and/or form various Co–S compounds, which contributes to the chiral selectivity.

Chapter 5 CoSO₄/SiO₂ Catalyst for Selective Synthesis of (9,8)

SWCNTs: Effect of Catalyst Calcination

In Chapter 4, a sulfate promoted CoSO₄/SiO₂ catalyst was developed for chirally selective synthesis of large diameter (9,8) SWCNTs. To further investigate this unique catalyst and its (*n,m*) selectivity, CoSO₄/SiO₂ catalysts were calcined under different temperatures, and then employed in the SWCNT growth.

5.1 CoSO₄/SiO₂ catalyst preparation

The CoSO₄/SiO₂ catalyst was prepared by the incipient wetness impregnation method, which was described in Chapter 4. During the catalyst calcination, the airflow rate, temperature increasing rate, and calcination time can affect the catalyst performance. The calcination temperature is the most critical parameter among them. Therefore, other calcination parameters were held at their optimal conditions (*i.e.* airflow of 20 sccm per gram of catalyst from room temperature to a desired calcination temperature at 1 °C/min, 5 g of the catalyst each batch), and only the calcination temperature was varied from 400 to 950 °C.

5.2 SWCNT synthesis and purification

SWCNT growth was carried out in a horizontal CVD reactor. Catalysts were loaded in a ceramic boat at the center of the reactor. The catalyst was reduced in H₂ at 540 °C before exposed to 6 bar CO at 780 °C. The same growth conditions were employed for all catalysts. The detailed SWCNT synthesis and purification of as-synthesized SWCNTs were described in Chapter 2.

5.3 SWCNT (*n,m*) analysis

5.3.1 Raman spectroscopy

Figure 5-1 Raman spectra of SWCNTs grown from catalysts calcined at different conditions marked on the right side of figures. (a) under the excitation of 514 nm laser, (b) under the 785 nm laser. The region on the left of each graph between 100 and 350 cm^{-1} correspond to RBM peaks, while the region on the right corresponds to D and G bands.

Raman spectroscopy is used to evaluate the quality and (*n,m*) selectivity of SWCNTs based on the RBM, D band and G band features.¹³⁵ Figure 5-1 shows Raman spectra of as-synthesized SWCNTs from catalysts calcined at different conditions under 514 and 785 nm laser excitations. All spectra have strong RBM and G band peaks with weak D band peaks, suggesting that high quality SWCNTs have been synthesized. The RBM peaks can be correlated with the (*n,m*) structures of SWCNTs according to the Kataura plot calculated by the tight-binding model.¹¹⁸ RBM frequencies are calculated as $223.5 \text{ cm}^{-1}/d_t + 12.5 \text{ cm}^{-1}$, where d_t is the diameter of SWCNTs.¹¹⁹ A combination of empirical¹¹⁹ and theoretical¹¹⁸ Kataura plots was used to identify the (*n,m*) structures of SWCNTs in the samples because the empirical plot¹¹⁹ is

more accurate for the E_{11} and E_{22} van Hove transitions of semiconducting SWCNTs. Figure 5-1a and 5-1b display a shift in the nanotube (n,m) structures with the change of catalyst calcination temperatures. Besides that, the (n,m) distribution of SWCNTs gradually becomes broader with the increase of calcination temperature. The catalysts calcined below 700 °C mainly grow large diameter ($d_t \geq 1.1$ nm) SWCNTs. Based on the empirical Kataura plot,¹¹⁹ the RBM peaks at 193 (Figure 5-1a), 213 (Figure 5-1a), 203 (Figure 5-1b) and 215 cm^{-1} (Figure 5-1b) come from the (10,8), (10,6), (9,8) and (9,7) nanotubes, respectively.

Table 5-1 Summary of RBM peaks identified in Figure 5-1 from SWCNT samples synthesized from the $\text{CoSO}_4/\text{SiO}_2$ catalysts uncalcined and calcined at different temperatures.

Excitation	514 nm						785 nm					
RBM, cm^{-1}	193	213	226	246	270	312	203	215	227	236	270	280
d_t , nm	1.24	1.11	1.03	0.97	0.90	0.76	1.17	1.10	1.03	0.97	0.90	0.83
uncalcined	√	√	×	×	×	√	√	√	×	×	×	√
400°C	×	√	×	×	×	×	√	√	×	×	×	√
500°C	√	√	×	√	×	√	√	√	×	×	×	√
600°C	√	√	×	√	√	√	√	√	×	×	×	√
700°C	√	√	√	√	√	√	√	√	√	√	×	√
800°C	×	×	√	√	√	√	√	√	√	√	√	×
900°C	×	×	√	√	√	√	√	√	√	√	√	×

When the catalyst calcination temperature is higher than 700 °C, the distribution of RBM peaks becomes broader, and the strongest RBM peaks shift to larger wavelength, suggesting more small diameter ($d_t < 1.0$ nm) SWCNTs are produced. The strongest RBM peaks at 270 (Figure 5-1a) and 246 cm^{-1} (Figure 5-1b) belong to the (7,6) and (8,6) nanotubes, respectively.

Table 5-1 lists SWCNTs identified by their RBM peaks in Figure 5-1. Due to the Raman

resonance effect,¹³⁵ it is difficult to quantify the abundance of various (n,m) species using only two excitation lasers in Raman analysis; hence, PL spectroscopy was employed to assign the (n,m) structure of semiconducting tubes.

5.3.2 PL spectroscopy

Figure 5-2 sketches the PL contour plots of SWCNTs grown from catalysts calcined at different temperature conditions. The spikes from the resonance behaviour of both excitation and emission events represent the transition pair belonging to individual semiconducting (n,m) species. The relative abundance of semiconducting (n,m) tubes identified in Figure 5-2 was calculated based on their PL peak intensity. The detailed results are listed in Table 5-2 to 5-8.

Figure 5-2 PL contour plots as a function of excitation and emission energies of SDBS-dispersed SWCNTs grown from catalysts calcined at different conditions. (a) uncalcined, (b) 400, (c) 500, (d) 600, (e) 700, and (f) 800 °C. Major chiral species identified in PL are marked with their (n,m) indices.

Table 5-2 Tabulated values of PL peak intensity and the relative abundance of (n,m) species in SWCNTs grown on the uncalcined $\text{CoSO}_4/\text{SiO}_2$ catalyst.

(n,m)	Diameter	Chiral angle	E_{11}	E_{22}	PL intensity	Relative
index	d_t (nm)	θ ($^\circ$)	(nm)	(nm)	(counts)	abundance, (%)
(6,5)	0.76	27.00	993	566	774.3	8.32%
(7,3)	0.71	17.00	996	498	427.5	4.59%
(7,5)	0.83	24.50	1022	634	239.9	2.58%
(7,6)	0.90	27.46	1126	642	301.1	3.23%
(8,4)	0.84	19.11	1124	574	454.6	4.89%
(8,6)	0.97	25.28	1162	710	147.7	1.59%
(8,7)	1.03	27.80	1273	726	468.8	5.04%
(9,7)	1.10	25.87	1329	790	1214.4	13.05%
(9,8)	1.17	28.05	1424	818	3857.4	41.46%
(10,6)	1.11	21.79	1380	754	527.4	5.67%
(10,8)	1.24	26.30	1470	870	325.7	3.50%
(10,9)	1.31	28.30	1567	886	565.9	6.08%

Table 5-3 Tabulated values of PL peak intensity and the relative abundance of (n,m) species in SWCNTs grown on the $\text{CoSO}_4/\text{SiO}_2$ catalyst calcined at 400 $^\circ\text{C}$.

(n,m)	Diameter	Chiral angle	E_{11}	E_{22}	PL intensity	Relative
index	d_t (nm)	θ ($^\circ$)	(nm)	(nm)	(counts)	abundance, (%)
(6,5)	0.76	27.00	981	566	157.2	4.34%
(7,3)	0.71	17.00	995	498	136.1	3.76%
(7,5)	0.83	24.50	1021	638	66.8	1.85%
(7,6)	0.90	27.46	1112	642	65.9	1.82%
(8,4)	0.84	19.11	1103	578	101.9	2.82%
(8,6)	0.97	25.28	1163	710	44.5	1.23%
(8,7)	1.03	27.80	1265	726	99.7	2.75%
(9,7)	1.10	25.87	1319	790	437.4	12.1%
(9,8)	1.17	28.05	1413	818	1828.6	50.52%
(10,6)	1.11	21.79	1380	754	222.9	6.16%
(10,8)	1.24	26.30	1465	870	113.3	3.13%
(10,9)	1.31	28.30	1559	886	344.7	9.52%

Table 5-4 Tabulated values of PL peak intensity and the relative abundance of (n,m) species in

SWCNTs grown on the CoSO₄/SiO₂ catalyst calcined at 500 °C.

(<i>n,m</i>)	Diameter	Chiral angle	E ₁₁	E ₂₂	PL intensity	Relative
index	d _t (nm)	θ (°)	(nm)	(nm)	(counts)	abundance,(%)
(6,5)	0.76	27.00	985	570	2746.6	19.51%
(7,3)	0.71	17.00	990	502	963.4	6.85%
(7,5)	0.83	24.50	1026	642	1167.5	8.29%
(7,6)	0.90	27.46	1114	642	824.2	5.86%
(8,4)	0.84	19.11	1110	574	940.6	6.68%
(8,6)	0.97	25.28	1166	710	296.3	2.11%
(8,7)	1.03	27.80	1263	726	875.8	6.22%
(9,7)	1.10	25.87	1319	790	1136.1	8.07%
(9,8)	1.17	28.05	1414	822	3572.9	25.38%
(10,6)	1.11	21.79	1382	758	648.6	4.61%
(10,8)	1.24	26.30	1469	874	405.3	2.88%
(10,9)	1.31	28.30	1559	886	499.0	3.54%

Table 5-5 Tabulated values of PL peak intensity and the relative abundance of (*n,m*) species in SWCNTs grown on the CoSO₄/SiO₂ catalyst calcined at 600 °C.

(<i>n,m</i>)	Diameter	Chiral angle	E ₁₁	E ₂₂	PL intensity	Relative
index	d _t (nm)	θ (°)	(nm)	(nm)	(counts)	abundance,(%)
(6,5)	0.76	27.00	983	570	3394.1	19.55%
(7,3)	0.71	17.00	990	502	1182.8	6.81%
(7,5)	0.83	24.50	1026	642	1886.4	10.86%
(7,6)	0.90	27.46	1114	642	1373.1	7.91%
(8,4)	0.84	19.11	1108	578	1401.4	8.07%
(8,6)	0.97	25.28	1166	710	580.2	3.34%
(8,7)	1.03	27.80	1263	726	1227.4	7.07%
(9,7)	1.10	25.87	1319	790	1294.0	7.45%
(9,8)	1.17	28.05	1414	822	2993.0	17.24%
(10,6)	1.11	21.79	1381	754	803.8	4.63%
(10,8)	1.24	26.30	1467	874	564.9	3.25%
(10,9)	1.31	28.30	1558	886	663.0	3.82%

Table 5-6 Tabulated values of PL peak intensity and the relative abundance of (*n,m*) species in

SWCNTs grown on the CoSO₄/SiO₂ catalyst calcined at 700 °C.

(n,m)	Diameter	Chiral angle	E ₁₁	E ₂₂	PL intensity	Relative
index	d _t (nm)	θ (°)	(nm)	(nm)	(counts)	abundance,(%)
(6,5)	0.76	27.00	983	574	1618.2	15.45%
(7,3)	0.71	17.00	990	498	469.8	4.48%
(7,5)	0.83	24.50	1026	646	1468.7	14.01%
(7,6)	0.90	27.46	1114	646	1487.0	14.19%
(8,4)	0.84	19.11	1108	582	1315.4	12.55%
(8,6)	0.97	25.28	1166	714	1022.3	9.75%
(8,7)	1.03	27.80	1263	730	1102.2	10.52%
(9,7)	1.10	25.87	1319	790	623.5	5.95%
(9,8)	1.17	28.05	1414	826	509.3	4.86%
(10,6)	1.11	21.79	1380	758	390.0	3.72%
(10,8)	1.24	26.30	1468	870	171.7	1.64%
(10,9)	1.31	28.30	1559	890	302.2	2.88%

Table 5-7 Tabulated values of PL peak intensity and the relative abundance of (n,m) species in SWCNTs grown on the CoSO₄/SiO₂ catalyst calcined at 800 °C.

(n,m)	Diameter	Chiral angle	E ₁₁	E ₂₂	PL intensity	Relative
index	d _t (nm)	θ (°)	(nm)	(nm)	(counts)	abundance,(%)
(6,5)	0.76	27.00	981	570	4571.9	17.68%
(7,3)	0.71	17.00	990	498	1098.8	4.25%
(7,5)	0.83	24.50	1022	650	5174.5	20.01%
(7,6)	0.90	27.46	1112	646	3426.3	13.25%
(8,4)	0.84	19.11	1102	594	5188.8	20.07%
(8,6)	0.97	25.28	1166	714	2292.6	8.86%
(8,7)	1.03	27.80	1263	726	1496.6	5.79%
(9,7)	1.10	25.87	1320	790	884.5	3.42%
(9,8)	1.17	28.05	1413	826	690.5	2.67%
(10,6)	1.11	21.79	1376	758	480.4	1.86%
(10,8)	1.24	26.30	1467	862	273.6	1.06%
(10,9)	1.31	28.30	1557	886	279.9	1.08%

Table 5-8 Tabulated values of PL peak intensity and the relative abundance of (n,m) species in

SWCNTs grown on the CoSO₄/SiO₂ catalyst calcined at 900 °C.

(<i>n,m</i>)	Diameter	Chiral angle	E ₁₁	E ₂₂	PL intensity	Relative
index	d _t (nm)	θ (°)	(nm)	(nm)	(counts)	abundance,(%)
(6,5)	0.76	27.00	980	570	3984.6	16.19%
(7,3)	0.71	17.00	994	498	896	3.64%
(7,5)	0.83	24.50	1022	634	5147	20.92%
(7,6)	0.90	27.46	1114	646	3977.3	16.16%
(8,4)	0.84	19.11	1105	582	5161.7	20.98%
(8,6)	0.97	25.28	1166	714	2298.8	9.34%
(8,7)	1.03	27.80	1263	726	1368.5	5.56%
(9,7)	1.10	25.87	1320	790	645.5	2.62%
(9,8)	1.17	28.05	1414	822	470.7	1.91%
(10,6)	1.11	21.79	1378	758	396.9	1.61%
(10,8)	1.24	26.30	1463	870	129.6	0.53%
(10,9)	1.31	28.30	1557	886	132.7	0.54%

Corroborating with Figure 5-1, Figure 5-2 suggests that the diameter of SWCNTs shifts from the large diameters to small diameters with increasing calcination temperature. This is also showed on the chiral map in Figure 5-3b. More importantly, Figure 5-2b has an intense peak from the (9,8) nanotubes with minor peaks from the (10,9) and (9,7) nanotubes. As shown in Figure 5-3a, the relative abundance of the (9,8) nanotubes is 50.52%, which suggests that the catalyst calcined at 400 °C has an excellent single chiral selectivity towards the large diameter (9,8) nanotubes. The uncalcined catalyst can also grow the (9,8) nanotubes; however, the peaks from the (10,9), (9,7), (8,7) and (6,5) nanotubes are more intense as compared to Figure 5-2b. The relative abundance of the (9,8) nanotubes is 41.46% for the uncalcined catalyst. When the catalyst calcination temperature raised from 400 to 600 °C, the (*n,m*) distribution of the resulting SWCNTs becomes broader, including (10,9), (10,6), (9,8), (9,7), (8,7), (7,6), (7,5), (8,4), and (6,5) nanotubes. The intensity of PL peaks from small diameter

nanotubes, such as the (6,5) and (7,5) nanotubes, continues to increase. When the catalyst calcination temperature reaches 700 °C, the dominant (n,m) species shifts from the (9,8) to the (6,5) nanotubes. The relative abundance of the (6,5) nanotubes is 15.45%, a few times higher than that of the (9,8) nanotubes at 4.86%. When the catalyst calcination temperature is further increased to 800 or 900 °C, their PL plots show some major changes: the large diameter nanotubes, such as (10,9), (9,8) and (9,7), disappear, and the main species are small diameter nanotubes such as (6,5), (7,5), (7,6) and (8,4). The catalyst calcined at 950 °C was also examined; the catalyst becomes inactive to SWCNT growth.

Figure 5-3 (a) The change of relative abundance of semiconducting (n,m) tubes at different catalyst calcination temperatures. The relative abundance is calculated from the intensity of PL peaks of various (n,m) species. (b) A chiral map of (n,m) species identified in PL plots. The few major species shown in (a) are highlighted in different colors.

5.3.3 UV-vis-NIR absorption spectroscopy

As PL spectroscopy can only detect semiconducting SWCNTs, UV-vis-NIR absorption spectroscopy was used to complement the results from PL analysis. Figure 5-4 shows that the chirality distribution of SWCNTs varies in a similar trend as that in the PL plots. The spectra of SWCNTs grown from the uncalcined catalyst and the catalyst calcined at 400 °C have a single main peak in their E_{11}^S transition bands, which belongs to the (9,8) nanotubes. Similarly, the strongest peaks in their E_{22}^S transition bands also come from the (9,8) nanotubes. There are a few absorption peaks below 700 nm, which can be assigned to the E_{11}^M transition of metallic tubes or E_{22}^S transition of semiconducting tubes. Based on the positions of these peaks, they likely belong to metallic (9,6) and (10,10) nanotubes. When the catalyst calcination temperature increases to 600 °C, the dominant (n,m) species remains as (9,8); however, the E_{11}^S peak from the (6,5) nanotubes at 980 nm becomes larger. When the catalyst calcination temperature reaches 800 °C, the (6,5), (7,5), (7,6) and (8,4) become dominant species. Based on the relative intensity of their absorption peaks and the reconstruction analysis in Chapter 4, it can be concluded that when the catalyst is calcined at low calcination temperatures, the dominant semiconducting (9,8) nanotubes have much higher abundance than metallic tubes.

Figure 5-4 UV–vis–NIR absorption spectra of SDBS-dispersed SWCNTs grown from catalysts calcined at different conditions. The label E_{11}^S (shaded purple) marks the absorption bands of the first one-dimensional van Hove singularities from semiconducting SWCNTs; the E_{22}^S and E_{11}^M (shaded yellow) correspond to the overlapping absorption bands of the first van Hove singularities from metallic SWCNTs and the second van Hove singularities from semiconducting SWCNTs. All spectra were normalized at 1420 nm for easy comparison.

Raman, PL, and UV–vis–NIR absorption spectroscopy analyses consistently show that: (a) the $\text{CoSO}_4/\text{SiO}_2$ catalyst is highly selective towards the large diameter single chirality (9,8) nanotubes; (b) the chiral selectivity of the catalyst is correlated with the catalyst calcination temperatures; (c) the catalyst calcined at 400 °C has the highest selectivity towards the (9,8) nanotubes; and (d) the chiral selectivity would shift to small diameter nanotubes when the catalyst is calcined above 700 °C.

5.4 Carbon yield

Figure 5-5 TG and DTG profiles of carbon deposits grown on the CoSO₄/SiO₂ catalysts (with ~1 wt% Co) calcined at three different temperatures. (a) 400 °C, (b) 700 °C, and (c) 900 °C.

The total carbon yield and selectivity to SWCNTs are both important in evaluating the performance of catalysts used for SWCNT synthesis. TGA was adopted to determine the carbon yield and different carbon species in the carbon deposits grown from the CoSO₄/SiO₂ catalyst. As depicted in Figure 5-5, the total carbon yield of three representative samples grown on the catalysts (with ~1 wt% Co) calcined at 400, 700 and 900 °C is 3.8, 5.3, and 3.2 wt% respectively. This suggests that the carbon yield from the CoSO₄/SiO₂ catalyst is passable for developing scalable SWCNT production processes. The carbon yield increases slightly with the increase of catalyst calcination temperature from 400 to 700 °C, and then decreases when the calcination further increases to 900 °C. The DTG profiles of the carbon deposits in Figure 5-5 can be divided into three oxidation regions including amorphous carbon from

250-400 °C, CNTs (SWCNTs and MWCNTs) usually between 400 and 700 °C, and graphite above 800 °C.¹⁵⁹ The weight loss below 250 °C is likely from the adsorbed water or the removal of surface hydroxyl groups on the catalysts. The DTG profile in Figure 5-5a shows that 92% of carbon deposits are SWCNTs, which are oxidized at 563 °C. The other three peaks in Figure 5-5b and 5-5c at 486, 586, and 490 °C can also be credited to SWCNTs of different diameters, which have been confirmed in the earlier works.^{56,136,160,161} The selectivity to SWCNTs is 73 and 55 % based on the integrated peak areas. The appearance of peaks at ~ 490 °C suggests the growth of smaller diameter SWCNTs after catalyst calcination at higher temperatures, which is in agreement with the spectroscopic results. Furthermore, the peaks from graphite become more intense with the increase of catalyst calcination temperature.

5.5 Morphology of carbon deposits

Figure 5-6 TEM images of SWCNTs and other carbon species grown from the $\text{CoSO}_4/\text{SiO}_2$ catalyst. (a–b) the catalyst calcined at 400 °C. (d–f) the catalyst calcined at 800 °C. (c) AFM

image of purified SWCNTs deposited on silicon wafer and the height profile of nanotubes along the red line.

To further examine the morphology of carbon deposits, TEM images were captured on as-synthesized SWCNTs with catalysts. As seen in Figure 5-6, SWCNTs grown from the catalyst would bundle together. The catalyst calcined at 400 °C yields mainly SWCNTs with diameter around 1.2nm. The AFM image of purified SWCNTs also shows the height of individual tubes deposited on the silicon wafer is about 1.2 nm. It is difficult to find large metal particles on this catalyst. But a small amount of carbon fibers and graphite were observed on the catalyst calcined at 800 °C. Large metal particles can also be found on this catalyst, as well as in SWCNT bundles (see Figure 5-6 d-f). Large metal particles are covered by graphene layers (Figure 5-6f). The TEM and AFM images agree with the results obtained from spectroscopies and TGA.

5.6 Characterization of the CoSO₄/SiO₂ catalyst

5.6.1 Catalyst morphology

To understand how the different catalyst calcination temperature can affect performances of the CoSO₄/SiO₂ catalyst in SWCNT synthesis, several characterization techniques were used to study its physicochemical properties. The catalyst is supported on fumed silica. As shown in Figure 5-6, the catalyst consists of SiO₂ particles with size around 20 nm. SEM images in Figure 5-7 indicate that SiO₂ particles can aggregate together to form micrometer scale large particles. No significant changes were observed in the morphology of these SiO₂ particles after different calcination treatments and SWCNT growth.

Figure 5-7 SEM of the $\text{CoSO}_4/\text{SiO}_2$ catalyst calcined at (a) 400 °C and (b) 900 °C.

5.6.2 Structure by XRD and physisorption

The structure of the catalyst is further characterized by XRD and nitrogen physisorption. As shown in Figure 5-8, the catalysts have a broad diffraction peak near $2\theta = 21^\circ$ originating from the SiO_2 supports. No diffraction peaks from bulk Co oxides or Co silicates are observed on the XRD spectrum of the uncalcined catalyst. After different calcination treatments, their XRD spectra show insignificant changes. Even though some surface Co oxides or Co silicates may have formed, XRD analysis didn't detect them.

Figure 5-8 XRD patterns of the $\text{CoSO}_4/\text{SiO}_2$ catalyst calcined at different conditions.

$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ is a reference.

In Figure 5-9, N₂ physisorption isotherms show that the catalyst is a porous material with the pore size around 32 nm. The pores likely come from the gaps among SiO₂ particles. For the catalyst calcined at 400 °C, it has a surface area of 208 m²/g, and a large pore volume of 1.54 mL/g. When the catalyst is calcined at 800 °C, its surface area is 205 m²/g, and its pore volume is 1.58 mL/g. These findings suggest that the observed chiral selectivity changes in SWCNT synthesis are unlikely due to the morphology or physical structure changes of the catalysts.

Figure 5-9 Nitrogen physisorption isotherms and pore size distributions (insert) of the CoSO₄/SiO₂ catalyst calcined at 400 and 800 °C.

5.6.3 H₂-TPR

Figure 5-10 H₂-TPR profiles of the CoSO₄/SiO₂ catalyst calcined at different conditions and several Co references (Co₃O₄, CoO, CoSO₄·7H₂O and CoSiO₃).

Figure 5-10 illustrates the TPR profiles of the uncalcined CoSO₄/SiO₂ catalyst and those calcined at different temperatures in comparison with several references. The CoSO₄·7H₂O displays a sharp peak around 585 °C, which is ascribed to the reductive decomposition of bulk CoSO₄. Co oxides are usually reduced below 400 °C, which is shown by the two Co oxides references (Co₃O₄ and CoO). Co silicates typically show a high reduction temperature above 600 °C. The uncalcined catalyst and those calcined at 400 and 600 °C all have a sharp peak around 460–470 °C, which can be attributed to the reductive decomposition of highly dispersed CoSO₄ on the SiO₂ substrate. The reduction peaks from Co oxides and Co silicates are minor on their TPR profiles. When the catalyst calcination temperature increases to 800 °C,

there is a strong peak at 310 °C, and its position lies between the peaks of CoO and Co₃O₄, suggesting that the calcination at 800 °C may lead to the formation of Co oxides. When the catalyst is calcined at 950 °C, a broad low intensity peak shows up from 600 to 950 °C. This indicates the formation of various Co silicates, such as Co hydrosilicate, surface and bulk Co silicate.^{162,163} H₂-TPR results demonstrate that different Co species can be formed after catalyst calcination at different conditions. This could be the key reason for the observed chiral selectivity changes.

5.6.4 UV-vis diffuse reflectance spectroscopy

The surface chemistry of catalysts was further investigated by UV-vis diffuse reflectance spectroscopy. Figure 5-11 shows that the uncalcined catalyst and those calcined at 400 and 600 °C have a broad peak around 535 nm similar to that of CoSO₄·7H₂O. These three catalysts are light pink in color. When the calcination temperature increases to 800 °C, the catalyst turns into gray and black. Its UV-vis spectrum is similar to that of Co₃O₄ with two broad peaks around 400 and 720 nm, respectively. These two peaks can be assigned to ν_1 ⁴A_{1g}→¹T_{1g} and ν_2 ¹A_{1g}→¹T_{2g} transitions, suggesting the existence of octahedral configured Co³⁺ ions.¹³² The UV-vis spectrum of CoO is same as that of Co₃O₄ below 400 nm. Thus, it is difficult to judge whether the calcined catalysts also contain CoO based on their UV-vis spectra alone. When the catalyst is calcined at 950 °C, its UV-vis spectrum has several peaks at 250-300nm and 500-600nm, just like that of CoSiO₃. The peak around 580nm indicates the formation of amorphous Co silicate.^{164,165}

Figure 5-11 UV-vis diffuse reflectance spectra of the $\text{CoSO}_4/\text{SiO}_2$ catalyst calcined at different conditions and references (Co_3O_4 , CoO , CoSO_4 , CoSiO_3 and fumed SiO_2).

5.6.5 XANES spectra at Co K-edge

Figure 5-12 XAS spectra of $\text{CoSO}_4/\text{SiO}_2$ catalysts calcined at different conditions and several references ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, CoSiO_3 , CoO , Co_3O_4 and Co foil). (a) XANES spectra near the Co K-edge. The inset shows the enlarged spectra near the Co K-edge. (b) Fourier transforms of EXAFS spectra in r -space at the Co K-edge for samples in (a).

XAS was utilized to characterize the local chemical environment of Co atoms in the CoSO₄/SiO₂ catalyst. Figure 5-12a shows the normalized XANES spectra of Co species in catalysts calcined at different conditions. CoSO₄·7H₂O, CoSiO₃, CoO, Co₃O₄ and Co foil were used as references. CoSO₄·7H₂O contains octahedrally coordinated Co ions. Co atoms are situated in a distorted octahedral environment in Co silicates. CoO has all Co atoms sitting in an octahedral environment. In Co₃O₄, Co²⁺ ions are in a tetrahedral coordination and Co³⁺ are in an octahedral coordination.^{164,166} Two spectroscopic features reveal significant differences among these catalysts. One is their preedge peaks and edge jumps shown in the insert of Figure 5-12a. The preedge peak was ascribed to the dipole forbidden 1s → 3d transitions whose intensities are strong functions of the local symmetry of the Co species.¹⁶⁷ The edge jump was assigned to the 1s → np transition when 1s electron is excited and the position of the K edge varies linearly with the valence of the Co species.⁵⁴ In Figure 5-12a, the preedge spectra of three catalysts (uncalcined, calcined at 400 and 600 °C) at 7709 eV almost overlap, and are similar to that of the CoSO₄·7H₂O, suggesting that Co atoms in these three catalysts are in an octahedrally coordinated structure. Their edge jumps around 7717 eV indicate that Co(II) is the dominant oxidation state of Co atoms in these catalysts.^{136,168} In comparison, the peak at 7709 eV of the catalyst calcined at 800 °C locates between those of the CoO and Co₃O₄ references, and its edge jump is close to those of the Co₃O₄ and CoSiO₃ references, suggesting that Co atoms in this catalyst are in a distorted tetrahedral structure.¹⁶⁸ The other spectroscopic feature is the white line peak at 7725 eV, which is attributed to the unfilled d states of Co atoms at the Fermi level. The intensity of the white line peak increases with the number of unfilled d states.⁵⁴ Cobalt foil has a weak white line peak, while the CoSO₄·7H₂O has a strong

white line peak. When the hydrated water is removed, the intensity of white line decreases a bit. The uncalcined $\text{CoSO}_4/\text{SiO}_2$ catalyst has a strong white line peak, which indicates that Co atoms are in an oxidized state. The white line of the catalyst calcined at 400 °C is almost identical to that of the uncalcined catalyst, suggesting that most of Co atoms in the catalyst are in an oxidized state after calcination at 400 °C. The white line peak intensity of the catalyst calcined at 600 °C slightly decreases. In contrast, after the calcination at 800 °C, the white line peak of the catalyst splits into two peaks, in which one at 7729 eV can be attributed to the existence of Co_3O_4 , and the other at 7726 eV is similar to those from CoO and CoSiO_3 , which advocates the formation of Co oxides and Co silicates in the catalyst.

Table 5-9 Structure parameters of the first Co–O coordination shell in catalysts determined from the EXAFS data (Figure 5-12b) at the Co K-edge by fitting using FEFF 9.

Catalysts	Co–O first shell fitting by the Co_3O_4 model		
	$N_{\text{Co-O}}$	$dR(\text{\AA})$	$\Delta\sigma^2$
uncalcined	4.8 ± 0.1	0.271 ± 0.011	0.006
400 °C	5.2 ± 0.2	0.266 ± 0.016	0.008
600 °C	4.6 ± 0.1	0.258 ± 0.011	0.007
800 °C	2.6 ± 0.1	0.154 ± 0.014	0.008
Catalysts	Co–O first shell fitting by the CoSO_4 model		
	$N_{\text{Co-O}}$	$dR(\text{\AA})$	$\Delta\sigma^2$
uncalcined	5.7 ± 0.2	-0.010 ± 0.009	0.007
400 °C	6.0 ± 0.3	-0.015 ± 0.013	0.009
600 °C	5.4 ± 0.1	-0.022 ± 0.008	0.008
800 °C	3.2 ± 0.2	-0.124 ± 0.015	0.009

The EXAFS of catalysts was Fourier transformed to r -space to separate the contribution from different coordination shells of Co atoms. Figure 5-12b shows the uncalcined catalyst has

a strong Co–O peak at 1.96 Å, similar to that of CoSO₄ · 7H₂O. With the increase of catalyst calcination temperature, the Co–Co peak appears. The spectrum of the catalyst calcined at 800 °C is similar to those of Co₃O₄ and CoSiO₃. The spectra in *r*-space were fitted using Co paths in both Co₃O₄ and CoSO₄ generated by the FEFF 9 program¹¹⁵ to get the first shell coordination number (N_{Co-O}) and the bond distance (R_{Co-O}). In theoretical references, N_{Co-O} is 4, 2, and 6, and R_{Co-O} is 1.816, 2.099, and 2.133 Å in Co₃O₄, CoSO₄, and CoO, respectively. The fitting results are listed in Table 5-9. The Debye–Waller factors ($\Delta\sigma^2$) are 0.006–0.009, which means that the fitting is within acceptable limits. The N_{Co-O} is in the range of 2.6–6.0, suggesting that Co atoms are in the distorted octahedral or tetrahedral environment. The N_{Co-O} slightly increases when the catalyst calcined at 400 °C as compared to that of the uncalcined catalyst, and then drops when the calcination temperature was further increased, indicating that the catalyst is undergoing transitions. The fitting results of N_{Co-O} obtained by using the Co paths from CoSO₄ are higher than those obtained by using the Co paths from Co₃O₄. The deviation of the fitted bond distances (dR) is larger when the Co paths from Co₃O₄ are used, except for the catalyst calcined at 800 °C. This indicates that the local environment of Co atoms is similar to that in CoSO₄, when calcination temperature is below 600 °C. Then, the environment of Co atoms changes to become more like that in Co₃O₄, when the calcination temperature increases to 800 °C.

5.7 Sulfur in the $\text{CoSO}_4/\text{SiO}_2$ catalyst

Figure 5-13 The weight fraction of sulfur in $\text{CoSO}_4/\text{SiO}_2$ catalysts calcined at different temperatures and after reduction in H_2 at 540 °C during SWCNT growth.

Since sulfur may play an important role in the chiral selectivity of the $\text{CoSO}_4/\text{SiO}_2$ catalyst,¹⁶⁹ elemental analysis was firstly used to corroborate the existence of sulfur in the catalyst. Figure 5-13 depicts the weight fraction of sulfur in the $\text{CoSO}_4/\text{SiO}_2$ catalysts after calcination at different temperatures. There is 0.64 wt% sulfur in the uncalcined catalyst. Sulfur content shows a slight decrease to 0.61 wt% when the catalyst calcination temperature increases to 600 °C. A sharp drop to 0.20 wt% occurs when the calcination temperature is elevated to 700 °C. The sulfur content continues to drop to 0.12 wt% after catalyst calcination at 900 °C. Although the changing trend of sulfur content does not exactly mirror the chiral selectivity change demonstrated in Figure 5-3a, it is similar to the changing trend of TPR results in Figure 5-10 and the white line peak change in Figure 5-12. This suggests that the

SO_4^{2-} deposited on SiO_2 may have decomposed during calcination, and different amount of sulfur is removed from the catalyst after catalyst calcination at different conditions. I also measured the sulfur content in catalysts after reduction in H_2 at 540°C during SWCNT growth. The sulfur content in reduced catalysts is lower due to the reduction in H_2 . A sharp drop can still be observed when the calcination temperature changes from 600 to 700°C .

5.8 Effect of catalyst calcination

Figure 5-14 Schematic illustration of catalyst transitions at different calcination temperatures.

Silica particles are around 20 nm in diameter, thus a curved surface is used to represent the surface of silica particles.

Based on characterization results of the $\text{CoSO}_4/\text{SiO}_2$ catalyst, it is proposed that the catalyst undergoes transitions at different calcination temperatures as illustrated in Figure 5-14. The zero points of charge of SiO_2 is about $2-3$; therefore, SiO_2 particles are negatively charged at $\text{pH} > 3$.¹⁷⁰ The aqueous solution of CoSO_4 has a pH around 5 . Cations can adsorb on SiO_2 by

ion exchange with H^+ from silanol groups ($SiOH$).¹⁶² $CoSO_4 \cdot 7H_2O$ dissolved in deionized water forms $[Co(H_2O)_6]^{2+}$ ions. For the uncalcined catalyst, Co ions adsorb on SiO_2 surface through electrostatic interaction. Another possibility is to form strongly bonded Co to the SiO_2 surface through oxolation reaction.¹⁶² When the catalyst calcination temperature is low (*e.g.* 400 °C), sulfur in the $CoSO_4/SiO_2$ catalyst may exist as chelating bidentate SO_4^{2-} , which is a common structure on sulfate promoted metal oxide catalysts.¹⁷¹ Cobalt ions would stay in either the octahedral environment surrounded by H_2O , or the tetrahedral environment, where each Co atom links to one sulfur atom through two O atoms, and is also bonded to the SiO_2 surface through silanol groups. With the increase of calcination temperature, $S=O$ bonds would decompose. The removal of sulfur causes the formation of surface Co oxides.¹⁷² When the calcination temperature further raises to 800 °C, $S=O$ bonds in the catalyst decompose completely, while most of Co atoms are converted into Co oxides.¹⁶² Some of them would form rather large CoO or Co_3O_4 particles. At very high calcination temperature (for example higher than 950 °C), the reaction between Co oxides and SiO_2 may also lead to the formation of Co silicates.¹⁷³

The above discussion suggests that the unique Co and S structures formed on SiO_2 surface at different catalyst calcination temperatures may influence the formation of Co particles for SWCNT growth. For the uncalcined catalyst and the catalyst calcined at 400 °C, Co species are well spread on the large surface of SiO_2 particles. Therefore, Co metal particles with a suitable size could be formed on SiO_2 surface during SWCNT growth without severe aggregation. On one hand, the coexistence of sulfur atoms near Co atoms may limit the aggregation of Co atoms, compared with other catalysts prepared using other Co precursors without sulfur. On

the other hand, sulfur atoms may also form various Co–S compounds, which could lead to the specific chiral selectivity towards the (9,8) nanotubes. Based on the current results, it cannot be concluded beyond doubt which of the above two roles played by sulfur atoms is more important. With the increase of catalyst calcination temperature, some fractions of sulfur atoms have been removed from the catalyst. The formation of surface Co oxides or Co silicates leads to the growth of Co metal particles in different sizes during the SWCNT synthesis. This is evident by the growth of the small diameter (6,5) nanotubes. Besides that, the abundance of the (6,5) nanotubes increases with the increase of catalyst calcination temperature and the decrease of the sulfur content in the catalyst. A previous study also reports that well dispersed Co silicates on SiO₂ surface result in the growth of small diameter tubes, such as (6,5), (7,5), (7,6) and (8,4).¹³⁶ When the catalyst calcination temperature further increases to 800 and 900 °C, it may lead to the formation of some bulk Co oxides and Co silicates, although XRD cannot detect them. The bulk Co silicates are inactive for SWCNT growth. This correlates with the drop of the observed carbon deposit yield. Furthermore, bulk Co oxides can be reduced into large Co particles, which leads to the growth of carbon fibers and graphite observed in TEM analysis.

As was proposed in Chapter 4, the selectivity toward (9,8) may be due to the matching between carbon caps and the most stable Co particles in their size range and the higher growth rate of high chiral angle tubes, and the shift of (*n,m*) selectivity from small diameter (6,5) to large diameter (9,8) could be credited to the jump in the diameter of stable Co particles.¹⁶⁹ However, it should be noted that the complexity of the chemical nature of the compound catalyst, especially sulfur may also influence the nucleation of Co particles, making it difficult

to obtain a more detailed mechanism at present. More theoretical simulation or experimental studies on simplified model catalysts would be very useful to obtain a better understanding of the mechanism on chiral selection for SWCNT growth.

5.9 Conclusion

The $\text{CoSO}_4/\text{SiO}_2$ catalyst was prepared and calcined at different temperature for SWCNT growth. The chiral selectivity of the catalyst is correlated with the catalyst calcination temperatures. When the catalyst is calcined in air at 400 °C, it yields 50.52% of (9,8) nanotubes among all semiconducting SWCNTs. The selectivity would shift to small diameter nanotubes when the catalyst is calcined above 700 °C.

The catalyst calcination plays a crucial role in the formation of active Co species on SiO_2 surface for SWCNT growth. TEM, XRD and physisorption results show that the chiral selectivity change is not resulting from the morphology or physical structure changes of the catalyst. H_2 -TPR, UV-vis spectroscopy and XAS studies show that at low calcination temperature (≤ 400 °C), Co ions adsorb on SiO_2 surface through electrostatic interaction and/or form strongly bonded Co to the SiO_2 surface through the oxolation reaction. Sulfur exists as chelating bidentate SO_4^{2-} on the surface with Co atoms. The coexistence of sulfur atoms near Co atoms may limit the aggregation of Co atoms or form various Co-S compounds, which may lead to the specific chiral selectivity towards the (9,8) nanotubes. With the increase of calcination temperature, some sulfur atoms are removed from the catalyst, leading to the formation of surface Co oxides and Co silicates which are more selective to the small diameter SWCNTs.

Chapter 6 Sulfur Doped Co/SiO₂ Catalysts for Chirally Selective Synthesis of SWCNTs

Chapter 4 and 5 demonstrated that the presence of sulfur in the CoSO₄/SiO₂ catalyst is related to the growth of (9,8) nanotubes. Therefore, It is hypothesized that it is possible to activate non-selective catalysts via sulfur doping for synthesis of (9,8) nanotubes. Since cobalt catalysts supported on silica substrates (Co/SiO₂) is the most often used catalyst for SWCNT growth,^{50,51,127,136,174} three regular Co/SiO₂ catalysts were doped by sulfur for SWCNT growth.

6.1 Sulfur doped Co/SiO₂ catalyst preparation

Three Co/SiO₂ catalysts with 1 wt% Co were prepared by the impregnation method using three Co precursors, including Co (II) acetylacetonate (Co(acac)₂, Sigma-Aldrich, 97%), Co (II) chloride (CoCl₂, Alfa Aesar, 97%) and Co (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, Sigma-Aldrich, 99%). Co(acac)₂ was dissolved in dichloromethane (Sigma-Aldrich, anhydrous, ≥99.8%), while Co(NO₃)₂·6H₂O and CoCl₂ were dissolved in deionized water. The Co precursor solutions were then added to fumed silica (Cab-O-Sil[®]M-5, Sigma-Aldrich) with surface area of 254 m²/g. The mixtures were aged at room temperature for 1 h, and subsequently dried in an oven at 100 °C for 2h. The dried catalyst was further calcined under airflow of 20 sccm per gram of catalyst from room temperature to 400 °C at 1 °C/min, and then kept at 400 °C for 1 h. These three catalysts were denoted as CoACAC/SiO₂, CoCl/SiO₂, and CoN/SiO₂. To dope sulfur into these Co/SiO₂ catalysts, the above calcined catalysts were impregnated by dilute sulphuric acid (H₂SO₄, 0.04 mol/L) at 8 mL solution/g catalyst for 1 h. Afterwards, the mixtures were dried and calcined again using the same procedure described

above. The resulting sulfur doped catalysts were denoted as CoACAC/SiO₂/S, CoCl/SiO₂/S, and CoN/SiO₂/S, respectively.

6.2 SWCNT synthesis and purification

Catalysts were introduced into a CVD reactor, and first reduced in pure H₂ at 540 °C before exposed to 6 bar CO at 780 °C. The same growth conditions were used for all catalysts. The detailed SWCNT synthesis and purification of as-synthesized SWCNTs were described in Chapter 2.

6.3 SWCNT (*n,m*) analysis

PL maps in Figure 6-1a-f show that two undoped Co/SiO₂ catalysts (CoACAC/SiO₂ and CoCl/SiO₂) grow small diameter nanotubes (< 0.9 nm), such as (6,5), (7,5), (7,6) and (8,4). CoN/SiO₂ is not active for SWCNT growth, and this is in agreement with previous studies using various SiO₂ supported Co catalysts.^{68,136,175} In contrast, after doping with sulfur, the major (*n,m*) species are large diameter tubes (> 1.1 nm), such as (9,8), (9,7), (10,6), and (10,9). The abundance of these four species calculated using their PL intensity is 52.4–69.1% among all semiconducting species identified, out of which, 32.7–40.5% is (9,8) (see Table 6-1—6-3). PL results were corroborated by UV–vis–NIR absorption spectra. Figure 6-1g shows that SWCNTs from CoACAC/SiO₂ and CoCl/SiO₂ have intense absorption peaks at 992, 1025 and 1137 nm from (6,5), (7,5), (7,6), and (8,4). SWCNTs grown on CoN/SiO₂ have weak absorption peaks. In contrast, Figure 6-1h shows that SWCNTs grown on sulfur doped catalysts all have strong absorption peaks at 1420 and 818 nm, corresponding to the E₁₁^S and E₂₂^S transitions of (9,8). A few other absorption peaks below 700 nm can be assigned to either

the E_{11}^M transition of metallic (9,6) (1.02 nm) and (10,10) (1.36 nm) or the E_{22}^S transition of semiconducting (6,5). Since the intensity of (6,5) PL peaks in Figure 6-1d-f is low, the absorption peaks below 700 nm in Figure 6-1h are likely to be from those metallic tubes.

Figure 6-1 PL maps and UV-vis-NIR absorption spectra of SDBS-dispersed SWCNTs grown on undoped and sulfur doped Co/SiO₂ catalysts. PL maps: (a) CoACAC/SiO₂, (b) CoCl/SiO₂, (c) CoN/SiO₂, (d) CoACAC/SiO₂/S, (e) CoCl/SiO₂/S, and (f) CoN/SiO₂/S. Some major (*n,m*) species identified on PL maps are marked. Absorption spectra: undoped (g) and sulfur doped (h). The shaded pink indicates the E_{11}^S absorption band and the shaded blue shows the overlapping E_{22}^S and E_{11}^M bands.

Table 6-1 Tabulated values of PL intensities and relative abundances of (n,m) species in SWCNTs produced on the CoACAC/SiO₂/S catalyst.

(n,m) index	Diameter d_t (nm)	Chiral angle θ (°)	E ₁₁ (nm)	E ₂₂ (nm)	PL intensity (counts)	Relative abundance, (%)
(6,5)	0.76	27.00	983	570	537.5	7.7
(7,3)	0.71	17.00	990	510	264.9	3.8
(7,5)	0.83	24.50	1023	642	155.0	2.2
(7,6)	0.90	27.46	1122	646	169.5	2.4
(8,4)	0.84	19.11	1111	578	241.0	3.4
(8,6)	0.97	25.28	1165	714	113.5	1.6
(8,7)	1.03	27.80	1264	726	403.8	5.8
(9,7)	1.10	25.87	1321	790	995.2	14.2
(9,8)	1.17	28.05	1414	822	2836.2	40.5
(10,6)	1.11	21.79	1380	754	535.4	7.7
(10,8)	1.24	26.30	1467	870	277.0	4.0
(10,9)	1.31	28.30	1562	886	469.5	6.7

Table 6-2 Tabulated values of PL intensities and relative abundances of (n,m) species in SWCNTs produced on the CoCl/SiO₂/S catalyst.

(n,m) index	Diameter d_t (nm)	Chiral angle θ (°)	E ₁₁ (nm)	E ₂₂ (nm)	PL intensity (counts)	Relative abundance, (%)
(6,5)	0.76	27.00	982	570	182.4	12.4
(7,3)	0.71	17.00	986	502	131.6	8.9
(7,5)	0.83	24.50	1023	642	96.1	6.5
(7,6)	0.90	27.46	1113	642	72.3	4.9
(8,4)	0.84	19.11	1109	578	75.4	5.1
(8,6)	0.97	25.28	1162	714	49.0	3.3
(8,7)	1.03	27.80	1265	722	59.5	4.0
(9,7)	1.10	25.87	1319	790	106.6	7.2
(9,8)	1.17	28.05	1412	818	478.2	32.7
(10,6)	1.11	21.79	1376	758	63.2	4.3
(10,8)	1.24	26.30	1469	866	36.4	2.5
(10,9)	1.31	28.30	1558	890	119.9	8.2

Table 6-3 Tabulated values of PL intensities and relative abundances of (n,m) species in SWCNTs produced on the CoN/SiO₂/S catalyst.

(n,m) index	Diameter d_t (nm)	Chiral angle θ (°)	E ₁₁ (nm)	E ₂₂ (nm)	PL intensity (counts)	Relative abundance, (%)
(6,5)	0.76	27.00	979	566	228.4	8.8
(7,3)	0.71	17.00	986	506	135.4	5.2
(7,5)	0.83	24.50	1024	642	121.8	4.7
(7,6)	0.90	27.46	1113	642	101.6	3.9
(8,4)	0.84	19.11	1110	578	120.8	4.7
(8,6)	0.97	25.28	1165	714	63.9	2.5
(8,7)	1.03	27.80	1263	726	120.6	4.7
(9,7)	1.10	25.87	1319	790	259.1	10.0
(9,8)	1.17	28.05	1413	818	1020.8	39.5
(10,6)	1.11	21.79	1377	750	143.7	5.6
(10,8)	1.24	26.30	1469	866	81.5	3.1
(10,9)	1.31	28.30	1558	886	189.4	7.3

Figure 6-2 Raman spectra of SWCNTs grown on undoped Co/SiO₂ catalysts (a and c) and

sulfur doped Co/SiO₂ (b and d) under 785 and 514 nm laser excitations, respectively. The regions on the left correspond to RBM peaks, while the regions on the right correspond to D and G bands.

SWCNTs were further characterized by Raman spectroscopy under two excitation lasers (785 and 514 nm) shown in Figure 6-2. The intense RBM peaks and weak D band peaks from carbon deposits grown on CoCl/SiO₂ and CoACAC/SiO₂ suggest that high quality SWCNTs are produced. In contrast, the low intensity RBM peaks and intense D band peaks from carbon deposits grown on CoN/SiO₂ suggest that this catalyst is not active for SWCNT growth. The RBM peaks can be correlated with the (*n,m*) structures of SWCNTs according to the Kataura plot generated by the tight-binding model.¹¹⁸ The diameter of SWCNTs was calculated using the equation $\omega_{\text{RBM}} = 223.5 \text{ cm}^{-1}/d_t + 12.5 \text{ cm}^{-1}$, where ω_{RBM} and d_t are the RBM frequency and the diameter of SWCNTs.¹¹⁹ The RBM peaks in Figure 6-2a and 6-2c at 238 and 267 cm⁻¹ can be assigned to (8,6) and (7,6) according to the empirical Kataura plot,¹¹⁹ suggesting that the undoped catalysts mainly produce SWCNTs with diameters less than 1 nm. In comparison, all sulfur doped Co/SiO₂ catalysts produce SWCNTs with high quality, as indicated by their intense RBM peaks and weak D band peaks (see Figure 6-2b and 6-2d). The major RBM peaks centered around 202 and 213 cm⁻¹ can be ascribed to the (9,8) and (9,7) with diameters around 1.1–1.17 nm. Therefore, Raman results agree with the findings from PL and UV–vis–NIR spectra. Overall, the three spectroscopic techniques show that sulfur doping can shift the (*n,m*) selectivity of Co/SiO₂ catalysts from small diameter tubes near (6,5) to large diameter tubes with a narrow distribution around (9,8).

6.4 Catalyst characterization

Co species deposited on SiO_2 would first be partially reduced in H_2 , and then nucleate into Co nanoparticles to initiate SWCNT growth. The change in (n,m) selectivity shown in Figure 6-1 may be attributed to the changes of Co species caused by sulfur doping. Firstly, elemental analysis of sulfur doped catalysts was conducted. The sulfur content in $\text{CoACAC/SiO}_2/\text{S}$, $\text{CoCl/SiO}_2/\text{S}$, and $\text{CoN/SiO}_2/\text{S}$ was found to be 0.91, 1.17 and 0.83 wt%, respectively, which confirms the existence of sulfur.

Next, H_2 -TPR was employed to study the reducibility of Co species. Figure 6-3 shows that CoACAC/SiO_2 displays a peak around 797 °C, which is ascribed to surface Co silicate.¹³⁶ CoCl/SiO_2 has multiple peaks at 360–800 °C, which may come from the reduction of CoO , CoCl_2 , and surface Co silicate. CoN/SiO_2 possesses a broad peak around 290 °C which can be attributed to Co_3O_4 and CoO . In contrast, all the TPR profiles of the three sulfur doped Co/SiO_2 catalysts have a sharp peak at 493-506 °C, similar to the chiral selective $\text{CoSO}_4/\text{SiO}_2$ catalyst.¹⁶⁹ In addition, the CoO_x peaks of undoped catalysts become significantly smaller after sulfur doping, and new peaks around 800 °C appear on $\text{CoCl/SiO}_2/\text{S}$ and $\text{CoN/SiO}_2/\text{S}$, suggesting the formation Co hydrosilicate or surface Co silicate,¹⁶² while the 797 °C peak of CoACAC/SiO_2 becomes smaller.

Figure 6-3 H₂-TPR profiles of undoped and sulfur doped Co/SiO₂ catalysts and several Co references (CoO, Co₃O₄, CoSiO₃, CoCl₂ and CoSO₄·7H₂O).

Lastly, UV–vis diffuse reflectance spectroscopy was employed to probe the surface chemistry of the catalysts. As shown in Figure 6-4, CoACAC/SiO₂ has two peaks around 570 and 650 nm, suggesting the formation of surface Co silicates.¹⁷⁶ The spectrum of CoCl/SiO₂ shows two broad peaks at 550 and 720 nm, indicating the presence of CoO_x and CoCl₂. The spectrum of CoN/SiO₂ is similar to that of Co₃O₄, having two broad peaks at ~400 and 720 nm, which can be assigned to the transitions of octahedral configured Co³⁺ ions.¹³² In contrast, all the three sulfur doped Co/SiO₂ catalysts have a broad peak around 535 nm similar to that of CoSO₄, implying the existence of Co species bonded to SO₄²⁻.

Figure 6-4 UV-vis diffuse reflectance spectra: (a) Co/SiO₂ catalysts and references (Co₃O₄, CoO and CoSiO₃), (b) sulfur doped Co/SiO₂ catalysts as well as the reference CoCl₂ and CoSO₄.

6.5 Mechanism

Figure 6-5 Schematic illustration of changes in Co species on Co/SiO₂ catalysts caused by sulfur doping.

Doping sulfate ions to metal oxides has created various solid acid catalysts, such as SO₄²⁻/ZrO₂, SO₄²⁻/TiO₂, and SO₄²⁻/Fe₂O₃.^{171,177} Based on characterization of the Co/SiO₂ catalysts, the following mechanism is proposed to explain their (*n,m*) selectivity in SWCNT growth. As shown in Figure 6-5, undoped Co/SiO₂ catalysts contain CoO_x, Co hydrosilicate,

and surface Co silicates,¹⁶² which are evidenced by their H₂-TPR profiles and UV-vis spectra. Surface Co silicates on CoACAC/SiO₂ and CoCl/SiO₂ would be reduced and nucleate into small Co nanoparticles, which are selective to small diameter SWCNTs,¹³⁶ as shown in Figure 6-1. CoO_x on CoN/SiO₂ is reduced to form large Co particles, which are not selective to SWCNTs. Doping sulfur through H₂SO₄ leads to the formation of chelating bidentate SO₄²⁻, where one sulfur atom is linked to one Co atom through two O atoms, a common structure found in sulfate promoted metal oxide catalysts.¹⁷¹ This is supported by the sharp peaks at 493–506 °C in the TPR profiles and the broad peak around 535 nm in the UV-vis spectra. Windle *et al.* showed that adding thiophene or carbon disulfide in gas phase would restrict the growth of Fe particles for selective growth of (9,9).¹⁵⁸ Similarly, it is proposed that the coexistence of sulfur atoms near Co atoms may limit the nucleation of Co and/or form Co–S compounds, which change the selectivity of catalysts to (9,8). As discussed in my previous study,¹⁶⁹ the selectivity toward (9,8) may be due to the close match between carbon caps and the most stable Co particles in their size range and the higher growth rate of high chiral angle tubes.¹⁰⁸ Because active Co nanoparticles would be embedded under or near SiO₂ surface, their size and composition still can't be quantified in TEM. Furthermore, it is proposed that H⁺ ions would react with CoO_x, releasing Co ions to form well dispersed Co hydrosilicate and surface Co silicate on SiO₂, which are more selective to SWCNTs than CoO_x. This is evidenced by the increased SWCNT selectivity of CoN/SiO₂/S.

6.6 (NH₄)₂SO₄ doped Co/SiO₂ catalyst

6.6.1 Doping method

To further verify the proposed mechanism, CoN/SiO₂ was doped using ammonium sulfate ((NH₄)₂SO₄, 0.2 mol/L). The doping method is the same with other sulfur doped catalysts described in 6.1. The resulting sulfur doped catalyst was denoted as CoN/SiO₂/AS. And the subsequent SWCNT growth and purification were described in 6.2.

6.6.2 PL and abundance of (*n,m*) species

The PL map in Figure 6-6 shows that CoN/SiO₂/AS catalyst produces dominantly (6,5) tubes (35.4% in Table 6-4). However, it can still grow (9,8) tubes (11.3% in Table 6-4), which can be attributed to the doping of sulfur. CoN/SiO₂/AS is less selective to (9,8) SWCNTs as compared to CoN/SiO₂/S.

Figure 6-6 PL map of SDBS-dispersed SWCNTs grown on the CoN/SiO₂/AS catalyst.

Table 6-4 Tabulated values of PL intensities and relative abundances of (*n,m*) species in

SWCNTs produced on the CoN/SiO₂/AS catalyst.

(<i>n,m</i>) index	Diameter <i>d_t</i> (nm)	Chiral angle <i>θ</i> (°)	E ₁₁ (nm)	E ₂₂ (nm)	PL intensity (counts)	Relative abundance, (%)
(6,5)	0.76	27.00	991	566	1928.3	35.40%
(7,3)	0.71	17.00	989	502	734.1	13.50%
(7,5)	0.83	24.50	1025	638	408.4	7.50%
(7,6)	0.90	27.46	1127	642	409.7	7.50%
(8,4)	0.84	19.11	1120	574	486.4	8.90%
(8,6)	0.97	25.28	1163	718	138.3	2.50%
(8,7)	1.03	27.80	1269	726	173.7	3.20%
(9,7)	1.10	25.87	1330	790	216.7	4.00%
(9,8)	1.17	28.05	1428	822	613.6	11.30%
(10,6)	1.11	21.79	1377	754	123.1	2.30%
(10,8)	1.24	26.30	1470	866	105.7	1.90%
(10,9)	1.31	28.30	1557	890	107.2	2.00%

6.6.3 Absorption spectra

Figure 6-7 UV–vis-NIR absorption spectra of SDBS-dispersed SWCNTs grown on CoN/SiO₂/AS catalyst.

The strong absorption peaks at 1415 and 810 nm in Figure 6-7 correspond to the E₁₁^S and E₂₂^S transition of (9,8). The peak around 983 nm from the E₁₁^S transition of (6,5) is much more intense compared to that of SWCNTs grown from CoN/SiO₂/S, indicating more (6,5) tubes are

grown on CoN/SiO₂/AS. Because the absorption coefficient of (9,8) is higher than that of (6,5), the absorption peaks from (9,8) look larger than that of (6,5). A few absorption peaks below 700 nm can be assigned to either the E^M₁₁ transition of metallic (9,6) and (10,10) or the E^S₂₂ transition of semiconducting (6,5).

6.6.4 H₂-TPR and UV-vis diffuse reflectance spectroscopy

The TPR profile of CoN/SiO₂/AS has an intense peak around 519 °C, which is similar to that of CoN/SiO₂/S shown in Figure 6-3c. However, the large peak around 800 °C of CoN/SiO₂/S shown in Figure 6-3c is very weak in Figure 6-8a. The CoN/SiO₂/AS has a broad peak from 425–800 °C, suggesting the existence of several Co species, including unreacted CoO_x, Co hydrosilicate, and surface Co silicate. Figure 6-8b shows that the UV-vis spectrum of CoN/SiO₂/AS catalyst has a broad peak around 535 nm similar to that of CoN/SiO₂/S, suggesting the existence of Co species bonded to SO₄²⁻.

Figure 6-8 H₂-TPR profile (a) and UV-vis diffuse reflectance spectrum (b) of CoN/SiO₂/AS catalyst.

Overall, $(\text{NH}_4)_2\text{SO}_4$ doped CoN/SiO₂ catalyst can grow (9,8) nanotubes due to the sulfur doping. However, it is less selective to (9,8) nanotubes as compared to CoN/SiO₂/S because NH_4^+ is less reactive than H^+ . This provides strong credibility to the proposed mechanism.

6.7 Conclusion

In conclusion, three types of Co/SiO₂ catalysts, which are either inactive for the SWCNT growth or only selective to small diameter nanotubes, can be converted into chirally selective catalysts to grow SWCNTs enriched with large diameter (9,8) tubes by doping catalysts with sulfur. H^+ ions may react with CoO_x to form well dispersed Co hydrosilicate and surface Co silicate on SiO₂, which increases the selectivity to SWCNTs. Sulfur atoms near Co atoms believed to assist the formation of Co nanoparticles which are selective to (9,8) tubes.

Chapter 7 Application of (9,8) SWCNTs in Field Effect Transistors

Electronic properties of SWCNTs are important in their practical applications, such as SWCNT based field effect transistors (FETs). A key property of SWCNT-FET devices is the ratio between the current through the transistor in its “on” state and the leakage current in the “off” state (the on/off ratio). Mobility is another important property of SWCNT-FET devices, which describes the motion of an electron or hole influenced by an applied electric field. High on/off ratio and mobility are desired for the good performance of FET devices. Compared to larger diameter tubes, smaller diameter tubes usually have lower mobilities and are more prone to Schottky barrier effects.¹⁷⁸ Therefore, larger diameter tubes are more desired to construct high performance FETs. In this chapter, the electronic performance of (9,8) SWCNTs from the previous synthesis process were investigated.

7.1 Fabrication of SWCNT thin film FETs

As shown in Figure 7-1, SWCNT thin film FETs consist of two Au electrodes (100 nm thickness) patterned on top of the SiO₂/Si substrate. The device channels are ~ 75 μm long and ~ 100 μm wide. SiO₂ of 300 nm thickness serves as gate dielectric. SDBS dispersed SWCNTs were dropped across device channels to form active layers. About 25 μL of SWCNT suspension was dropped on the device, and the device was then dried at room temperature and rinsed by deionized water. This procedure was repeated until the density of SWCNTs is high enough to yield a drain current ($> 10^{-8}$ A) between two electrodes under a bias voltage (V_d) of 2 V at zero gate voltage.

Figure 7-1 A schematic drawing of the device composed of SWCNT thin films bridging a pair of Au source and drain electrodes.

Thirty five FETs were fabricated and tested for each SWCNT samples. All electrical measurements of SWCNT thin film FETs were carried out in ambient conditions using a Keithley semiconductor parameter analyzer (4200-SCS).

7.2 Electronic performances of SWCNT thin film FETs

A motivation to control the (n,m) structure of larger diameter nanotubes is their potential improvement in electronic performances. To compare electronic characteristics of SWCNTs with different diameters, SWCNT produced from Co–TUD-1 and (6,5) nanotubes from Co-Mo catalysts were both used in device fabrication. (6,5) nanotubes were produced using Co-Mo catalysts supported on silica particles. The catalyst preparation and SWCNT characterization details can be found in the previous publication.¹²⁴ PL map and absorption spectrum of surfactant dispersed (6,5) nanotubes used in this study are shown in Figure 7-2.

Figure 7-2 (a) PL map and (b) UV-vis-NIR spectrum of (6,5) SWCNTs produced on Co-Mo catalysts.

Figure 7-3 shows typical AFM images of SWCNT networks obtained in FET device channels. SWCNT networks consist of both individual nanotubes and small nanotubes bundles. The bundles could be formed when SWCNT suspensions were dried on the SiO₂ surface. Similar amount of SWCNT suspensions were dropped on each device. (9,8) enriched SWCNTs formed networks with the nanotube density of ~ 21 tubes/ μm^2 and the average length of ~ 0.37 μm . In comparison, (6,5) enriched SWCNTs formed similar networks with the nanotube density of ~ 20 tubes/ μm^2 and the average length of ~ 0.41 μm .

Figure 7-3 Typical AFM images of SWCNT networks in FET device channels. (a) (9,8) enriched SWCNTs produced on Co-TUD-1, (b) (6,5) enriched SWCNTs produced on Co-Mo

catalysts.

Figure 7-4 Current–voltage characteristics (I_d – V_d) of devices at different V_g from -100 to 100 V with the step of 10 V from bottom to top. (a) A typical device fabricated by (9,8) nanotubes from Co–TUD-1 catalysts. (b) A typical device fabricated by (6,5) nanotubes from Co-Mo catalysts.

Typical drain current (I_d) – drain voltage (V_d) curves of FETs fabricated from (9,8) and (6,5) nanotubes are presented in Figure 7-4. Gate voltage (V_g) varied from -100 to 100 V with the step of 10 V from bottom to top. The high gate bias voltage was required because the thick SiO_2 (300 nm) layers were used as gate dielectric.

Transfer characteristics (typical I_d – V_g curves) of FETs at $V_d = 2$ V are shown in Figure 7-5(a). Percentage histograms of FET I_{on} – I_{off} ratios from two types of SWCNTs are also showed in Figure 7-5(b). Percentage histograms of FET device mobilities are presented in Figure 7-6. The average electronic characteristics of semiconducting FETs (with $I_{on}/I_{off} > 10^3$) from two types of nanotubes were listed in Table 7-1.

Figure 7-5 (a) Typical drain current–gate voltage curves of the thin film FETs from (9,8) and (6,5) SWCNTs. (b) Percentage histogram of FET on-off ratios from the two types of SWCNTs.

Figure 7-6 Percentage histogram of FET device mobilities from (9,8) and (6,5) SWCNTs.

Figure 7-5, Figure 7-6 and Table 7-1 demonstrate that semiconducting (9,8) devices have a higher average mobility than that of (6,5) devices (0.903 vs. $0.135 \text{ cm}^2/(\text{V}\cdot\text{s})$). Smaller diameter SWCNTs are known to have poorer contacts and lower carrier mobilities.¹⁷⁹ Moreover, compared under similar nanotube densities and length distributions, a higher percentage of (9,8) devices have semiconducting characteristics ($I_{on}/I_{off} > 10^3$) compared to (6,5)

devices. (9,8) nanotubes from this synthesis process demonstrate superior FET device performances.

Table 7-1 Average electronic characteristics of semiconducting FETs (with $I_{on}/I_{off} > 10^3$) fabricated with (9,8) and (6,5) nanotubes.

Sample	I_{off} (A)	I_{on} (A)	Threshold V forward (V)	Threshold V reverse (V)	Hysteresis ΔV (V)	Effective mobility ($\text{cm}^2/(\text{V s})$)
(9,8)	6.42×10^{-10}	2.42×10^{-6}	61.1	-50.2	111.3	0.903
(6,5)	2.37×10^{-10}	4.99×10^{-7}	44.8	-76.0	120.8	0.135

7.3 Conclusion

SWCNT thin film field effect transistors were fabricated using (9,8) nanotubes from this synthesis process, which have higher average device mobility and a higher fraction of semiconducting devices than those using (6,5) nanotubes. However, this application is only preliminary. In future, the as-synthesized (9,8) SWCNTs will be further enriched for fabrication of FET devices with better electronic performance.

Chapter 8 Summary and Future Research

SWCNTs with a defined chirality are of fundamental importance to nanoscience and technology. Although single chirality nanotubes can be separated from SWCNT mixtures through different techniques, the yield, scalability, and cost of such separation, as well as the properties (length and functionality) of resulting SWCNTs, depends on the initial chirality distribution determined during SWCNT growth. Countless catalysts have been investigated for SWCNT synthesis over the past two decades, but only a few of them show certain selectivity towards small diameter nanotubes. Synthesis of specific monochiral SWCNT is clearly complicated and still remains a challenge at present. Work in this thesis attempted to make progress on chirally selective growth of SWCNTs on novel catalysts.

First, Co-TUD-1 catalyst was developed by hydrothermal method for SWCNT synthesis. The chirality distribution was analyzed by PL spectroscopy, UV-vis-NIR absorption spectroscopy, and Raman spectroscopy with multilaser excitation. When the catalyst was reduced in H_2 at an optimized temperature, 59.1% of semiconducting nanotubes were (9,8) nanotubes ($d = 1.17$ nm). A mechanism was proposed to explain the selectivity toward (9,8) nanotubes: Co species on the mesoporous TUD-1 can nucleate in two steps. First, Co^{2+} ions are partially reduced in H_2 during prereduction, but they are still dispersed isolatedly on the large surface of TUD-1. Second, Co atoms aggregate quickly into clusters under CO to initiate SWCNT growth. Co ions are incorporated into the amorphous silica walls of TUD-1, and the large surface area of TUD-1 and the strong metal-support interaction are sufficient in stabilizing these clusters with a narrow diameter distribution at around 1.2 nm, responsible for the growth of (9,8) nanotubes.

Next, a novel sulfate-promoted $\text{CoSO}_4/\text{SiO}_2$ catalyst was prepared by the incipient wetness impregnation method, which selectively grew (9,8) nanotubes with 51.7% abundance among semiconducting tubes, and 33.5% over all tube species. After reduction in H_2 at 540 °C, the catalyst containing 1 wt% Co had a carbon yield of 3.8 wt%, in which more than 90% was SWCNT. $\text{CoSO}_4/\text{SiO}_2$ catalyst is unique with a narrow Co reduction window under H_2 centered at 470 °C, which can be attributed to the reduction of highly dispersed CoSO_4 . XAS results suggested the formation of Co particles with average size of 1.23 nm which matches with the diameter of (9,8) tubes. Density functional theory study indicated that the diameter of structurally stable pure Co particles is scattered, matching with the most abundant chiral tubes, such as (6,5) and (9,8). Moreover, the formation of such large Co particles on the $\text{CoSO}_4/\text{SiO}_2$ catalyst depends on sulfur in the catalyst. XAS results showed that sulfur content in the catalyst changes after catalyst reduction at different conditions, which correlates with the change in (n,m) selectivity observed. The potential roles of sulfur were proposed to be limiting the aggregation of Co atoms and/or forming Co–S compounds, which enables the chiral selectivity towards (9,8) nanotubes.

Then, to further investigate the $\text{CoSO}_4/\text{SiO}_2$ catalyst and its (n,m) selectivity, the catalyst was calcined at different temperatures and then applied into the SWCNT growth. The chiral selectivity of the catalyst is found correlated with the catalyst calcination temperatures. When the catalyst is calcined in air at 400 °C, it yields 50.52% of (9,8) nanotubes among all semiconducting SWCNTs. The selectivity would shift to small diameter nanotubes when the catalyst is calcined above 700 °C. The catalyst calcination results in different Co species on SiO_2 surface for SWCNT growth. At low calcination temperature (≤ 400 °C), Co ions adsorb

on SiO₂ surface through electrostatic interaction and/or form strongly bonded Co to the SiO₂ surface through the oxolation reaction. Sulfur exists as chelating bidentate SO₄²⁻ on the surface with Co atoms. The coexistence of sulfur atoms near Co atoms may limit the aggregation of Co atoms or form various Co–S compounds, which may lead to the specific chiral selectivity towards the (9,8) nanotubes. With the increase of calcination temperature, some sulfur atoms are removed from the catalyst, leading to the formation of surface Co oxides and Co silicates which are more selective to the small diameter SWCNTs.

Since the sulfur is found to be important for selective synthesis of large diameter (9,8) SWCNTs with narrow (*n,m*) distribution, a sulfur doping method was developed to convert those non-selective catalysts to chirally selective catalysts. Three regular Co/SiO₂ catalysts, which are either inactive for the SWCNT growth or only selective to small diameter nanotubes, can be converted into chirally selective catalysts to grow SWCNTs enriched with large diameter (9,8) nanotubes by sulfur doping. H⁺ ions help to change CoO_x into well dispersed surface Co species, which increases the selectivity to SWCNTs. Sulfur atoms near Co atoms are believed to assist the formation of Co nanoparticles which are selective to (9,8) nanotubes.

Last, SWCNT thin film FETs were fabricated using (9,8) nanotubes from the synthesis process, which demonstrated better electronic performances than those using (6,5) nanotubes.

As for future work on the chirally selective growth of SWCNTs, the following studies are proposed based on the work in this thesis.

(1) Increase of SWCNT yield

Large diameter (9,8) SWCNTs show promising applications in electronics and optoelectronics, however, their large-scale applications are only possible when they are

available in large amounts. Currently, the yield of (9,8) SWCNT is not very high. Therefore, yield increase of (9,8) SWCNT is a primary task. Several ways can be considered. First, increase the interaction between the metal Co and silica supports. Second, increase the Co loading. Third, add additives, such as sulfur during the SWCNT growth.

(2) Mechanism exploration

In this thesis, comprehensive techniques were conducted to characterize catalysts and SWCNTs. Theoretical simulation was also carried out to relate the size of Co clusters with the diameter of the (9,8) SWCNT. Those results evidenced the growth of (9,8) SWCNT is dependent on the presence of sulfur. But how does the sulfur influence Co clusters (size, morphology, composition, melting point and crystal structures) to control the chiral selectivity during the SWCNT growth? How does the chemical state of Co and sulfur change during the SWCNT growth? Does the presence of sulfur affect the carbon solubility? Does any carbide form during the SWCNT growth? Therefore, in-situ XPS or in-situ XAS at Co-edge and S-edge should be further conducted to disclose those mysteries. The exploration of mechanism can also offer new methods to improve the catalysts and the (9,8) SWCNT yield.

(3) Metal sulfate and sulfide catalyst

$\text{CoSO}_4/\text{SiO}_2$ catalyst was found selective for (9,8) SWCNT growth, and since nickel and iron are neighbors of cobalt in the periodic table of elements, nickel sulfate or iron sulfate supported on SiO_2 may behave similarly to $\text{CoSO}_4/\text{SiO}_2$ catalyst in the SWCNT synthesis. On the other hand, Co sulfide may be one of the reasons for the (9,8) selectivity. It is possible that Co sulfide well dispersed on catalyst supports can also serve as a unique catalyst for chirality control.

In all, this study offered efficient methods to prepare catalysts to achieve a unique chiral selectivity. Those catalysts show good selectivity towards (9,8) SWCNTs, but there are some hurdles needed to be crossed for the commercial synthesis. First, multiple batches of SWCNT synthesis by recycling catalysts is not easy so far, because cobalt in the catalysts have been reduced and aggregated after the SWCNT growth. Multi-use of these catalysts would result in low selectivity to SWCNTs. Second, carbon nanotubes are usually embedded in the pore of catalysts after growth. SWCNTs are obtained by removal of catalysts in NaOH solution especially for the Co-TUD-1 catalyst. However, considering the easier preparation and lower cost, the $\text{CoSO}_4/\text{SiO}_2$ catalyst will be further investigated to scale up of the SWCNT production. And since the (9,8) nanotubes exhibit interesting electronic properties, I am optimistic that a lot of applications can be explored using such unique samples.

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Appendix

List of related publications

Chapter 3

Hong Wang, Bo Wang, Xian-Yang Quek, Li Wei, Jianwen Zhao, Lain-Jong Li, Mary B. Chan-Park, Yanhui Yang, and Yuan Chen; *Selective Synthesis of (9,8) Single Walled Carbon Nanotubes on Cobalt Incorporated TUD-1 Catalysts*, Journal of the American Chemical Society, 2010, 132, 16747–16749

Chapter 4

Hong Wang, Li Wei, Fang Ren, Qiang Wang, Lisa D. Pfefferle, Gary L. Haller, Yuan Chen, *Chiral-selective CoSO₄/SiO₂ Catalyst for (9,8) Single Walled Carbon Nanotubes Growth*, ACS Nano, 2013, 7, 614-626

Chapter 5

Hong Wang, Fang Ren, Changchang Liu, Rongmei Si, Dingshan Yu, Lisa D. Pfefferle, Gary L. Haller, Yuan Chen, *CoSO₄/SiO₂ Catalyst for Selective Synthesis of (9,8) Single Walled Carbon Nanotubes: Effect of Catalyst Calcination*, Journal of Catalysis, 2013, 300, 91-101

Chapter 6

Hong Wang, Kunli GOH, Rui Xue, Dingshan Yu, Wenchao Jiang, Raymond Lau, Yuan Chen, *Sulfur Doped Co/SiO₂ Catalysts for Chirally Selective Synthesis of Single Walled Carbon Nanotubes*, Chemical Communications, 2013, 49, 2031-2033

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Wang, Qiang, **Wang, Hong**, Wei, Li, Yang, Shuo-Wang, Chen, Yuan; *Reactive Sites for Chirally Selective Growth of Single Walled Carbon Nanotubes: A DFT Study of $Ni_{55}-C_n$ Complexes*, Journal of Physical Chemistry A, 2012, 116, 11709–11717

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