Chirality selective growth of single-walled carbon nanotube in chemical vapor deposition

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Chirality Selective Growth of Single-Walled Carbon Nanotube in Chemical Vapor Deposition

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Summary

Chirality Selective Growth of Single-Walled Carbon Nanotube in Chemical Vapor Deposition

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Nanyang Technological University

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This thesis focuses on the chirality selective growth of Single-Walled Carbon Nanotube (SWCNT) in Chemical Vapor Deposition (CVD). SWCNT possesses exceptional properties which are (n,m) structure dependent. Preferential growth of SWCNTs with specific (n,m) structures is desired for many potential applications. SWCNT chirality may be controlled by the dynamic interaction between catalytic metal particles and carbon networks formed on the metal particle surface. Therefore, three factors, which could influence the SWCNT chirality in CVD growth, are explored: (1) carbon precursor, (2) pressure, and (3) catalyst substrate. Several techniques are employed to characterize catalysts (e.g. X-ray diffraction, N_2 physisorption, ultraviolet-visible diffuse reflectance spectroscopy, and temperature programmed reduction) and SWCNTs (e.g. Raman spectroscopy, photoluminescence spectroscopy, ultraviolet-visible-near infrared absorption spectroscopy, thermogravimetric analysis) in order to understand the chirality selectivity of SWCNTs.

Four different carbon precursors (CO , C_2H_5OH , CH_3OH and C_2H_2) are used to grow SWCNTs on Co-Mo bimetallic catalysts supported on SiO_2 . Pressure is found to be a key factor for obtaining narrowly (n,m) distributed SWCNTs. The (n,m) abundance evaluation based on an

electron-phonon interaction model reveals that the (n,m) selectivity can be shifted by using different carbon precursors. The reconstruction of E_{11}^S SWCNT near infrared absorption spectra confirms that the dominant (n,m) SWCNTs produced by different carbon precursors are all at the high chiral angle region. (7,6), (7,5) and (6,5) can be selectively enriched by tuning the CO pressure from 2 to 18 bar. A mechanism study indicates that the (n,m) selectivity is controlled by CO partial pressure other than the total pressure. Different catalyst supports may perturb the interaction between Co and Mo species leading to the formation of diverse metal clusters. Co-Mo supported on SiO_2 and Co-Mo supported on MgO have the ability to grow SWCNTs with similarly narrow (n,m) distribution. Co-Mo supported on TiO_2 and Co-Mo supported on Al_2O_3 produce MWCNTs (Multi-Walled Carbon Nanotubes) due to their interruptions of the synergistic effect between Co and Mo. Monometallic Co incorporated TUD-1 (Co-TUD-1) is synthesized and applied for SWCNT growth for the first time. A mixture of MWCNTs and SWCNTs are produced using Co-TUD-1. However, further improvement of Co-TUD-1 synthesis is necessary. Overall, towards a better control of SWCNT (n,m) structures, work in this thesis successfully makes two achievements: (1) produce narrowly (n,m) distributed SWCNTs, and (2) shift the (n,m) distribution by different carbon precursors, pressures and catalyst substrates.

List of Abbreviations

BET	Brunauer-Emmett-Teller
BJH	Barret-Joyner-Halenda
CNT	Carbon Nanotube
CVD	Chemical Vapor Deposition
DOC	Sodium Deoxycholate
DTG	Differential Thermogravimetric
DWCNT	Double-Walled Carbon Nanotube
HiPCo	High Pressure Co
IGA	InGaAs
MCM-41	Mobil Composition of Matter 41
MD	Molecular Dynamic
MWCNT	Multi-Walled Carbon Nanotube
OD	Optical Density
PL(E)	Photoluminescence (Excitation)
RBM	Radial Breathing Mode
RRS	Resonance Raman Spectra / Spectroscopy
SC	Sodium Cholate
SDBS	Sodium Dodecyl Benzene Sulfonate
SDS	Sodium Dodecyl Sulfate
SEM	Scanning Electron Microscope
STM	Scanning Tunneling Microscope

SWCNT	Single-Walled Carbon Nanotube
TCD	Thermal Conductivity Detector
TEA	Triethanolamine
TEAOH	Tetraethyl Ammonium Hydroxide
TEM	Transmission Electron Microscope
TEOS	Tetraethyl Orthosilicate
TGA	Thermogravimetric Analysis
TPR	Temperature Programmed Reduction
TUD-1	Technische Universiteit Delft 1
UV-vis-NIR	Ultraviolet-visible-Near infrared
VHS	Van Hove Singularity
VLS	Vapor-Liquid-Solid
XRD	X-Ray Diffraction

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Chapter 1

Introduction

The work of this thesis focuses on a nanometer scale material, Single-Walled Carbon Nanotube (SWCNT). This thesis studies how to control the chiral structure of SWCNTs during their growth in Chemical Vapor Deposition (CVD).

The term “nanotechnology” was brought to light by physicist Richard Feynman[1] in 1959 and promoted by Dr. K Eric Drexler[2] in 1986. Since then, especially following the invention of scanning tunneling microscope (STM), nanotechnology research has received substantial attention, and developed quickly. Many nanoscale materials have been successfully synthesized, and they exhibit exceptional properties compared to their macro-scale states.[3-5] These properties make them promising for many applications which are considered to be capable of remaking the world.[2] However, these applications will not be realized until the structure of nanoscale materials can be well controlled. Furthermore, to realize the commercialization of nanomaterials, several obstacles have to be resolved, such as scalability of production methods, efficient assembling of individual nanomaterials into complex devices, etc. This thesis focuses on the chiral structure control of SWCNTs during their synthesis in CVD.

1.1 SWCNT

Carbon nanotube (CNT) was discovered by Iijima in 1991.[5] CNT is considered to be a cylinder rolled by graphene sheets. It can be categorized into SWCNT formed by one single graphene sheet and multi-walled carbon nanotube (MWCNT) formed by multiple graphene sheets,

illustrated in Figure 1-1. SWCNT can be as long as centimeters,[6] but with only ~1 nanometer in diameter, which yields an extremely high length/diameter aspect ratio exceeding 10^7 .

Figure 1-1 Schematic illustration of SWCNT[7]

1.1.1 SWCNT structures

SWCNT exhibits a unique chiral structure which is described by a chiral index (n,m) . As illustrated in Figure 1-2, on a graphene sheet, any two carbon atoms can be connected (dotted line). A SWCNT forms through rolling up the graphene sheet along this dotted line. If one atom is considered as origin (O), the other atom is chosen arbitrarily and marked by a index (n,m) (n and m are integers). Each (n,m) corresponds to one particular SWCNT structure with a certain diameter (d) and chiral angle (θ) ($0^\circ < |\theta| < 30^\circ$). SWCNT diameter can be determined by the (n,m) index using $d = 0.0783\sqrt{(n^2 + m^2 + nm)}$ nm. Chiral angle (θ) can also be calculated by the (n,m) index using equation $\theta = \tan^{-1}(\sqrt{3}m/(2n + m))$. Figure 1-2 also shows two families of special SWCNTs with $(n,0)$ and (m,m) chiral indices, namely zigzag ($\theta = 0^\circ$) and armchair ($\theta = 30^\circ$) SWCNTs, respectively. The total number of possible (n,m) SWCNT chiral structures is more than 200 since a stable SWCNT can reach more than 2 nm in diameter.[8] Because the physical and chemical properties of SWCNT are sensitively dependent on its (n,m) structure,[9] the chiral structure diversity brings significant challenges to SWCNT applications.

Figure 1-2 Schematic representation of zigzag, armchair and chiral SWCNTs (the schematic illustrations of SWCNT are adapted from [10])

1.1.2 SWCNT properties

SWCNT possesses a well-defined one-dimensional nanostructure with a very high length/diameter aspect ratio. This structural perfection provides SWCNT many extraordinary properties. The electronic properties of SWCNT are chirality dependent. A SWCNT can be either metallic if its chiral index (n,m) meets $n - m = 3l$ (l equals to 0 or other integers) or semiconducting if $n - m \neq 3l$. Therefore, by random selection, SWCNT should have a 1:2 distribution between metallic and semiconducting tubes.[11] However, recent experiments and calculations suggested that the possibility of forming high chiral angle tubes is higher than others.[12-14] Metallic SWCNT is an excellent conductor[15] with an extremely high current density up to $4 \times 10^9 \text{ A/cm}^2$ and a carrier mobility of $10,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. [16] These properties are originated from the “ballistic conductance” due to the weak acoustic phonon scattering in this one-dimensional metallic SWCNT.[17] In contrast, semiconducting SWCNT possesses varied

band gaps ranging between 0.4-0.7 eV, and the band gap is inversely proportional to its diameter.[18] This property diversity among different chiral SWCNTs hinders many potential electronic applications, where either pure metallic or semiconducting SWCNTs with particular band gaps are desired. Meanwhile, the current synthesis has yet been capable of selectively producing SWCNTs with a single chiral structure. Therefore, synthesis of SWCNTs with controlled chiral structures is desired. In addition, SWCNT has excellent thermal and mechanical properties. Its thermal conductivity is extremely high along its axis (400-5800 W/m · K). The Young's modulus and tensile strength of SWCNT can be as high as ~1 TPa and ~20 GPa respectively, which exceed those of stainless steel in a few folds.

1.1.3 SWCNT applications

SWCNT is promising for many applications due to its extraordinary electronic, thermal and mechanical properties. Intensive research efforts have been invested towards these applications. Some of them are listed in Table 1-1.

Table 1-1 Potential SWCNT applications in a variety of industrial fields

Electronics	Energy	Bio-applications
Field effect transistors[19]	Super capacitors[20]	Cell and tissue imaging[21]
EMI shielding[22]	Solar cell materials[23]	Drug delivery[24]
Thin film transistors[25]	Mechanics	
Memory devices[26]	Polymer composite[27]	
Sensors[28]	Probe tips[29]	
Field emission displays[30]	Membrane filters[31]	

Among listed applications in Table 1-1, one important application is to apply SWCNTs as the block materials for next generation nanoscale electronics. However, the realization of this application is still challenged by (1) large scale production of SWCNT with an affordable cost, and (2) availability of high purity SWCNTs with specific (n,m) structure.

1.2 SWCNT synthesis

Several techniques have been developed to synthesize SWCNTs including arc discharge, laser ablation and CVD.[32-34] Arc discharge can generate high temperature between two carbon electrodes so that solid carbon electrodes can be vaporized and form SWCNTs by carbon vapor condensation. Laser ablation has a similar mechanism while a laser is used to vaporize carbon, and gaseous carbon atoms further condense into SWCNTs. High quality SWCNTs have been produced by laser ablation using a Co/Ni contained graphite composite[35] and also by arc discharge using a Y-Ni catalyst.[36] However, it is difficult to control the SWCNT structures (diameter and chirality) during the synthesis by these two techniques. In addition, arc discharge and laser ablation only can produce powdered SWCNT samples. It is challenging to achieve controlled synthesis on planar substrates by these methods. These drawbacks bring significant challenges to the SWCNT purification, manipulation, and assembling for building nanotube-device architectures.[37]

In contrast, CVD provides a more controllable route to produce high quality SWCNTs than arc discharge and laser ablation. CVD provides three advantages: (1) the morphology and structure of SWCNTs can be controlled; (2) it is feasible to scale up to industrial scale SWCNT production; (3)

it is able to grow ordered SWCNT structures (e.g. vertically aligned SWCNT forest,[38] crossed SWCNT architecture[39]) on planar substrates.

Figure 1-3 Schematic representation of the CVD system used in this thesis work

In general, CVD involves the deposition of carbon precursors on catalytic metal particles supported on various substrates. Figure 1-3 illustrates the lab scale CVD system used in this thesis work. The basic principle of CVD is to decompose carbon precursors, such as carbon monoxide,[40, 41] methane,[42] ethanol,[34] and other hydrocarbons, under a high reaction temperature. The decomposed carbon radicals then form SWCNTs on catalytic metal particles. The SWCNT growth mechanism in CVD is discussed in Section 1.4. Tube reactor, furnace and mass flow controllers are the main components for a CVD system. Tube reactor must be able to stand up to 1000 °C which is necessary for decomposing carbon precursors. Mass flow controllers control the variable gas flow rates and pressures in the reactor. A number of parameters, such as temperature, pressure, gas flow rate, reaction time, catalyst and carbon precursors, are working together to achieve an optimized synthesis condition leading to a good selectivity to SWCNTs over other carbon impurities.

1.3 Catalysts for SWCNT synthesis

Catalyst plays a crucial role in SWCNT synthesis. Catalyst contains nanoscale particles serving as seeds for SWCNT growth. Different transition metals, such as Co, Fe, Ni, Mo and their alloys have been used to construct catalysts for SWCNT growth. More recently, precious metals, such as Au,[43] Pt,[44] Ag,[45] even Si nanoparticles[46, 47] have been used for SWCNT growth. In general, transition metals are more efficient to catalyze carbon precursor decomposition. Since the reaction temperature for SWCNT growth in CVD is high, small metal particles (<1 nm) are actively migrating to form larger particles (>5~10 nm), and large metal particles are not selective for SWCNT growth. Therefore, substrates must be used to disperse and stabilize these small metal particles.

Two types of substrates are widely used in catalysts for SWCNT growth, namely structural and planar substrates. A structural substrate usually possesses several properties: (1) high thermal stability, which allows a substrate to stand high reaction temperatures necessary for decomposing carbon precursors; (2) a large surface area, which makes metal particles well dispersed with high loading; (3) simplicity of dissolving in acid or alkaline solutions, so that SWCNTs can be easily removed from substrates if necessary; (4) strong “metal-support interaction”,[48] which is expected to favor the SWCNT growth by limiting the sintering of metal particles. Most structural substrates possess internal structures (e.g. cylindrical or spherical pores) so that a large surface area can be obtained. High surface area porous SiO_2 [32], Al_2O_3 [49] and MgO [50] are widely used structural substrates.

Several approaches have been explored to load metal species on structural substrates for SWCNT growth such as: impregnation,[51] incorporation,[52] combustion,[53] and sol-gel process.[54] Impregnation is a process of depositing metallic ions on the surface of structural substrates by immersing substrates into metallic ion aqueous (or organic solvents) solutions. After drying and calcination, metal oxides form on the surface of the substrate. Before SWCNT growth, metal oxides need to be reduced into metal particles. It is noteworthy that a substrate itself may not be sufficient to stabilize the supported metal particles. Bimetallic composites may be employed to assist the stabilization of metal particles. For example, Co-Mo catalyst uses Mo oxides to stabilize Co nanoparticles.[55] Incorporation, also called co-precipitation, uses one type of metallic ions to substitute the other type of metallic ions originating from the substrate itself (e.g. Si ions of silica substrate, Al ions of Al_2O_3 substrate). The substitution process takes place simultaneously with the substrate structure formation. A catalyst synthesized by incorporation can be viewed as a solid solution of metal oxide and substrate which has a well defined structure.[56] An example is the Co incorporated MCM-41 (Mobil Composition of Matter 41), in which Co ions replace some Si ions in the mesoporous MCM-41.[57] Prereduction is also necessary to activate metal particles for SWCNT growth. Moreover, the incorporated metal oxide is relatively more stable in reduction compared to impregnated catalysts. Combustion is an accelerated decomposition and oxidization process for synthesizing catalysts. Various metal nitrites (Mg, Al, Fe, Co, Ni, Mo) can be heated to their combustion points resulting in fine metal oxide particles after cooling.[53] Sol-gel process can uniformly disperse metallic ions in a gel-like porous substrate (e.g. Al_2O_3).[54] The gel needs to be dried under supercritical ethanol or carbon

dioxide, and calcined to form catalysts with a large surface area. Among these catalyst preparation methods, impregnation is relatively simple, and has been widely used.[51, 55, 58] Even though incorporation is a more tedious process, it is also very popular. Because catalysts prepared by incorporation result in very stable metal particles supported on substrates, leading to a high selectivity towards SWCNTs [41, 57, 59] with a narrow (n,m) distribution.[60]

The other family of catalysts for SWCNT growth is metal particles supported on planar substrates. Unlike their structural rivals, planar substrates do not possess a large surface area. Therefore, the loading of metal particles on planar substrates is low. However, this type of catalyst possesses its unique advantage in some applications such as SWCNT based electronic device fabrication,[61] SWCNT alignment (either vertically[62] or horizontally[63]), patterning,[64] and even SWCNT structure control.[65] SiO_2/Si wafer, quartz, sapphire and many others have been utilized as catalyst substrates. There are two challenges for catalyst preparation on a planar substrate. Firstly, metal particles supported on planar surfaces should be small enough for SWCNT growth. Secondly, metal particles have to be dispersed uniformly on the surface for preventing them from severe aggregation during SWCNT growth. To overcome such challenges, various approaches have been applied such as dip-casting,[66] spin-coating,[67] and sputtering.[68] Through these methods, metallic thin films or discrete metal particles can be deposited on planar substrates. After calcination and reduction, uniformly distributed metal particles can be obtained for SWCNT growth.

1.4 CNT growth mechanism in CVD

A thorough understanding of CNT growth mechanism in CVD is crucial for the synthesis and application of CNTs. Although CVD has been intensively investigated for CNT growth, the growth mechanism is still poorly understood.

Vapor-liquid-solid (VLS) model[69] is often used to explain the CNT growth. In this theory, carbon precursors are decomposed on the surface of catalytic metal particles. The resulting supersaturated liquid metal precipitates carbon atoms continuously in the form of faceted cylinders.[70] The catalytic metal particles are considered to be liquid and serve as (1) a catalyst for decomposing carbon precursors, (2) a solvent to dissolve atomic carbon, and (3) a template for the nucleation and growth of CNT.[71] Furthermore, Hofmann et al. proposed a four-step CNT growth process (Figure 1-4) based on the VLS model: (1) adsorption of the gas precursor molecules on the catalyst surface, (2) dissociation of precursor molecules, (3) diffusion of precursor species in or on the catalyst particle, and (4) nucleation and incorporation of carbon into a growing structure.[72] VLS model was supported by many experimental results. Homma et al. utilized Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) to characterize iron and cobalt catalysts applied for CNT growth in CVD.[73] Harutyunyan and Tokune conducted similar studies on iron and cobalt nanoparticles during SWCNT growth in CVD by Raman spectroscopy, SEM and calorimetric measurements.[74-76] Solid-liquid and solid-liquid-solid phase transitions of these nanoparticles were observed during SWCNT growth confirming the liquid state of metal particles. It is also believed that the diffusion of carbon

through the particles can reduce the melting temperature of metal significantly. Hence metal particles can be liquefied at a relatively low temperature.

Figure 1-4 Schematic of CNT growth process: (1) precursor adsorption, (2) dissociation, (3) carbon transport, and (4) carbon incorporation.[72]

VLS model provides a good explanation for CNT growth. However, many issues are still controversial: (1) are metal particles always liquid? (2) are metal particles really metallic or carbide? (3) can carbon atoms diffuse into the particle or only on its surface? Many efforts from both experimental and theoretical approaches have been made to answer these questions.

Sophisticated atomic *in-situ* observation using TEM on metal particles during nanofiber and CNT growth in CVD was realized recently. These direct observations revealed that the particles were actually crystalline other than liquid during CNT growth in CVD.[77-79] Other observations discovered that metal particles are pure metal other than carbide.[80, 81] Besides experimental approaches, *ab initio* molecular dynamic (MD) simulations were also employed to study the growth mechanism of CNT. Raty et al. argued that carbon atoms are unlikely to penetrate inside

the particles, especially for the particles less than 1 nm involving SWCNT growth.[82] Another MD simulation showed that either solid or liquid particles are capable of producing CNT, however it is much easier for carbon atoms to penetrate into liquid particles than solid ones.[71] These results suggested that VLS model might not be the only possibility and other models may also exist. More systematic experiments or simulations are necessary to have a better understanding of the CNT growth mechanism.

1.5 SWCNT structure control in CVD

Although the growth mechanism of SWCNTs in CVD is still not fully understood, some empirical principles have been discovered, and have been employed for the controlled growth of SWCNTs in terms of diameter, chirality, orientation and length.

1.5.1 Diameter

The size of catalyst metal particles is found to be closely related to the diameter of CNTs.[83] SWCNT growth requires smaller metal particles than the growth of double-walled carbon nanotube (DWCNT) and MWCNT. Lamouroux et al. reviewed literatures about CNT growth and constructed a linear correlation between metal particle size and CNT diameter shown in Figure 1-5.[48] This correlation suggests that the diameter of CNT can be controlled by tuning the size of metal particles. Many efforts have been made to control the size of metal particles. Thermal annealing ($>1000\text{ }^{\circ}\text{C}$) in Ar ambient can evaporate cobalt particles leading to the growth of SWCNT with narrow diameter distribution.[84] The size of metal particles is also dependent on the SWCNT synthesis temperature. Metal particles can sinter under higher temperature to larger

sizes leading to the growth of SWCNTs with larger diameters.[59, 85] It is reported that SWCNT diameters increase from 0.8-1.4 nm to 1.2-2.2 nm if the synthesis temperature hikes from 900 °C to 1000 °C.[86] Carbon precursor supply rate can also influence the SWCNT diameter. A decrease of the mean diameter of SWCNTs can be obtained by increasing the gas flow rate of carbon precursor.[87] Bimetallic catalysts (two metals supported on substrate, e.g. Co-Mo, Fe-Co) can produce SWCNTs with a narrow diameter distribution because one metal can be stabilized by the other.[51, 88] Good dispersion of catalytic metal particles can also be achieved if the substrate has a strong interaction with metal particles. The strong interaction between substrate and metal particles could prevent them from sintering and migrating.[89]

Figure 1-5 Correlation between metal particle size and CNT diameter.[48]

1.5.2 Chirality

The nature of SWCNT structure implies that SWCNTs with the same diameter could have different chiral angles. Therefore, SWCNT chirality control is more challenging than just diameter control. O'Connell et al. discovered that semiconducting SWCNTs dispersed individually in aqueous solution have near-infrared fluorescence emission.[90] Since then, fluorescence spectroscopy has been used to assign the chirality of semiconducting SWCNTs. It is still not

known how the SWCNT chirality is determined in CVD process. The *ab initio* calculations showed that controlling the carbon cap formed on a metal particle during SWCNT growth is crucial for the chirality selective growth of SWCNTs.[91, 92] The *in situ* experimental study discovered that metal particles are dynamically reshaping during CNT growth. It is also suggested that SWCNT chirality selectivity is related dynamically to catalytic metal particle-carbon network interactions.[78] Therefore, not only metal particles, but also carbon precursors could influence the SWCNT chirality selectivity.

Efforts have been made towards SWCNT chirality control in CVD. High temperature was discovered to facilitate the nucleation of metal particles producing SWCNT with wider (n,m) distribution.[93-95] The synergistic effect of bimetallic catalysts (Co-Mo, Fe-Mo, Fe-Ru) can lead to well dispersed and stabilized metal particles producing SWCNTs with very narrow (n,m) distribution.[13, 58, 93] Various crystal planes of sapphire affected the diameter and (n,m) distribution of SWCNTs when tubes were grown aligning on the surface of sapphire.[65] Preferential growth of 95% semiconducting SWCNTs on quartz substrate was also reported. The introduction of methanol as a carbon precursor and the strong interaction between SWCNTs and the substrate were found to be key factors for selective growth of semiconducting SWCNTs.[63] Metallic SWCNTs could also be directly enriched if the ratio of carbon atoms to oxygen atoms of the carbon precursors increased.[96]

1.5.3 Orientation

Perfectly aligned SWCNTs on planar substrates are desired for the fabrication of SWCNT based electronic devices [25, 61] or field emitters for display.[97] The alignment of SWCNTs can be categorized into horizontal alignment and vertical alignment. Both have been achieved by various methods recently. For example, Co-Mo bimetallic catalyst deposited on Si wafer has been used to grow vertically aligned SWCNTs in CVD.[66, 68, 98-101] Optimum Co/Mo molar ratio and particle density on substrates are crucial for achieving vertical aligned growth of SWCNTs.[68] This is because an individual SWCNT needs to interact with its neighbors via van der Waals force to gain rigidity, which helps SWCNTs to self-orient vertically to the substrate.[102] CVD is also effective to produce horizontally aligned SWCNTs on planar substrates. Various external forces can be adopted to enhance the alignment, such as electric field,[103] gas flow,[104] or atomic steps on substrates.[105]

1.5.4 Length

Ultralong SWCNTs (millimeter scale or longer) are desired for producing lightweight, high strength fibers.[106] CVD has been employed to grow ultralong SWCNTs from Fe nanoparticles supported on Si wafer. SWCNTs with 4 cm length have been successfully grown.[6] Fe-Mo bimetallic catalysts have also been used to grow ultralong SWCNTs in CVD. In addition, by varying the direction of Si wafer, crossed SWCNT network can also be fabricated.[39, 104]

1.6 Motivation and scope of this thesis

Obtaining SWCNTs with specific chirality is essential for their future applications. Two different approaches can possibly lead to this goal: (1) chirality control during the SWCNT synthesis and (2) post-synthesis chirality selective separation. Although chirality selective separation has drawn great research interests,[107-110] this thesis focuses on the first approach based on the following considerations: (1) Direct chirality control in synthesis could avoid inducing defects during SWCNT functionalization in separation process, which usually would compromise the performance of SWCNTs in electronic devices. (2) Post-synthesis separation often involves wrapping SWCNTs by surfactant,[109] DNA,[107] polymers,[108] or other dispersion agents. To my best knowledge, the method for effective removal of these agents is still unavailable. Significant amount of surfactant residues remain on the surface of SWCNTs after separation, which could hinder SWCNT applications when high purity tubes are needed. (3) (n,m) narrowly distributed tube samples may also show some advantages over tubes samples having a wide diameter distribution for various post-synthesis chiral selective separation processes.

As discussed in section 1.5.2, SWCNT chirality may be controlled by the dynamic interaction between catalytic metal particles and carbon networks.[78] This interaction may be influenced by both carbon precursor supply rate and metal particle nucleation.

Carbon precursors decompose on the surface of metal particles (Figure 1-4) supplying carbon atoms to form SWCNTs. Although many carbon precursors have been demonstrated to be effective for SWCNT growth, their decomposition rates are distinct due to their different chemical compositions. Therefore, using different carbon precursors with different decomposition rates may

lead to different chirality selectivity in SWCNT synthesis. Similarly, pressure also has a direct impact on the carbon precursor supply rate. Hence, carbon precursor pressure may be another crucial factor resulting in the change of SWCNT chirality selectivity. On the other hand, the metal particle nucleation plays another important role in this dynamic SWCNT chirality selective process. Since metal particles can be supported on various substrates. The interaction between metal particles and substrates may influence the morphology of metal particles and lead to the shift of SWCNT chirality selectivity. Lolli et al.[95] have attempted to change the SWCNT (n,m) growth selection by employing SiO₂ and MgO as substrates for Co-Mo catalysts. The comparison between different substrates revealed that smaller chiral angle SWCNTs were produced from MgO supported catalysts due to the strong interaction between MgO and Co.[95] Based on these considerations, attempts towards SWCNT chirality selective growth were made via applying: (1) different carbon precursors, (2) different carbon precursor pressures, and (3) different catalyst substrates.

This thesis will be presented in the following structure. The basic experimental methods and characterization techniques related to SWCNTs and catalysts are discussed in Chapter 2. Chapter 3 presents the methodology for SWCNT chirality abundance evaluation. The effects of different carbon precursors and pressures on the SWCNT chirality selectivity are investigated in Chapter 4 and 5, respectively. Chapter 6 discusses the effect of different catalyst substrates on the chirality selective growth of SWCNTs. In Chapter 7, a novel monometallic catalyst Co incorporated TUD-1 (Technische Universiteit Delft 1) is synthesized and applied for SWCNT growth. Chapter 8 summarizes the conclusions in this thesis and discusses directions for future research.

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Chapter 2

General Experimental Methods

This thesis focuses on chirality selective growth of SWCNTs from experimental approaches. One catalyst was applied to investigate parameters of CVD which could affect the chirality selectivity of SWCNTs. In this chapter, synthesis and purification methods of catalysts and SWCNTs are introduced first. A wide range of experimental techniques have been applied for characterizing catalysts and SWCNTs. The characterization techniques discussed in this chapter focuses on two aspects: (1) their basic physical principles and (2) their applications in this thesis.

2.1 Catalyst synthesis

Cobalt-molybdenum supported on porous silica (Co-Mo/SiO₂) was used in this study for two reasons: (1) it is capable of growing SWCNTs with narrow (*n,m*) distribution,[1] and (2) the synthesis procedure is relatively simple. Catalysts supported on planar substrates were not used because the SWCNT yield is too low to collect enough samples for performing solution phase spectroscopic studies. On the other hand, a novel catalyst, Co incorporated TUD-1 (Co-TUD-1), has also been developed for SWCNT growth. The synthesis of this new catalyst is discussed in Chapter 7. Here, the synthesis method for Co-Mo/SiO₂ is introduced.

Two metal salts Co(NO₃)₂ · 6H₂O and (NH₄)₆Mo₇O₂₄ · 4H₂O were dissolved in 20 mL deionized (DI) water separately and slightly stirred for 10 minutes. These two solutions then were mixed together and stirred for another 10 minutes. The silica gel (used as received from Sigma-Aldrich, possessing 6 nm average pore size and Brunauer-Emmett-Teller (BET) surface area of

480 m²/g) was slowly added into the solution with stirring at room temperature. The Co/Mo molar ratio was kept at 1:3 and Mo loading at 4.6 wt.% over the final catalyst weight. The metal-silica suspension was then slowly dried in a heated oven for overnight. The dried solid powder was finally ground and calcined at 500 °C for 3 hours.

2.2 SWCNT synthesis

In a typical SWCNT synthesis, Co-Mo/SiO₂ catalyst (200 mg) was loaded into a ceramic boat and placed into a stainless steel tube reactor. The catalyst was firstly reduced under 1 bar flowing H₂ (80 mL/min) using a temperature ramp of 10 °C/min to 500 °C. Once the temperature reached 500 °C, the reactor was purged using flowing Ar (250 mL/min), while the temperature was further increased to 800 °C. Then the carbon monoxide (CO, the carbonyls were eliminated by Nanochem Purifier by Matheson Gas Products) flow (100 mL/min) was introduced into the reactor and kept at 6 bar for 30 minutes or 1 hour. Finally, the reactor was purged by Ar and cooled down under the protection of a steady Ar flow. The SWCNT growth process is illustrated in Figure 2-1.

The growth conditions varied according to different carbon precursors used. For C₂H₅OH and CH₃OH, a vacuum condition (5 mbar) was necessary due to their high decomposition rates at high temperature. C₂H₂ needed to be further diluted in Ar at 1:1000 ratio before being introduced into the reactor at 5 mbar and a total flow rate of 500 mL/min. The details of SWCNT synthesis parameters are discussed in respective chapters in this thesis.

Figure 2-1 Schematic illustration of SWCNT growth process in CVD: (A) Induce H₂ at room temperature, (B) metal oxide is reduced by H₂ to form metal nanoparticles at 500°C, (C) CO is induced and decomposed at 800°C and (D) SWCNT forms on metal particles.

2.3 SWCNT purification

The as-synthesized SWCNTs were mixed with impurities including amorphous carbon, graphite, MWCNTs, catalyst support and metal particles. The existence of impurities not only interferes the characterization of SWCNTs, but also hinders their potential applications. Due to the complicity of the impurities, multi-step purification process is required to obtain high purity SWCNTs.[2, 3] Since SWCNT purification is not the main focus of this study, a simplified purification procedure was adapted only for the purpose of characterizing SWCNT samples. The as-synthesized SWCNT samples were firstly refluxed in 0.15 mol/L NaOH solution to remove the silica support. Then the solid samples were recovered by filtration through a membrane with 0.22 μm pore size. The recovered black solid powder was dispersed in 1 wt.% sodium dodecyl benzene

sulfonate (SDBS)/D₂O (or 2 wt.% sodium cholate(SC)/D₂O) solution and sonicated using a cup-horn ultrasonicator (SONICS, VCX-130) at 100 W for 1 hour. After ultrasonication, the suspension was centrifuged for 1 hour at ca. 53,000 g (up to 120,000 g) to remove metal particles, SWCNT bundles and other carbon impurities. The purification process is illustrated in Figure 2-2. The clear supernatant enriched with surfactant wrapped SWCNTs was extracted and kept for further characterizations (such as photoluminescence spectroscopy and UV-vis-NIR absorption spectroscopy).

Figure 2-2 Schematic illustration of SWCNT purification process: (A) reflux of as-synthesized SWCNT sample in NaOH solution to remove catalyst substrate, (B) ultrasonicate the filtered solid powder in surfactant/D₂O solution to debundle SWCNTs, and (C) ultracentrifuge the solution to remove MWCNT, metal particles and other carbon impurities.

2.4 Catalyst characterizations

The characterizations of catalysts were conducted to examine (1) their physical structures such as surface area and pore size of substrates, and (2) their chemical properties such as the domain size of metal oxides and the reducibility of metal particles. The following techniques were employed to characterize these properties.

2.4.1 X-Ray diffraction (XRD)

XRD is a powerful characterization tool to reveal the crystallographic structure of materials. A crystal lattice is a regular three-dimensional distribution of atoms in space. These atoms can form different planes with different orientations and specific distance (d) between two neighbor planes. If a monochromatic X-ray beam (wavelength λ) strikes on the crystal at an angle θ , the diffraction occurs when Bragg's Law is satisfied: $n\lambda = 2d\sin\theta$. By varying the X-ray incoming angle θ , Bragg's Law can be satisfied by different d spaces in polycrystalline materials. The pattern of the diffraction against θ can be considered as the fingerprint of a certain crystalline material. In this study, XRD was used to probe the ordered structure of Co-TUD-1 catalyst. XRD measurement was carried out on a Shimadzu X-ray diffractometer (Cu $K\alpha$, $\lambda=0.154$ nm, 40 kV, 30 mA).

2.4.2 N₂ physisorption

The surface area and pore size distribution of catalysts were characterized by N₂ physisorption. During the measurement, N₂ (at 77 K) is adsorbed on the solid surface of catalyst and meanwhile its converse process, desorption occurs. If the adsorption curve and the desorption curve do not coincide, an adsorption hysteresis forms. The relation between the amount of adsorbed N₂ and the

equilibrium pressure of nitrogen is called adsorption isotherm. Adsorption isotherms can be classified into several common types.[4] Mesoporous materials, such as MCM-41 and TUD-1, have the type IV isotherm. At low pressure ($P/P_0 < 0.25$), a monolayer of nitrogen molecules is absorbed on the pore wall surface of materials. At higher pressure, adsorption in mesopores leads to multilayer formation until condensation takes place when $P/P_0 \approx 0.25-0.5$, giving a sharp increase in adsorption volume,[5] which results in a sharp step in the nitrogen physisorption isotherm. The surface area can be calculated from the nitrogen physisorption isotherm by Brunauer-Emmett-Teller (BET) method.[6] Pore volume and size can be obtained by Barret-Joyner-Halenda (BJH) method.[7] In this study, nitrogen adsorption-desorption isotherms were measured at 77 K with a static volumetric instrument Autosorb-6B (Quanta Chrome).

2.4.3 UV-vis diffuse reflectance spectroscopy

Diffuse reflectance spectroscopy is an excellent tool for powdered or crystalline materials and intractable solid samples. Diffuse reflection is the reflection of light from an uneven or granular surface such that an incident ray is seemingly reflected at a number of angles.[8] The reflecting power of the incident ray is called 'reflectance'. In the measurement, the light with different wavelengths was shot to the solid powder. This incident light is partially absorbed and partially scattered. The scattered light is then collected by a detector. If the sample is infinitely thick, the diffuse reflection of the sample (R_∞) is in correlation with apparent absorption (K) and apparent scattering coefficient (S) via Kubelka-Munk function: $F(R_\infty) = (1 - R_\infty)^2 / 2R_\infty = K/S$. $F(R_\infty)$ has a linear relation with transition metal ions concentration supported on the catalyst surface and it measures their d-d transitions which depend on the oxidation state and coordination

environment of the metal ions.[9] In this study, diffuse reflectance was used to probe the metal oxide domain size of Co-Mo catalyst supported on different substrates. It was also used to investigate the local environment of cobalt in the TUD-1 structure. Diffuse reflectance spectra were obtained by a Varian Cary 5000 UV-vis-NIR spectrophotometer equipped with a Praying Mantis accessory kit.

2.4.4 Temperature programmed reduction (TPR)

TPR is a useful characterization technique for investigating the chemistry of the metal-support interaction and the surface chemical information of catalysts (e.g. material species, stability and metal distribution). The reduction temperature of metal oxides can be influenced by the interaction with catalyst supports and the synergy among different metals. In this study, TPR was performed from 50 °C to 950 °C, within which the metal oxides in catalyst can be reduced in a flowing H₂. Before the TPR measurement, a catalyst sample (200 mg) was loaded into a customized quartz cell and pre-calcined using air at 500 °C for 1 hour to obtain a clean surface. After cooling the sample to room temperature, 5 % H₂/Ar was introduced through the sample at a steady flow rate of 30 mL/min. The sample cell was placed in a furnace and heated at 5 °C/min from room temperature to 950 °C and held for 30 minutes at 950 °C to ensure the completion of metal reduction. If the metal oxide was reduced at a certain temperature, some of H₂ would be consumed. Water formed due to the reduction was then condensed in an acetone/liquid nitrogen cold trap. The gas mixture finally flowed into a gas chromatograph (Techcomp 7900) equipped with a thermal conductivity detector (TCD). The H₂/Ar composition change induced by the H₂

consumption during metal oxide reduction was detected and recorded by TCD so that the reduction temperature of metal oxides in the catalyst can be determined.

2.5 SWCNT characterization

In this study, four experimental techniques have been utilized to characterize SWCNTs in order to answer the following questions: (1) What are different carbon species existing in a sample? (2) What is the content and purity of SWCNTs in a sample? (3) What is the (n,m) distribution of a SWCNT sample? The discussion for each experimental technique mainly focuses on its application related to this thesis.

2.5.1 Raman spectroscopy

For a molecule, the electrons usually stay at the ground electronic state. When a monochromatic light encounters this molecule and interacts with its electron cloud, the molecule polarizability will change, or the electron cloud will deform. This short electron cloud deformation could be considered as the electron is excited into a “virtual state”, which is not a true quantum state of a molecular vibration. If there is no gain or loss of energy in this scattering process, similar to an elastic collision, it is called Rayleigh scattering. If the molecular vibration does not return to the ground state but an excited molecular vibrational state, this is called Stokes Raman Scattering. When the incident photons have the same energy as an electronic transition, the resonance Raman scattering may happen, leading to much stronger Raman scattering compared to non-resonant Raman scattering. Figure 2-3 illustrates these three types of vibrational Raman spectroscopy.

Figure 2-3 Schematic representation of different types of Raman scattering

Resonant Raman scattering of SWCNTs are much more intense compared to the non-resonant Raman scatterings. SWCNTs have unique electronic band structures. When the electronic band gap energy of a SWCNT is close to the incoming laser energy, strong Raman signal can be observed. The electronic transitions in SWCNTs range from 0.25 eV to 2.5 eV, and different (n,m) tubes have distinct electronic transition energies. Theoretically, by changing the laser excitation energy, each type of (n,m) SWCNTs can be resonant under a particular laser energy, therefore the existence of (n,m) tubes can be confirmed in Raman spectroscopy. However, the Raman spectrometer equipped with lasers having continuously tunable energies is not widely available. SWCNT (n,m) distribution exploration cannot be easily done by Raman spectroscopy in this thesis.

Resonance Raman Spectra (RRS) of SWCNTs show three main features as illustrated in Figure 2-4: the Radial Breathing Mode (RBM) (100-400 cm^{-1}), the Disorder-induced band (D band) ($\sim 1300 \text{ cm}^{-1}$) and the Graphite-like band (G-band) (1500-1600 cm^{-1}). The RBM comes from the vibration of carbon atoms in the radial direction with the same phase, as if the tube is breathing. The RBM is not only used to identify the existence of SWCNTs in a sample, but also applied to estimate the SWCNT diameter. The RBM position is correlated with the SWCNT diameter (d) following the equation $\omega_{\text{RBM}} = A/d + B$, [10] where A and B are constants. G band comes from the graphite tangential vibration mode, in which, two atoms in the graphite sheet are vibrating tangentially against each other. Unlike the single peak of graphite G band, the G band from SWCNTs gives multi-peak features. The G^+ and G^- bands shown in Figure 2-4 are correlated with atomic displacements along the tube axis and along the circumferential direction, respectively. G^- band is strongly sensitive to the metallicity of SWCNTs. For Raman spectroscopy experimental data analysis, G band from SWCNT samples containing more metallic tubes are usually fitted with Breit-Wigner-Fano (BWF) line shape, while samples with more semiconducting tubes are fitted with Lorentzian line shape. [11] The D band is commonly related to defects in SWCNTs and amorphous carbon. The D/G ratio sometimes can be used to evaluate the SWCNT quality. Lower D/G ratios may indicate that less defects exist on a SWCNT sample. G, D and RBM modes are used in this study for two purposes: (1) to identify the presence of SWCNT in a sample and (2) to determine the diameter distribution of SWCNT samples. Raman spectra in this thesis were recorded by a Renishaw Ramanscope in the backscattering configuration using 514.5 nm (2.41

eV), 633 nm (1.96 eV) and 785 nm (1.58 eV) lasers. Spectra were averaged over five random spots on each sample.

Figure 2-4 A typical Raman spectrum of SWCNT with three featured modes (The schematic illustration of SWCNT was modified from [12])

2.5.2 Photoluminescence (PL) spectroscopy

The term PL describes a process in which a photon is absorbed by a medium, generating an electron excited state and then a new photon with lower frequency is emitted upon the relaxation of excited electron to its ground state. PL spectroscopy can be used to probe the electronic structure of materials.

SWCNT possesses a unique electronic band structure which is strongly dependent on its physical structure described by the (n,m) index. PL methods have emerged as a basic characterization tool to determine the (n,m) structure of SWCNTs.[13, 14] SWCNTs have a set of sharp maxima called van Hove singularities (VHS) in their electronic density of states (DOS). VHS are labeled with $v_1, v_2, \dots, v_i$ for valence bands and $c_1, c_2, \dots, c_i$ for conduction bands (subscripts are the sub-band indices) shown in Figure 2-5. $E_{11}, E_{22}, \dots, E_{ii}$ represents the van Hove transition energy between v_i and c_i . The relation between electronic transitions and all possible (n,m) SWCNTs can be described in a Kataura plot calculated using a tight binding model.[15] Very strong van der Waals force exists among SWCNTs, so they tend to form bundles other than existing as individual tubes. However, very weak PL signal can be observed from SWCNT bundles, because excited electrons can be transferred to other tubes in a bundle other than relaxation to the ground state. The transfer of excited electrons among tubes in a bundle quenches photon emission. Therefore, to measure PL spectrum, SWCNT samples have to be debundled. Bachilo et al. dispersed SWCNTs individually by wrapping them with sodium dodecyl sulfate (SDS) in ultrasonication. They measured the first and second van Hove optical transitions (E_{11}, E_{22}) of more than 30 different semiconducting SWCNTs.[13] An empirical Kataura plot describing the relation between SWCNT optical transitions (E_{11}, E_{22}) and its (n,m) structure was developed based on their experimental measurements.[16] The SWCNT (n,m) assignment in this study is based on this empirical Kataura plot because it gives a better correlation than theoretical Kataura plot.[15] It is noteworthy that only semiconducting SWCNTs can be detected in PL spectroscopy, and metallic tubes are not detectable.

Figure 2-6 is a typical PL spectrum of a SWCNT sample in this study. Figure 2-6(A) is a 3-D plot, x,y coordinates stand for excitation wavelength and emission wavelength, respectively. Figure 2-6(B) is its 2-D contour plot. This spectrum was generated by the accumulation of emission spectra excited by discrete excitation wavelengths with small constant intervals. Each peak in Figure 2-6(A) or each bright spot in (B) shows an optical transition pair (E_{22} , E_{11}) correlated with the electronic band structure of a semiconducting SWCNT. (n,m) structure of this tube can be assigned by referring to the empirical Kataura plot.[16] PL spectroscopy was intensively used to probe the (n,m) distribution of SWCNT samples in this study. They were measured by a Jobin-Yvon Nanolog-3 spectrofluorometer equipped with an IGA (InGaAs) near-infrared (NIR) detector.

Figure 2-5 Schematic density of electronic states for a semiconducting SWCNT [13]

Figure 2-6 Typical PL spectra of SWCNTs: (A) 3D plot and (B) contour plot of PL intensity measured as a function of excitation and emission wavelength

2.5.3 UV-vis-NIR absorption spectroscopy

Absorption spectroscopy is a technique measuring the absorption of light at a particular wavelength by a sample. PL spectroscopy is only capable of detecting semiconducting SWCNTs. UV-vis-NIR absorption spectroscopy is able to detect both semiconducting and metallic SWCNTs.

As illustrated in Figure 2-5, electrons can be excited from valence bands to conduction bands upon the absorption of incoming photons. E_{22}^S (S for semiconducting SWCNT) and E_{11}^S absorptions of semiconducting SWCNTs are in the near infrared range. Metallic SWCNTs absorb photons with energies of E_{11}^M (M for metallic SWCNT) at a lower wavelength range. Figure 2-7 is a typical SWCNT absorption spectrum. E_{22}^S and E_{11}^S peaks come from semiconducting tubes, and E_{11}^M peaks come from metallic tubes. Because optical transitions of different SWCNTs could be very close, one peak in an absorption spectrum may represent the combination of several (n,m) SWCNT species. Therefore, in order to identify different (n,m) species in an absorption spectrum,

the spectrum deconvolution is necessary. Another important feature of SWCNT absorption spectrum is the π -plasmon background, which can be contributed to both carbonaceous impurities and SWCNTs. The π -plasmon background can be used to evaluate the purity of SWCNT. Purity index ($AA(S)/AA(T)$) is often applied for such a purpose. $AA(S)$ is the area of the E_{22} transition after the π -plasmon background removal. $AA(T)$ is the total area under the E_{22} transition spectral curve.[17] In this study, the UV-vis-NIR absorption was mainly used to evaluate the (n,m) distribution of SWCNT samples. The spectra were obtained on a Varian Cary 5000 UV-vis-NIR spectrophotometer.

Figure 2-7 A typical UV-vis-NIR absorption spectrum of SWCNT

2.5.4 Thermogravimetric analysis (TGA)

TGA is an analytical method monitoring the weight change of a sample against a temperature ramp under flowing gases which can react with the sample. Through reactions, the sample can gain or lose weight. Such an analysis requires precise temperature control and weight sensing. Differential thermogravimetric (DTG) profile is usually used to reveal the decomposition temperature of a substance. If this substance has multiple decomposition temperatures and they are overlapped, the deconvolution of DTG curves may be required.

In this study, TGA was used to analyze the carbon loading on catalysts and the composition of different carbon species in SWCNT samples. An as-synthesized SWCNT sample contains not only SWCNTs but also other impurities like MWCNTs, amorphous carbon and graphite. TGA is a useful tool to measure the abundance of those impurities, because they are usually oxidized at different temperatures. The amorphous carbon is fully decomposed below 300 °C in air, while the graphite can only be burned above 800 °C. The decomposition temperature of SWCNTs or MWCNTs can be varied remarkably between 400 °C and 700 °C depending on the presence of metal particles.[18-20] In general, MWCNTs have a higher decomposition temperature than SWCNTs if they are in the same environment. Before each TGA measurement, samples were kept at 110 °C to remove the moisture until the weight was stable. Then the sample was heated at 10 °C/minute to 1000 °C meanwhile the weight change was recorded. After cooling down to room temperature, the second temperature ramp was carried out as a baseline to correct the first one. TGA was conducted on a PerkinElmer Diamond TG/DTA equipment.

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Chapter 3

SWCNT (n,m) Abundance Evaluation

This thesis focuses on the (n,m) selective growth of SWCNTs, hence a methodology to evaluate the (n,m) abundance in a SWCNT sample is essential. For typical SWCNT samples (diameter ranges 0.6-1.5 nm), there are >100 different (n,m) species with distinct electronic properties.[1] Many efforts have been made to obtain SWCNT with selective (n,m) by controlled CVD synthesis or separation.[2-11] These studies must be based on the precise (n,m) abundance evaluation of SWCNTs. However, accurately characterizing (n,m) SWCNT abundance in a given sample is still challenging. In this chapter, characterization methodologies based on currently available experimental techniques are discussed. The strategies which were applied to determine the (n,m) abundance of SWCNT samples are outlined in the following chapters.

3.1 Spectroscopic techniques

As discussed in Chapter 2, Resonance Raman spectroscopy (RRS),[12] UV-vis-NIR absorption spectroscopy,[13] and PL spectroscopy[14] are currently available techniques that can be used for the non-destructive (n,m) characterization of SWCNT species. Among these techniques, PL spectroscopy provides a quick identification for the majority of semiconducting SWCNTs. UV-vis-NIR absorption spectroscopy measures the optical absorption of SWCNTs. Both semiconducting and metallic SWCNTs can be detected. However, the deconvolution of absorption spectra of bulk SWCNT samples into distinct (n,m) contributions is very difficult, because electron transitions of these tubes with different diameters are overlapped especially for samples

having a wide (n,m) distribution. Both PL and absorption spectra require a surfactant dispersed SWCNT sample. RRS has the advantage for being applicable to SWCNTs in bundles, and for measuring metallic tubes as well, either in solid or solution phases, through the RBM vibration of SWCNTs. However, these three spectroscopical techniques have the same problem concerning the abundance determination. Measured optical signal intensity (I^{EXP}) can be simplified as $I^{\text{EXP}} = \eta \cdot I^{\text{CAL}} \cdot A \cdot I^{\text{EXC}}$, where η is the detection efficiency of an experimental system, I^{CAL} is the intrinsic photophysical parameter for a particular SWCNT structure, A is the abundance of one particular SWCNT, and I^{EXC} is the excitation intensity. The intrinsic photophysical parameter I^{CAL} is Raman cross section for RRS,[12] PL quantum efficiency for PL spectroscopy,[14] and absorption extinction coefficient for optical absorption spectroscopy,[13] respectively. Ideally, if an accurate intrinsic intensity (I^{CAL}) is available, then the population of individual (n,m) SWCNT in a mixture can be obtained by the equation $A(n,m) = I^{\text{EXP}}(n,m)/[\eta \cdot I^{\text{CAL}}(n,m) \cdot I^{\text{EXC}}]$.

3.2 Intrinsic SWCNT property I^{CAL}

Recently, several theoretical models have emerged to predict the intrinsic photophysical parameter I^{CAL} . However, these predictions are difficult to be validated by experimental measurement because of the lack of chiral resolved samples (where the abundance A is known).

Reich S. et al proposed an exciton-exciton resonance model for obtaining PL quantum efficiency.[15] The exciton-exciton resonance depends on the electronic structure of the SWCNTs. If the presence of two excitons in E_{11}^{S} subband is allowed, when E_{22}^{S} energy is larger than $2E_{11}^{\text{S}}$, excitons in E_{22}^{S} decay into E_{11}^{S} . It liberates enough energy to create a second exciton, other than leads to PL emission (Figure 3-1). They showed that the PL intensity of SWCNTs is much

stronger in tubes with large chiral angles, because exciton resonances make the PL intensity of zigzag tubes (small chiral angles) intrinsically weak. Two seemingly similar tubes can show very different exciton dynamics, which depend on the SWCNT chirality.

Figure 3-1 (a) PL process: an electron excited from ground state to E_{22}^S , relaxes to E_{11}^S and back to ground state with emitting; (b) and (c) different structure dependent SWCNT exciton decay routes.(modified from [15])

Oyama et al proposed a single particle tight-binding theory [16] for PL quantum efficiency and absorption extinction coefficient. They consider (1) an induced absorption of light at E_{22}^S , (2) relaxation from E_{22}^S to E_{11}^S by an electro-phonon interaction, and (3) spontaneous emission at E_{11}^S . The PL intrinsic intensity is expressed by the product of these three factors. Based on the assumption, intrinsic PL intensity can be obtained by multiplying the photon-absorption,

relaxation and photon-emission matrix elements. Results for various SWCNTs are shown in Figure 3-2.

Figure 3-2 Intrinsic PL intensity for semiconducting SWCNTs predicted by a tight binding theory.[16] Type I: $\text{mod}(m-n, 3) = 1$; Type II: $\text{mod}(m-n, 3) = 2$.

For Raman spectroscopy, the resonant Raman intensities for 50 semiconducting SWCNTs were calculated by Popov V. et al. using a symmetry-adapted nonorthogonal tight binding model.[17] The results are shown in Figure 3-3. More recently, Jiang et al. extended such calculation to various metallic SWCNTs and provided guidance for intrinsic resonance Raman scattering intensities.[18] SWCNTs were divided into five groups as semiconducting I with small diameter and small chiral angle, semiconducting II with large diameter and chiral angle either $< 25^\circ$ or

$\geq 25^\circ$, metallic SWCNTs and armchair SWCNTs. For each group, different fitting parameters were applied to calculate the intrinsic Raman intensity.

These three models have yet been verified experimentally. Experimental studies are needed to validate these theoretical predictions and push forward the characterization techniques.

Figure 3-3 Calculated resonance Raman profiles for 50 semiconducting SWCNTs in the diameter range $0.56 \text{ nm} < d < 1.3 \text{ nm}$. [17]

3.3 Spectroscopic strategies for SWCNT (n,m) abundance evaluation

Although the theoretical prediction of SWCNT intrinsic property I^{CAL} is still in debate, they have already been applied to estimate the abundance of (n,m) SWCNT species. Jorio A. et al. measured SWCNTs grown from Co-Mo catalyst dispersed in SDS solution using a Ar-Kr and dye lasers excited Raman spectrometer. [19] Raman RBM intensity ($I_{\text{RBM}}^{\text{EXP}}$) for each tube under full

resonance condition was divided by the predicted RBM Raman cross section ($I_{\text{RBM}}^{\text{CAL}}$). [18] The researchers expected that the ratio ($A = I_{\text{RBM}}^{\text{EXP}} / \eta \cdot I_{\text{RBM}}^{\text{CAL}} \cdot I^{\text{EXC}}$) reflects the real population. Similar strategy was applied for PL measurement by Oyama Y. et al. [16] The abundance of each (n, m) SWCNT prepared by high pressure CO (HiPCo) CVD and alcohol CVD was obtained by equation, $A(n, m) (I_{\text{PL}}^{\text{EXP}}) / (I_{\text{PL}}^{\text{CAL}})$.

Since there are multiple theoretical models to predict the SWCNT intrinsic property I^{CAL} , the choice of different models directly leads to different results on the (n, m) abundance determination. Luo et al. evaluated the (n, m) abundance of SWCNT grown from Co-MCM-41 [20] by applying an exciton-exciton resonance model [15] and an electron-phonon interaction model. [16] These two models were compared by the reconstruction of absorption spectra. The results indicated that the electron-phonon interaction model provided a better prediction than the exciton-exciton model. [20] Therefore, PL quantum efficiency predicted by the electron-phonon model was used in this thesis to evaluate (n, m) abundance of SWCNTs grown by different carbon precursors and under different pressures. The reconstruction of absorption spectra was also employed to reveal the existence of small chiral angle tubes in SWCNT samples. The details are stated in Chapter 4 and Chapter 5, respectively.

Measured spectroscopical intensity I^{EXP} has also been directly used to quantify the SWCNT (n, m) abundance [21-23] by empirical weighting parameters without considering their intrinsic properties. For example, in $I^{\text{EXP}}(n, m) = \eta \cdot I^{\text{CAL}}(n, m) \cdot A(n, m) \cdot I^{\text{EXC}}$, set all the $I^{\text{CAL}}(n, m) = 1$, so $A(n, m)$ is direct proportional to the measured $I^{\text{EXP}}(n, m)$. [21, 22] Recent research measured the product of absorption cross section and PL quantum yield for 12 (n, m) structural species of

semiconducting SWCNT in SDS suspension.[24] The results showed that the PL quantum efficiencies among various (n,m) SWCNT species may not be as large as the theoretical model predicted. This result gave supports to the direct use of measured intensity to quantify the SWCNT (n,m) abundance. However, there is a drawback for this strategy. A broadly varying background of measured PL profile versus excitation wavelength can be observed shown in Figure 3-4b. In this case, directly applying the measured intensity to quantify the SWCNT (n,m) abundance is not accurate. Arnold et al. suggested a scenario to minimize the background issue:[25] the partial derivative of the PL intensity versus excitation wavelength was computed and the amplitude of the partial derivative was used to determine the SWCNT abundance (Figure 3-4d). This method was used in this study to evaluate the (n,m) abundance of SWCNTs grown from different catalyst substrates in Chapter 6.

Figure 3-4 (a) A measured SWCNT PL intensity map; (b) extracted emission intensity curve versus excitation wavelength from one SWCNT species, a background can be observed indicated by the black arrow beneath the curve; (c) and (d) the computed partial derivative of PL intensity versus excitation wavelength.[25]

When a SWCNT sample has narrow (n,m) distribution and enriched with a few types of high chiral angle tubes, these two methods (applying PL quantum efficiency or not applying) were observed to provide similar abundance distribution. On the other hand, for SWCNT samples with wide (n,m) distribution, applying PL quantum efficiency together with absorption spectra

reconstruction yields more accurate abundance evaluation results. The details will be further discussed in the following chapters.

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Chapter 4

SWCNT (n,m) Selective Growth by Different Carbon Precursors on Co-Mo Catalyst

This chapter investigates the SWCNT (n,m) selectivity induced by different carbon precursors (CO, C₂H₅OH, CH₃OH and C₂H₂), which have distinct decomposition rates resulting in different carbon supply rates. If the narrow chirality selectivity is kinetically controlled, SWCNTs with distinct and narrow (n,m) distribution should be obtained. In this study, PL and UV-vis-NIR absorption spectroscopies were utilized to analyze the abundance of semiconducting (n,m) SWCNTs on four representative samples synthesized from CO, C₂H₅OH, CH₃OH and C₂H₂. It was found that by carefully adjusting the pressure on these precursors, narrowly (n,m) distributed SWCNTs can be obtained from CO, C₂H₅OH, CH₃OH and majority of these SWCNTs were predominately in the same higher chiral angle region. SWCNT (n,m) selectivity can be shifted among different precursors.

4.1 SWCNT synthesis from different carbon precursors

Co-Mo/SiO₂ catalysts were prepared using impregnation method described in Chapter 2. The SWCNT growth method from CO adopted the typical synthesis method in CVD described in Chapter 2. For C₂H₅OH and CH₃OH, narrow (n,m) distribution SWCNTs were only obtained under vacuum conditions. Once the SWCNT growth temperature (800 °C) was reached, the reactor was evacuated by a rotary pump to 5 mbar. C₂H₅OH or CH₃OH vapor from a reservoir, of which the temperature was maintained at 30 °C and 0 °C respectively, was introduced for 30

minutes at a constant total pressure of 5 mbar. Due to its extremely fast decomposition rate, C_2H_2 was further diluted in Ar at 1:1000 ratio before being introduced into the reactor at 5 mbar and a total flow rate of 100 mL/min. Three runs for each carbon source under identical conditions were tested to validate the run-to-run fluctuation vs. differences among runs using different carbon precursors. The synthesized SWCNTs were purified using the methods described in Chapter 2. PL spectroscopy and UV-vis-NIR absorption spectroscopy were utilized to determine the SWCNT (n,m) distributions grown from different carbon precursors.

4.2 SWCNTs (n,m) distributions and abundances

Figure 4-1 illustrates two-dimensional PL excitation (PLE) maps for the aqueous dispersion of SWCNTs produced by four carbon precursors with excitation scanned from 300 to 800 nm and emission collected from 830 to 1360 nm. The resonance behavior of both excitation and emission events results in spikes corresponding to transitions pair from individual (n,m) SWCNTs.[1] Figure 4-1 suggests that narrowly (n,m) distributed SWCNTs were produced using four different carbon precursors.

The chirality map for SWCNT samples in Figure 4-2 shows that (n,m) distribution are predominantly in the same higher chiral angle region originating from (7,5), (7,6), (8,4) and (8,6). The strength of the (n,m) chirality from PLE map was determined from the amplitude of the partial derivative, as suggested by Arnold et al[2] to minimize the effect of the slowly varying background. CO produced the narrowest (n,m) distribution dominated at (7,6), (7,5) and (8,4).

C₂H₅OH and CH₃OH produced more (8,6), (9,5) and (8,7) as shown in Figure 4-1 and Table 4-1 to Table 4-3.

Taking into consideration of the relative PL quantum efficiency of various (*n,m*) SWCNTs, using the methodology developed by Luo et al.[5] based on a single-particle electron-phonon interaction model,[4] the abundance of each (*n,m*) SWCNT was obtained listed in Table 4-1 to Table 4-4. In order to validate the run-to-run fluctuation vs. differences among runs using different carbon precursors, three parallel runs for each carbon precursor under identical conditions were tested. Figure 4-3 indicates that (*n,m*) distribution changes are caused by different carbon precursors and the run-to-run fluctuation is in a reasonable range. Figure 4-4 illustrates the histograms of diameter distribution of SWCNTs that were extracted from Figure 4-3 and Table 4-1 to Table 4-4. The error bars in Figure 4-4 show the run-to-run fluctuation of three parallel experiments.

As PL intensity of different (*n,m*) SWCNTs could be altered by the effects of different surfactants, sonication-induced changes and nanotube lengths on the quantum yields,[6] a series of controlled experiments using four different surfactants were performed. Although the PL intensity can be different due to the SWCNT concentration in solution, the (*n,m*) abundance distribution is not affected as shown in Figure 4-5.

Figure 4-1 PL intensity maps as a function of excitation and emission wavelength for SDBS micellarized SWCNTs in D₂O produced from four different carbon precursors on Co-Mo/SiO₂ catalysts.

Figure 4-2 Chirality maps of SWCNT samples produced from three different carbon precursors, CO, C₂H₅OH and CH₃OH. Red and orange hexagons are dominant (*n,m*) species produced, yellow hexagons are other minor (*n,m*) species produced. Blue hexagons are those included in absorption spectra reconstruction as discussed later. (6,5) were dominant tubes from Bachilo et. al.[3]

Table 4-1 Tabulated values of the relative PL intensities for SWCNT samples, calculated PL intensities from the electro-phonon interaction model,[4] and (n,m) abundances for samples produced from CO.

(n,m)	Diameter	Chiral Angle	Amplitude of the partial derivative of PL intensity[2]			Calculated PL Intensity	Normalized Average Abundance
(6,5)	0.757	27	3.07	5.85	6.39	0.67	18.0
(8,3)	0.782	15.3	0.40	0.49	0.48	2.13	1.6
(7,5)	0.829	24.5	18.47	19.22	20.10	0.71	67.8
(8,4)	0.84	19.11	21.25	17.57	18.17	0.46	66.8
(10,2)	0.884	8.95	1.12	0.85	1.03	2.38	3.5
(7,6)	0.895	27.46	27.36	28.21	29.69	0.47	100.0
(9,4)	0.916	17.48	8.50	7.05	6.54	0.7	25.9
(10,3)	0.936	12.73	2.55	2.57	2.38	0.28	8.8
(8,6)	0.966	25.28	9.68	10.81	7.88	0.49	33.3
(9,5)	0.976	20.63	4.47	4.60	3.74	0.28	15.0
(8,7)	1.032	27.8	1.74	2.78	1.84	0.3	7.5
(10,5)	1.05	19.11	0.69	1.05	0.92	0.47	3.1
(9,7)	1.103	25.87	0.71	1.25	0.83	0.27	3.3

Table 4-2 Tabulated values of the relative PL intensities for SWCNT samples, calculated PL intensities from the electro-phonon interaction model,[4] and (n,m) abundances for samples produced from C_2H_5OH .

(n,m)	Diameter	Chiral Angle	Amplitude of the partial derivative of PL intensity[2]			Calculated PL Intensity	Normalized Average Abundance
(6,5)	0.757	27	1.73	4.05	5.67	0.67	17.4
(8,3)	0.782	15.3	0.21	0.49	0.75	2.13	2.2
(7,5)	0.829	24.5	8.09	9.54	11.50	0.71	44.3
(8,4)	0.84	19.11	10.93	12.09	13.56	0.46	55.7
(10,2)	0.884	8.95	0.37	0.68	0.49	2.38	2.3
(7,6)	0.895	27.46	22.20	21.19	22.33	0.47	100.0
(9,4)	0.916	17.48	4.65	4.96	5.22	0.7	22.6
(10,3)	0.936	12.73	3.08	5.04	5.10	0.28	20.1
(8,6)	0.966	25.28	20.16	15.05	14.34	0.49	75.4
(9,5)	0.976	20.63	11.53	8.74	6.62	0.28	40.9
(8,7)	1.032	27.8	9.55	9.25	8.02	0.3	40.8
(10,5)	1.05	19.11	2.63	3.00	2.18	0.47	11.9
(9,7)	1.103	25.87	4.88	5.93	4.21	0.27	22.9

Table 4-3 Tabulated values of the relative PL intensities for SWCNT samples, calculated PL intensities from the electro-phonon interaction model,[4] and (n,m) abundances for samples produced from CH₃OH.

(n,m)	Diameter	Chiral Angle	Amplitude of the partial derivative of PL intensity[2]			Calculated PL Intensity	Normalized Average Abundance
(6,5)	0.757	27	2.53	3.96	3.05	0.67	16.5
(8,3)	0.782	15.3	0.75	1.06	0.41	2.13	3.8
(7,5)	0.829	24.5	9.40	10.15	9.53	0.71	50.3
(8,4)	0.84	19.11	12.90	13.62	12.97	0.46	68.2
(10,2)	0.884	8.95	0.64	0.55	0.52	2.38	3.0
(7,6)	0.895	27.46	18.67	19.01	20.19	0.47	100.0
(9,4)	0.916	17.48	2.09	4.70	5.24	0.7	20.8
(10,3)	0.936	12.73	10.80	6.61	6.78	0.28	41.8
(8,6)	0.966	25.28	12.17	13.56	14.58	0.49	69.7
(9,5)	0.976	20.63	11.78	9.64	8.97	0.28	52.5
(8,7)	1.032	27.8	8.59	8.70	9.16	0.3	45.7
(10,5)	1.05	19.11	3.79	3.45	3.14	0.47	17.9
(9,7)	1.103	25.87	5.90	5.00	5.44	0.27	28.2

Table 4-4 Tabulated values of the relative PL intensities for SWCNT samples, calculated PL intensities from the electro-phonon interaction model,[4] and (n,m) abundances for samples produced from C_2H_2

(n,m)	Diameter	Chiral Angle	Amplitude of the partial derivative of PL intensity[2]			Calculated PL Intensity	Normalized Average Abundance
(6,5)	0.757	27	5.39	5.26	5.94	0.67	37.8
(8,3)	0.782	15.3	0.66	0.52	0.53	2.13	3.9
(7,5)	0.829	24.5	11.87	9.44	10.62	0.71	72.7
(8,4)	0.84	19.11	13.26	14.71	13.30	0.46	93.9
(10,2)	0.884	8.95	0.24	0.28	0.32	2.38	1.9
(7,6)	0.895	27.46	15.79	13.69	14.45	0.47	100.0
(9,4)	0.916	17.48	3.68	4.09	3.90	0.7	26.6
(10,3)	0.936	12.73	7.03	7.17	7.85	0.28	50.2
(8,6)	0.966	25.28	12.43	13.77	12.48	0.49	88.0
(9,5)	0.976	20.63	11.22	10.84	10.22	0.28	73.5
(8,7)	1.032	27.8	9.06	8.88	9.25	0.3	61.9
(10,5)	1.05	19.11	2.85	4.09	3.95	0.47	24.8
(9,7)	1.103	25.87	6.51	7.26	7.20	0.27	47.7

Figure 4-3 PL intensity maps as a function of excitation and emission wavelength for SDBS micellized SWCNTs in D₂O produced from four different carbon precursors on Co-Mo/SiO₂ catalysts, three parallel runs for each carbon precursor.

Figure 4-4 Calculated diameter distribution histograms (bars) obtained from PL analysis and their log normal fits. Dashed bars in panel indicate the possible position of the (10,0) and (11,0) zigzag SWCNTs and (11,1) small chiral angle SWCNTs.

Figure 4-5 Comparison of PL spectra of SWCNTs produced by CO in different surfactants including SDBS, single strain DNA, sodium deoxycholate (DOC) and SDS. Abundance analysis indicates that the (n,m) abundance distribution is not affected by different surfactants in this study.

4.3 NIR absorption spectra reconstructions

Two issues may complicate the accuracy of a particular (n,m) SWCNT abundance determined from PL experimental results. (1) Experimental results have shown that the relative PL intensity of the zigzag and small chiral angle semiconducting SWCNTs is significantly lower than those from large chiral angle tubes at the same tube diameter range.[1, 7-10] The absence of PL signals from zigzag tubes (10,0), (11,0) and small chiral angle tube (11,1) in the samples may be due to their low PL quantum efficiencies.[4] (2) The large diameter SWCNTs also have relative lower PL intensity than that of smaller diameter tubes as pointed out by researchers.[11-15] Especially, for SWCNTs produced from C_2H_2 , some larger diameter SWCNTs may not be detected by PL analysis.

In order to reconcile my findings, the methodology developed by Luo et al.[5] was adopted to reconstruct the NIR absorption manifold of the E_{11}^S transition. The overall contribution to the expected optical density (OD) of all (n,m) SWCNTs at a specific optical energy (E) can be calculated by using the following equation,

$$OD(E) = C \sum_{n,m} A(d_t) I_{cal}^{abs}(n, m) \frac{\gamma_e}{4(E - E_{11}(n, m))^2 + \gamma_e^2}$$

where C is the normalization factor introduced to account for sampling conditions and the collection geometries. $I_{cal}^{abs}(n, m)$ values for E_{11}^S transitions were taken from the calculated E_{22}^S extinction coefficients for the single-particle tight-binding theoretical model. $E_{11}(n, m)$ values were obtained from PL measurements of Figure 4-1 and γ_e is the width of the optical transitions, which is related to the lifetime of the excited states, it is approximated that $\gamma_e = C_1 + C_2/I_{cal}^{abs}(n, m)$ with C_1 and C_2 as adjustable parameters.

A single-mode log-normal distribution line shape[5] was applied to fit the experimental data as shown in Figure 4-4. The log-normal diameter distribution function for the CO produced sample, $A(d_t)$ obtained in Figure 4-4 for all (n,m) tubes, was first utilized in reconstruction. For one extreme case, where it is assumed that no diameter-induced chirality was imparted by the catalyst, zigzag (10,0) and (11,0) and small chiral angle tube (11,1) were introduced. The other extreme case corresponded to the complete absence of these small chiral angle tubes. However, as shown in Figure 4-6, the reconstructions of E_{11}^S transition for both cases are unsuccessful. It is noticed that the (n,m) abundance determined by PL analysis in my sample is quite apart from the proposed single-mode log-normal distribution compared with the sample studied by Luo et al.[5]. One scenario might be that the chiral selective growth is at play. Particular chirality could be favored in CVD growth. To verify this, a three-steps fitting strategy was applied. First, the $A(d_t)$ determined by PL analysis (Table 4-1 to Table 4-4) was directly used to reconstruct the NIR absorption spectrum. The fitting result shown in Figure 4-7 is significantly improved compared with those in Figure 4-6. Second, I added in the two zigzag tubes and one small chiral angle tube using their abundance obtained by the log-normal diameter distribution from Figure 4-4a. The result in Figure 4-7d shows that part of the reconstruction result (>1100 nm) is improved, while the other part (<1100 nm) gets worse. Third, the (10,0), (11,0) and (11,1) tubes were included, however, their abundance was set approximately at the average abundance level of those minor tubes identified in Figure 4-2. An improved reconstruction was obtained as shown in Figure 4-7c. Based on intensity variation between the experimental and reconstructed spectra in Figure 4-6 and Figure 4-7, it is concluded that the actual SWCNTs produced by CO in my sample is close to the

abundance distribution obtained by PL analysis. Zigzag tubes present at lower concentrations compared with higher chiral angle tubes. The main (n,m) species are predominately in the higher chiral angle region.

Figure 4-6 Experimental E_{11}^S optical absorption spectrum and spectral reconstruction of aqueous SDBS dispersed SWCNT suspensions grown by CO. Reconstruction is by the summation of the thin Lorentzian peak contribution from each (n,m) SWCNT using the abundance determined by single-mode log-normal distribution line shape fitting.[5] (a) Spectra reconstruction without the (10,0) and (11,0) zigzag nanotubes and small chiral angle (11,1) tube. (b) Spectra reconstruction with the (10,0) and (11,0) zigzag nanotubes and small chiral angle (11,1) tube included.

Figure 4-7 (a) Experimental E_{11}^S optical absorption spectrum (circles) and background curve (solid line) of aqueous SDBS dispersed SWCNT suspensions grown by CO. The spectra indicated with circles in panels b, c and d were obtained by subtracting the two curves in panel a. (b) Spectral reconstruction by the summation of the thin Lorentzian peak contribution from each (n,m) SWCNT using the abundance determined by PL analysis without (10,0), (11,0) and (11,1) nanotubes. (c) Reconstruction by adding (10,0), (11,0) and

(11,1) which abundance are at the average level of minor tubes identified in Figure 4-2. (d) Reconstruction adding (10,0), (11,0) and (11,1) nanotubes which abundance determined by the log-normal diameter distribution.

Similar analysis routines were conducted for samples produced from C_2H_5OH , CH_3OH and C_2H_2 . As in the same case as that of CO , it is clear that if the abundance of a specific (n,m) tube obtained by the single-mode log-normal distribution line shape is directly adopted, no matter whether the zigzag tubes are included or not, reconstruction of the E_{11}^S absorption spectra is unsuccessful. Results are shown in Figure 4-8, Figure 4-9 and Figure 4-10 for C_2H_5OH , CH_3OH and C_2H_2 respectively. On the other hand, if $A(d_t)$ determined by PL analysis was utilized to reconstruct the NIR absorption spectrum for C_2H_5OH and CH_3OH , the reconstruction can be achieved as shown in Figure 4-11 and Figure 4-12. There are mismatches of experiential and reconstructed spectra between 900 nm and 1000 nm, especially for CH_3OH (Figure 4-12). This could be due to the overlap of E_{22}^S bands from some larger diameter tubes and E_{11}^S bands of smaller diameter tubes. Even so, based on the intensity in absorption spectra, their abundance should be low compared with dominant (n,m) tubes. It is concluded that the samples produced by C_2H_5OH and CH_3OH also have the similar (n,m) abundance distribution to that obtained by PL analysis. The main (n,m) species are predominately in the higher chiral angle region.

However, the reconstruction of C_2H_2 spectra cannot be achieved as shown in Figure 4-10 and Figure 4-13. These results suggest that large diameter SWCNTs having relative lower PL intensity constitute a significant fraction of SWCNTs produced by C_2H_2 . Much broader (n,m) distribution is obtained in the SWCNT samples.

Figure 4-8 Experimental E_{11}^S optical absorption spectrum and spectral reconstruction of aqueous SDBS dispersed SWCNT suspensions grown by C_2H_5OH . Reconstruction is by the summation of the thin Lorentzian peak contribution from each (n,m) SWCNT using the abundance determined by single-mode log-normal distribution line shape fitting.[5] (a) Spectra reconstruction without the (10,0) and (11,0) zigzag nanotubes and small chiral angle (11,1) tube. (b) Spectra reconstruction with the (10,0) and (11,0) zigzag nanotubes and small chiral angle (11,1) tube included.

Figure 4-9 Experimental E_{11}^S optical absorption spectrum and spectral reconstruction of aqueous SDBS dispersed SWCNT suspensions grown by CH_3OH . Reconstruction is by the summation of the thin Lorentzian peak contribution from each (n,m) SWCNT using the abundance determined by single-mode log-normal distribution line shape fitting.[5] (a) Spectra reconstruction without the (10,0) and (11,0) zigzag nanotubes and small chiral angle (11,1) tube. (b) Spectra reconstruction with the (10,0) and (11,0) zigzag nanotubes and small chiral angle (11,1) tube included.

Figure 4-10 Experimental E_{11}^S optical absorption spectrum and spectral reconstruction of aqueous SDBS dispersed SWCNT suspensions grown by C_2H_2 . Reconstruction is by the summation of the thin Lorentzian peak contribution from each (n,m) SWCNT using the abundance determined by single-mode log-normal distribution line shape fitting.[5] (a) Spectra reconstruction without the (10,0) and (11,0) zigzag nanotubes and small chiral angle (11,1) tube. (b) Spectra reconstruction with the (10,0) and (11,0) zigzag nanotubes and small chiral angle (11,1) tube included.

Figure 4-11 (a) Experimental E_{11}^S optical absorption spectrum (circles) and background curve (solid line) of aqueous SDBS dispersed SWCNT suspensions grown by C_2H_5OH . The spectra indicated with circles in panels b, c and d were obtained by subtracting the two curves in panel a. (b) Spectral reconstruction by the summation of the thin Lorentzian peak contribution from each (n,m) SWCNT using the abundance determined by PL analysis without (10,0), (11,0) and (11,1) nanotubes. (c) Reconstruction by adding (10,0), (11,0) and (11,1)

which abundance are at the average level of minor tubes identified in Figure 4-2. (d) Reconstruction adding (10,0), (11,0) and (11,1) nanotubes which abundance determined by the log-normal diameter distribution.

Figure 4-12 (a) Experimental E_{11}^S optical absorption spectrum (circles) and background curve (solid line) of aqueous SDBS dispersed SWCNT suspensions grown by CH_3OH . The spectra indicated with circles in panels b, c and d were obtained by subtracting the two curves in panel a. (b) Spectral reconstruction by the summation of the thin Lorentzian peak contribution from each (n,m) SWCNT using the abundance determined by PL analysis without $(10,0)$, $(11,0)$ and $(11,1)$ nanotubes. (c) Reconstruction by

adding $(10,0)$, $(11,0)$ and $(11,1)$ which abundance are at the average level of minor tubes identified in Figure 4-2. (d) Reconstruction adding $(10,0)$, $(11,0)$ and $(11,1)$ nanotubes which abundance determined by the log-normal diameter distribution.

Figure 4-13 (a) Experimental

E_{11}^S optical absorption spectrum

(circles) and background curve

(solid line) of aqueous SDBS

dispersed SWCNT suspensions

grown by C_2H_2 . The spectra

indicated with circles in panels b,

c and d were obtained by

subtracting the two curves in

panel a. (b) Spectral

reconstruction by the summation

of the thin Lorentzian peak

contribution from each (n,m)

SWCNT using the abundance

determined by PL analysis

without (10,0), (11,0) and (11,1)

nanotubes. (c) Reconstruction by

adding (10,0), (11,0) and (11,1)

which abundance are at the

average level of minor tubes identified in Figure 4-2. (d) Reconstruction adding (10,0), (11,0) and

(11,1) nanotubes which abundance determined by the log-normal diameter distribution.

It is found that the pressure of carbon precursor is a key factor for the chirality control in this study. Only at high CO pressure, narrow (n,m) distribution SWCNTs were obtained. On the contrary, C_2H_5OH and CH_3OH only grew SWCNTs under vacuum conditions. C_2H_2 needed to be further diluted by 1000 times in Ar at 5 mbar, otherwise no SWCNT was produced, even so narrowly (n,m) distributed SWCNTs have not been obtained. Lu et al.[16] have proposed a hypothesis that the diameters of SWCNTs were closely related to the carbon supply rate by selective activation of nanoparticles. It is reasoned that the pressure determines the striking frequency of a carbon precursor on the cobalt particle surfaces. Meanwhile these four different carbon precursors would have different decomposition rates on the cobalt surface at 800 °C, e.g. C_2H_2 decomposes much faster than CO. The carbon feeding rate to cobalt surfaces is then tuned by pressure, leading to different (n,m) selectivity.

The narrow (n,m) selectivity of Co-Mo catalyst has been attributed to small Co clusters formed *in-situ* and stabilized by Mo carbide.[3] Lolli et al.[17] have found that different (n,m) distributions were produced by CO and CH_4 . Although their abundance analysis did not consider the absorption extinction coefficients, absorption spectra of SWCNTs produced by CH_4 did indicate much wider (n,m) distribution compared with that by CO, due to the different kinetic behavior of CH_4 decomposition. They argued that the kinetic rather than thermodynamic effect should be considered toward the chirality control. The results in this study show that narrow (n,m) selectivity on Co-Mo catalyst can be shifted using different carbon precursors. The dominant (n,m) species produced by CO in this research is about 0.1 nm larger in diameter compared with previous results,[3] probably owing to the different catalyst prereduction condition and CO

pressure applied. The spread of (n,m) distribution produced in this study is at the similar level compared with Bachilo et al.,[3] while much narrower compared with HiPco nanotubes. Moreover, C_2H_5OH and CH_3OH increased the diameter of dominant (n,m) species by 0.05-0.2 nm (Figure 4-4). Because the cobalt clusters were continuously agglomerating due to high temperature sintering during the SWCNT growth, it is argued that other than one (n,m) tube with global minimum stability energy (e.g. (7,6)) on metal cluster surfaces, several local minimum could coexist with a small difference in stability. When different carbon supply rates match with these local minimum stabilities, SWCNTs enriched with various (n,m) can be produced. By fine tuning the growth conditions, the controlled production of specific (n,m) structures could be achieved.

In addition to the pressure effect, the carbon precursor chemistry may also play an important role for attaining narrow diameter distribution nanotubes. Lolli et al.[17] have discussed the difference between CO and CH_4 and attributed the broader distribution of SWCNTs produced by CH_4 to the evolution of hydrogen, a byproduct of the CH_4 decomposition. Hydrogen may not only increase the rate of reduction and sintering of metal clusters, but also may hinder the nucleation of carbon species on the surface of the cluster by decreasing the carbon surface fugacity.[17] Zhang et al.[18] also pointed out that hydrogen radicals were damaging the formation of sp^2 -like SWCNTs in plasma enhanced CVD and showed that the addition of oxygen in the carbon precursors scavenges H species providing an environment which favors the SWCNT growth. It is reasoned that the broader distribution of SWCNTs produced by C_2H_2 may have the similar cause as that produced by CH_4 , in which a reducing agent (H_2) is the byproduct of C_2H_2 decomposition. However, for C_2H_5OH and CH_3OH , oxygen-containing species, like OH radicals, have been

suggested to facilitate the oxidation of amorphous carbon.[19] OH radicals may also provide a balance of C and H ratio to favor SWCNT growth, which leads to a narrower (n,m) distribution. H_2 (1 mL/min) was co-fed for C_2H_5OH and CH_3OH growth while few SWCNTs were produced with H_2 . It is suspected that the difference between C_2H_5OH and CH_3OH may be due to the different C/H/O ratios (2/6/1 and 1/4/1 respectively) or the difference between C-C bond of C_2H_5OH and single carbon atom in CH_3OH .

4.4 Conclusion

SWCNTs using four different carbon precursors on Co-Mo/SiO₂ catalyst have been synthesized successfully. Semiconducting (n,m) abundance has been evaluated by a method based on a single-particle tight-binding theoretical model using PL and UV-vis-NIR absorption spectroscopies. Narrowly (n,m) distributed SWCNTs can be obtained under high pressure CO or vacuumed C_2H_5OH and CH_3OH predominately in the same higher chiral angle region. For SWCNTs produced by diluted C_2H_2 , reconstruction failure of E_{11}^S NIR absorption spectra suggests that PL spectrum may miss tube fractions with larger diameters and smaller chiral angles. Carbon precursor pressure is found to be a key factor to the chirality control in this study. The carbon precursor chemistry may also play an important role in obtaining narrowly (n,m) distributed SWCNTs. The (n,m) selectivity on Co-Mo/SiO₂ catalysts can be shifted by applying different carbon precursors.

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Chapter 5

Pressure-induced SWCNT (*n,m*) Selective Growth on Co-Mo catalyst

Previous investigations of SWCNT chirality selectivity induced by different carbon precursors in Chapter 4 showed that the pressure of carbon precursor is a key factor to control the SWCNT chirality. Carbon supply rate is directly related to the pressure of carbon precursor during the SWCNT growth. Because the pressure can be continuously tuned, the SWCNT chirality distribution may be shifted systematically other than distinctly. Based on this motivation, this chapter investigates the influence of the carbon precursor pressure on the SWCNT chirality selectivity.

5.1 Effect of the CO pressure on SWCNT (*n,m*) selectivity

Co-Mo/SiO₂ catalysts and SWCNTs were synthesized as described in Chapter 2. The CVD system used in this study was specially designed to allow the pressure to be increased from one atmosphere to a desired pressure ranging from 2 to 18 bar in less than 3 seconds, avoiding SWCNT growth heterogeneity during the pressure-increasing period. PL spectroscopy was utilized to characterize SDBS-micellarized SWCNT samples. Figure 5-1 illustrates the PL intensity maps for SWCNTs with excitation scanned from 500 to 800 nm and emission collected from 850 to 1350 nm. The resonance behavior of both excitation and emission events results in spikes corresponding to transition pairs from individual semiconducting (*n,m*) SWCNTs. Figure 5-1 suggests that SWCNTs with narrow chirality distribution are produced under CO pressure from 2 to 18 bar. Dominant PL peaks are originated from the (6,5), (7,5) and (7,6) SWCNTs. The

pressure induced chirality selectivity can be identified among these three chiral SWCNTs. (6,5) has the highest intensity under 18 bar CO, and its intensity decreases when the CO pressure drops from 18 to 2 bar. In contrast, (7,6) has the highest intensity under 2 bar CO, and its intensity goes down with the increase of CO pressure. The changing trend of (7,5) intensity lies in the middle, showing the highest intensity around 12 bar CO pressure.

Figure 5-1 Pressure-induced SWCNT (n,m) selectivity on Co-Mo catalyst monitored by PL spectroscopy. Normalized PL intensity map is a function of excitation and emission wavelengths for SDBS-micellarized SWCNT samples in D_2O . Locations of three dominate chiral tubes (6,5), (7,5) and (7,6) are labeled. Pressures marked on the graph indicate the CO pressure under which SWCNTs were produced.

5.2 SWCNT (n,m) abundance analysis

The electron-phonon interaction model[1] was applied to analyze the SWCNT (n,m) abundance. The strengths of chiral tubes from Figure 5-1 were obtained by the amplitude of the partial derivative, as recommended by Arnold et al. to minimize the effects of the slowly varying background.[2] The method details were described in Chapter 3. The relative PL intensities, calculated PL quantum yields, and (n,m) abundances for SWCNTs produced under different pressures are listed from Table 5-1 to Table 5-9. Several other (n,m) species at lower chiral angles, such as (8,3), (8,4), (9,4) and (8,6), also have pronounced PL intensity. However, their intensities are significantly lower than those from the three dominant species at higher chiral angles. Figure 5-2 shows that the abundance of (6,5) tubes can be systematically increased from less than 2 % (among semiconducting tubes identified in PL analysis) to 48 % by increasing the pressure from 2 to 18 bar. The abundance of (7,6) tubes decreases from 26 % to 7 % when CO pressures are altered in the same range. The (7,5) tube abundance shows a volcano-shaped correlation with pressure, and the maximum abundance of (7,5) exists around 12 bar at 28 %. The content of secondary (n,m) tubes identified in PL analysis (Figure 5-2) also shows the pressure dependence. Abundance of (8,3) tubes increases with pressure similarly at that of (6,5) tubes. Abundance of (8,6) and (9,4) tubes decreases with pressure. And (8,4) tubes have the very similar pattern as that of (7,5) tubes.

Table 5-1 Tabulated values of the relative PL intensities for SWCNT samples, calculated PL intensities from the electro-phonon interaction model,[1] and (n,m) abundance for samples produced under **2 bar** CO on Co-Mo/SiO₂ catalysts

(n,m)	Diameter	Chiral Angle	Amplitude of the partial derivative of PL intensity[2]	Calculated PL Intensity[1]	Normalized Average Abundance
(6,5)	0.757	27	12.03	0.67	6.9
(7,5)	0.829	24.5	60.29	0.71	32.5
(8,4)	0.84	19.11	70.94	0.46	59.0
(7,6)	0.895	27.46	120.88	0.47	100.0
(10,2)	0.884	8.95	10.26	2.38	1.6
(9,4)	0.916	17.48	41.67	0.7	22.8
(8,6)	0.966	25.28	80.5	0.49	62.8
(8,7)	1.032	27.8	24.47	0.3	17.6
(9,5)	0.976	20.63	27.38	0.28	37.4
(10,3)	0.936	12.73	17.17	0.28	26.5

Table 5-2 Tabulated values of the relative PL intensities for SWCNT samples, calculated PL intensities from the electro-phonon interaction model,[1] and (n,m) abundance for samples produced under **4 bar** CO on Co-Mo/SiO₂ catalysts

(n,m)	Diameter	Chiral Angle	Amplitude of the partial derivative of PL intensity[2]	Calculated PL Intensity[1]	Normalized Average Abundance
(6,5)	0.757	27	100.6	0.67	22.0
(8,3)	0.782	15.3	26.6	2.13	1.8
(7,5)	0.829	24.5	350.2	0.71	72.2
(8,4)	0.84	19.11	207.4	0.46	66.0
(10,2)	0.884	8.95	51.9	2.38	3.2
(7,6)	0.895	27.46	340.3	0.47	100.0
(9,4)	0.916	17.48	126.7	0.7	26.5
(10,3)	0.936	12.73	18.5	0.28	26.5
(8,6)	0.966	25.28	136.0	0.49	40.6
(9,5)	0.976	20.63	33.1	0.28	17.3

Table 5-3 Tabulated values of the relative PL intensities for SWCNT samples, calculated PL intensities from the electro-phonon interaction model,[1] and (n,m) abundance for samples produced under **6 bar** CO on Co-Mo/SiO₂ catalysts

(n,m)	Diameter	Chiral Angle	Amplitude of the partial derivative of PL intensity[2]	Calculated PL Intensity[1]	Normalized Average Abundance
(6,5)	0.757	27	72.43	0.67	34.8
(8,3)	0.782	15.3	19.9	2.13	3.0
(7,5)	0.829	24.5	194.15	0.71	88.0
(8,4)	0.84	19.11	94.71	0.46	66.3
(7,6)	0.895	27.46	123.7	0.47	100.0
(10,2)	0.884	8.95	28.21	2.38	3.8
(9,4)	0.916	17.48	46.83	0.7	21.5
(8,6)	0.966	25.28	62.06	0.49	40.8
(8,7)	1.032	27.8	7.57	0.3	17.6
(9,5)	0.976	20.63	13.65	0.28	15.7
(10,3)	0.936	12.73	7.79	0.28	26.5

Table 5-4 Tabulated values of the relative PL intensities for SWCNT samples, calculated PL intensities from the electro-phonon interaction model,[1] and (n,m) abundance for samples produced under **8 bar** CO on Co-Mo/SiO₂ catalysts

(n,m)	Diameter	Chiral Angle	Amplitude of the partial derivative of PL intensity[2]	Calculated PL Intensity[1]	Normalized Average Abundance
(6,5)	0.757	27	83.72	0.67	39.0
(8,3)	0.782	15.3	24.73	2.13	3.6
(7,5)	0.829	24.5	217.55	0.71	95.6
(8,4)	0.84	19.11	88.57	0.46	60.1
(7,6)	0.895	27.46	112.44	0.47	100.0
(10,2)	0.884	8.95	34.07	2.38	4.5
(9,4)	0.916	17.48	54.94	0.7	24.5
(8,6)	0.966	25.28	68.38	0.49	43.5
(8,7)	1.032	27.8	12.58	0.3	17.6
(9,5)	0.976	20.63	15.64	0.28	17.4
(10,3)	0.936	12.73	9.52	0.28	26.5

Table 5-5 Tabulated values of the relative PL intensities for SWCNT samples, calculated PL intensities from the electro-phonon interaction model,[1] and (n,m) abundance for samples produced under **10 bar** CO on Co-Mo/SiO₂ catalysts

(n,m)	Diameter	Chiral Angle	Amplitude of the partial derivative of PL intensity[2]	Calculated PL Intensity[1]	Normalized Average Abundance
(6,5)	0.757	27	294.78	0.67	78.1
(8,3)	0.782	15.3	144.76	2.13	12.1
(7,5)	0.829	24.5	410.78	0.71	102.7
(8,4)	0.84	19.11	231.58	0.46	89.4
(7,6)	0.895	27.46	162.34	0.47	100.0
(10,2)	0.884	8.95	49.84	2.38	3.7
(9,4)	0.916	17.48	65.92	0.7	16.7
(8,6)	0.966	25.28	32.41	0.49	11.7

Table 5-6 Tabulated values of the relative PL intensities for SWCNT samples, calculated PL intensities from the electro-phonon interaction model,[1] and (n,m) abundance for samples produced under **12 bar** CO on Co-Mo/SiO₂ catalysts

(n,m)	Diameter	Chiral Angle	Amplitude of the partial derivative of PL intensity[2]	Calculated PL Intensity[1]	Normalized Average Abundance
(6,5)	0.757	27	392.88	0.67	89.3
(8,3)	0.782	15.3	154.96	2.13	11.1
(7,5)	0.829	24.5	484.18	0.71	103.9
(8,4)	0.84	19.11	250.09	0.46	82.8
(7,6)	0.895	27.46	184.29	0.47	100.0
(10,2)	0.884	8.95	48.3	2.38	3.1
(9,4)	0.916	17.48	72	0.7	15.7
(8,6)	0.966	25.28	32.67	0.49	10.2

Table 5-7 Tabulated values of the relative PL intensities for SWCNT samples, calculated PL intensities from the electro-phonon interaction model,[1] and (n,m) abundance for samples produced under **14 bar** CO on Co-Mo/SiO₂ catalysts

(n,m)	Diameter	Chiral Angle	Amplitude of the partial derivative of PL intensity[2]	Calculated PL Intensity[1]	Normalized Average Abundance
(6,5)	0.757	27	383.79	0.67	116.8
(8,3)	0.782	15.3	120.49	2.13	11.5
(7,5)	0.829	24.5	345.28	0.71	99.2
(8,4)	0.84	19.11	160.59	0.46	71.2
(7,6)	0.895	27.46	123.17	0.47	100.0
(10,2)	0.884	8.95	27.59	2.38	2.4
(9,4)	0.916	17.48	45.12	0.7	13.1
(8,6)	0.966	25.28	19.61	0.49	8.2

Table 5-8 Tabulated values of the relative PL intensities for SWCNT samples, calculated PL intensities from the electro-phonon interaction model,[1] and (n,m) abundance for samples produced under **16 bar** CO on Co-Mo/SiO₂ catalysts

(n,m)	Diameter	Chiral Angle	Amplitude of the partial derivative of PL intensity[2]	Calculated PL Intensity[1]	Normalized Average Abundance
(6,5)	0.757	27	313.2	0.67	140.7
(8,3)	0.782	15.3	71.16	2.13	10.1
(6,4)	9.692	23.41	16.14	1.48	3.3
(7,5)	0.829	24.5	234.55	0.71	99.5
(8,4)	0.84	19.11	119.59	0.46	78.3
(7,6)	0.895	27.46	68.67	0.47	100.0

Table 5-9 Tabulated values of the relative PL intensities for SWCNT samples, calculated PL intensities from the electro-phonon interaction model,[1] and (n,m) abundance for samples produced under **18 bar** CO on Co-Mo/SiO₂ catalysts

(n,m)	Diameter	Chiral Angle	Amplitude of the partial derivative of PL intensity[2]	Calculated PL Intensity[1]	Normalized Average Abundance
(6,5)	0.757	27	99.31	0.67	179.4
(8,3)	0.782	15.3	22.12	2.13	12.6
(6,4)	9.692	23.41	7.68	1.48	6.3
(7,5)	0.829	24.5	46.46	0.71	79.2
(8,4)	0.84	19.11	27.05	0.46	71.2
(7,6)	0.895	27.46	10.52	0.47	100.0

Figure 5-2 Abundances of three main chiral tubes systematically alter with changing CO pressure.

Chirality map of aqueous suspensions of SWCNTs indicates three dominant chiral tubes identified in PL analysis ((6,5), (7,5) and (7,6)) and other tubes observed. The abundance evaluation is based on the electron-phonon interaction model [1] considering the PL quantum yield difference among semiconducting tubes.

The relative PL intensity of zigzag, small chiral angle, and large diameter semiconducting SWCNTs is significantly lower than that from large chiral angle and small diameter SWCNTs.[3-5] The absence of PL signal from these tubes in my samples may be due to their low PL quantum efficiency.[1] To reconcile the findings, UV-vis-NIR absorption spectra of SDBS-micellarized SWCNT samples were taken. Figure 5-3 suggests that the three dominant chiral tubes identified in PL analysis are the main species produced. Their abundances vary with CO pressure in the same pattern as that in PL analysis. Deconvolution of the absorption spectra of SWCNTs into distinct chiral contributions is complicated because their transition energies are closely spaced. The reconstruction of absorption spectra in Chapter 4 indicated that a good reconstruction was obtained when zigzag and smaller chiral angle tubes were included at the average abundance level of minor tubes identified in PL analysis, other than including them as the same abundance as dominant high chiral angle tubes. It reaffirms that the main (n,m) species produced are those high chiral angle tubes identified in PL analysis.

Raman spectroscopy was also conducted for trying to quantify the SWCNT (n,m) abundance. Raman spectra were taken for SWCNT samples under 514.5 nm, 633 nm and 785 nm laser energies shown from Figure 5-4 to Figure 5-6, respectively. RBM peaks in Raman spectra suggest that smaller diameter tubes are produced under higher CO pressure. Yao et al. [6] have used Raman spectroscopy to monitor the diameter and chirality variation of individual tubes with growth temperature changes. However, the abundance evaluation of (n,m) tubes for bulk SWCNT samples are more complicated requiring both continuous tunable laser excitation Raman spectroscopy and intrinsic properties for each chiral species. The three laser energies used in this

study are not sufficient to determine the population of semiconducting tubes identified in PL by Raman spectroscopy.

Figure 5-3 UV-vis-NIR absorption spectra of SWCNTs produced under different CO pressures.

The relative strengths of the E_{11} and E_{22} transitions for semiconducting (6,5) (highlighted in blue), (7,5) (highlighted in green) and (7,6) (highlighted in red) indicate their abundance changes with CO pressure variation.

Figure 5-4 Raman spectra of SWCNTs produced under different CO pressures on Co-Mo/SiO₂ catalysts. Raman spectra were taken at 514.5 nm. Dashed and dotted lines are calculated positions of those dominant (*n,m*) tubes identified in PL analysis based on Bachilo's 4-parameter tight binding fitting model.[7]

Figure 5-5 Raman spectra of SWCNTs produced under different CO pressures on Co-Mo/SiO₂ catalysts. Raman spectra were taken at 633 nm. Dashed and dotted lines are calculated positions of those dominant (*n,m*) tubes identified in PL analysis based on Bachilo's 4-parameter tight binding fitting model.[7]

Figure 5-6 Raman spectra of SWCNTs produced under different CO pressures on Co-Mo/SiO₂ catalysts. Raman spectra were taken at 785 nm. Dashed and dotted lines are calculated positions of those dominant (*n,m*) tubes identified in PL analysis based on Bachilo's 4-parameter tight binding fitting model.[7]

5.3 Mechanism

To understand the mechanism of (n,m) selectivity under different CO pressures, the SWCNT growth under the pure CO of 8 bar and a mixture (CO/Ar=1:1) of 16 bar were compared. PL intensity maps are shown in Figure 5-7. The result shows that the similar chirality distribution is obtained under these two conditions. It suggests that the partial pressure of CO other than the total pressure in the CVD reactor is the determining factor in (n,m) selectivity. The (n,m) selectivity also appears to start at the early stage of the SWCNT structure formation. If CO was introduced slowly (in 1 minute rather than 3 seconds) from 1 bar to the desired pressure, the distinct difference among various pressures was blurred. It is also found that the chirality distribution of SWCNTs produced under 6 bar CO (pressure increasing period is approximate 30 seconds) in previous study (Chapter 4) is similar to that of SWCNTs produced under 4 bar CO in this study (pressure increasing period is less than 3 seconds).

Figure 5-7 Normalized PL intensity map as a function of excitation and emission wavelength for SWCNT samples produced (left) under pure CO of 8 bar and (right) under a gas mixture (CO/Ar=1:1) of 16 bar.

Hofmann et al. has proposed that the SWCNT growth on a size-fixed metal cluster has four steps described in Chapter 1.[8] It is reasoned that the direct impact of increasing CO pressure is to increase the striking coefficient of CO molecules on the Co particles. It may lead to a faster dissociation rate of CO, releasing more active carbon atoms to interact with Co particles. Theoretical calculations have shown that the binding energies of CO to cobalt particles and preferred chemisorption sites depend on the particle size and surface coverage.[9] Shibuta et al.[10] and Balbuena et al.[11] have proposed that carbon caps formed when the catalytic clusters reaches saturation with carbon atoms. SWCNT growth may be initiated faster under higher CO pressure because of the higher concentration of active carbon atoms available, which leads to smaller diameter tubes like (6,5) and (8,3). When CO pressure is lower, it may take a longer period of time for enough active carbon atoms to form a stable carbon cap structure on the Co cluster surface. Because Co clusters are continuously aggregating during SWCNT growth owing to the high-temperature sintering, Co clusters might grow larger before the carbon caps could be stabilized on their surfaces. When the dynamic interaction between carbon caps and Co clusters is stabilized under lower CO pressure, larger diameter SWCNTs like (7,6) and (9,4) are produced.

On the other aspect, the concentration of large chiral angle tubes determined in PL (such as (6,5), (7,5), and (7,6)) is much higher than their small chiral angle tube counterparts (such as (8,3), (8,4), and (9,4), respectively) as shown in Figure 5-2. A theoretical calculation[12] has compared the total energy of nanotube caps on a Ni(111) surface and found that large chiral angle tubes such as (7,5) and (7,6) have lower formation energies compared with small chiral angle tubes. On the basis of this calculation,[12] Reich et al. proposed that chiral selectivity must start during

nucleation, and once a cap is formed, it is quenched in and grows into a unique nanotube. The selectivity of larger chiral angle tubes shown in my study may be owing to the higher stability between large chiral angle carbon caps with Co clusters surface.

5.4 Conclusion

CO pressure is a critical factor in SWCNT (n,m) control for Co-Mo catalyst. SWCNT samples enriched with three dominant tubes at (6,5), (7,5), and (7,6) can be obtained. Semiconducting tube abundance was evaluated by PL and UV-vis-NIR absorption spectroscopy. Selective growth of SWCNTs enriched with different chiral tubes can be achieved. By increasing the pressure from 2 to 18 bar, the amount of the (6,5) with respect to the amount of the (7,6) can be tuned. The partial pressure of CO other than the total pressure is the determining factor in (n,m) selectivity.

5.5 References

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Chapter 6

Effect of Different Catalyst Supports on the (n,m) Selective Growth of SWCNTs on Co-Mo Catalyst

SWCNT synthesis in CVD is an extremely sensitive catalysis reaction. A critical SWCNT growth condition window may exist, in which the right balance is necessary between carbon supply and metal cluster nucleation for SWCNT growth.[1, 2] Furthermore, this dynamic balance can be changed by varying growth conditions, which leads to the production of SWCNTs with different (n,m) distributions. Catalysts for SWCNT synthesis can be prepared by first dispersing metal ions on a catalyst support (e.g. a high surface area oxide). The metal ions are reduced, and nucleate into small clusters, which trigger tube growth under a carbon source. Various catalyst supports, including SiO_2 , [3] Al_2O_3 , [4] MgO , [5] zeolites, [6] silica-alumina, [7] clay, [8] and MCM-41, [9] have been utilized owing to their large surface area, high temperature stability, and simplicity for removal by either acid or alkaline. [10] Lolli et al. [11] have attempted to change the (n,m) selectivity by modifying the morphology of metal clusters via their interactions with different catalyst supports. They compared the SWCNT growth from Co-Mo catalysts supported on SiO_2 and MgO , and concluded that smaller chiral angle tubes are produced from MgO supported catalysts due to the stronger interaction between MgO and Co. [11] Lamouroux et al. [10] further proposed that a strong “metal-support interaction” is necessary to limit the high temperature sintering of metal clusters, but catalyst supports such as TiO_2 , which has been reported to have a strong interaction with supported metal particles, [12] has not been tested for SWCNT growth. Therefore, it is useful to evaluate the feasibility of (n,m) selectivity control

through different catalyst supports, which may help to achieve the ultimate goal of (n,m) selective growth of SWCNTs.

Driven by this aim, four oxide catalyst supports, including SiO_2 , Al_2O_3 , MgO , and TiO_2 were studied. To systematically elucidate the effect of catalyst supports, SWCNTs were synthesized under the same growth condition while maintaining the Co-Mo molar ratio and loading-to-surface-area ratio constant for all catalysts. The resulting carbon deposits were evaluated by Raman spectroscopy, TGA, PL and UV-vis-NIR absorption spectroscopies. UV-vis diffuse reflectance spectroscopy was used to measure the domain size of transition metal oxides. The reducibility of Co and Mo on different catalyst supports was characterized by TPR.

6.1 Co-Mo catalysts on different substrates

Bimetallic Co-Mo catalysts supported on different catalyst substrates (SiO_2 , Sigma-Aldrich, No. 288624; Al_2O_3 , Sigma-Aldrich, No. 267740; MgO , Sigma-Aldrich, No. 342793; and TiO_2 , Degussa, Aeroxide P25) were prepared by impregnation. The Co (from $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, 99.999 %) to Mo (from $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, Sigma-Aldrich, 99.98 %) molar ratio was fixed at 1:3 molar ratios. Mo loading was 4.6 wt.% for SiO_2 supported catalysts with the surface area of $480 \text{ m}^2/\text{g}$. The metal contents for other supports, such as Al_2O_3 ($155 \text{ m}^2/\text{g}$), MgO ($145 \text{ m}^2/\text{g}$), and TiO_2 ($45 \text{ m}^2/\text{g}$) were adjusted according to the same loading-to-surface-area ratio. To better clarify the role of catalytic supports, monometallic catalysts, Co/support and Mo/support, were also prepared with identical Co or Mo loadings compared to those of Co-Mo/support

catalysts. After impregnation, catalysts were dried overnight in an oven at 60 °C and then calcined for 3 hours at 500 °C in air. Samples prepared are listed in Table 6-1.

Table 6-1 Synthesized Co, Mo, and Co-Mo catalysts supported on various substrates

	Type of	Metal Content		Surface	Metal/Surface Area	
	Substrate	(wt.%)		Area	(μmol/m ²)	
		Co	Mo	(m ² /g)	Co	Mo
Co/SiO ₂	SiO ₂	0.942	-	480	0.333	-
Mo/SiO ₂	SiO ₂	-	4.6		-	0.999
Co-Mo/SiO ₂	SiO ₂	0.942	4.6		0.333	0.999
Co/Al ₂ O ₃	Al ₂ O ₃	0.304	-	155	0.333	-
Mo/Al ₂ O ₃	Al ₂ O ₃	-	1.486		-	0.999
Co-Mo/Al ₂ O ₃	Al ₂ O ₃	0.304	1.486		0.333	0.999
Co/MgO	MgO	0.285	-	145	0.333	-
Mo/MgO	MgO	-	1.39		-	0.999
Co-Mo/MgO	MgO	0.285	1.39		0.333	0.999
Co/TiO ₂	TiO ₂	0.0883	-	45	0.333	-
Mo/TiO ₂	TiO ₂	-	0.431		-	0.999
Co-Mo/TiO ₂	TiO ₂	0.0883	0.431		0.333	0.999

6.2 Carbon deposit composition analysis

Figure 6-1 Raman spectra of carbon deposits grown from Co-Mo catalysts supported on SiO₂, Al₂O₃, MgO, and TiO₂. (a-d) are under 514 nm laser excitation. (e-h) are under 633 nm laser excitation.

Figure 6-1 shows Raman spectra of carbon deposits grown from Co-Mo catalysts supported on SiO₂, Al₂O₃, MgO, and TiO₂. The RBM is the fingerprint for SWCNT structure identification.[13] Strong RBM peaks (between 100 and 400 cm⁻¹ range) are displayed in Figure 6-1 for carbon deposits grown from Co-Mo catalysts supported on SiO₂ and MgO. Under a 514 nm laser (Figure 6-1a and c), the dominant RBM peaks for Co-Mo/SiO₂ and Co-Mo/MgO are both centered at around 266 cm⁻¹. It suggests that SWCNTs grown from Co-Mo/MgO are similar in diameter compared to tubes grown from Co-Mo/SiO₂ because the RBM peak position is inversely

proportional to the diameter of SWCNT.[13] Raman spectra conducted under a 633 nm laser (Figure 6-1e and g) also reveal that Co-Mo/SiO₂ and Co-Mo/MgO grow the same tube species. The RBM peaks of tubes from Co-Mo/MgO are more intense at the higher wavenumber region (278 cm⁻¹). Due to the resonance effect, it is difficult to accurately determine the (*n,m*) distribution of a SWCNT sample using Raman spectroscopy. The (*n,m*) distribution of SWCNTs produced on Co-Mo/SiO₂ and Co-Mo/MgO were characterized by PL and UV-vis-NIR spectroscopies, which will be discussed in the next section.

Figure 6-1b and f show that carbon deposits from Co-Mo/Al₂O₃ have no RBM peaks, suggesting that Co-Mo/Al₂O₃ is not selective for SWCNT growth. Furthermore, the single-peak featured G bands (1590 cm⁻¹) and the intense D bands (1310 cm⁻¹) on Figure 6-1b and f demonstrate the presence of MWCNTs or graphite.[14] For carbon deposits grown on Co-Mo/TiO₂, Raman spectra of carbon deposits, shown in Figure 6-1d and h, are strongly affected by Raman features of TiO₂ support. TiO₂ was characterized to elucidate its impact on Raman spectra. Degussa P25 is a mixture of 80 % anatase and 20 % rutile. The Raman spectrum (grey curve in Figure 6-1d) from fresh TiO₂ displays several peaks, similar to previous studies.[15] However, after impregnating metal ions, calcination, and SWCNT growth, Raman spectrum in the RBM region of Co-Mo/TiO₂ resembles that of pure rutile TiO₂. [15] The structure change of TiO₂ is beyond the scope of the present study. An important message is that the RBM peaks on Figure 6-1d are mainly contributed by TiO₂ rather than SWCNTs. Based on the shape of G band and D band on Figure 6-1d and h, it is concluded that Co-Mo/TiO₂ is more selective for MWCNT growth than SWCNT growth.

To further verify the results obtained by Raman spectroscopy, TGA was applied to distinguish carbon species in the produced carbon deposits. Figure 6-2 shows the TGA profiles of carbon deposits grown from four different supports. In Figure 6-2a, weak peaks from amorphous carbon (below 300 °C) can be observed. Both the two major DTG peaks centered at 420 and 530 °C can be assigned to SWCNTs, similar to a previous study.[1] The two oxidation peaks from SWCNTs are caused by different interactions between SWCNTs and metal residues. The weak and broad peak around 800 °C comes from Mo residues. Figure 6-2b demonstrates that carbon deposits grown on Co-Mo/Al₂O₃ are mainly amorphous carbon and MWCNTs; this is consistent with Raman results presented in Figure 6-1. Figure 6-2c illustrates that most carbon deposits grown on Co-Mo/MgO are SWCNTs, having one oxidation peak at 460 °C. The DTG results in Figure 6-2d demonstrate the presence of MWCNTs in carbon deposits grown from Co-Mo/TiO₂, which is consistent with Raman results shown in Figure 6-1. Moreover, DTG in Figure 6-2d also indicates the presence of a small fraction of SWCNTs.

Figure 6-2 TGA of carbon deposits from: (a) Co-Mo/SiO₂; (b) Co-Mo/Al₂O₃; (c) Co-Mo/MgO; and (d) Co-Mo/TiO₂. Weight loss profiles are dotted lines, while the corresponding DTG profiles are solid lines. The proposed temperature regions for oxidation of SWCNTs and MWCNTs are highlighted in light grey and dark grey, respectively.

6.3 SWCNT (n,m) abundance analysis

Since only Co-Mo/SiO₂ and Co-Mo/MgO are selective to SWCNTs, as indicated by Raman spectroscopy and TGA, further evaluations toward their (n,m) and diameter distributions were conducted on these two samples. The resonance behavior of both excitation and emission events results in spikes corresponding to transition pairs from individual (n,m) SWCNTs. The PL maps in Figure 6-3 show that SWCNTs with narrow (n,m) distribution were produced using both Co-Mo/SiO₂ and Co-Mo/MgO. In order to confirm that the observed narrow (n,m) distribution is not induced by our dispersion or centrifugation, SWCNTs were also dispersed by three surfactants separately: SC, SDBS and SDS. Furthermore, the dispersed SWCNT solutions were centrifuged under different centrifugation forces from 20,000 to 120,000 g prior to PL studies. In subsequent PL studies, no significant changes in their (n,m) distribution were observed as compared to those results shown in Figure 6-3. To estimate the abundance of various (n,m) tubes, It was considered that PL intensities are proportional to tube abundances. PL efficiencies of various (n,m) species were not considered here because a recent experimental study on individual tubes recommends that the actual PL efficiency differences among various (n,m) species may not be as large as previous theoretical estimations.[16] Furthermore, it was also noticed that when a SWCNT sample has narrow (n,m) distribution and enriched with a few types of high chiral angle tubes (e.g. SWCNTs grown from Co-Mo/SiO₂ and Co-Mo/MgO in this study), these two (n,m) abundance evaluation methods (applying PL quantum efficiencies or not) provide similar results (Table 6-3). To minimize the influence of varying spectrum backgrounds, PL intensities were determined from the amplitude of the partial derivatives of each single emission profile extracted from PLE

maps.[17] Figure 6-3d to f present the (n,m) abundance for each species identified in PLE maps as a function of its diameter. The abundance and the properties of identified (n,m) species are also listed in Table 6-2. Based on PLE maps, (7,5) is the most dominant species, and SWCNTs grown from both Co-Mo/SiO₂ and Co-Mo/MgO have a narrow diameter distribution.

Figure 6-3 Two-dimensional excitation versus emission PLE contour maps of SWCNTs from: (a) Co-Mo/SiO₂, prereduced at 500 °C; (b) Co-Mo/MgO, prereduced at 500 °C; and (c) Co-Mo/MgO, prereduced at 550 °C. Calculated diameter distribution histograms of SWCNTs obtained from corresponding PLE contour maps: (d) from (a), (e) from (b), (f) from (c).

Table 6-2 Abundance of (n,m) tubes from Co-Mo/SiO₂ and Co-Mo/MgO determined by PL spectroscopy

(n,m)	Diameter (nm)	Chiral Angle (degree)	E ₁₁ ^a (nm)	E ₂₂ ^b (nm)	SiO ₂ , 500 °C	MgO, 500 °C	MgO, 550 °C
(6,5)	0.757	27.0	986	570	13.46	18.76	18.79
(8,3)	0.782	15.3	962	666	4.30	10.98	12.35
(9,2)	0.806	9.8	1144	552	0.00	2.79	3.34
(7,5)	0.829	24.5	1036	646	30.68	39.92	36.75
(8,4)	0.840	19.1	1120	590	8.66	11.46	12.81
(10,2)	0.884	8.9	1070	736	4.83	2.69	2.44
(7,6)	0.895	27.5	1134	648	13.96	4.81	4.69
(9,4)	0.916	17.5	1112	726	7.94	2.60	1.90
(10,3)	0.936	12.7	1258	648	1.58	1.20	0.91
(8,6)	0.966	25.3	1182	722	10.49	2.40	3.06
(9,5)	0.976	20.6	1254	680	2.65	0.60	0.72
(8,7)	1.032	27.8	1274	732	1.46	1.79	2.24

^a and ^b. Excitation and absorption energies of (n,m) tubes were determined by spike positions

observed on PLE maps shown in Figure 6-3

Table 6-3 Comparison of (n,m) abundance evaluation between applying PL quantum efficiency and using PL intensity directly. Method A: directly use PL intensity, Method B: applying PL quantum efficiencies predicted from electron-phonon interaction model.[18]

(n,m)	SiO ₂ , 500 °C		MgO, 500 °C		MgO, 550 °C	
Method	A	B	A	B	A	B
(6,5)	13.46	11.92	18.76	18.23	18.79	18.09
(8,3)	4.30	1.20	10.98	3.36	12.35	3.74
(9,2)	0.00	0.00	2.79	4.54	3.34	5.39
(7,5)	30.68	25.64	39.92	36.60	36.75	33.38
(8,4)	8.66	11.17	11.46	16.22	12.81	17.96
(10,2)	4.83	1.20	2.69	0.73	2.44	0.66
(7,6)	13.96	17.61	4.81	6.66	4.69	6.44
(9,4)	7.94	6.72	2.60	2.42	1.90	1.75
(10,3)	1.58	3.34	1.20	2.78	0.91	2.10
(8,6)	10.49	12.69	2.40	3.19	3.06	4.02
(9,5)	2.65	5.62	0.60	1.39	0.72	1.65
(8,7)	1.46	2.88	1.79	3.87	2.24	4.82

Figure 6-4 UV-vis-NIR spectra of SC dispersed SWCNTs from: (a) Co-Mo/SiO₂; (b) Co-Mo/MgO reduced at 500°C; and (c) Co-Mo/MgO reduced at 550°C. The relative absorption peaks at E₁₁ transitions for tubes with different diameters are highlighted.

The dispersed SWCNT solutions were also characterized by UV-vis-NIR absorption spectroscopy. The UV-vis-NIR spectra shown in Figure 6-4 reaffirmed that SWCNTs from Co-Mo/MgO contain more tube species with smaller diameter than those from Co-Mo/SiO₂. More specifically, SWCNTs from Co-Mo/MgO contains more (8,3) and (6,5) tubes, as highlighted in light grey color. The highlighted light grey color peaks (from (8,3) and (6,5) tubes) of spectra b and c in Figure 6-4 are more intense relative to the grey color peaks from (7,5) tubes. This is

different from the PL results in Figure 6-3, in which peaks from (7,5) tubes have the highest intensity. The similar differences between UV-vis-NIR and PL spectroscopies have been observed in chapter 5. There are two reasons which may explain the apparent discrepancy between UV-vis-NIR and PL results: (1) The absorption peaks of (6,5) and (8,3) tubes are overlapped. Both (8,3) and (6,5) may contribute to the same broad absorption peak in UV-vis-NIR spectra, while they are clearly separated in PLE maps. (2) Different (n,m) species have different absorption and PL efficiency, which may lead to dissimilar peak intensities in PL and UV-vis-NIR spectroscopies.

Figure 6-5 (n,m) map of SWCNTs from Co-Mo/SiO₂ and Co-Mo/MgO. Tubes detected in PL spectroscopy were highlighted in black and grey colors (darker color represents higher abundance).

As claimed by Lolli et al.,[11] MgO supported catalysts are more selective to small chiral angle tubes (e.g. (8,4)) compared to SiO₂ supported catalysts. Their claim was obtained by evaluating (n,m) abundance through fitting absorption spectra of different samples.[11] However, it is found

that their absorption spectrum fitting method may have underestimated the abundance of smaller chiral angle tubes (e.g. (8,3)) produced from SiO₂ supported catalysts. As illustrated in Figure 6-5, (8,3) has a similar diameter as (6,5), while (8,4) has a similar diameter as (7,5). E₁₁ transition energies of (7,5) and (8,4) are quite different (at 1028 and 1116 nm respectively), as listed in Table 6-2. It is relatively simple to differentiate the contribution from those two species on absorption spectra. However, E₁₁ transition energies of (6,5) and (8,3) are closer at 989 and 955 nm, respectively, which makes them harder to be deconvolved from absorption spectra, as illustrated in Figure 6-4. In contrast, PL results in Figure 6-3 clearly highlight the existence of (8,3) tubes from SiO₂ supported catalysts. As shown in Figure 6-5, (8,3) has even smaller chiral angle than (8,4) (15.3° vs. 19.1°). Therefore, it is concluded that the MgO supported catalysts do not possess particular selectivity towards smaller chiral angle tubes compared to SiO₂ supported catalysts.

6.4 Characterizations of Co-Mo catalysts supported on different substrates

There are two unexpected findings in SWCNT characterization results (1) MgO and SiO₂ supported catalysts produce SWCNTs with similar (*n,m*) distribution, although MgO is known to interact more strongly with Co than SiO₂, and to form solid solutions with Co ions.[11] (2) TiO₂ supported catalysts are not SWCNT selective, although reducible TiO₂ exhibits strong interaction with group VIII metals.[12] The influence of the catalyst supports on the stabilization of metal particles usually can be explained by several dynamics processes such as: encapsulation or mechanical trapping, formation of new chemical compounds, alloying with the elements constituting the lattice of support, anchoring of the metal particle by the surface sites.[19]

Figure 6-6 UV-vis diffuse reflectance spectroscopy for band-gap extrapolation of Co-Mo catalysts supported on four different catalyst supports. Gaps for two reference compounds are pointed using arrows.

Lolli et al.[11] reported that domain size of small metal oxides can be changed due to the different interaction between supports and metals leading to the growth of SWCNTs at different chiral angles. However, our results in PL and UV-vis-NIR studies present a different trend. To clarify the influence of metal oxide domain size changes, the UV-vis diffusive reflectance spectroscopy was applied to measure the band energy gap of catalysts, which is inversely proportional to the metal oxide domain size. As recommended,[11, 20] the square root of the

Kubelka-Munk function multiplied by the photon energy is used to plot the resulting function versus the photon energy. The spectra data for calcined Co-Mo catalysts supported on four different catalyst supports are shown in Figure 6-6. Energy gaps of two references (indicated in Figure 6-6) were also used to validate our experimental procedure. SiO₂ supported catalysts have a band gap of 3.25 eV, while MgO supported catalysts have a band gap of 3.4 eV, indicating that MgO supported catalysts have a smaller metal oxide domain size than SiO₂ supported catalysts. However, disordered metal clusters on MgO do not produce SWCNTs significantly different from those found on SiO₂. Apart from this, Al₂O₃ supported catalyst has a smaller metal oxide domain size (band gap of 3.6 eV) than TiO₂ supported catalyst (band gap of 2.94 eV); however, both TiO₂ and Al₂O₃ supported catalysts are not selective to SWCNT growth. These results consistently demonstrate that different domain size of metal oxides induced by various catalyst supports is not directly responsible for the (n,m) selective growth of SWCNTs.

The chemistry of the metal-support interaction is one of the key factors to understand the catalytic performance of different catalysts.[19] TPR is a useful characterization technique for investigating the chemistry of the metal-support interaction and surface chemical information (e.g. material species, stability, and metal distribution).[21] Figure 6-7 shows the TPR profiles of metal species on four catalyst supports. For each support, monometallic Co and Mo catalysts were compared with bimetallic Co-Mo catalysts to reveal the possible synergistic effect between Co and Mo.

Figure 6-7 TPR profiles of monometallic Co, Mo and bimetallic Co-Mo catalysts supported on various catalyst supports: (a) SiO₂, (b) Al₂O₃, (c) MgO, and (d) TiO₂

Figure 6-7a presents TPR profiles of catalysts supported on SiO₂. The first two peaks on the TPR profile of Co supported on SiO₂ are at 380 °C and 470 °C, which are due to the Co oxide reduction under H₂ following these steps: Co₃O₄ → CoO → Co.[22] Co oxides (Co₃O₄ and CoO) formed during the calcination of catalysts. They can be reduced at relatively low temperatures and are likely to form large metal particles under high temperature reduction during SWCNT growth. The peak above 900 °C can be attributed to the reduction of Co silicates (CoSiO₃ and Co₂SiO₄).[23] Co silicates are formed through the strong interaction between Co ions and SiO₂ support. Because

of their less reducibility, it is difficult to reduce Co silicates for SWCNT growth. The TPR profile of monometallic Mo supported on SiO₂ has one major peak at 770 °C, which can be explained by the reduction of MoO₃ (formed in calcination) in two steps: MoO₃→MoO₂→Mo.[24, 25] With the assistance of TPR profiles from monometallic Co and Mo catalysts, the peaks on the TPR profile of Co-Mo catalyst supported on SiO₂ can be allocated accordingly. It should be noted that the peak of Co silicates is absent on the TPR profile of Co-Mo catalyst. This may be due to the presence of Mo, which may curb the interaction between Co ions and SiO₂ to form Co silicates. Nonetheless, the most important feature related to SWCNT growth is the new peak at 575 °C, as highlighted in grey color. This peak can be attributed to the reduction of CoMoO₄ following a route of CoMoO₄→CoMoO₃→Co₃Mo→Co₂Mo₃, in which Co ions are well dispersed by Mo.[23, 24] The existence of CoMoO₄ has previously been verified by XRD.[23, 24] The highly dispersed Co ions are then further reduced by CO forming small metal clusters than result in (*n,m*) selective SWCNT synthesis.

Figure 6-7b shows TPR profiles of catalysts supported on Al₂O₃. It can be noted that the reduction peak at 570 °C for monometallic Mo supported on Al₂O₃ is very small, as compared with that in TPR profiles of catalysts supported on SiO₂. However, a large peak can be observed above 900 °C. Previous TPR and XRD studies on Mo catalysts indicated that Al₂O₃ interact strongly with Mo oxides to form tetrahedral Mo species that are difficult to be reduced.[26] This accounts for the Mo reduction peak above 900 °C. The TPR profile of Co-Mo catalyst supported on Al₂O₃ also presents a large peak above 900 °C, suggesting that most Mo species still interact strongly with Al₂O₃ rather than Co. TPR peaks of Co oxides upshift to 535 °C, which is still

significantly lower than the 575 °C peak of SiO₂ supported catalyst. Therefore, it is proposed that there is a strong interaction between Mo and Al₂O₃, interrupting the synergistic effect between Co and Mo. Without interaction with Mo, Co species are easily reduced to form larger metal particles that are more selective for MWCNTs than SWCNTs.

Figure 6-7d also illustrates the interruption of the synergistic effect between Co and Mo supported on TiO₂. TiO₂ possesses strong interaction with metal species, which is confirmed by the multiple peaks of monometallic Co and Mo catalysts. No intense peaks exist between 500 °C and 600 °C on the TPR profile of Co-Mo catalysts. It is proposed that the absence of these peaks is caused by the strong interactions of Co or Mo with TiO₂ individually, which disrupts the synergistic effect between Co and Mo. Moreover, part of Co oxides supported on TiO₂ can be easily reduced, as indicated by the peak at 315 °C. Even though some Co species (which are reduced at higher temperature) can bring about the growth of SWCNTs, Co-Mo/TiO₂ produce large amount of MWCNTs owing to Co species reduced at low reduction temperatures.

Figure 6-7c illustrates different TPR profiles for catalysts supported on MgO. A strong peak contributed by MgCo₂O₄ species is observed at 635 °C for monometallic Co catalysts.[27] The TPR profile of monometallic Mo catalyst also shows one major peak that belongs to the reduction of MoO₃. The main peak of Co-Mo catalyst suggests a strong interaction between Co and Mo. The reduction temperature of CoMoO₄ upshifted by 70 °C compared to the SiO₂ supported Co-Mo catalyst (Figure 6-7a). This upshifted temperature may be the reason for smaller diameter SWCNTs produced on MgO supported catalyst, as indicated in Figure 6-3. Since the reduction temperature of the monometallic Co catalyst on MgO is almost the same as the Co-Mo catalyst, an

intriguing question may raise: whether or not Co/MgO and Co-Mo/MgO have the same performance in SWCNT synthesis? To answer this question, Co/MgO was tested for SWCNT growth. After 500 °C prereduction in H₂ and growth under CO at 800 °C, small amount of carbon deposits were observed. MWCNTs were the main species inside this carbon deposits, suggesting that the MgCo₂O₄ species formed on Co/MgO are different from Co ions dispersed by Mo from Co-Mo/MgO. This finding also confirms that the synergistic effect between Co and Mo is critical for good SWCNT selectivity.

In my SWCNT synthesis experiments, all catalysts have been prereduced in H₂ at 500 °C for better comparison among different samples. Based on the TPR profile of MgO supported catalysts in Figure 6-7c, 500 °C may not be the optimum reduction temperature for Co-Mo/MgO. Therefore, another batch of SWCNTs was synthesized at 550 °C prereduction temperature in H₂ using Co-Mo/MgO, considering that the reduction peak of CoMoO₄ upshifted by 70 °C. Raman spectra of SWCNT samples were shown in Figure 6-1. Compared with spectra from SWCNT samples reduced at 500 °C, a stronger RBM can be found. This suggests that more SWCNTs were produced, because more metal Co clusters are available after prereduction at a higher temperature. TGA profile in Figure 6-2 also indicates that less amorphous carbon was produced, hence more selective to SWCNTs. Furthermore, no considerable changes were observed in the (*n,m*) selectivity in Figure 6-3 and Figure 6-4, indicating that the prereduction temperature change on Co-Mo/MgO has no significant impact on its (*n,m*) selectivity.

Based on TPR results and the structure of carbon produced on different catalyst supports, it is proposed that the formation of CoMoO₄, in which Co ions are well dispersed by Mo oxides, is

critical for a good SWCNT selectivity on catalysts impregnated with Co. Previous studies have shown that the selectivity of the Co-Mo catalyst strongly depends on the stabilization of Co by Mo oxides. The non-interacting Co phase is reduced to metallic Co that is not selective to SWCNTs, while the Co phase interacting with Mo remains as well-dispersed Co ions that are highly selective to SWCNT production.[28] In this study, it is demonstrated that cobalt oxides, cobalt silicates, and solid solutions such as MgCo_2O_4 are all not selective for SWCNT growth. TPR results indicate that different catalyst supports may perturb the interaction between Co and Mo species, leading to the formation of different Co phases responsible for the observed differences in carbon growth. That is, SiO_2 and MgO support enhance the selectivity toward SWCNTs in a narrow diameter range between 0.75-0.85 nm, because the formation of well dispersed CoMoO_4 . In contrast, Al_2O_3 and TiO_2 have strong interactions with Co or Mo individually, which disrupts the synergistic effect between Co and Mo. Co-Mo catalysts supported on these two supports are not selective to SWCNTs.

Two conditions must be satisfied for the selective growth of particular (n,m) SWCNTs. First, metal clusters with narrow diameter distribution should be stabilized during growth, which would manage the diameter variation of SWCNTs. Second, the chiral angle of SWCNTs at a particular diameter should be controlled. This study shows that SiO_2 and MgO provide well dispersed Co species on Mo oxides, which result in Co clusters in a narrow diameter range suitable for SWCNT growth with diameter between 0.75-0.85 nm under CO at 800 °C. However, it is not feasible to elucidate how the chiral angle is manipulated based on current results. Several theoretical studies have proposed that the SWCNT chirality is controlled by the formation of carbon cap structure on

a metal nanoparticles catalyst.[29, 30] An interesting observation from this study and previous publications [3, 31-33] is that most of the narrow (n,m) selective SWCNT synthesis produces tubes in the same near-armchair range including (6,5), (7,5) and (7,6) tubes. A recent work has shown that near-zigzag tubes can be grown on the A-plane of sapphire.[34] Unlike the aligned growth on sapphire planes, oxide supports studied in the present study would have limited contact with growing SWCNTs. Oxide catalyst supports are unlikely to change the chiral angle of tubes after the carbon cap structures are formed on metal clusters. Thus, the role of catalyst support could be limited to regulate the formation of metal clusters.

Lastly, in term of large scale SWCNT production, an essential criterion for choosing a catalyst support is its removal simplicity after SWCNT growth. In this aspect, SiO_2 and MgO are superior to TiO_2 and Al_2O_3 . SiO_2 can be removed by alkaline solution, while MgO can be removed in diluted acid solution. Moreover, SiO_2 nanoparticles have larger surface areas than MgO , which implies that more metal ions can be loaded to produce more SWCNTs using the same amount of catalysts.

6.5 Conclusion

Co-Mo catalysts supported on four catalyst supports (SiO_2 , Al_2O_3 , MgO , and TiO_2) were evaluated for SWCNT growth. SiO_2 and MgO supported catalysts have good selectivity toward SWCNTs; however, there are no significant differences in their (n,m) selectivities. Both supports initiate the growth of near-armchair tubes; even though MgO supported catalysts produce more tubes with slightly smaller diameter due to their less reducibility. TiO_2 supported catalysts produce a mixture of MWCNTs and SWCNTs, while Al_2O_3 supported catalysts mainly produce

MWCNTs. UV-vis diffuse reflectance spectroscopy study of catalysts demonstrates that the domain size of metal oxides on various supports is not directly responsible for the (n,m) selectivity. TPR analyses of monometallic catalysts (Co and Mo) and bimetallic Co-Mo catalysts indicate that supports can change the reducibility of metal species. The different supports may perturb the interaction between Co and Mo species, leading to the formation of diverse metal clusters responsible for the observed carbon deposits distinction in SWCNT synthesis.

6.6 References

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Chapter 7

Co incorporated TUD-1 Catalyst for SWCNT Synthesis

In Chapter 6, it has been demonstrated that the synergistic effect between Co and Mo is essential for growing SWCNTs with narrow (n,m) distribution. Some catalyst supports (such as Al_2O_3 and TiO_2), which have strong interactions with Co or Mo, could interrupt this synergistic effect resulting in the formation of MWCNTs. Monometallic catalyst has its advantage over bimetallic Co-Mo catalyst because of the simplicity in SWCNT purification. Mo is very stable against acid treatment, and Mo residues exist on purified SWCNTs grown from bimetallic Co-Mo catalysts. However, without the assistance of Mo, Co supported on impregnated catalysts intends to sinter and form large particles on the substrate surface during SWCNT growth. For Co incorporated monometallic catalyst, such as Co-MCM-41, Co can be well dispersed in the supporting amorphous SiO_2 matrix due to the anchoring effect in the MCM-41 mesopores.[1] Without the assistance of Mo, these well dispersed Co particles can lead to the growth of SWCNTs with narrow (n,m) distribution. However, the drawbacks of Co-MCM-41 catalyst are the high cost (various expensive surfactants for catalyst synthesis), long synthesis time (7 days in autoclave),[2] and relative low carbon loading (1.25 wt.% carbon/1 wt.% cobalt),[3] which significantly increases the cost of SWCNTs. Therefore, it is worth investigating new catalysts using monometallic (Co) for SWCNT synthesis.

7.1 Co incorporated TUD-1

TUD-1[4] is a mesoporous silica material. Unlike the 2D tubular structure of MCM-41, TUD-1 is featured to be a sponge-like 3D structure with a large surface area (~several hundreds of m^2/g , up to $1000 \text{ m}^2/\text{g}$) and high thermal stability (little degradation at 1000°C). These properties make TUD-1 potentially effective as catalyst substrate for SWCNT growth. More importantly, inexpensive triethanolamine (TEA) molecules are used as the structure templates in TUD-1 synthesis other than expensive surfactants used in MCM-41 synthesis. Many researchers have investigated M (M for various metals, such as Fe,[5] Al,[6] Ti[7] and Co[8, 9]) incorporated TUD-1 for catalyzing various reactions. However, TUD-1 has yet been applied for SWCNT growth. In this study, a simple and economic synthesis of Co-TUD-1 and its application for SWCNT growth are reported.

7.1.1 Co-TUD-1 synthesis

Co-TUD-1 with 1 wt.% Co loading was synthesized following a modified method reported by Hamdy et al.[8] In a typical synthesis, 0.14 g of cobalt (II) sulphate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, >99 %, Sigma-Aldrich) was dissolved in DI water. The CoSO_4 aqueous solution then was added dropwise into 10 g tetraethyl orthosilicate (TEOS, >98 %, Sigma-Aldrich) under vigorous stirring. After stirring for 30 minutes, 7.2 g triethanolamine (TEA, >98.5 %, Fluka) and 1.8 g DI water were added dropwise and further stirred for 2 hours. 6.1 g tetraethyl ammonium hydroxide (TEAOH, 35 %, Sigma-Aldrich) was subsequently added to the mixture and aged for 24 hours at room temperature. After aging, the solution was dried in an oven at 100°C for 24

hours and hydrothermally treated in a Teflon-lined stainless steel autoclave at 180 °C for 8 hours.

The final product was calcined at 600 °C for 10 hours under a steady airflow to remove the templates.

7.1.2 Characterizations of Co-TUD-1

In order to investigate the physical and chemical properties of Co-TUD-1, synthesized Co-TUD-1 was characterized using XRD, N₂ physisorption, UV-vis diffuse reflectance, and TPR shown in Figure 1a~d, respectively.

Figure 7-1 1 wt.% Co-TUD-1 characterizations: (a) small angle XRD, (b) N₂ physisorption showing isotherms and pore size distribution (insert), (c) UV-vis diffuse reflectance and (d) TPR.

XRD is an important characterization technique on the structure of crystalline or other ordered materials. The small angle XRD pattern in Figure 7-1a shows an intense diffraction peak observed at the vicinity of $2\theta = 0.8^\circ$ to 1.0° indicating the highly ordered mesoporous structure of Co-TUD-1.[4] The isotherm in Figure 7-1b shows a step increase in nitrogen uptake within the relative pressure (P/P_0) range of 0.5-0.8, representing a typical mesostructured feature. The adsorption/desorption shows a hysteresis of type IV isotherm. 1 wt.% Co-TUD-1 sample exhibits well defined pore size around 7.4 nm with a narrow pore size distribution (insert in Figure 7-1b). N_2 physisorption also revealed that 1 wt.% Co-TUD-1 possesses a large surface area ($740 \text{ m}^2/\text{g}$) and pore volume (1.42 ml/g) calculated by BET[10] and BJH[11] methods, respectively. UV-vis diffuse reflectance was conducted to investigate the local environment of Co in the TUD-1 structure (Figure 7-1c). The UV-vis spectra of Co-TUD-1 and pure Co_3O_4 are almost identical suggesting the existence of Co_3O_4 on the surface of TUD-1. The TPR profile of Co-TUD-1 is illustrated in Figure 7-1d. A distinct and narrow reduction peak is located at a reduction temperature of 460°C . The position of this main peak is higher than the reduction temperatures of cobalt oxides at surface which appear as two shoulders at 380°C and 420°C corresponding to the reduction process $\text{Co}_3\text{O}_4 \rightarrow \text{CoO} \rightarrow \text{Co}$. [12] The peak at 460°C may be assigned to the reduction of incorporated Co in TUD-1 structure. However, the two shoulders suggest that a fraction of Co is still on the surface of TUD-1 as Co_3O_4 other than being incorporated into the Si template. This result is in agreement with UV-vis spectra in Figure 7-1c. The characterizations show that Co-TUD-1 possesses comparable physical structure with Co-MCM-41: highly ordered mesoporous structure, large surface area, and narrowly distributed pore size. On the other hand, the Co

incorporation in TUD-1 is incomplete and the reducibility of Co (460 °C) is much lower than that of Co in MCM-41(750 °C).

7.2 SWCNT growth on Co-TUD-1

The SWCNT growth conditions in CVD have been systematically studied using Co-MCM-41.[13, 14] The reduction temperature was discovered to play a crucial role for the quality of SWCNTs grown from Co-MCM-41.[14] Hence, experiments in this section were designed to systematically study the influence of the prereduction in H₂ on the quality of SWCNTs produced. SWCNTs were synthesized following the procedure described in Chapter 2, except that prior to exposure to pure CO the catalyst was heated in flowing H₂ at one atmosphere at 10°C per minute rate from room temperature to different reduction temperatures at 400 °C, 500 °C, and 600 °C. After the prereduction period, the catalyst was purged with pure Ar and then heated to 800 °C. SWCNTs were grown for 1 hour under 6 bar CO.

The Raman spectroscopy was conducted using a 633 nm laser on the as-synthesized SWCNT samples produced from Co-TUD-1, which was prereduced at different reduction temperatures (Figure 7-2). As illustrated in Figure 7-2, the samples grown from Co-TUD-1 prereduced at 400 °C shows distinct G and D bands located at 1587 cm⁻¹ and 1325 cm⁻¹, respectively. However, the D band shows a high intensity and the D/G ratio is around 0.5. Meanwhile, the intensity of RBM peaks is very low in this Raman spectrum. As reduction temperature was further increased to 500 °C, the D/G ratio remains at a similar level, but a clear RBM peak appears at 188 cm⁻¹ suggesting the existence of SWCNTs. If the catalyst was prereduced at 600 °C, the D/G ratio decreases to

0.25 and the RBM peak becomes much more intense. Since the D band is originated from the amorphous carbon and defects in SWCNTs or MWCNTs. The coexistence of a high D/G ratio and RMB peaks suggests that SWCNTs grown from Co-TUD-1 are mixed with other carbon impurities such as MWCNTs and amorphous carbon. A previous study[15] performed quantitative Raman characterization on the SWCNT-MWCNT mixtures with different SWCNT/MWCNT ratios. The results showed that with the increase of MWCNTs in a sample, the intensity of RBM and the G band gradually decreases, while the D band increases.[15] The Raman spectra in this study show a similar trend suggesting that SWCNT selectivity increases when the catalyst prereduction temperature increases. At low reduction temperature (400 °C), more MWCNTs or amorphous carbon other than SWCNTs were produced.

Figure 7-2 Raman spectra of as-synthesized solid samples from Co-TUD-1 prereduced at different reduction temperatures (400 °C, 500 °C, and 600 °C)

To further verify the results obtained by Raman spectroscopy, TGA was applied to distinguish the carbon species in the produced samples. Figure 7-3 shows the DTG profiles of carbon deposits grown from Co-TUD-1 prereduced at different temperatures. In Figure 7-3, the positive peaks around 300 °C can be attributed to weight gain by Co oxidation. It may compromise the oxidation of amorphous carbon, and the abundance evaluation of amorphous carbon is difficult. The major peak at 560 °C can be assigned to MWCNTs, in agreement with TGA results in Chapter 6. peaks located at 430 °C come from the oxidation of SWCNTs. It is shown that with the increase of reduction temperature, the intensity of the SWCNT peaks increases. This is consistent with the Raman results presented in Figure 7-2. The small peaks at 940 °C are attributed to the decomposition of graphite. There is no recognizable change of this peak among different reduction temperatures. The TGA results confirm that significant amount of MWCNTs were produced from Co-TUD-1, and high reduction temperature increases the selectivity to SWCNTs.

Figure 7-3 DTG profiles of carbon deposits produced from Co-TUD-1 prereduced at 400 °C, 500 °C, and 600 °C. The proposed temperature regions for oxidation of SWCNTs and MWCNTs are highlighted in light grey and dark grey, respectively.

The test of Co/MgO for SWCNT growth revealed that MWCNTs were the main species produced (Chapter 6). In this study, Co is incorporated into TUD-1 structure other than deposited on its surface leading to the increase of Co reduction temperature to 460 °C shown in Figure 7-1d. However, the Co incorporation is incomplete. Two peaks in TPR profile at 380 °C and 420 °C reveal that a portion of Co is deposited on the surface of TUD-1 as Co_3O_4 which can be easily

reduced to large particles leading to the formation of MWCNTs and graphite. With the increasing of reduction temperature, the incorporated Co can be reduced to metal particles which are relatively smaller and more stable. Then, SWCNTs can grow from these metal particles.

7.3 SWCNT (n,m) analysis

Since the abundance of SWCNTs produced by Co-TUD-1 prereduced at 600 °C is relatively high, the sample was dispersed in 1 wt.% SDBS/D₂O solution. After ultracentrifugation at 72,000 g, the supernatant enriched with SDBS wrapped SWCNTs was obtained for (n,m) analysis using PL spectroscopy. Figure 7-4 is the PLE 2D contour map with the excitation wavelength from 300 to 850 nm and the emission wavelength from 900 to 1600 nm. It is observed that the (n,m) distribution is relatively wide and the dominant SWCNT species are (6,5) and (9,8) with the diameter range between 0.757 nm and 1.17 nm. Because the Co reduction temperature in TUD-1 is relatively low, the incorporated Co in TUD structure can be fully reduced at 600 °C. Therefore, the anchoring effect[1] observed on partially reduced Co ions in Co-MCM-41 may play a limited role on Co-TUD-1. Therefore, the Co particles may sinter and migrate into larger sizes leading to the wide diameter distribution of SWCNTs. On the other hand, the dominant SWCNT species (6,5) and (9,8) are both high chiral angle tubes. This result is in agreement with previous studies in Chapter 4, 5 and 6. A recent theoretical study indicated that carbon caps with high chiral angle facilitate thermodynamically and kinetically C₂ addition and offer more alternative reaction paths than the zigzag caps.[16]

Figure 7-4 PL intensity map as a function of excitation and emission wavelength for SDBS micellarized SWCNTs in D₂O produced from Co-TUD-1 prereduced at 600 °C.

7.4 Conclusion

Co incorporated TUD-1 was successfully synthesized and applied for SWCNT growth in CVD. The characterization of catalysts shows that Co-TUD-1 possesses a large surface area and well defined pore structure. Co-TUD-1 was prereduced at different reduction temperatures before SWCNT growth. Raman spectroscopy and TGA results indicated that the carbon deposits produced from Co-TUD-1 are mainly MWCNTs. A certain portion of SWCNTs can be produced under high reduction temperatures (600 °C). However, the (n,m) distribution is wide with two dominant SWCNT species (6,5) and (9,8). Both of them are at the high chiral angle region.

7.5 References

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Chapter 8

Summary and Future Research

Intensive research efforts have been invested to CNTs since 1991. Thereafter, researchers have gained substantial progress on CNT synthesis, purification, separation, applications as well as its environmental impacts. Although CNTs possess many potentials, the major challenges towards commercialization have yet been conquered. Firstly, the structure of CNTs must be precisely controlled in terms of diameter, chirality and length. Secondly, techniques have to be developed to precisely organize CNTs in terms of their position and orientation. Last but not least, the CNTs must be produced in large scale, low cost and high purity.

Work in this thesis attempts to make progress on one aspect: chirality selective growth of SWCNTs in CVD. Based on fundamental studies on the growth mechanism of SWCNTs, three factors which may influence the SWCNT chirality in CVD are explored: (1) carbon precursor, (2) pressure, and (3) catalyst substrate. Several techniques are employed to characterize both catalysts and SWCNTs in order to have a better understanding of the chirality selectivity. One method is developed to evaluate the SWCNT (n,m) abundance. Co-Mo catalyst is chosen for this study due to its simplicity in synthesis and its outstanding performance of growing SWCNTs with narrow (n,m) distribution.

Four different carbon precursors (CO, C₂H₅OH, CH₃OH and C₂H₂) are used to grow SWCNTs on Co-Mo/SiO₂. To obtain narrowly (n,m) distributed SWCNTs, the growth conditions for different carbon precursors must be varied (high pressure CO, vacuumed C₂H₅OH and CH₃OH,

vacuumed and diluted C_2H_2). Therefore, carbon precursor pressure is considered to be a key factor for the SWCNT (n,m) selective growth. (n,m) abundance of semiconducting SWCNTs is evaluated based on an electron-phonon interaction model using PL spectroscopy. The evaluation results reveal that the (n,m) selectivity can be shifted by using different carbon precursors. The dominant (n,m) tubes produced by different carbon precursors are all at the high chiral angle region. E_{11}^S NIR absorption spectrum reconstruction is applied to probe small chiral angle tubes. The results indicate that the abundance of small chiral angle tubes is low.

The pressure of CO is systematically varied from 2 to 18 bar in order to study its impact on SWCNT (n,m) selectivity. PL spectroscopy results indicate that (6,5), (7,5) and (7,6) can be selectively enriched one by one by tuning the CO pressure. High pressure favors the growth of small diameter tubes and (6,5) can be enriched under 18 bar. Conversely, low pressure leads to the growth of large diameter tubes, and (7,6) is dominant under 2 bar. In this study, the dominant SWCNTs are also found at the high chiral angle region. The mechanism study indicates that the (n,m) selectivity is controlled by CO partial pressure other than the total pressure in the reactor.

Co-Mo catalysts supported on four different catalyst substrates (SiO_2 , Al_2O_3 , MgO, and TiO_2) are evaluated for SWCNT growth. It is shown that different supports may perturb the interaction between Co and Mo species, leading to the formation of diverse metal clusters. Therefore, only Co-Mo/ SiO_2 and Co-Mo/MgO have the ability to grow SWCNTs. The (n,m) distribution analysis shows that the SWCNTs produced by Co-Mo/ SiO_2 and Co-Mo/MgO have narrow (n,m) distributions. Moreover, no significant differences in their (n,m) selectivities are observed. On the other hand, due to the strong “metal-support interaction”, TiO_2 and Al_2O_3 perturbs the synergistic

effect between Co and Mo leading to the formation of large Co particles. MWCNTs are the main product for Co-Mo/TiO₂ and Co-Mo/Al₂O₃.

To avoid the contamination of Mo in purified SWCNT samples and develop more cost effective monometallic catalysts, one monometallic Co incorporated TUD-1 is synthesized and applied for SWCNT growth for the first time. However, MWCNTs constitute significant fraction of produced carbon deposits. SWCNTs can be grown under a relatively high reduction temperature. The incomplete Co incorporation may lead to the sintering of Co clusters, which are responsible for the growth of MWCNTs. The improvement of Co-TUD-1 synthesis method is necessary to achieve a complete Co incorporation in the TUD-1 template.

Work in this thesis successfully makes two achievements: (1) produce narrowly (n,m) distributed SWCNTs, and (2) shift the (n,m) distribution. However, all produced (n,m) species at different diameters are found to be at the high chiral angle region. The chiral angle of SWCNTs is yet managed to be controlled.

In future work on the chirality selective growth of SWCNT in CVD, the following studies are proposed.

- (1) The work in this thesis only focuses on semiconducting SWCNTs. Metallic SWCNTs are not in the scope due to the lack of (n,m) resolved characterization techniques on metallic SWCNTs. Raman spectroscopy equipped with lasers having continuous tunable energies is a good candidate for this purpose. The study on selective growth of metallic SWCNTs or

semiconducting SWCNTs in CVD is significant for the fabrication of SWCNT based electronic devices.

- (2) Currently, to obtain narrowly (n,m) distributed SWCNTs, the diameter of SWCNTs has to be refined at about 1 nm. However, SWCNTs with large diameter (for example, >1.4 nm) have their advantages for electronic device fabrication because smaller diameter SWCNTs usually have poor contacts with electrodes and lower current mobilities compared with larger diameter tubes. Therefore, the narrowly (n,m) distributed large diameter SWCNTs are highly desired. Research on new catalyst designs has potential to achieve this goal.
- (3) The research on SWCNT growth mechanism still lags behind. The SWCNT chirality selection mechanism is poorly understood. More efforts should be invested on this issue, which is crucial to achieve a good control of the SWCNT chirality in terms of diameter and chiral angle, so that any desired type of SWCNTs can be produced by design.

Many nanoscale materials emerged in the last few years, such as nanowires and graphene. They have become strong competitors to CNTs in many potential applications. Techniques developed for CNTs have high potentials to be transferred to those new nanomaterials, and these techniques will play more and more important roles in the future for manipulating different nanomaterials.

Appendix

List of related publications

Chapter 4

Wang, B., Poa, C. H., Wei, L., Li, L. J., Yang, Y. , Chen, Y., *(n,m) Selectivity of Single-Walled Carbon Nanotubes by Different Carbon Precursors on Co-Mo catalysts*, Journal of the American Chemical Society, 2007, **129**(29), 9014-9019

Chapter 5

Wang, B., Wei, L., Yao, L., Li, L. J., Yang, Y. H., Chen Y., *Pressure-induced single-walled carbon nanotube (n,m) selectivity on Co-Mo catalysts*, The Journal of Physical Chemistry C, 2007, **111**(40), 14612-14616

Chapter 6

Wang, B., Li, L., Yang, Y., Chen Y., *Effect of different catalyst supports on the (n,m) selective growth of single-walled carbon nanotube from Co-Mo catalyst*, Journal of Materials Science, 2009, **44**, 3285-3295

Other publications

Wei, L., **Wang, B.**, Liu, D., Li, L. J., Yang, Y., and Chen, Y., *In-situ formation of cobalt nanoclusters in sol-gel silica films for single-walled carbon nanotube growth*, Nano, 2009, **4**(2), 99-106

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Wei, L., **Wang, B.**, Goh, T. H., Li, L. J., Yang, Y., Chan-Park, M., and Chen, Y., *Selective Enrichment of (6,5) and (8,3) Single-Walled Carbon Nanotubes via Co-Surfactant Extraction from Narrow (n,m) Distribution Samples*, The Journal of Physical Chemistry B, 2008, **112**(10), 2771 -2774.

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Chen, Y., Wei, L., **Wang, B.**, Lim, S., Ciuparu, D., Zheng, M., Chen, J., Zoican, C., Yang, Y., Haller, G., and Pfefferle, L., *Low defect, purified, narrowly (n,m)-dispersed single walled carbon nanotubes growing from cobalt incorporated MCM-41*, ACS Nano, 2007, **1**(4), 327-336

Chen, Y., **Wang, B.**, Li, L. J., Yang, Y., Ciuparu, D., Lim, S., Haller, G. L., and Pfefferle, L., *Effect of different carbon sources on the growth of single-walled carbon nanotube from MCM-41 containing nickel*, Carbon, 2007, **45**(11), 2217-2228