Sulfur-modified cobalt catalysts for the chirality-selective synthesis of single-walled carbon nanotubes

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NANYANG
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**SULFUR-MODIFIED COBALT CATALYSTS FOR THE
CHIRALITY-SELECTIVE SYNTHESIS OF SINGLE-WALLED
CARBON NANOTUBES**

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ABSTRACT

Selective synthesis of single-walled carbon nanotubes (SWCNTs) with a specific (n , m) chirality is desired for many potential applications. Current research has been focused on achieving high chirality selectivity. In this thesis, I expand the research on this issue into two aspects: (1) optimizing chemical vapor deposition (CVD) conditions and catalyst properties to achieve both good chirality selectivity and carbon yield, (2) developing low cost catalysts and scalable synthesis strategies to reduce the production cost of SWCNTs with high chirality purity.

On the first aspect, a sulfur-assisted CVD method using ethanol as carbon feedstock was demonstrated. The results show that introducing sulfur-containing compounds into carbon feedstock dramatically influences the carbon yield, and alters the chirality selectivity. For instance, when 0.0001 wt.% of carbon disulfide (CS_2) was added to ethanol, the carbon yield increased significantly from 4.8 to 14 wt.% without chirality changes. With the further increase of CS_2 concentration, the chirality distribution shifted from smaller diameter (of multiple chiralities) toward larger diameter species of a narrow chiral window, such as (8,7) at 1 nm and (9,8) at 1.2 nm, with the cost of a sharp decrease in the carbon yield. In a similar manner, 0.001 wt.% of thiophene enhanced the carbon yield from 4.8 to 5.9 wt.%. Further increase of thiophene concentration reduced carbon yield significantly. More importantly, thiophene (0.1 wt.%) in ethanol led to the selective growth of (9,8) nanotubes with a relative abundance of 43.1% among all semiconducting nanotubes.

Moreover, a new sulfidized Co/SiO₂ catalyst was prepared to synthesize SWCNTs. Co/SiO₂ catalyst was first sulfided with the mixture of H₂S and H₂, and then, SWCNTs were grown by CVD using CO as carbon feedstock. The results indicate that the sulfided Co/SiO₂

catalyst has a good selectivity to (9,8) nanotubes, without decreasing the carbon yield compared to original Co/SiO₂ catalyst. The characterization results of the catalysts show that the formation of Co₉S₈ nanoparticles during sulfidation plays a critical role in modulating the chirality selectivity of the catalyst.

On the second aspect, first, low cost porous silica particles were used to replace high purity expensive porous fumed silica as catalyst substrates. Both the photoluminescence (PL) and UV-vis-NIR absorption results showed that SWCNTs with a narrow diameter distribution of around 1.2 nm can be synthesized using the catalyst made of low cost silica particles (Co/SiO₂ particle). Next, SWCNT synthesis in different reactor designs was compared in an attempt to improve SWCNT production yield. Comparing a horizontal and a vertical CVD reactor in the same diameter, about 5 times more catalysts (1 g vs. 200 mg) can be loaded in the vertical reactor. Similar chirality selectivity and carbon yield can be obtained in the vertical fixed-bed reactor at 25% of the carbon feedstock gas flow rate of that used in the horizontal reactor. Further, large silica gel particles (60 wt.% of total catalyst mixture) were added to the Co/SiO₂ particle catalyst so the catalyst mixture can be fluidized in a vertical fluidized-bed reactor. However, SWCNT synthesis results obtained in the fluidized-bed reactor suggest that the fast mass transfer in the fluidized bed is not beneficial for SWCNT chirality control, which led to fast metal cluster nucleation and saturation of metal catalysts by carbon.

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NOMENCLATURE

BET	Brunauer-Emmet-Teller
CJH	Barret-Joyner-Halenda
CNT	Carbon Nanotube
CVD	Chemical Vapor Deposition
DTG	Differential Thermogravimetric
FESEM	Field Emission Scanning Electron Microscopy
ICP	Inductively Coupled Plasma
MWCNT	Multi-Walled Carbon Nanotube
PL	Photoluminescence
RBM	Radial Breathing Mode
SDBS	Sodium Dodecyl Benzene Sulfonate
SEM	Scanning Electron Microscope
SWCNT	Single-Walled Carbon Nanotube
TCD	Thermal Conductivity
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TPR	Temperature Programmed Reduction
UV-vis-NIR	Ultraviolet-visible-Near Infrared
XPS	X-ray Photoelectron Spectroscopy
XRF	X-ray Fluorescence

Chapter 1: Literature Background

1.1. Single-walled carbon nanotubes

Single-walled carbon nanotubes (SWCNTs) were discovered in 1993¹⁻² and from then on, they have attracted a lot of research efforts because of their potential applications in polymer composites,³ energy devices,⁴ nanoelectronics,⁵ and nanosensors.⁶ However, despite the remarkable effort of numerous researchers, real-life use of SWCNTs are still scarce mainly due to two reasons: (1) lack of control in the material properties, (2) high cost of production. Conventional synthesis methods produce many different types of SWCNTs at the same time and it is challenging to sort them out. Therefore, there is still a viable need to advance the control over the properties of SWCNTs by synthesis which ultimately reduces the cost of SWCNT production for specific applications. Below, I first introduce the basic feature of SWCNTs that determine their material properties dramatically, “chirality”. Then, I briefly explain the methods available for chirality enrichment of SWCNTs. Later, I provide a thorough account of the SWCNT synthesis with a special focus on catalyst design. Last, I introduce “sulfur-modified cobalt catalyst” which I further deepen in the main chapters of the thesis later on (see Chapter 3 and 4).

1.2. Chirality of SWCNTs

SWCNTs are hollow cylinders of carbon with a unique chiral structure, which is defined by a pair of chiral indices: (n,m) . **Figure 1-1** shows that SWCNTs can be conceptually formed by rolling up a graphene sheet along the vector $\mathbf{R} = n\mathbf{a}_1 + m\mathbf{a}_2$ (where $\mathbf{a}_1$ and $\mathbf{a}_2$ are lattice unit vectors of the graphene sheet) from the origin point (0,0) towards

any (n,m) point on the graphene sheet. The resulting (n,m) SWCNT has a diameter of $d = 0.0783\sqrt{(n^2 + m^2 + nm)}$ [unit: nm] with an angle of $\theta = \tan^{-1}[\sqrt{3}m/(2n + m)]$.⁷

Figure 1-1. Schematic illustration of the chiral structures of SWCNTs. The chiral index (n,m) ($0 \leq m \leq n$) uniquely defines the structure of a single SWCNT. SWCNTs are known as armchair nanotubes when $n = m$, and as zigzag nanotubes when $m = 0$.

The electronic, optical, thermal, mechanical, and magnetic properties of SWCNTs all depend on their chiralities.⁷⁻¹² For electronic applications, when the (n,m) index satisfies $n - m = 3j$, where j is an integer, the SWCNTs are metallic, and they can work as conductive wires. In contrast, when $n - m = 3j + 1$ or $3j + 2$, SWCNTs are semiconducting with different band gaps. In these cases they can be applied as gate materials in transistors.¹³⁻¹⁵ SWCNTs within specific diameter ranges with suitable band gaps have revealed superior transistor performances.¹⁶⁻²⁰ For photovoltaic applications, SWCNTs of single chirality show better performances compared to SWCNT mixtures of different chiral species.²¹⁻²² For biomedical applications, chirality enriched SWCNTs demonstrate much brighter photoluminescence emissions, leading to lower SWCNT doses and less toxicity concerns.²³⁻²⁵ With these advantages to offer, it has been a long-standing goal to selectively obtain single-

chirality SWCNTs for potential applications ranging from electronics to biomedicine.^{19, 26-27}

1.3. Applications of single-chirality SWCNTs

As we said above, one of the most important driving forces for the selective synthesis of SWCNTs is their applications in different research areas, including the energy storage and biological applications²⁸⁻²⁹.

In energy storage applications, solar energy harvesting is considered as a very important way to solve the energy challenge for the world. Since the light in the near-infrared (IR) regime can be absorbed by SWCNTs efficiently, it is a promising way to incorporate SWCNTs into solar cells. For solar cell devices, the purity of the SWCNTs is critical to the overall solar energy conversion efficiency. The presence of impure SWCNTs could result in the nonuniform band gaps and energy levels of SWCNTs, which is harmful for the power conversion efficiency (PCE). For example, in Strano *et al.*'s job, they fabricated two polymer-free solar cells with pure (6,5) SWCNTs and nanotubes with a 20% impurity of (6,4) SWCNTs, which indicated that the impurity led to a huge decrease in PCE.³⁰ Isborn, Tung *et al.* also reported that the chirality of the SWCNT is a key factor determining the efficiency of SWCNT/fullerene devices by comparing the performance of solar cells prepared with (9,7), (7,6) and (6,5) SWCNTs.³¹ Recently, Flavel *et al.* reported that they succeeded in determining the diameter limit of SWCNTs used in SWCNT/fullerene solar cells, providing the guidance for establishing a family of (n,m) species that can be efficiently used in SWCNT/fullerene solar cells.³² Since the energy band alignment is very important for all devices where charge transport is involved, the selective synthesis of SWCNTs with desired chirality is quite needed.

In addition, the nature of SWCNTs makes them of great interest for photothermal therapy and biological imaging³³⁻³⁵. Dai *et al.* developed a gel filtration method to enrich

semiconducting (12,1) and (11,3) SWCNTs and a higher photoluminescence intensity was observed from the sorted SWCNTs than that from unsorted SWCNTs.³³ It indicates that further efforts should be made to achieve the SWCNTs with single chirality for improving the performance of SWCNTs for biological imaging. In fact, SWCNTs with single chirality may find the most promising future in the bio-related applications.

1.4. SWCNT enrichment

The enrichment of SWCNTs is very important for driving the applications of SWCNT research forward. Usually, the as-produced SWCNTs inevitably contain many impurities, which can be classified into two types: (1) carbonaceous particles (e.g. carbon nanoparticles, amorphous carbon, MWCNTs, and graphite); (2) catalyst residues (e.g. catalyst supporting substrates and metal nanoparticles).³⁶ Many methods have been applied to purify the as-produced SWCNT samples. It is well known that the density and oxidation temperature vary with the species of carbon impurities because of their different structure and the purification methods are developed based on the difference. For examples, oxygen/air,³⁷⁻³⁸ H₂O₂,³⁹⁻⁴⁰ and water⁴¹ are used to remove amorphous carbon efficiently. However, as the oxidation temperature of MWCNTs and graphite is higher than that of SWCNTs, it is not suitable to apply this method to them. The centrifugation is chosen to remove MWCNTs due to the fact that their densities are higher than that of SWCNTs.⁴²⁻⁴³ For the metal catalysts and catalyst substrates, strong acid (e.g. HF or HNO₃⁴⁴⁻⁴⁷) or strong alkaline treatment is widely used.

After purification, SWCNTs with different chiralities should be sorted by different separation methods. Generally, SWCNTs are separated by methods such as ultracentrifugation, chromatography, and electrophoresis.

Centrifugation, especially density gradient ultracentrifugation (DGU), separates SWCNTs *via* buoyant density.⁴⁸⁻⁴⁹ In this method, SWCNTs are dispersed by the noncovalent

functionalization of surfactants, leading to density variations. In the centrifugation process, different SWCNTs move to their locations where their densities match the local density of the gradient. The selectivity can be tuned by changing the density gradient, centrifugal force and time easily.⁵⁰

Chromatography, especially ion-exchange chromatography (IEX), is a useful method to separate SWCNTs with different chiralities. In this method, SWCNTs are surrounded by a charged polymer like single-strand DNA molecules (ssDNA), which are negatively charged. Then, the dispersion is introduced to an IEX column, which contains positively charged substrates. Due to electrostatic attractions, SWCNT-ssDNA complexes will be attracted to the surface of the substrates and with the increase of the salt concentration, the SWCNT-ssDNA complexes become positively charged and can be eluted from the surface.⁵¹ The separation selectivity can be influenced by surface charges induced by ssDNA and the length of SWCNTs.⁵²

Agarose gel-based electrophoretic separation has been applied recently and shown promising results.⁵³ Agarose gel retards the movement of molecules subjected to the electric field by electrophoresis cells and smaller molecules can pass through the pores of the gel matrix easier yielding to a separation effect. In addition, when dispersed SWCNTs are loaded to the agarose gel under electrical bias, metallic SWCNTs can move faster while semiconducting SWCNTs in small bundles are trapped in the agarose gel.⁵⁴ Therefore, agarose gel electrophoresis can separate SWCNTs both according to their sizes and electrical conductivity.

In recent years, supported by the aqueous-two polymer phase separation, a novel approach for sorting nanotubes has been applied,⁵⁵⁻⁵⁷ which is an auspicious route for the scalable enrichment of high-purity SWCNTs.⁵⁸ But the separation yield, the cost, and as well as the quality in terms of their physical and chemical properties largely depend on the starting

as-synthesized SWCNTs, and therefore, chirality-selective synthesis of SWCNTs is still highly desired.⁵⁹⁻⁶⁰

1.5. SWCNT synthesis routes

Currently, CNTs can be synthesized by several different techniques: arc-discharge, laser evaporation, and chemical vapor deposition (CVD) techniques.⁶¹ In the arc-discharge method, a high-current electric arc goes through two high-purity graphite electrodes in hydrogen or inert gas.⁶² During arcing, carbon vapor is created by consuming solid carbon electrodes and SWCNTs are formed by carbon vapor condensation. (Laser evaporation, method has a similar mechanism with that of the arc-discharge method. The difference is that instead of the current, a laser is shot at a graphite target containing a metal catalyst.⁶¹ In catalytic CVD,⁶³⁻⁶⁴ a carbon precursor (normally in gaseous phase) is catalytically converted into solid SWCNTs by decomposition upon interacting with the catalysts. Although high-quality SWCNTs can be yielded by the first two methods,⁶⁵⁻⁶⁶ a critical problem is that there is little control over the diameter, chirality, and length of SWCNTs through the two processes. Catalytic CVD has become the prevalent method for chirality-selective synthesis of SWCNTs as it offers more parameters to achieve better control of the catalysts, carbon precursors and growth conditions.⁶⁷ Previous studies did show that the chirality selectivity can be changed to some extent by the CVD method using different methods, such as varying growth temperature⁶⁸⁻⁶⁹ and gas feedstock,⁷⁰ modulating the pressure of gas feedstock⁷⁰, changing catalyst metal compositions⁷¹ and employing different catalyst supports.⁷²⁻⁷³ In all these methods, it has been proved that the catalysts play quite crucial roles in the selective synthesis of SWCNTs.⁷⁴⁻⁷⁷ The effort trying to optimize the composition or shape of the catalyst samples accounted for the highest reported proportion, 55%, of SWCNT selective synthesis.⁷⁸

1.6. Fundamentals of catalyst design

A typical definition of a catalyst is that the material increases the rate of a chemical reaction while itself is not consumed. In chemical reactions, catalysts play two major roles: i) accelerating reactions, and ii) influencing the selectivity. Based on different needs, various catalysts are chosen for a particular industrial process according to their activity, stability, selectivity, and cost. As summarized by Jourdain and Bichara, it is generally accepted that catalysts play four roles in the CVD-based synthesis of SWCNTs.⁷⁹ First, they catalyze the dissociation of carbon precursors. Second, they involve in the diffusion of carbon intermediates and influence the reactions to take place on the surface. Third, they serve as nanoscale templates for the nucleation of carbon caps and extension of nanotubes. Fourth, they keep the reactive sites active for incorporation of more carbon for continuous growth. The first two roles are similar to those in many heterogeneous catalytic reactions, while the last two are distinctive for the synthesis of SWCNTs. Theoretical studies have tried to link the chirality selectivity to different aspects of the interactions between catalysts and the growing carbon structures.⁸⁰⁻⁹⁴ Electron microscopy studies have shown that the carbon caps first sprout on catalyst nanoparticles, then lift themselves by incorporating more carbon atoms and eventually grow into well-defined tubes before the termination of growth.⁹⁵⁻⁹⁹ As the overall growth process is a dynamic event dependent on many parameters, it is not fully clear at which stage catalysts do specifically determine the chirality of SWCNTs. It is also not quite clear catalysts whether really involve in the control of nanotube chirality at any specific stage of growth process or not.

Several hypotheses have been proposed to explain the chirality-selection process and some of those are back up with experimental evidence. The first hypothesis is that the chirality of SWCNTs can be fixed by well-defined carbon caps or nanotube edges if suitable carbon intermediates are continuously supplied.¹⁰⁰ This hypothesis lays the foundation for the

two most frequently used approaches in chirality-selective synthesis. One is the SWCNT “cloning” method by amplifying SWCNTs from shortened SWCNT seeds¹⁰¹ or nanocarbon pieces¹⁰² with defined chiral structures. It is anticipated that the “cloned” SWCNTs would have the same chirality as the seeds. The other method is to control the formation of carbon caps by catalysts. Reich *et al.* showed that some caps are preferentially stabilized on specific local crystalline lattices of metal surfaces.^{82, 84} This opens up the possibility of designing catalysts that influence the nucleation of carbon caps, suggesting the importance of the second and third roles of catalysts in the chirality-selective synthesis of SWCNTs stated above. The second hypothesis is that the growth rate of SWCNTs is chirality-dependent, and represented by the dislocation growth mechanism.¹⁰³ This mechanism has been substantiated by several experimental studies.¹⁰⁴⁻¹⁰⁵ The different growth rates relate to the continuous incorporation of carbon species into the growing carbon structures, which in turn strongly depends on the second and forth roles of the catalysts for SWCNT synthesis. According to this explanation, the catalysts determine where and how carbon atoms are incorporated, as well as prepare suitable carbon intermediates and keep the active incorporation sites “alive”. Recently, Yakobson *et al.* combined SWCNT/catalyst interface thermodynamics with the dislocation kinetic growth theory to show that the selectivity toward near-armchair SWCNTs, such as (6,5) and (9,8), emerges from the two antagonistic trend: energetic preference toward achiral SWCNT/catalyst interfaces versus faster growth of chiral SWCNT. The third hypothesis suggests that the termination of growth or the changes of chirality during SWCNTs growth are dependent on the chirality of SWCNTs. Although there is little experimental evidence to support this hypothesis, the termination of growth obviously links to the fourth role of catalysts. Furthermore, since the catalysts affect the incorporation of carbon species into growing carbon structures, if the chirality of nanotubes frequently changes during SWCNT synthesis, catalysts would play important roles in controlling such

changes. Overall, although the chirality selection mechanism in SWCNT synthesis is still under debate, current experimental and theoretical evidence have shown that catalysts strongly influence many aspects of the chirality-selection during the synthesis of SWCNTs. As the mechanism is not fully understood, it is not possible to design a specific catalyst and the search for the development of effective catalysts to produce SWCNTs is still highly desirable for both fundamental and practical interest.

Nowadays, SWCNT can be produced by many kinds of catalysts, including (1) metal catalysts,¹⁰⁶ which are the dominating catalysts in the chiral-selective synthesis of SWCNTs. They can be divided into two groups: supported catalysts and unsupported catalysts; (2) non-metal catalysts, such as semiconductor particles (Si, Ge, SiC),¹⁰⁷ insulator particles and substrates (SiO₂),¹⁰⁸⁻¹⁰⁹ metal oxide particles (ZrO₂)¹¹⁰ and even diamond;¹¹¹ (3) SWCNT “cloning” seeds;¹¹²⁻¹¹³ (4) Organic structure (C₉₆H₅₄).¹¹⁴⁻¹¹⁵ Considering the selectivity, carbon yield, and the cost, metal catalysts are more efficient than the alternatives for the synthesis of SWCNTs. The problem in the SWCNT growth by metal catalysts is the lack of a precise understanding regarding how the size of metal nanoparticles control the chirality selectivity. To tackle this problem and realize the selective synthesis of SWCNTs, three approaches have been proposed to design catalyst. In the first approach, a second metal is used to modify the crystal structure or size of catalysts. Resasco *et al.*¹¹⁶ reported their Co-Mo catalyst in 2003. This catalyst was prepared by the impregnation method, using the cobalt nitrate (Co(NO₃)₂) and ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) as precursors. The ratio of Co and Mo was controlled at 1:3 with a total metal loading of 2 wt.%. Based on the breakthrough of SWCNT spectrofluorimetric analysis, the catalyst showed an obvious selectivity to (6,5) and (7,5) nanotubes, which together accounted for more than 50 % of the semiconducting tubes. They suggested that under high temperature, the interplay between Mo oxides and Co optimized the Co catalyst aggregation.¹¹⁷ Then in the growth process, the Co²⁺

ions formed well-dispersed Co nanoparticles, leading to a narrow chirality distribution. Maruyama *et al.*¹¹⁸ prepared a kind of Fe/Co catalyst, which also showed a similar selectivity by CVD method using ethanol as the carbon source. This catalyst was produced by the impregnation of iron acetate $(\text{CH}_3\text{CO}_2)_2\text{Fe}$ and cobalt acetate $(\text{CH}_3\text{CO}_2)_2\cdot 4\text{H}_2\text{O}$ on a Y-type zeolite, in which the amounts of Fe and Co were 2.5 wt.% each. Their results showed that when the growth temperature was 650 °C, (6,5) and (7,5) nanotubes were selectively synthesized. In 2012, Ren *et al.*¹¹⁹ also reported a kind of Co-Pt catalyst by impregnating cobalt (II) acetate tetrahydrate $(\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O})$ and hexachloroplatinic (IV) acid hexahydrate $(\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O})$ on porous silica with Co and Pt ratio at 1:1. The catalyst showed a selectivity toward the (6,5) nanotubes at a relatively high temperature of 800 °C and 850 °C. It was ascribed that the stable CoPt alloy stopped the catalyst against sintering to relative large nanoparticles. Apart from Co bimetallic catalysts, FeRu catalyst was also proved to be an efficient one to selective synthesis SWCNTs by Dai *et al.*¹²⁰ A kind of silica support (average particle size of 7 nm and BET surface area of $380 \pm 30 \text{ m}^2/\text{g}$) and iron nitrate and ruthenium chloride hydrate was mixed in methanol. After being sonicated for 1 h, the solvent in catalysts was removed by rotary evaporator. In the CVD process, the catalysts were first reduced by H_2 till the growth temperature before the CH_4 was introduced for growth. According to their results, the FeRu catalyst showed a selectivity to (6,5) nanotubes at a growth temperature of 600 °C. Under this temperature, the small FeRu nanoparticles are stable with the diameters in 1-2 nm range, leading to the good selectivity.

Silica catalyst supports are usually dissolved by hydrofluoric acid (HF), which is toxic and not economical. In contrast, MgO can be easily removed by HCl. He *et al.*¹²¹⁻¹²² designed a Fe-Cu catalyst by impregnating $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ on a porous MgO in ethanol first. After drying, the mixture was then added into a $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ ethanol solution and sonicated following by drying and annealing at 450 °C for 2 hours. The catalyst showed a chirality

selectivity to small diameter nanotubes. It was proposed that Cu inhibited the sintering of Fe nanoparticles in the growth process, leading to the unique selectivity. All the catalysts discussed above lead to a narrow selectivity to SWCNTs with a small diameter. In 2014, Li *et al.*⁷⁸ reported a W-Co alloy catalyst with high melting points to synthesize a relatively large diameter SWCNTs by controlling the structure of the catalyst. The catalyst was prepared by depositing the clusters $(\text{Na}_{15}[\text{Na}_3\{\text{Co}(\text{H}_2\text{O})_4\}_6\{\text{WO}(\text{H}_2\text{O})\}_3(\text{P}_2\text{W}_{12}\text{O}_{48})_3]\cdot n\text{H}_2\text{O})$ on silicon wafers and then being calcined in air. The results indicated that the (12,6) nanotubes could be produced with the amount of more than 92%. The XRD patterns of the catalysts corresponded to W_6Co_7 , which leads to the selective growth of (12,6) SWCNTs.

Besides changing the composition of the catalyst, the other approach is to incorporate metal species on porous substrates with high surface area. The metal catalyst is well-dispersed with a high homogeneity in the frame structure of the support rather than only on the surface. Several kinds of the mesoporous SiO_2 framework have been applied to prepare catalysts with high chirality selectivity in SWCNT synthesis, such as MCM-41 (Mobil Composition of Matter 41)¹²³⁻¹²⁸ and TUD-1¹²⁹. Lim *et al.*¹³⁰ prepared Co-incorporated MCM-41 (Co-MCM-41) first and it showed a good selectivity to (7,5) nanotubes.^{123, 131-132} The X-ray absorption spectroscopy was used to understand the mechanism of reduction and nucleation of Co.^{123, 133-134} The results showed that the Co^{2+} ions were partially reduced to Co^{1+} intermediate species in the reduction process by H_2 at 500 °C, which were still individually dispersed in the frame structure of MCM-41. After exposure to CO, the Co^{1+} species were converted to Co carbonyl-like compounds with a high mobility and it led to fast migration and formation of metal nanoclusters capable of dissociating CO and initiating the growth of SWCNTs.¹²³ Based on these results, several bimetallic catalysts were prepared by MCM-41, such as Co-Cr-MCM-41¹²⁶, Co-Mn-MCM-41¹²⁷, and Co-Mo-MCM-41¹²⁸. All these catalysts showed a selectivity to SWCNTs with small diameters. Furthermore, only Co

resulted in the growth of SWCNTs while the other metal species played the role of anchoring sites for Co particles instead of being involved in the growth of SWCNTs directly.

In an earlier study of our group, Co was also incorporated into TUD-1, another mesoporous silica template. Different from the catalyst supported by MCM-41, the as-produced Co-TUD-1 showed a high selectivity to relatively large diameter nanotubes such as (9,8) species.¹²⁹ The low reduction temperature was believed to be the reason for the uniqueness of this catalyst, increasing the amount of reduced Co atoms. As a result, when CO was introduced, Co atoms were enough to form relative large Co nanoclusters. At the same time, the size of these nanoclusters was also controlled by TUD-1 within a narrow diameter distribution around 1.2 nm, which resulted in the synthesis of (9,8) nanotubes.¹²⁹

Both of the two approaches explained above have certain advantages, however, considering the need for mass production, they have an obvious drawback of high cost. Compared to the mono-metallic catalysts, the bimetallic catalysts (e.g. containing Mo, Cr, Ru, and Pt) are usually more difficult to be removed. Then, for the catalysts supported by MCM-41 and TUD-1, the preparation time is six days¹³⁰ and three days¹²⁹ respectively. In addition, some expensive surfactants are also needed. Naturally, all these factors explained above greatly increase the cost of SWCNT production which hampers their possible use in mass production.

Another approach is to modify the mono-metallic catalysts by non-metal species, in which sulfur and sulfur-containing compounds play interesting roles in carbon nanotube (CNT) synthesis. Sulfur is usually considered as an impurity in various industrial fields. However, the well-controlled poisoning of metals by sulfur can afford beneficial effects.¹³⁵ Bartholomew *et al.* increased the selective production of heavier hydrocarbons by adding a small amount of sulfur.¹³⁶ In the field of carbon deposition, Rostrup-Nielsen reported that carbon-free steam reforming of CH₄ can be obtained by nickel catalyst with the presence of

sulfur¹³⁷ and then studied the detailed effects of sulfur on carbon formation. He claimed that the sulfur decreased the rate of steam reforming less than that of carbon formation.¹³⁸ In contrast, some studies claimed that the introduction of sulfur could increase the formation of carbon deposits. Gardner *et al.*¹³⁹ reported a process to accumulate carbon on sulfidized alumina supported Ni catalysts by the methanation of CO. When the temperature was below 380 °C, the rate of carbon deposition on sulfidized catalysts was less than that of catalysts without sulfur. However, above 380 °C, this trend was reversed. They explained that the sulfur stopped hydrogasification of surface carbon and therefore, lead to the increase of carbon deposition. Baker *et al.*¹³⁵ studied to investigate the influence of sulfur on the catalytic formation of carbon by investigating the decomposition of ethylene on sulfidized cobalt catalysts. They found that when the cobalt was treated by low levels of H₂S (4-100 ppm), the production of filamentous carbon was dramatically increased. However, when the levels of H₂S were above 500 ppm or the H₂S was introduced continuously together with the carbon precursor with the concentration of >60 ppm, the catalysts were poisoned. Donald S. Bethune *et al.*¹⁴⁰ investigated the effects of sulfur on the synthesis of SWCNTs by arc-discharge. They incorporated sulfur in the form of CoS and mixture of S and Co respectively in the anode. Their results showed that the production of SWCNTs is increased while the diameter distribution of SWCNTs becomes wider. In CVD method, Cheng *et al.*¹⁴¹ succeeded in increasing the yield of SWCNTs by introducing thiophene to growth system. Barreiro *et al.*¹⁴² reported an aerosol-assisted CVD method to produce high-purity and long SWCNTs with ferrocene as catalyst and sulfur as the promoter. They also concluded that the sulfur could enhance the growth of SWCNTs.

Sulfur is also linked to the formation of Y-shaped CNT branches. Vallés *et al.*¹⁴³ prepared Co-Mo/MgO sol-gel catalyst to produce CNTs in a horizontal CVD system. Thiophene was introduced with the carbon precursor of methane. The SEM images show that

Y-shaped CNTs are densely organized. It is believed that sulfur controlled the growth direction of the produced nanotubes. Li *et al.*¹⁴⁴ designed a process to produce CNTs by pyrolysis of thiophene. The catalyst was prepared by grinding the mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, following the 1 h calcination at 600 °C in air. Then the resulted powder of Co and Mg oxides was reduced under hydrogen (H_2 , 100 sccm) and argon (Ar, 200 sccm) for 0.5 hours at 600 °C. Finally, the cobalt nanoparticles supported by MgO were obtained. In the growth process, the catalysts were placed in a quartz boat or on a silicon wafer surface located in the center of a horizontal quartz tubular reaction chamber. After a typical reduction process by H_2 , thiophene ($\text{C}_4\text{H}_4\text{S}$) was introduced along with the H_2 flow for 15 min. Their results showed that high concentration of thiophene poisoned the catalyst, resulting in bad graphitization of carbon nanofibers of short CNTs. In contrast, the high concentration of thiophene produced Y-junction and multibranched CNTs. They suggested that the active sites of catalysts were changed by the interaction between Co and S, which changed the growth direction, leading to the formation of branched CNTs. Terrones *et al.*¹⁴⁵ presented an atomistic branching mechanism for the role of sulfur in the synthesis of CNTs. The accumulation of S atoms in the nanotubes promoted the formation of a bump, leading to the deformations on the opposite side of the tube. These changes altered the growth direction of the main stem and thus promoted the growth of the second arm.

Sulfur can also alter the formation of CNTs towards multi-walled CNTs, double-walled CNTs, or SWCNTs of different diameters. Xie *et al.*¹⁴⁶ intended to enhance the synthesis of SWCNTs by thermally decomposing ferrocene mixed with sulfur under the flow of argon and acetylene, however, instead of which, the DWCNTs dominated as the main products. Subsequently, they varied the molar ratio of ferrocene to sulfur from 512:1 to 2:1 to resolve the influence of sulfur concentration. It was found that only small amount of sulfur worked.¹⁴⁷ Cheng *et al.*¹⁴⁸ investigated the detailed influence of sulfur on the structure of

CNTs by a floating catalyst method using ferrocene as the catalyst precursor and methane or ethanol as the carbon source. Thiophene was chosen as the sulfur source and was introduced as a part of methane or argon flow. Firstly, the HRTEM images showed that without sulfur, only a few MWCNTs and SWCNTs were observed while most of the products were amorphous carbon. However, with the increase of sulfur concentration, small-diameter SWCNTs, large-diameter SWCNTs, small-diameter DWCNTs, large-diameter DWCNTs and a mixture of large-diameter SWCNTs, DWCNTs and MWCNTs were successively produced. From the correlation observed between SWCNTs and attached catalysts in HRTEM figure, they proposed that the root growth mechanism resulted in the growth of SWCNTs and the nucleation of SWCNTs began with the formation of small caps. Combining all results together, it was concluded that sulfur influenced the diameter and wall number of CNTs through reconstructing the surface of catalyst particles. Finally, they observed the sulfur-assisted catalytic growth of SWCNTs by *in-situ* TEM.¹⁴⁹ The hollow core of MWCTs with open ends were used as a nanoreactor, in which the catalyst of ferrocene and sulfur were loaded. Their *in-situ* TEM observation showed that sulfur promoted the nucleation and growth of SWCNTs by forming inhomogeneous local active sites and modifying the interface bonding between catalysts and precipitated graphitic layers. As a result, carbon caps can be formed and lifted off.

More interestingly, unique chirality selectivity towards armchair metallic SWCNTs, such as (9,9) and (12,12), was observed in the sulfur assisted CNT fiber spinning process with Fe-based floating catalysts.¹⁵⁰ Windle *et al.* claimed that the sulfur controlled the growth of iron catalyst size, keeping the particles of appropriate dimensions for SWCNTs synthesis.

1.7. Sulfur-modified cobalt catalysts

There are a few catalysts having chirality-selectivity towards relatively large-diameter

(>1 nm) SWCNTs. Among those, cobalt-based catalysts deposited on porous substrates can be produced in large quantities in a relatively easy manner which makes them more promising for scalable SWCNT production.^{59, 129, 151-153} The Co(AcAc)₃ impregnated SiO₂ catalyst (Co/SiO₂) was chosen to investigate the effect of sulfur on its chirality selectivity because of the following considerations. First, two monometallic Co catalysts supported on porous or flat substrates have previously shown a chirality selectivity towards (6,5) nanotubes, indicating the possibility of obtaining chirality selectivity from similar monometallic Co catalysts.¹⁵⁴⁻¹⁵⁵ Second, the mono-metallic catalyst serves as a simpler platform to understand the effect of sulfur without considering a more complex bimetallic alloys in other chirality selective catalysts.¹⁵⁶⁻¹⁵⁷ Third, a previous study¹⁵⁸ has shown that the Co/SiO₂ catalyst from Co(AcAc)₃ offered one of the highest SWCNT yields up to 75 wt.% among several Co catalysts when CO was used as a carbon feedback.

Besides the results reported by other groups, in our previous work, it has been found that sulfate-promoted CoSO₄/SiO₂ catalyst has good chirality selectivity towards (9,8) nanotubes when CO is used as carbon feedstock¹⁵⁹ and the selectivity is shifted towards small-diameter nanotubes when sulfur in the catalyst is removed at higher catalyst calcination temperatures¹⁶⁰. In addition, doping sulfate ions into metal oxides during catalyst preparation can convert Co/SiO₂ catalysts into chiral-selective catalysts producing SWCNTs enriched with large-diameter (9,8) nanotubes.¹⁶¹

The discussion above leads to the study on the effects of sulfur-modified cobalt catalyst on both chirality-selection and carbon yield. In this thesis, the cobalt catalysts were modified by sulfur on two aspects. First, SWCNTs will be produced by a new *in-situ* sulfur-assisted CVD method, in which ethanol will be chosen as a green carbon precursor. Different amount of thiophene and carbon disulfide (CS₂) was introduced to a gas phase to *in-situ* dope Co/SiO₂ catalyst to tune its chirality selectivity. Second, sulfidized catalysts (S-Co/SiO₂) are

intended to be directly synthesized by sulfidation of Co/SiO₂ using H₂S. The sulfidation conditions, such as temperature, reaction time and sulfur concentration were optimized. The controllable transition of Co species can be achieved as verified by catalyst characterization. The sulfidized catalyst will be further tested in SWCNT synthesis. In the last chapter, the preliminary attempts in scaling up the synthesis of large-diameter SWCNTs will be shown.

1.8. Scalability of chirality selective SWCNT synthesis

Apart from the efforts made to selectively synthesize SWCNTs by designing new catalysts, various potentially scalable processes have also been studied to build a road between the basic scientific research and industrial applications of SWCNTs, such as the patent of “Process and apparatus for producing single-walled carbon nanotubes” from the University of Oklahoma,¹⁶² “HiPCO Process” designed by Rice University¹⁶³ and “Fluidized Bed” process from Tsinghua University.¹⁶⁴ “Aerosol method for SWCNT synthesis” from the Helsinki University of Technology.¹⁶⁵

A horizontal furnace is usually used in a typical CVD system. An obvious trend is that most of the investigations on the synthesis of SWCNTs used the catalysts with the amount ≤ 1 g^{122, 125, 129, 159, 166-169}. Considering that the catalysts are usually put in a quartz boat located in the center of the horizontal furnace, large amounts of catalysts would just increase the bed depth. As a result, the catalyst powders at the bottom of the boat would face the diffusion issue.¹⁷⁰ Kathyayini *et al.*¹⁷¹ got a similar carbon yield by using 0.5 g and 1 g catalysts. Zeng *et al.*¹⁷² investigated the influence of contact area by using two layers of boats instead of a single-layer boat and they found the carbon yield increased by 2 times. For a horizontal CVD process, the contact area between the catalysts and carbon precursors limits the scalable synthesis of SWCNTs and it is believed that the good mixing is a solution to this issue. Thus, the fluidized-bed CVD (FBCVD) method is regarded as a choice for the scalable synthesis of

SWCNTs. The detailed demonstration will be introduced in Chapter 5.

1.9. Motivation and scope

After the development of more than 20 years, the scalable synthesis of SWCNTs with chirality selectivity is still the hindrance for their wide potential applications. The overall objective of my research is to modify the present catalysts to obtain SWCNTs with chirality selection and apply this new catalyst into the scalable reactor.

Figure 1-2. The graphical abstract for the thesis.

This thesis will be presented in the following structure. After this introductory section, Chapter 2 presents the basic methods and techniques used for the synthesis and characterization of both catalysts and SWCNTs. Then in Chapter 3, the *in-situ* effects of sulfur on the synthesis of SWCNTs are illustrated. Sulfur-containing compounds (thiophene and CS₂) were introduced into the CVD system together with carbon source (ethanol) and the results show that both thiophene and CS₂ can *in-situ* shift the chirality selection. Chapter 4 investigates the S-Co/SiO₂ catalyst for (9,8) SWCNT growth. In this chapter, the Co/SiO₂ catalyst was first sulfided by H₂S, then the resulting S-Co/SiO₂ catalyst was used to

synthesize SWCNT in a CVD system. Our findings show that this catalyst has a good selectivity to (9,8) nanotubes. More characterizations of the catalysts were carried out to investigate the mechanism. Chapter 5 shows our preliminary attempts on the scalable synthesis of SWCNTs using a cheaper version of S-modified Co/SiO₂ catalyst prepared by different support materials and different reactors. Chapter 6 summarized the thesis and the future work.

Chapter 2: General Experimental Methods

This thesis focuses on sulfur-modified cobalt catalyst for the chiral selective growth of SWCNTs. In this chapter, catalyst and SWCNT synthesis and characterization methods were discussed in detail.

2.1. Catalyst preparation

Impregnation method was used for catalyst preparation, in which the desired metal ions and substrates were directly mixed in solutions, followed by drying and calcination. In this process, metal atoms are randomly distributed on the substrate surface.

2.2. Catalyst characterization

2.2.1. Nitrogen physisorption

Nitrogen physisorption was used to investigate the specific surface area and pore size distribution of the catalyst. In this study, nitrogen adsorption-desorption isotherms of catalysts were measured at 77 K with a Quantachrome Autosorb-6b static volumetric instrument. The catalyst powders should be first degassed at 250 °C under high vacuum (<0.01 mbar). Based on the Brunauer, Emmet, and Teller (BET) method, the surface area was calculated. To calculate their pore size and pore size distribution, the Barrett, Joyner, and Halenda (BJH) method from the desorption branch of their isotherms was used.¹⁷³⁻¹⁷⁴

2.2.2. Elemental analysis

Elemental analysis is used to analyze the materials quantitatively for the elemental composition. The weight fraction of carbon and sulfur in the catalyst after SWCNT synthesis

was measured by an elemental analyzer (Elementarvario, CHN). Before each test, all samples should be dried at 100 °C for 8 hours. In each test, about 5 mg samples were used and tested for three times to obtain the average and standard errors.

2.2.3. Scanning electron microscope

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

2.2.4. Transmission electron microscopy

Transmission electron microscopy (TEM) is the most compelling tool to image nanoscale materials with atomic-scale resolution. TEM images of catalysts were recorded on a Philips Tecnai 12 microscope (Chapter 3) or JEOL, JEM-1400 (Chapter 4). The samples were typically first dropped into anhydrous ethanol and then dispersed by bath sonication for 30 min, and then one drop of the suspension was deposited on a TEM grid covered with holey carbon film.

2.2.5. X-ray diffraction

X-ray diffraction (XRD) is commonly applied to reveal the crystallographic structure of catalysts. In this thesis, XRD measurements of catalysts were carried out using a Bruker AXS D8 X-ray diffractometer (Cu K α , λ = 0.154 nm, 40 kV, 30 mA).

2.2.6. H₂-temperature programmed reduction

H₂-temperature programmed reduction (H₂-TPR) is very useful in investigating the metal support interaction and providing surface chemical information, such as stability, metal species, and metal distribution.¹⁷⁵ In this thesis, the reducibility of catalysts was investigated by TPR system equipped with a thermal conductivity (TCD) detector of a gas

chromatography (Techcomp 7900). 200 mg of the catalyst or reference samples were loaded into a quartz cell. H₂ (5%) in Ar was introduced into the quartz cell at a flow rate of 30 sccm. Pure Ar gas was used as a reference for the TCD. After the TCD baseline was stable, the temperature of the quartz cell was increased to a high temperature at 5 °C/minute, and then held for 30 minutes. An acetone–liquid N₂ trap was installed between the quartz cell and the TCD to condense water or H₂S produced during catalyst reduction.

2.2.7. X-ray photoelectron spectroscopy

The chemical nature of catalysts was also studied using X-ray photoelectron spectroscopy (XPS) with a monochromatized Al-K α radiation source (Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer System). In all measurements, the pass energy was set at 50 eV, which approximately corresponds to an energy resolution of 0.5 eV, and a flood gun was used for charge compensation. Due to the flood gun, the base pressure of the chamber which is around 2×10^{-9} mbar at start rose to roughly 2×10^{-7} mbar during the measurements. Data was analyzed with Advantage Software Version 5.27.

2.2.8. Inductively Coupled Plasma

All the samples were first total digested in a microwave system (Milestone SK-10) which is able to run ten samples per cycle (one acid blank and nine samples). At each cycle, approximately 100 mg of the samples were weighed into teflon tubes and a mixture of acid (1 mL of ~37% HCl + 3 mL of 65% of HNO₃ + 6 mL of 70% HF) was added on each. After the addition of acid mixture, the samples were heated to 200 °C in 20 minutes and were kept at that temperature isothermally for 30 minutes. After natural cooling, 25 mL of 4% boric acid was added into each vessel and a second cycle of digestion was performed with the same program. Finally, all digested solutions were topped up to 50 g with 2% nitric acid. Three replicate dilutions were prepared for each sample and the results were calculated by

averaging all three after the subtraction background obtained by the average of acid blank solutions. The elemental determinations were performed on an Agilent 7700x ICP-MS (Agilent Technologies Inc.) equipped with an Octopole Reaction System with Helium Collision Cell for the removal of spectral interference. The system was operated with a MicroMist glass concentric nebulizer, a (Scott-type) quartz spray chamber, and nickel sampler/skimmer cones. SpexCertiprep Multi-element calibration standard-1 and standard-2A were used as external calibration solutions. Data analysis was performed using MassHunter software.

2.2.9. X-ray fluorescence

X-ray fluorescence (XRF) measurements were carried out on a Bruker S8 Tiger XRF spectrometer under helium atmosphere using an X-ray tube with Rh anode for the generation of X-rays. Prior to the measurements, the instrument was calibrated with its own standards. Powder samples were placed in the liquid holders with Prolene film (4 μm) as the supporting material and “Loose Powder” method was selected. SiO_2 was selected as the matrix for the calculations.

2.3. SWCNTs synthesis

For a typical CVD method, the growth process usually begins with heating a catalyst to high temperatures in hydrogen (for reduction) or inert gas atmosphere, and then a carbon precursor decomposes on the catalyst in the quartz tube over a period of time. During the heating and growth period, the gas flow rate and pressure can be controlled depending on different requirements. Finally, after the system is cooled to room temperature, the SWCNTs grown on the catalysts can be collected.

2.4. SWCNTs purification

To obtain SWCNT suspension, the as-synthesized powders with carbon deposits were dispersed in 2 wt.% sodium dodecyl benzene sulfonate (SDBS) (Aldrich) D₂O (99.9 atom % D, Sigma-Aldrich) solution by sonication in a cup-horn ultrasonicator (SONICS, VCX-130) at 20 W for 0.5 hours. Subsequently, the SWCNT suspension was centrifuged for 1 hour at 50,000 g. SWCNT supernatant obtained after centrifugation was further characterized by several spectroscopies. This method was demonstrated in the previous job of our research group, which has been proved that it could lead little damage to the samples.¹⁷⁶

2.5. SWCNTs characterization

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

2.5.1. Raman Spectroscopy

Raman spectroscopy is a noncontact and nondestructive technique, which is commonly used to characterize CNT. SWCNTs have special electronic and vibrational structures, which result in unique characteristic peaks in Raman spectroscopy. The Radial Breathing Mode (RBM) is a totally symmetric vibrational mode associated with the vibration of carbon atoms in a radial direction from the nanotube axis, as if the tube is breathing. RBM always locates at the low frequency range (100 – 400cm⁻¹), which can be used to identify the existence of SWCNTs in a sample, and it is also applied to estimate SWCNT diameters. The Disorder-induced band (D band) and the Graphite-like band (G band) are three main features

corresponding to SWCNT structures. Briefly, different RBM indicates different SWCNTs; the D/G ratio can be used to evaluate the SWCNT quality.

Raman spectroscopy is used in this study for the following purposes: (1) to determine the diameter distribution of SWCNT samples, (2) to identify the existence of SWCNT in samples and (3) to evaluate the SWCNT quality by D/G ratio. Raman spectra were obtained by a Renishaw Ramanscope in the backscattering configuration. Three lasers with different energy (514.5 nm (2.41 eV), 633 nm (1.96 eV), and 785 nm (1.58 eV)) were used. Each spectrum was the average of five scans at different locations of the same sample.

2.5.2. PL spectroscopy

Photoluminescence (PL) studies of SWCNT focus on electronic transitions of semiconducting tubes because metallic tubes do not show light emission due to the available electronic states between their valence and conduction bands. The relation between electronic transitions and all possible (n,m) SWCNTs can be described in a Kataura plot based on a calculation using a tight binding model.¹⁷⁷ New empirically-based Kataura plots were developed to obtain more reliable predictions of (n,m) structures using measured SWCNT optical transitions (E_{11} , E_{22}).¹⁷⁸

PL spectroscopy can provide a quick identification for the chirality distribution of semiconducting SWCNTs. In the early studies, PL intensity of individual (n,m) specie was directly applied to determine their relative abundance.^{9, 116} Some theoretical studies later suggested that (n,m) species may have significantly different photoluminescence quantum efficiencies, which could introduce errors in their relative abundances calculated by the PL intensity alone.¹⁷⁹⁻¹⁸⁰ Some experiments indicate that the quantum efficiency difference among different (n,m) SWCNT species may not be the same with the theoretical predictions.¹⁸¹ In our previous studies, we have compared the abundance values calculated

with or without considering (n,m) photoluminescence quantum efficiency coefficients.⁷⁰ No significant differences were observed. These findings support the direct use of measured PL intensity in determining the SWCNT (n,m) abundance. Thus, in this study, the relative abundance of (n,m) species was calculated by dividing the PL intensity of individual (n,m) species by the sum of intensities of all (n,m) species. In this thesis, PL spectra were measured by a Jobin-Yvon Nanolog-3 spectrofluorometer.

2.5.3. UV-Vis-NIR absorption spectroscopy

Absorption spectroscopy is a technique measuring the optical absorption of a sample in a particular wavelength range. The application of UV-vis-NIR absorption spectroscopy in SWCNT characterization is based on electronic transitions between energy bands of SWCNT caused by incoming photons. Both semiconducting and metallic SWCNTs can be detected. Because transition energies of different SWCNTs could be very close, each peak in an absorption spectrum may represent the combination of several (n,m) SWCNT species. In order to identify different (n,m) species in an absorption spectrum, several spectrum deconvolution scenario (Lorentz, Gauss or Voigt) have been used.¹⁸²

In this thesis, UV-vis-NIR absorption spectroscopy was mainly used to analyze the (n,m) distribution of SWCNT samples. The Varian Cary 5000 spectrophotometer was used to measure the UV-vis-NIR absorption spectra.

2.5.4. Thermogravimetric analysis

The carbon deposit was also characterized by TGA. The total carbon yield was determined by analyzing weight loss of as-synthesized carbon deposits with catalysts on a TG instrument (PerkinElmer, Diamond TG/DTA). For a typical test, about 2 mg of as-synthesized catalyst was placed in an alumina pan. The sample was heated to 150 °C and held for 0.5 hours under air flow (200 sccm) to remove moisture. Subsequently, its temperature

was continuously raised from 150 to a high temperature at the 10 °C/minute ramping rate. The weight loss was monitored and recorded as a function of the temperature.

Chapter 3: Sulfur-induced Chirality Changes in Single-walled Carbon Nanotube Synthesis by Ethanol Chemical Vapor Deposition on Co/SiO₂ Catalyst

3.1. Introduction

In previous studies, the CoSO₄/SiO₂ catalyst was prepared by the wetness impregnation method with CoSO₄ and fumed silica. The whole preparation process takes around two days. To change the concentration of sulfur in the catalyst, it is needed to produce new catalyst with different CoSO₄, leading to two major issues: first, it will take a lot of time in the catalyst preparation; second, the concentration of Co in the catalyst will also change, which will make the research inconsistent. However, by supplying sulfur as an additive into the precursor, it is much easier to precisely adjust the concentration of sulfur in the carbon feedstock. Thus, the effect of different amounts of sulfur on the SWCNT synthesis can be investigated efficiently. As a result, I hypothesized that introducing sulfur into carbon feedstock in gas phase may efficiently alter the chirality selectivity of catalysts towards different (*n,m*) nanotube species by modifying the catalyst.

In this chapter, SWCNT synthesis was carried out using a Co monometallic catalyst supported on a porous SiO₂ using ethanol CVD. Two types of sulfur-containing compounds with different chemical compositions, carbon disulfide, and thiophene, were added to the ethanol at different concentrations. The effects of these two sulfur-containing compounds on the chirality distribution of SWCNTs were monitored by photoluminescence (PL) and ultraviolet–visible–near-infrared (UV–vis–NIR) absorption spectroscopy. The carbon yield

reflecting the activity of the catalyst was tracked by thermogravimetric analysis (TGA). The results have shown a strong correlation between chirality change/carbon yield and sulfur concentration. It suggests good potential of using sulfur-containing compounds to change the chirality selectivity of catalysts in SWCNT synthesis.

3.2. Catalyst preparation

The Co/SiO₂ catalyst with ~1 wt.% Co (based on the starting materials used) was prepared following a previous reported incipient wetness impregnation method.¹⁵⁸ Co (III) acetylacetonate (Co(AcAc)₃, 99.99%, Sigma–Aldrich) was dissolved in dichloromethane solution and then added to fumed silica (Cab–O–Sil M-5, surface area 200 m²/g, Sigma–Aldrich,). Fumed silica is produced by hydrolysis of SiCl₄ at high temperature. It is a common substrate material for catalysts because it is stable after high-temperature treatment, and has a large specific surface area to accommodate Co species. Further, it can be easily dissolved in a NaOH solution, which facilitates the purification of SWCNTs. The wet solids were aged at room temperature for 1 hour and dried on a glass plate at 60 °C for 8 hours. The dried catalyst (5 g each batch) was ground into fine powders, and then calcined under a dry air flow (20 sccm per gram of catalyst) from room temperature to 440 °C at 1 °C/minute and kept at that temperature for 5 hours before cooling to room temperature.

3.3. SWCNTs synthesis

SWCNT synthesis was carried out in a horizontal tube reactor using low-pressure ethanol CVD (**Figure 3-1** shows its schematic drawing). The calcined Co/SiO₂ catalyst (50 mg) was loaded into a ceramic boat at the center of the reactor and was reduced under flowing H₂ (1 bar, 50 sccm, 99.99%, Soxal) from room temperature to 780 °C at a ramping rate of 15 °C/minute. Subsequently, the reactor was evacuated by a vacuum pump to 0.1 mbar. During SWCNT synthesis, ethanol (>99.5%, Sigma–Aldrich) was carried into the

reactor from a reservoir (its temperature was kept at 25 °C) by a H₂ flow for 0.5 hours. The pressure in the reactor was maintained constant. Eventually, the reactor was cooled to room temperature under Ar flow. When sulfur compounds, carbon disulfide (>99.5%, purity, Sigma–Aldrich) or thiophene (>99%, Aldrich), were introduced to the ethanol reservoir, all other parameters were kept the same. The concentration of carbon disulfide in ethanol was changed from 0.001 to 0.045 wt.%, while that of thiophene was varied from 0.001 to 0.2 wt.%. The experiments were repeated at least three times for each set of synthesis parameters to minimize system errors.

Figure 3-1. Schematic diagram of the ethanol chemical vapor deposition reactor.

3.4. SWCNT characterization

After SWCNT synthesis, the catalyst (5 mg) loaded with carbon deposits was directly suspended in 2 wt.% sodium dodecyl benzene sulfonate (SDBS, Sigma–Aldrich) D₂O (99.9%, Sigma–Aldrich) solution by sonication in a cup-horn ultrasonicator at 20 W for 0.5 hours. After sonication, the suspension was centrifuged at 50,000 g for 1 hour. The clear SWCNT supernatant obtained after centrifugation was characterized by PL and UV–vis–NIR absorption spectroscopy. PL signals were collected on a spectrofluorometer with the excitation wavelength scanned from 400 to 900 nm and the emission wavelength collected from 650 to 1700 nm. The UV–vis–NIR absorption spectra were measured from 400 to 1600 nm on a spectrophotometer. The carbon deposit was also characterized by TGA. The total

carbon yield was determined by analyzing weight loss of as-synthesized carbon deposits with catalysts on a TG instrument. For a typical test, about 2 mg of as-synthesized catalysts were placed in an alumina pan. The sample was heated to 150 °C and held for 0.5 hours under air flow (200 sccm) to remove moisture. Subsequently, its temperature was continuously raised from 150 to 1000 °C at the 10 °C/minute ramping rate. The weight loss was monitored and recorded as a function of the temperature. The same procedure was repeated after the sample was cooled to room temperature to get the second weight–temperature curve for baseline correction.

3.5. Results and discussion

Physicochemical properties of the Co/SiO₂ catalyst

Figure 3-2. SEM (left) and TEM (right) images of the Co/SiO₂ catalyst and SWCNTs. (a) the catalyst after calcination in air, (b) SWCNTs on the catalyst grown without adding sulfur compounds, (c) SWCNTs on the catalyst after adding 0.0001 wt.% carbon disulfide, (d) SWCNTs on the catalyst after adding 0.1 wt.% thiophene. The scale bar in the SEM image of (a) is 200 nm in length, and the other SEM image scale bars are 100 nm in length.

Figure 3-3. Nitrogen physisorption of the Co/SiO₂ catalyst. The inserts show the pore size distribution determined by the Barrett, Joyner, and Halenda (BJH) method.

The SEM and TEM images in **Figure 3-2a** shows that the catalyst after calcination in the air is comprised of small SiO₂ particles. The structure of the catalyst is further characterized by N₂ physisorption and XRD. The physisorption isotherm (**Figure 3-3**) indicates that the catalyst is a porous material with a surface area of 227 m²/g and a pore volume of 1.5 mL/g. Its average pore size is around 35 nm, which likely comes from the gaps among individual SiO₂ particles. Its XRD pattern shown in **Figure 3-4** has a broad diffraction peak near $2\theta = 21^\circ$ originating from SiO₂ particles. No diffraction peaks from bulk Co oxides or Co silicates are observed. This is similar to the result of the previous study that the Co/SiO₂ catalyst contains surface Co silicate, which is highly dispersed in the surface layer of SiO₂ without long-range crystallographic order.¹⁵⁸ The existence of surface Co silicate was further confirmed by H₂-TPR. **Figure 3-5** shows that its reduction profile has a single peak at around 830 °C, indicating Co species are tightly bonded to the SiO₂ substrate.

Figure 3-4. XRD patterns of Co/SiO₂ catalysts after calcination and SWCNT growth at different conditions.

Figure 3-5. H₂-temperature-programmed reduction profile of the Co/SiO₂ catalyst.

Since the H₂-TPR profile indicates that the Co/SiO₂ catalyst only starts to be reduced in H₂ at around 670 °C with the peak maximum at 830 °C, the catalyst was firstly activated by H₂ reduction to generate sufficient small Co particles for SWCNT growth. The chirality distribution of SWCNTs synthesized at three different H₂ reduction conditions: 540, 780 and 830 °C was compared. The PL and absorption spectroscopy results (**Figure 3-6**) show that

the chirality distribution of SWCNTs has minor changes at the first two reduction conditions. This can be attributed to the formation of small Co metal particles by reducing highly dispersed surface Co silicate species, resulting in small Co particles anchored to the SiO₂ surface.¹⁵⁸ The XRD pattern of the catalyst after SWCNT growth in **Figure 3-4** confirms that no large Co particles formed after SWCNT growth. The 830 °C reduction sample contains slightly larger diameter nanotubes.

Figure 3-6. (a) PL contour plots as a function of excitation and emission energies and (b) UV-vis-NIR absorption spectra of SDBS-dispersed SWCNTs grown on the Co/SiO₂ catalyst after catalyst reduction in H₂ at three different temperatures.

TGA results in **Figure 3-7** show that although more Co particles can be generated at higher reduction temperatures leading to higher SWCNT yield, a small amount of graphite was also produced, which can be attributed to the formation of aggregated Co particles. The pressure of ethanol was also varied to evaluate its impact on SWCNT synthesis. As shown in

Figure 3-8, when the pressure of ethanol in the reactor increases from 5 to 50 mbar, no significant chirality distribution changes in SWCNTs have been observed. The carbon yield does increase with the increase of ethanol pressure, although more amorphous carbon is produced at higher ethanol pressure. These findings of the effect of carbon feedback pressure and catalyst reduction temperature on the synthesis of SWCNTs are similar to several previous studies.¹⁸³⁻¹⁸⁶ Thus, the catalyst reduction temperature in H₂ was fixed at 780 °C (the same as the growth temperature) and the ethanol pressure was fixed at 25 mbar for the following studies.

Figure 3-7. TG and DTG profiles of carbon deposits grown on the Co/SiO₂ catalyst after catalyst reduction in H₂ at three different temperatures.

Figure 3-8. (a) PL contour plots as a function of excitation and emission energies and (b) UV-vis-NIR absorption spectra of SDBS-dispersed SWCNTs grown from Co/SiO₂ at different ethanol pressures.

Effect of carbon disulfide on chirality selectivity

I used liquid sulfur compounds (carbon disulfide and thiophene) other than sulfur compounds in solid (pure S) or gas (H₂S) states in this study because it is much easier to precisely adjust their concentration in carbon feedstock. As shown later, small changes of sulfur concentrations in carbon feedstock have significant impacts on the chirality selectivity of the Co/SiO₂ catalyst. **Figure 3-9a** sketches the PL contour plots (only six representative results are shown here) of SWCNTs grown from the Co/SiO₂ catalyst after adding different amounts of carbon disulfide in ethanol. The spikes from the resonance behavior of both excitation and emission events represent the transition pair belonging to individual semiconducting (*n,m*) species. The relative abundance of semiconducting (*n,m*) tubes

identified in **Figure 3-9a** was calculated based on their PL peak intensity. The detailed results are listed in **Table 3-1**. Using ethanol without sulfur, the major (n,m) species (their relative abundance is larger than 12%) include (7,5), (8,4), (7,6), and (8,6) at the diameter from 0.83 to 0.97 nm. When carbon disulfide was added to ethanol, the chirality selectivity shifts toward larger diameter nanotubes, such as (8,7) at 1.03 nm and (9,8) at 1.17 nm, while the relative abundance of smaller diameter nanotubes is declining. The changes in the relative abundance of (7,6), (8,7) and (9,8) nanotubes are shown in **Figure 3-9b**. The relative abundance of (8,7) nanotubes reaches the maximum at 20.6% when the carbon disulfide concentration is at 0.012 wt.%. Afterward, with the further increase of carbon disulfide concentration, the chirality distribution of SWCNTs shows minor changes.

Figure 3-9. (a) PL contour plots as a function of excitation and emission energies of SDBS-dispersed SWCNTs grown from Co/SiO₂ after adding different amounts of carbon disulfide in ethanol, (b) The change of relative abundance of three major (n,m) species determined by PL results at different carbon disulfide contents.

The changing trend of chirality distribution observed in PL contour plots corroborates with the UV-vis-NIR spectra shown in **Figure 3-10**. From UV-vis-NIR spectra, it is also noticed that the concentration of SWCNT dispersions vary greatly at different carbon disulfide concentrations, even though the same amount of carbon deposited catalysts were used to prepare the SWCNT dispersions. Thus, the TGA analysis was further carried out to determine the carbon yield at different synthesis conditions. According to the above experimental results, it is known that sulfur plays a very important role in the selective synthesis of SWCNTs. First, S is a necessity for (9,8) growth in this low-pressure CVD methods. Second, with the observed decreased the carbon yield, one proper hypothesis is that S may have poisoned the catalysts thus reduced the catalytic efficiency.

Figure 3-10. UV-vis-NIR absorption spectra of SDBS-dispersed SWCNTs grown from Co/SiO₂ after adding different amounts of carbon disulfide in ethanol. The label S₁₁ (shaded by yellow) marks the excitonic optical absorption bands for semiconducting SWCNTs corresponding to the first one-dimensional van Hove singularities; the S₂₂ and E₁₁ (shaded by blue) correspond to the overlapping absorption bands of the first van Hove singularities from metallic SWCNTs and the second van Hove singularities from semiconducting SWCNTs. All spectra were shifted in y-axis for easy comparison.

Table 3-1. The relative abundance of (n,m) species in SWCNTs grown on Co/SiO₂ after adding different amounts of carbon disulfide in ethanol.

(n,m) index	D (nm)	Carbon disulfide content in ethanol (wt.%)								
		0	0.0001	0.001	0.006	0.008	0.01	0.012	0.023	0.045
(6,5)	0.76	2.4	4.4	4.5	3.8	3.6	3.7	2.5	3.4	3.8
(8,3)	0.78	3.1	2.0	1.8	1.7	1.6	1.6	1.2	1.7	
(7,5)	0.83	12.1	18.4	12.5	11.7	9.5	6.8	4.0	5.4	5.0
(8,4)	0.84	16.5	20.2	14.1	12.0	12.2	9.4	6.3	8.4	7.6
(10,2)	0.88	3.0	3.8	3.8	3.4	2.9	2.0	1.6	2.3	2.3
(7,6)	0.90	19.1	18.7	14.1	11.9	11.7	10.5	8.9	11.2	11.8
(9,4)	0.92	8.5	7.3	8.2	6.5	5.6	4.6	4.0	5.1	5.7
(8,6)	0.97	17.9	10.5	13.3	11.9	11.9	11.4	11.5	11.6	12.2
(9,5)	0.98	5.5	5.8	8.4	10.3	9.8	11.4	12.4	10.8	10.9
(8,7)	1.03	5.5	4.7	8.2	11.8	13.4	17.7	20.6	18.0	14.8
(9,7)	1.10	3.2	1.5	5.3	6.2	7.5	8.4	10.4	8.9	9.4
(10,6)	1.11	1.8	1.3	3.3	4.5	4.8	5.6	6.9	5.5	7.9
(9,8)	1.17	1.5	1.3	2.7	4.2	5.5	6.8	9.8	7.5	8.5

Figure 3-11. (a) TG profiles of carbon deposits grown on Co/SiO₂ after adding different amounts of carbon disulfide in ethanol, (b) The weight fraction of carbon determined by TGA and EA in Co/SiO₂ catalysts after SWCNT synthesis with different amounts of carbon disulfide in ethanol, (c) The weight fraction of sulfur determined by EA.

As depicted in **Figure 3-11a**, the total carbon yield in the catalyst after synthesis without adding carbon disulfide is 4.8 wt.%. Although this carbon yield is lower than that previously reported on the Co/SiO₂ catalyst when CO was used as carbon feedstock,¹⁵⁸ it is comparable to the results reported for other Co catalysts using ethanol as carbon feedstock.^{185,}

¹⁸⁷ After adding a small amount of carbon disulfide (0.0001 wt.%), the carbon yield increases

sharply to 14.0 wt.%, consistent with previous findings that sulfur compounds are a promoter for carbon nanotube growth.^{141-142, 188-189} The higher SWCNT yield can be also observed in the SEM and TEM images (**Figure 3-2c**). However, with the increase of carbon disulfide concentration in ethanol, the carbon yield quickly drops. At 0.012 wt.% of carbon disulfide, the carbon yield is only 0.1 wt.%. To further corroborate the carbon yield results obtained by TGA, the carbon content in the carbon deposited catalysts was also determined by elemental analysis (EA). As shown in the **Figure 3-11b**, the results from EA are consistent with those from TGA. Comparing the dependences of the chirality distribution change and carbon yield on the carbon disulfide concentration, it is evident that the chirality selectivity change of the Co/SiO₂ catalyst (selectivity shifts from (7,6) toward (8,7) and (9,8) nanotubes) happens when the activity of the catalyst drops substantially (the carbon yield decreases from 4.8 to 0.1 wt.%), which is similar with the results from M.S. Kim's work¹³⁵. This finding suggests that the role of sulfur may be blocking some active sites of Co catalysts, which are initially active to grow different chiral species, resulting in the better selectivity toward some chiral species. In particular, small Co particles could be more susceptible to sulfur, thus the chirality distribution shifts from small diameter to large diameter nanotubes. If this hypothesis is true, one interesting question arises: does the similar trend happen using other sulfur compounds on Co catalysts?

Effect of thiophene on chirality selectivity

To answer this question, I further studied the effect of thiophene on SWCNT synthesis using the Co/SiO₂ catalyst. Thiophene was selected because it is less volatile (with the boiling point at 84 °C) than carbon disulfide (boiling point at 46.3 °C). Further, a previous study has shown that thiophene and carbon disulfide can promote the growth of carbon nanotubes (CNTs) with different structures.¹⁹⁰ **Figure 3-12a** sketches six representative PL contour plots of SWCNTs obtained after adding different amounts of thiophene into ethanol.

The relative abundance of semiconducting (n,m) tubes identified in **Figure 3-12a** is listed in **Table 3-2**. There are some similarities between the results of thiophene and carbon disulfide. When thiophene was added, the relative abundance of smaller diameter nanotubes (such as (7,6)) is decreasing, and that of larger diameter nanotube (such as (8,7)) is increasing. The chirality selectivity also shifts toward larger diameter nanotubes. However, when the thiophene concentration further increases, the catalyst shows excellent selectivity toward (9,8) nanotubes. The relative abundance of (9,8) nanotubes reaches the maximum at 43.1% when the thiophene concentration is at 0.1 wt.%. Afterward, with the further increase of thiophene concentration, the chirality distribution of SWCNTs shows a more even distribution among nanotubes from (6,5) to (10,6). Further, the effects of thiophene take place at much higher concentrations about one order higher than that of carbon disulfide.

Figure 3-12. (a) PL contour plots as a function of excitation and emission energies of SDBS-dispersed SWCNTs grown from the Co/SiO₂ catalyst after adding different amounts of thiophene in ethanol, (b) The change of relative abundance of three major (n,m) species determined by PL results at different thiophene contents.

The PL results corroborate with the UV-vis-NIR spectra shown in **Figure 3-13**. TGA results in **Figure 3-14** are similar to those in **Figure 3-11**. When a small amount of thiophene was added (0.001 wt.%), the total carbon yield increase to 5.9 wt.%. The carbon yield quickly drops to 1.8 wt.%, when 0.01 wt.% of thiophene was added. The carbon yield is only 0.4 wt.% when the relative abundance of (9,8) nanotubes reaches the maximum, which corroborates with the few nanotubes observed in the SEM and TEM images in **Figure 3-2d**. To answer the previous question, different sulfur compounds can also block active sites on Co catalysts, however, the trend observed in chirality selectivity changes are not the same. When suitable amount of thiophene is added, the catalyst shows good selectivity toward (9,8) nanotubes, which is not observed when carbon disulfide is used.

Figure 3-13. UV-vis-NIR absorption spectra of SDBS-dispersed SWCNTs grown from Co/SiO₂ after adding different amounts of thiophene in ethanol. The label S₁₁ (shaded by yellow) marks the excitonic optical absorption bands for semiconducting SWCNTs corresponding to the first one-dimensional van Hove singularities; the S₂₂ and E₁₁ (shaded by blue) correspond to the overlapping absorption bands of the first van Hove singularities from metallic SWCNTs and the second van Hove singularities from semiconducting SWCNTs. All spectra were shifted in y-axis for easy comparison.

Table 3-2. The relative abundance of (n,m) species in SWCNTs grown on Co/SiO₂ after adding different amounts of thiophene in ethanol.

(n,m) index	D (nm)	Thiophene content in ethanol (wt.%)								
		0	0.001	0.005	0.01	0.05	0.075	0.01	0.125	0.2
(6,5)	0.76	2.4	4.4	4.5	3.8	3.6	3.7	2.5	3.4	3.8
(8,3)	0.78	3.1	3.1	1.6	1.4	1.6	1.2			
(7,5)	0.83	12.1	13.9	9.8	9.0	6.8	4.1	2.1	3.7	6.0
(8,4)	0.84	16.5	16.6	11.0	12.6	12.0	7.2	4.1	6.5	8.9
(10,2)	0.88	3.0	4.4	2.1	2.5					
(7,6)	0.90	19.1	16.1	15.2	14.5	13.7	8.6	6.1	9.4	14.8
(9,4)	0.92	8.5	6.8	4.9	5.2	4.1	3.3	2.1	3.5	4.2
(8,6)	0.97	17.9	13.0	13.2	12.7	9.7	9.6	4.0	9.9	10.0
(9,5)	0.98	5.5	6.6	11.0	10.6	8.2	9.8		9.4	7.6
(8,7)	1.03	5.5	6.2	11.0	12.6	13.4	16.6	15.3	17.2	14.2
(9,7)	1.10	3.2	3.0	6.8	6.3	8.1	11.0	14.4	11.2	9.3
(10,6)	1.11	1.8	2.5	5.1	5.0	5.4	7.1	8.1	7.2	6.2
(9,8)	1.17	1.5	1.6	3.3	4.5	7.7	16.0	40.5	18.5	11.2

Figure 3-14. (a) TG profiles of carbon deposits grown on Co/SiO₂ after adding different amounts of thiophene in ethanol, (b) The weight fraction of carbon determined by TGA and EA in Co/SiO₂ catalysts after SWCNT synthesis with different amounts of thiophene in ethanol, (c) The weight fraction of sulfur determined by EA.

Discussion of the role of sulfur compounds on Co/SiO₂

Previous studies have observed several roles of sulfur in the synthesis of CNTs. Sulfur is generally regarded as a catalyst poison for transition metal catalysts in many industrial processes. Due to the strong bonding between sulfur and surface metal atoms, a small amount of sulfur can block the active sites on metal catalysts and decrease their activity by several

orders of magnitude.¹³⁵ However, a suitable amount of sulfur-containing compounds has been shown to be growth promoters for the synthesis of CNTs.^{141-142, 188-189} Several mechanisms were proposed to explain the roles of sulfur at different synthesis conditions. For Fe catalysts used in the direct CNT fiber spinning processes, a sulfur layer could be formed on the surface of Fe particles, which limits the dissolving of carbon in Fe particles and retards the diffusion of carbon inside Fe particles. The surface sulfur layer also assists the assembly of carbon atoms onto the edge of CNTs.¹⁹¹ Since Fe particles are directly introduced into CNT fiber spinning processes in the gas phase, they would continuously coarsen by the collision. Sulfur coated Fe particles may not coarsen as rapidly as uncoated ones, which would affect the selectivity towards SWCNTs or multiple walled CNTs.¹⁹² For Fe particles supported on substrates, sulfur may assist the formation of inhomogeneous local active sites on large Fe nanoparticles, and modifies the interface bonding between the catalysts and precipitated graphitic layers, so that carbon caps can be formed and lifted up.¹⁴⁸ These effects were observed in a recent *in-situ* transmission electron microscope study.¹⁴⁹

Based on the correlations between SWCNT chirality distribution/carbon yield and sulfur compound concentration observed in this study, several roles of sulfur compounds on the Co/SiO₂ catalyst proposed were illustrated in **Figure 3-15**. This mechanism is based on a consensus in the scientific literature that the outer diameter of formed nanotubes is directly correlated to the catalyst particles size.¹⁹³ The Co/SiO₂ catalyst in this study is different from Fe catalysts used in the direct CNT fiber spinning processes. Small Co particles are reduced by H₂ from the highly dispersed surface Co silicate on the Co/SiO₂ catalyst. They are anchored on the SiO₂ surface, as XRD results in **Figure 3-4** show that no large Co particles are formed. The Co particles on the SiO₂ surface would have a relatively wide diameter distribution. Without sulfur, carbon atoms would saturate smaller Co particles first, thus small diameter nanotubes, such as (7,5) and (7,6), are more likely to be initiated from those

smaller Co particles, resulting in the chirality distribution, similar to that observed in the previous studies.¹⁹⁴⁻¹⁹⁵ When a small amount of sulfur-containing compounds are introduced (0.0001 wt.% of carbon disulfide or 0.001 wt.% thiophene in ethanol), sulfur may play the role similar to that observed on Fe particles. A thin layer of sulfur was formed on Co particles, which assists the assembly of carbon atoms onto the growing nanotube edge, resulting in the significant carbon yield increase. The same influence of sulfur on the carbon yield was also observed in other studies.¹⁹⁶ They believed that the small amounts of sulfur in iron caused some liquefaction of the particle, which increased considerably the rate of the nucleation. Further increasing the concentration of sulfur compounds, carbon disulfide, and thiophene exhibit different effects. The thermal decomposition of carbon disulfide results in sulfur and carbon radicals on Co particles. The large amount of sulfur radicals could quickly block most of the active sites on Co particles, resulting in the sharp carbon yield reduction. Especially, smaller Co particles would be covered by sulfur first due to their relatively smaller surface areas, and become inactive in SWCNT growth, thus the chirality selectivity shifts towards larger diameter SWCNTs, which may still grow from larger Co particles. In contrast, the thermal decomposition of thiophene produces sulfur, carbon and hydrogen radicals. Although sulfur radicals may still block many active sites on Co particles, leading to the lower carbon yield, the hydrogen radicals could interact with sulfur on Co surface, weakening the blocking effect of sulfur. Some active sites on large Co particles may survive, and the small amount of sulfur may even promote SWCNT growth from those Co particles, thus leading to the unique chirality selectivity towards larger diameter nanotubes, such as (9,8). The content of sulfur on the Co/SiO₂ catalysts was quantified by EA. As shown in **Figure 3-11c** and **3-14c**, the sulfur content is about 0.2 wt.% at most conditions when sulfur compounds are added in ethanol. The higher sulfur content is correlated with the increase in carbon yield, suggesting some sulfur may be incorporated in SWCNTs. Although the EA

results cannot differentiate the surface composition changes of active Co particles, it is evident from the observed chirality distribution and carbon yield changes that the dynamic interactions among sulfur, hydrogen, carbon and Co metal particles are critical for the chirality selectivity of the Co/SiO₂ catalyst. TEM analysis was also performed in an attempt to determine the structures of Co metal particles, which are active for SWCNT growth. As shown in **Figure 3-2**, SWCNTs aggregate into small bundles of 10–20 nm in diameter. However, it is difficult to identify individual active Co particles in our TEM analysis. It may be due to the fact that only a small amount of Co is dispersed on the SiO₂ substrates of large surface area. Based on our current TEM results, it is difficult to elucidate the structure of potential Co–S phases. More theoretical simulation or experimental studies are needed to obtain a comprehensive understanding of the effect of sulfur on the chirality selection in SWCNT growth.

Figure 3-15. A schematic illustration of the potential effects of sulfur compounds on the Co particles supported on porous SiO₂ and their impact of SWCNT chirality selectivity.

3.6. Conclusion

Sulfur-containing compounds show strong effects on the synthesis of SWCNTs using ethanol CVD on the Co/SiO₂ catalyst in both carbon yield and chirality selectivity. When a small amount of sulfur compounds was added to ethanol, the carbon yield increases significantly from 4.8 to 14 wt.% (0.0001 wt.% carbon disulfide) or 5.9 wt.% (0.001 wt.% thiophene), while the chirality distribution of SWCNTs has minor changes. In contrast, when the sulfur compound concentration is further increased, the chirality distribution shifts from smaller diameter nanotubes, such as (7,6), toward larger diameter ones, such as (8,7) and (9,8), together with a sharp decrease in the carbon yield. In particular, when 0.1 wt.% thiophene is added, the catalyst shows good chirality selectivity toward (9,8) nanotubes with their relative abundance of 43.1% among all semiconducting nanotubes. The chirality selectivity changes are correlated with the significant changes in the catalytic activity of the catalyst. These effects of sulfur may be caused by the selective blocking of active sites on Co particles through the dynamic interactions among sulfur, hydrogen, carbon and Co metal particles. The results shown in this study suggests that sulfur compounds may be used as an efficient additive to tune the chirality selectivity of catalysts in SWCNT synthesis.

Chapter 4: “Smart poisoning” of Co/SiO₂ catalysts by sulfidation for chirality-selective synthesis of (9,8) single-walled carbon nanotubes

4.1. Introduction

Chirality-pure SWCNTs have attracted great interests because they have many potential applications ranging from electronics and photovoltaics to sensing and bioimaging.^{17, 30-31, 33, 78, 114, 197-198} In particular, relatively large SWCNTs ($d_t > 1$ nm) have certain advantages over small ones such as enabling better nanotube contacts and having higher carrier mobility, larger sensitivity, and faster response time, which make them interesting for electronic applications.^{129, 199-202} However, because no scalable chirality-selective SWCNT synthesis methods are currently available, costly separation procedures are required to obtain chirality-pure SWCNTs.^{58, 203} In recent years, a significant progress have been made in separating relatively large SWCNTs, such as (9,7) and (9,8) nanotubes.^{57, 204-207} However, the yield, cost and product quality of separation process still largely depend on the status of as-synthesized SWCNTs, which makes the chiral-selective synthesis of SWCNTs highly desired.⁵⁹⁻⁶⁰

There are a few catalysts that favor the chiral-selective synthesis of relatively large SWCNTs. Among those, being more suitable for large-scale production, Co-based catalysts seem more promising for the scalable production of SWCNTs.^{59, 129, 151-153} Importantly, despite S is generally considered as a catalyst “poison” for many catalytic chemical reactions,^{135, 208} several reports showed that S-containing species modulate the chiral distribution of SWCNTs.¹⁵¹⁻¹⁵³ For example, the variation of the concentration of S residues

on CoSO₄/SiO₂ catalysts, by reduction (in H₂) or calcination (in air) processes, influenced the chiral-selectivity towards (9,8) nanotubes.¹⁵¹⁻¹⁵² The introduction of S-containing compounds (*i.e.* carbon disulfide or thiophene) in C precursor (*i.e.* ethanol) at different ratios also modulated the chiral-selectivity of Co/SiO₂ catalysts.¹⁵³ However, the introduction of S compounds often leads to a significant decrease of catalysts activity for SWCNT production.¹⁵³ Putting all these observations together, there is no doubt that S dramatically influences SWCNT synthesis in favor of chiral-selectivity, however, the mechanism behind its influence is not fully understood, which limits its exploitation for better results.

In this study, a new approach, “smart poisoning” of Co/SiO₂ catalysts, was demonstrated for the chiral-selective synthesis of (9,8) SWCNTs. Co/SiO₂ catalysts were first sulfided with the mixture of H₂S and H₂, and then, SWCNTs were grown by chemical vapor deposition (CVD) using CO as the carbon precursor. Compared with ethanol, the decomposition of CO is slower, which is profitable to control the reaction rate. Combined with the modified catalyst, it is supposed to achieve a better control on the selective growth of SWCNT. In addition, CO is highly reductive, which can yield more metallic Co nanoparticles for carbon nanotube growth. Resulting SWCNTs were extensively characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and photoluminescence (PL), UV-vis-NIR absorption and Raman spectroscopies. Catalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), X-ray fluorescence (XRF) spectrometry, and H₂ temperature-programmed reduction (H₂-TPR) to elucidate the role of S. My findings show that the formation of Co₉S₈ nanoparticles by sulfidation plays a critical role in modulating the chirality selectivity of the catalyst. In addition, “smart poisoning” concept is also a promising method to create catalysts for chiral-selective synthesis of SWCNTs in a scalable manner.

4.2. Catalyst preparation

Synthesis of Co/SiO₂

Co/SiO₂ catalysts were prepared by an incipient wetness impregnation method.¹⁶⁹ Briefly, cobalt (III) acetylacetonate (Co(AcAc)₃, 99.99%, Sigma-Aldrich) was first dissolved in dichloromethane and then added to fumed silica (Cab-O-Sil M-5, surface area 200 m²/g, Sigma-Aldrich) at 1 wt.%. The wetted silica particles were aged at room temperature for 1 hour and were dried at 60 °C for another 8 hours. The dried silica particles were then ground into fine powders and were calcined at 440 °C under flowing air (20 sccm) for 5 hours. The heating rate from room temperature to calcination temperature was 1 °C/minute.

Sulfidation of Co/SiO₂

Co/SiO₂ catalysts were sulfided by H₂S/H₂. The experimental procedure is illustrated in **Figure 4-1a**. In a typical experiment, 0.5 g of Co/SiO₂ catalysts were loaded on top of a porous quartz frit in a vertical quartz reactor. The reactor was first purged with Ar flow and then the reactor system was heated at a heating rate of 10 °C/minute under H₂ flow at 50 sccm. When the reactor temperature was increased to ~635 °C, the catalysts were kept under this condition for 15 minutes. Subsequently, H₂S (10 vol% H₂S balanced by 90 vol% N₂) at 2 sccm and H₂ at 100 sccm were introduced to the reactor for 30 minutes and then cooled to room temperature under Ar flow. The sulfided catalyst was denoted as S-Co/SiO₂.

Figure 4-1. Schematic illustrations of three procedures used for catalyst treatments. (a) sulfidation of Co/SiO₂ catalysts, (b) SWCNT synthesis using Co/SiO₂ and S-Co/SiO₂ catalysts, (c) reduction of S-Co/SiO₂ catalysts. (a) & (c) was conducted in a vertical reactor where catalysts were placed on top of a porous quartz frit, (b) was carried out in a horizontal reactor where catalysts were loaded into a ceramic boat at the center of the reactor.

4.3. SWCNTs synthesis

SWCNT synthesis was carried out in a horizontal chemical vapor deposition reactor.

Catalysts were loaded in a ceramic boat at the center of the reactor. The experimental procedure is illustrated in **Figure 4-1b**. In a typical experiment, 100 mg of catalysts were first reduced under pure H₂ at 1 bar (50 sccm) from room temperature to 780 °C at 15 °C/minute. Once the temperature reached 780 °C, CO (99.9% from Alphagaz, Soxal, Singapore) was introduced into the reactor at 2 bar for 30 minutes at a flow rate of 400 sccm and then cooled to room temperature under flowing Ar. Carbonyl residues in CO gas were removed by a gas purifier (Nanochem, Matheson Gas Products, Montgomeryville, PA, USA) before CO enters the reactor. It should be noted that a relatively low CO pressure (2 bar) was used in this study which is a potentially important factor for the scalability of the process.

4.4. SWCNTs characterization

After SWCNT synthesis, 5 mg of carbon-loaded catalysts were dispersed in 8 mL of 2 wt.% sodium dodecyl benzene sulfonate (SDBS, Sigma-Aldrich) D₂O (99.9%, Sigma-Aldrich) solution by tip sonication for 0.5 hours in the ice-water bath. Subsequently, the solution was centrifuged at 50,000 g for 1 hour to obtain a clear SWCNT dispersion. PL and UV-vis-NIR absorption spectroscopies were then used to characterize the SWCNT dispersions. PL measurements were conducted with the excitation wavelength scanned from 500 to 900 nm and the emission wavelength collected from 800 to 1600 nm. The UV-vis-NIR absorption spectra were measured from 400 to 1800 nm on an optical absorption spectrophotometer. As-synthesized SWCNTs deposited on catalysts (solid powders) were also characterized by Raman spectroscopy under 514, 633, and 785 nm laser excitations. To prevent the damage of SWCNTs by laser heating, the laser energy was kept around 2.5-5.0 mW with an integration time of 10 seconds.

Carbon deposits on catalysts were also characterized by thermogravimetric analysis (TGA) to determine the total carbon yield. In a typical test, 2 mg of samples were first heated

in an alumina pan to 150 °C in air (200 sccm) and was held at that temperature for 30 minutes to remove adsorbed water. Subsequently, the temperature was raised from 150 to 950 °C at 10 °C/minute and the weight loss was recorded as a function of temperature during heating. The same procedure was repeated after the sample was cooled to room temperature. The second weight-temperature curve was used for baseline corrections.

4.5. Catalyst characterization

SWCNT SEM images of the catalysts were obtained at an accelerating voltage of 5 kV and TEM images were also recorded at 80 kV. Nitrogen adsorption-desorption isotherms were recorded on an adsorption analyzer. Their specific surface area values were calculated by the Brunauer-Emmet-Teller (BET) method, while their pore size and the pore size distribution were determined by the Barrett-Joyner-Halenda (BJH) method from the desorption branch of their isotherms.¹⁷³⁻¹⁷⁴ XRD measurements were carried out on Axs D8 X-ray diffractometer. H₂-TPR was conducted on a home-built TPR system equipped with a thermal conductivity detector (TCD) of a gas chromatograph.¹⁵³ For each test, 150 mg of samples were reduced under H₂ from room temperature to 900 °C at 5 °C/minute.

The chemical nature of the catalysts was also studied by using XPS and XRF. The detailed procedure was described in Chapter 2.

4.6. Results and discussion

4.6.1. Comparison of SWCNTs synthesized using Co/SiO₂ and S-Co/SiO₂

Before and after SWCNT synthesis, the Co/SiO₂ and S-Co/SiO₂ particles were examined by SEM and TEM. As seen in **Figure 4-2**, as-synthesized nanotubes bundle together and form large SWCNT ropes with length up to micrometers covering the catalyst surfaces well. The total carbon yields measured by TGA were also similar. **Figure 4-3** shows

that Co/SiO₂ has a carbon yield of 2.7 wt.% while the carbon yield of S-Co/SiO₂ is 2.5 wt.%. This result suggests that the sulfidation of Co/SiO₂ does not significantly change its catalytic activity for carbon deposition. This finding is particularly crucial because the majority of previous studies showed the trade-off between chiral-selectivity and SWCNT yield.⁵⁹

Figure 4-2. SEM and TEM (insets) images of Co/SiO₂ (a, b) and S-Co/SiO₂ (c, d) catalysts before (a, c) and after (b, d) SWCNT synthesis. The scale bars of SEM and TEM images are 200 and 20 nm in length, respectively.

Figure 4-3. TGA profiles of Co/SiO₂ and S-Co/SiO₂ catalysts after SWCNT synthesis.

Next, the chirality distribution of SWCNTs was analyzed using UV-vis-NIR, PL, and Raman spectroscopies (**Figure 4-4**). **Figure 4-4a** compares the UV-vis-NIR spectra of SWCNTs grown on both catalysts. Co/SiO₂-grown SWCNTs reveal five major peaks centered at 1030, 1130, 1185, 1275, and 1400 nm, which can be assigned to medium size species ($0.8 \text{ nm} < d_t < 1.0 \text{ nm}$), such as (9,4), (8,4), (7,6), (8,6), (9,5), and (10,3). The peak centered at 1400 nm comes from relatively large species ($d_t > 1.0 \text{ nm}$), such as (10,6) and (9,8) nanotubes. In contrast, for S-Co/SiO₂-grown SWCNTs, there is only one major peak centered at 1415 nm, which can be assigned to (10,6) and (9,8) nanotubes. The upshift in the position of peak maxima (*i.e.* from 1400 to 1415 nm) suggests that (9,8) nanotubes dominate in S-Co/SiO₂-grown SWCNTs as the absorption peak of (10,6) nanotubes appears at a wavelength lower. The significant increase in absorption peak intensity and the peak upshift suggest that S-Co/SiO₂ is much more selective in growing (9,8) nanotubes. It should be noted that the same preparation procedure of SWCNT dispersions was used for both samples. The absorbance of these two SWCNT dispersions in **Figure 4-4a** is comparable with the absorbance at around 0.20-0.35, which is consistent with the carbon yield measured by TGA.

Figure 4-4b shows PL contour plots of SWCNTs grown on both Co/SiO₂ and S-Co/SiO₂. The spikes from the resonance behavior of both excitation and emission events represent the transition pairs belonging to individual semiconducting SWCNT species.²⁰⁹ Among SWCNTs grown on Co/SiO₂, (7,6), (7,5), and (8,4) nanotubes have the highest concentration. The chirality selectivity shifts to (9,8) nanotubes in SWCNTs grown on S-Co/SiO₂. The relative abundance of semiconducting SWCNTs identified in **Figure 4-4b** was calculated based on their PL peak intensity. The detailed SWCNT abundance results are listed in **Table 4-1** and **4-2**. SWCNTs grown on Co/SiO₂ mainly comprise of medium-diameter nanotubes (>82%), including (7,5), (7,6), (8,4), (8,6), and (9,5) nanotubes. The total abundance of relatively large-diameter SWCNTs is around 10%. In contrast, SWCNTs grown

on S-Co/SiO₂ contain 67% of relatively large-diameter SWCNTs. Among them, the abundance of (9,8) nanotubes reaches 38%. Other prominent SWCNTs include (9,7) and (8,7) nanotubes, having similar diameters as that of (9,8) nanotubes.

Raman spectroscopy allows uncovering SWCNTs which are not easily detectable with PL, such as metallic nanotubes and nanotubes with small chiral angles.²¹⁰ I focused on radial breathing mode (RBM) peaks between 100 and 375 cm⁻¹ in order to identify the chirality of these SWCNTs. As shown in **Figure 4-4c and d**, Co/SiO₂-grown SWCNTs have much more RBM peaks under all three excitation wavelengths (*i.e.* 514, 633, and 785 nm), suggesting a much broader chirality distribution. The RBM peaks can be correlated to chirality properties of SWCNTs according to the empirical Kataura plot generated by the tight-binding model and experimental data.¹⁷⁷⁻¹⁷⁸ The diameter of SWCNTs can be calculated using $d_t = (\omega - 12.5 \text{ cm}^{-1}) / (223.5 \text{ cm}^{-1})$ where ω is the Raman shift of RBM peaks. The chirality of identified SWCNTs was marked by round dots on **Figure 4-4c and d**. The most abundant nanotubes observed in UV-vis-NIR and PL spectroscopies were also detected by Raman spectroscopy. Importantly, additional species were quite low in abundance.

Figure 4-4. (a) UV-vis-NIR absorption spectra, (b) PL contour plots, (c) Raman spectra under different laser energy of SWCNTs grown on Co/SiO₂ catalysts, and (d) Raman spectra under different laser energy of SWCNTs grown on S-Co/SiO₂ catalysts. The lower portions of (c) and (d) are empirical Kataura plots near to the laser energy at 514, 633 and 785 nm, showing the correction between SWCNT diameter and Raman shift of RBM peaks.²¹¹ The dotted horizontal lines correspond to the upper and lower limits of the resonance window of approximate 500 meV. The vertical dashed lines match with the Raman shift of RBM peaks.

Table 4-1. Tabulated values of PL peak intensities and the relative abundances of (n,m) species of SWCNTs grown on Co/SiO₂. The table is sorted based on the diameter of (n,m) species, and the most abundant species are highlighted in bold.

(n,m) index	SWCNT diameter d (nm)	Chiral angle θ (°)	E ₁₁ (nm)	E ₂₂ (nm)	PL intensity (counts)	Relative abundance (%)	Σ (%)
(8,3)	0.782	15.3	952	665	789	2.4	7.4
(6,5)	0.76	27	993	566	1636	5.0	
(7,5)	0.83	24.5	1022	634	5176	15.9	82.3
(8,4)	0.84	19.11	1124	574	5150	15.8	
(7,6)	0.9	27.46	1126	642	5161	15.8	
(9,4)	0.916	17.5	1100	722	1616	5.0	
(10,2)	0.936	12.7	1249	631	1681	5.2	
(8,6)	0.97	25.28	1162	710	4888	15.0	
(9,5)	0.976	20.6	1241	671	3128	9.6	
(8,7)	1.03	27.8	1273	726	1653	5.1	10.4
(9,7)	1.1	25.87	1329	790	833	2.6	
(10,6)	1.11	21.79	1380	754	416	1.3	
(9,8)	1.17	28.05	1424	818	462	1.4	

Table 4-2. Tabulated values of PL peak intensities and the relative abundances of (n,m) species of SWCNTs grown on S-Co/SiO₂. The table is sorted based on the diameter of (n,m) species, and the most abundant species are highlighted in bold.

(n,m) index	SWCNT diameter d (nm)	Chiral angle θ (°)	E ₁₁ (nm)	E ₂₂ (nm)	PL intensity (counts)	Relative abundance (%)	Σ (%)
(6,5)	0.76	27	993	566	1114	14.5	14.5
(7,5)	0.83	24.5	1022	634	305	4.0	18.4
(8,4)	0.84	19.11	1124	574	275	3.6	
(7,6)	0.9	27.46	1126	642	582	7.6	
(8,6)	0.97	25.28	1162	710	259	3.4	
(8,7)	1.03	27.8	1273	726	824	10.7	67.1
(9,7)	1.1	25.87	1329	790	827	10.7	
(9,8)	1.17	28.05	1424	818	2923	37.9	
(10,6)	1.11	21.79	1380	754	416	7.7	

Combining all the spectroscopic results discussed above as chirality distribution maps provides a better insight regarding the effect of “smart poisoning” as illustrated in **Figure 4-5**. The chirality distribution maps. **Figure 4-5a** shows that the diameter distribution of Co/SiO₂-grown SWCNTs is wide, ranging from 0.76 to 1.34 nm and major species are around 0.97 nm. In contrast, S-Co/SiO₂ is much more selective toward (9,8) nanotubes with a narrower chirality distribution around 1.2 nm.

Figure 4-5. Chirality distribution maps of SWCNTs grown on (a) Co/SiO₂ and (b) S-Co/SiO₂. The chiral indices (*n,m*) of nanotubes are marked if they are identified by any of three spectroscopic techniques used. Color fillings show the relative abundance of nanotubes identified in PL spectroscopy. SWCNTs identified by Raman spectroscopy are indicated with red and thicker honeycomb frames.

4.6.2. The effects of sulfidation on Co/SiO₂

The characterization of SWCNTs in the previous section indicates that S-Co/SiO₂ has a better selectivity toward (9,8) nanotubes at a similar total carbon yield with Co/SiO₂. To understand the origin of the observed chirality selectivity, I examined what are the major differences between Co/SiO₂ and S-Co/SiO₂. First, SEM and TEM images in **Figure 4-2** show that both Co/SiO₂ and S-Co/SiO₂ comprise of small SiO₂ particles of 20 nm in diameter. There is no significant morphological change before and after sulfidation. Next, the surface area and pore size distribution of both catalysts were measured by N₂ physisorption test. **Figure 4-6** shows that the surface area, pore volume, and pore size distribution of Co/SiO₂ and S-Co/SiO₂ are quite similar. This is reasonable considering that SiO₂ particles used in this study are stable at the sulfidation temperature. Overall, the physical structure of Co/SiO₂ shows no major changes after sulfidation.

Figure 4-6. Nitrogen physisorption isotherms of Co/SiO₂ and S-Co/SiO₂. The inset shows the pore size distributions of both catalysts determined by the BJH method.

Since Co/SiO₂ underwent H₂-based reduction during the heating step (from room temperature to 635 °C) before actual sulfidation step, it is needed to clarify whether H₂ reduction of Co/SiO₂ could be a contributor for the chirality selectivity of S-Co/SiO₂ or not. To do so, the Co/SiO₂ catalyst was reduced using the same procedure as used in the sulfidation process except the introduction of H₂S. The detailed procedure was illustrated in **Figure 4-1c**. The reduced Co/SiO₂ was used for SWCNT synthesis without further exposing to air. The same SWCNT growth procedure was used as shown in **Figure 4-1b**. SWCNTs grown from reduced Co/SiO₂ were characterized by UV-vis-NIR absorption spectroscopy. **Figure 4-7** indicates that their absorption spectrum is similar to that of SWCNTs grown on Co/SiO₂. This confirms that the origin of the chirality selectivity comes from sulfidation other than H₂ reduction.

Figure 4-7. UV-vis-NIR absorption spectra of SWCNTs grown using Co/SiO₂ and reduced Co/SiO₂. The reduction procedure followed the steps shown in **Figure 4-1c**. The SWCNT synthesis procedure followed the steps shown in **Figure 4-1b**.

The chemical structures of Co/SiO₂ and S-Co/SiO₂ were first examined by XRD. **Figure 4-8** shows their XRD patterns together with several reference samples. There are no clear diffraction peaks on 1 wt.% Co/SiO₂ and S-Co/SiO₂, which were used for SWCNT synthesis. Several previous studies have reported that at low weight loadings, Co forms well-dispersed surface Co silicates on high surface area SiO₂, which are difficult to be detected by XRD.^{169, 212-213} In order to identify possible chemical structures of Co found in Co/SiO₂ by XRD, I intentionally increased the weight loading of Co on SiO₂ to 10 wt.% using the same catalyst preparation procedure as that used for 1 wt.% catalysts. **Figure 4-8a** shows that there are minor peaks at around 35-38° on the XRD pattern of 10 wt.% Co/SiO₂. Based on the peaks of Co oxide references, these peaks likely come from Co oxides formed on SiO₂ surface. It is proposed that when the Co weight loading is too high, some Co would not be completely converted to surface Co silicates during catalyst calcination, resulting in the formation of Co oxides. The weak XRD peaks suggest that most of Co oxides have amorphous structures. On the other hand, **Figure 4-8b** shows that 10 wt.% S-Co/SiO₂ has

several clearer peaks at 30.1°, 31.4°, 47.8°, and 52.4°, corresponding to the (311), (222), (511), and (440) planes of Co_9S_8 (JCPDS No. 86-2273), which suggests the formation of small Co_9S_8 crystals during sulfidation.

Figure 4-8. XRD patterns of (a) Co/SiO_2 and (b) $\text{S-Co}/\text{SiO}_2$ with 1 and 10 wt.% of Co. The reference XRD patterns of CoO , Co_3O_4 , CoS , CoS_2 , and Co_9S_8 are from the database of The International Centre for Diffraction Data.

To further probe catalyst surfaces, the XPS analysis was carried out on both Co/SiO_2 and $\text{S-Co}/\text{SiO}_2$. **Figure 4-9a** shows two peaks appearing around 798 and 782 eV in $\text{Co}2\text{p}$ region of Co/SiO_2 correspond to cobalt-containing oxide species.²¹⁴ The XPS spectrum of $\text{S-Co}/\text{SiO}_2$, on the other hand, displays two other peaks around 778.5 eV and 794 eV, which suggests the presence of Co_9S_8 .²¹⁵⁻²¹⁶ $\text{S}2\text{p}$ region of XPS spectrum of $\text{S-Co}/\text{SiO}_2$ (**Figure 4-9b**) also indicates the formation of metal-sulfur bonds similar to those found in Co_9S_8 (and a sulfur ion in low coordination which might supposedly originate from the sulfur species adsorbed onto the support surfaces).^{215, 217-218} These XPS results are consistent with XRF results. **Table 4-3** lists the content (wt.%) of Co, S, and SiO_2 determined by XRF. After sulfidation, the mole ratio of Co and S is about 1.17, which is similar to that of Co_9S_8 . These results collectively suggest that the sulfidation process triggers the formation of Co_9S_8 species.

Figure 4-9. High-resolution XPS spectra of Co/SiO₂, S-Co/SiO₂, and reduced S-Co/SiO₂ catalysts at (a) Co2p and (b) S2p regions. Note that all samples are prepared by 10% Co to enhance signal intensity considering the fact that below 3-5% is virtually undetectable with regular XPS setups.

Table 4-3. Chemical composition of the catalysts as measured by XRF measurements.

Catalysts	Co, wt. %	S, wt. %	SiO ₂ , wt. %
Co/SiO ₂	0.93	0	99.07
S-Co/SiO ₂	0.80	0.37	98.83
S-Co/SiO ₂ , reduced	0.98	0	99.02

To further corroborate the XRD, XPS, and XRF findings, H₂-TPR experiments were performed, which allows valuable information to interpret the properties of catalysts. **Figure 4-10** compares the TPR profiles of Co/SiO₂, S-CO/SiO₂ catalysts, and two reference Co oxides. The reduction of Co/SiO₂ starts from 700 °C and completes at 900 °C with a peak maximum at 800 °C, which confirms the existence of surface Co silicates.^{152, 169, 212, 219-220} After sulfidation, there are two major peaks on the TPR profile of S-CO/SiO₂. The peak that appears at around 700-750 °C can be attributed to the reduction of Co₉S₈.²²¹⁻²²² The other peak centered at 250-300 °C can be credited to the reduction of Co oxides. The reduction peak of Co silicates at 800 °C mostly disappears. The TPR results suggest that some surface

Co silicates on Co/SiO₂ are reduced, and converted to Co₉S₈, while others may be converted to Co oxides. Since S-Co/SiO₂ was exposed to air after sulfidation, some Co₉S₈ formed during sulfidation may also be oxidized to Co oxides.²²²⁻²²³

Figure 4-10. H₂-TPR profiles of Co/SiO₂ and S-Co/SiO₂ and two reference Co oxides (*i.e.* CoO and Co₃O₄). The gray area corresponds to 20 minutes of isothermal run at 950 °C.

I initially attempted to directly characterize Co species on S-Co/SiO₂ (1 wt.%) using TEM. However, because SiO₂ has a large surface area (147 m²/g) and Co loading is low (1 wt.%), it is difficult to observe individual Co nanoparticles. The S-Co/SiO₂ (10 wt.% Co) with 10 times of Co loadings was also examined. As shown in **Figure 4-11**, multiple dark regions can be found on the SiO₂ surface with the diameters around 2-4 nm. It should be noticed that XRD pattern of S-Co/SiO₂ (10 wt.% Co) in **Figure 4-9b** has much broader peaks than that of the bulk Co₉S₈ reference. These broad XRD peaks of S-Co/SiO₂ (10 wt.% Co) suggest the existence of nanoparticles. Using Scherrer equation,²²⁴ the mean diameter of Co₉S₈ nanoparticles on S-Co/SiO₂ (10 wt.% Co) is estimated to be around 4.1 nm, which is comparable to the size of dark regions observed in TEM. For the catalysts prepared by 1 wt.% Co, therefore, the active catalysts should be even smaller, presumably 1-2 nm.

Figure 4-11. TEM image of S-Co/SiO₂ (10 wt.%). Note that there are darker spots typically around 1-3 nm.

4.6.3. A proposed mechanism

An important question is what is the role of Co₉S₈ nanoparticles in SWCNT synthesis. There are two possible scenarios. In the first scenario, SWCNTs directly grow from Co₉S₈ nanoparticles. The size and crystal structure of Co₉S₈ nanoparticles would directly affect the chirality selectivity of SWCNTs. This would be similar to the growth of (12,6) nanotubes on Co-W bimetallic alloy nanocrystals.⁷⁸ In the second scenario, Co₉S₈ nanoparticles are reduced to Co nanoparticles during SWCNT synthesis. The role of Co₉S₈ nanoparticles is assisting the formation of metallic Co nanoparticles with narrower diameter distribution. SWCNTs still grow from metallic Co nanoparticles. Because it was difficult to directly observe the structural and chemical transformation of Co₉S₈ nanoparticles on SiO₂ substrates by TEM, a series of additional experiments were designed to evaluate the likelihood of these two scenarios, which are discussed below.

Figure 4-12. UV-vis-NIR absorption spectra of SWCNTs grown using S-Co/SiO₂ and reduced S-Co/SiO₂. The reduction procedure followed the steps shown in **Figure 4-1c**. The SWCNT synthesis procedure followed the steps shown in **Figure 4-1b**.

Figure 4-13. H₂-TPR profiles of reduced S-Co/SiO₂, S-Co/SiO₂ and Co/SiO₂. The gray area corresponds to 20 minutes of isothermal run at 950 °C.

The S-Co/SiO₂ was first reduced in pure H₂ up to 635 °C using the procedure shown in **Figure 4-1c**. Reduction in H₂ at high temperature (above 600 °C) is expected to remove most S from the catalyst. Previous studies showed that CoSO₄/SiO₂ catalysts lose S after

reduction in H_2 at high temperature, and its chirality selectivity toward (9,8) nanotubes also disappears.¹⁵¹ XPS spectrum of reduced S-Co/SiO₂ (**Figure 4-9**) shows that S is removed after reduction. XRF results in **Table 4-3** also indicate that S cannot be detected on reduced S-Co/SiO₂, confirming the removal of S. Afterward, the reduced S-Co/SiO₂ was used for SWCNT synthesis using the growth procedure shown in **Figure 4-1b**. **Figure 4-12** shows the UV-vis-NIR absorption spectrum of SWCNTs grown on the reduced S-Co/SiO₂, which is identical to that of S-Co/SiO₂-grown SWCNTs. Importantly, the reduced S-Co/SiO₂ has practically the same chirality selectivity as that of S-Co/SiO₂. Further analysis of the reduced S-Co/SiO₂ by H_2 -TPR indicates that the reduction peak at around 700-750 °C comes from the disappearance of Co₉S₈ (see **Figure 4-13**), suggesting the total reduction of Co₉S₈. It should be noted that H_2 reduction of catalysts was carried under pure H_2 , while H_2 -TPR was conducted in 5% H_2 in Ar. Hence, Co₉S₈ would be reduced at a lower temperature in pure H_2 compared to the reduction in 5% H_2 . Overall, these experimental results strongly support the second scenario.

Based on experimental results discussed above, I proposed the following mechanism for the observed chirality selectivity changes upon sulfidation of Co/SiO₂. As illustrated in **Figure 4-14**, during SWCNT synthesis, Co/SiO₂ is first reduced under H_2 , which converts surface Co silicates into metallic Co atoms. These metallic Co atoms further nucleate into Co metal nanoparticles. The size distribution of Co metal nanoparticles is generally very broad, leading to SWCNTs with a wide diameter and chirality distribution. This is consistent with several previous studies.^{151, 225} In contrast, the sulfidation of Co/SiO₂ under H_2 and H_2 S results in the formation of Co₉S₈ nanoparticles. S limits the fast nucleation of metallic Co, resulting in Co₉S₈ nanoparticles likely well dispersed on the SiO₂ surface with a size of below 2 nm. Even their direct visualization is hard to achieve, the combination of XRD, XPS, XRF, and H_2 -TPR reveal the existence of super-fine Co₉S₈ nanoparticles. Importantly, during the

SWCNT synthesis, those Co_9S_8 nanoparticles are reduced back to Co metal nanoparticles. In comparison to metallic Co nanoparticles generated by the reduction of surface Co silicates, Co metal nanoparticles reduced from Co_9S_8 nanoparticles likely have narrower size distribution. As a result, “smart poisoned” catalysts lead to the chiral-selective growth of nanotubes, around (9,8) nanotubes.

Figure 4-14. Schematic illustration of Co/SiO₂ transformation under sulfidation and SWCNT synthesis.

4.6.4. Conclusion

Here I demonstrated a new and facile approach, “smart poisoning”, to achieve the chirality-selective synthesis of (9,8) SWCNTs by the sulfidation of Co/SiO₂ catalyst. It comprises three steps: (1) the production of conventional Co/SiO₂ catalyst, (2) the sulfidation of Co/SiO₂ by H₂S/H₂ treatment, and (3) then used to grow SWCNTs by chemical vapor deposition of CO. Resulting SWCNTs show a narrow diameter distribution around 1.2 nm. Photoluminescence results suggest chirality selectivity toward (9,8) nanotubes with the abundance of 37.9% among semiconducting nanotubes. More importantly, the carbon yield on sulfided Co/SiO₂ is 2.5 wt.%, which is similar to that of Co/SiO₂ at 2.7 wt.%. This suggests that the sulfidation of Co/SiO₂ does not decrease its activity for carbon deposition.

In contrast, Co/SiO₂ loses most of its activity for carbon deposition when S-containing compounds are directly introduced in gaseous carbon precursors during SWCNT growth. Catalysts characterizations by XRD, XPS, XRF and H₂-TPR collectively support that sulfidation of Co/SiO₂ leads to the formation of Co₉S₈ nanoparticles with a narrow size distribution. Co₉S₈ nanoparticles act as an intermediary compound, which is further reduced to stable Co metal nanoparticles during SWCNT growth; then Co metal nanoparticles achieve diameter and chirality control of SWCNTs. In contrast to many other applications that S acts as a “poison” for metal catalysts, here I find a quite peculiar benefit of S modification. I envision that this approach of forming structural controlled metal nanoparticles through an intermediary compound will lead to the mass-production of high-activity catalysts for the chiral-selective synthesis of SWCNTs in a scalable manner.

Chapter 5: Synthesis of SWCNTs in vertical CVD reactors

5.1. Motivation

In the previous chapter, I have succeeded in selectively synthesizing the (9,8) nanotubes with S-Co/SiO₂ catalyst. To produce the SWCNTs more efficiently, I tried to increase the amount of catalysts used in each synthesis batch. However, it was found that when the amount of catalyst was increased to 400 mg, the as-produced samples became inhomogeneous along the catalyst bed depth direction, which was caused by the diffusion limitation of carbon feedstock within the solid catalyst bed. The short constant temperature zone of the standard furnace also prevents further increasing the length of the catalyst bed. Thus, I attempted to solve the problem by using a vertical CVD reactor instead of a horizontal one. It is hoped that the gas flow can go through the catalyst bed, which may lead to increased SWCNT production yield by accommodating more catalysts in the CVD reactor. To some degree, the vertical reactor could overcome the diffusion limitation problem. Then for a fluidized-bed reactor, it has more advantages, including the more efficient gas-solid contact, the hence mass and heat transfer, leading to the more uniform temperature distribution. Furthermore, the fluidized-bed reactor could provide more space for the CNTs growth. It is a flexible process with the potential ability for operating reactors in continuous state and changing the parameters like gas mixture to achieve the desire product.²²⁶

For potential industrial applications, an important issue is to control the cost of raw materials. The synthesis process of the S-Co/SiO₂ catalyst has been demonstrated in Chapter 4. Before SWCNT synthesis, the Co/SiO₂ is sulfidized by H₂S first, which is relative time-

consuming, and the handling of H_2S also requires safety cautions. In addition, both high purity silica particles and H_2S are expensive. Thus, it is desirable to reduce the cost of catalysts.

In this chapter, I first show that high purity (9,8) nanotubes can be synthesized after changing the catalyst support from high purity silica particle to a cheaper alternative. Next, the new catalyst was used in a vertical CVD reactor. Carbon feedstock went through the fixed catalyst bed from the top. The amount of the catalyst can be increased up to 2 g per synthesis batch before the as-produced samples become inhomogeneous similar to what observed in horizontal CVD reactor. Finally, the catalyst was fluidized in the vertical CVD reactor in an attempt to enhance the homogeneity of SWCNT products.

5.2. SWCNTs synthesis in horizontal reactor

5.2.1. Catalyst preparation

The Co/SiO_2 particle catalyst was synthesized by the incipient wetness impregnation method described in Chapter 3. Briefly, in the first step, cobalt (III) acetylacetonate ($\text{Co}(\text{AcAc})_3$, 99.99%, Sigma-Aldrich) was dissolved in dichloromethane and then added to a new type of silica particles (60 mesh, Shanghai Biochemical Co., Ltd). The wet samples were aged at room temperature for 1 hour and were dried on a glass plate at $60\text{ }^\circ\text{C}$ for another 8 hours. The dried particles were ground into fine powders with ball-milling. Then fine powders were calcined at $440\text{ }^\circ\text{C}$ under flowing air (20 sccm) for 5 hours. and were cooled down naturally (heating rate from room temperature to calcination temperature: $1\text{ }^\circ\text{C}/\text{minute}$). The catalyst produced by this process was denoted as Co/SiO_2 particle.

5.2.2. SWCNT synthesis

In this part, SWCNT synthesis was carried out in a horizontal CVD reactor using

both Co/SiO₂ and Co/SiO₂ particle catalysts, respectively. The detailed procedure was the same as what described in Chapter 4. In addition, the depth of the Co/SiO₂ particle catalyst in the reactor was recorded. At 200 mg, the depth of catalyst was around 4 mm in the ceramic boat of 1×5 cm in size. The depth was 8 mm when 400 mg of catalysts were used.

5.2.3. Results and discussions

In **Figure 5-1a**, Co/SiO₂-grown SWCNTs reveal five major peaks centered at 1030, 1130, 1185, 1275, and 1400 nm, which can be assigned to medium size species ($0.8 \text{ nm} < d_t < 1.0 \text{ nm}$), such as (9,4), (8,4), (7,6), (8,6), (9,5), and (10,3). The peak centered at 1400 nm comes from relatively large species ($d_t > 1.0 \text{ nm}$), such as (10,6) and (9,8) nanotubes. In contrast, for Co/SiO₂ particle-grown SWCNTs, there is only one major peak centered at 1415 nm, which can be assigned to (10,6) and (9,8) nanotubes. The upshift in the position of peak maxima (*i.e.* from 1400 to 1415 nm) suggests that (9,8) nanotubes dominate in Co/SiO₂ particle-grown SWCNTs as the absorption peak of (10,6) nanotubes appears at a lower wavelength. The significant increase in absorption peak intensity and the peak upshift suggest that Co/SiO₂ particle catalyst is much more selective in growing (9,8) nanotubes. It should be noted that the same preparation procedure of SWCNT dispersions was used for both samples.

Figure 5-1. (a) UV-vis-NIR absorption spectra, (b) TGA profiles, and (c, d) PL contour plots of Co/SiO₂ particle catalysts after SWCNT synthesis.

Table 5-1. Tabulated values of PL peak intensities and the relative abundances of (n,m) species of SWCNTs grown on Co/SiO₂ particle.

(n,m) index	Diameter Dt(nm)	Chiral angle θ (°)	E ₁₁	E ₂₂	PLE Intensity (counts)	Relative Abundance (%)
(6,5)	0.76	27	993	566	430	6.86
(7,6)	0.9	27.46	1126	642	168	2.68
(8,4)	0.84	19.11	1124	574	101	1.61
(8,7)	1.03	27.8	1273	726	895	14.28
(9,7)	1.1	25.87	1329	790	1228	19.59
(9,8)	1.17	28.05	1424	818	2869	45.78
(10,6)	1.11	21.79	1380	754	576	9.19

Figure 5-1c&d show PL contour plots of SWCNTs grown on both Co/SiO₂ and Co/SiO₂ particle. The detailed SWCNT abundance results are listed in **Table 5-1**. The spikes from the resonance behavior of both excitation and emission events represent the transition

pairs belonging to the individual semiconducting SWCNT species.²⁰⁹ Among SWCNTs grown on Co/SiO₂, (7,6), (7,5), and (8,4) nanotubes have the highest concentration. The chirality selectivity shifts to (9,8) nanotubes in SWCNTs grown on Co/SiO₂ particle. SWCNTs grown on Co/SiO₂ mainly comprise of medium-diameter nanotubes (>82%), including (7,5), (7,6), (8,4), (8,6), and (9,5) nanotubes. The total abundance of relatively large-diameter SWCNTs is around 10%. In contrast, SWCNTs grown on Co/SiO₂ particle contain 89% of relatively large-diameter SWCNTs. Among them, the abundance of (9,8) nanotubes reaches 46%. Other prominent SWCNTs include (9,7) and (8,7) nanotubes, having similar diameters as that of (9,8) nanotubes. The selectivity towards (9,8) nanotubes can be attributed to the existence of sulfur in Co/SiO₂ particle catalysts.

5.2.4. Characterization of catalysts

Table 5-2 lists the content (wt.%) of the elements in the new silica particles determined by ICP. It should be noted that only the elements with a ratio of >0.1 wt.% were shown. Besides the Co and Si, only Na and Al were detected. There is no research work showing that Na or Al could affect the chirality selectivity of catalysts. To further investigate the chemical composition, XRF was used to provide more information. **Table 5-3** shows that sulfur exists in both silica particles and Co/SiO₂ particle catalysts. These results agreed with the early results in this thesis and suggest that the presence S on Co/SiO₂ particle catalysts may contribute to its chirality selectivity towards (9,8) nanotubes.

Table 5-2. Chemical composition (≥ 0.1000 wt.%) of the catalysts as measured by ICP measurements.

Samples	Co, wt.%	Si, wt.%
silica particles	0.0000	40.9259
Co/SiO ₂ particle	0.8756	38.8997
SiO ₂ (fumed)	0.0000	40.6731
Co/SiO ₂	1.0416	39.6610

Table 5-3. Chemical composition (≥ 0.1000 wt.%) of the catalysts as measured by XRF measurements.

Samples	Co, wt.%	SiO ₂ , wt.%	S, wt.%
silica particles	0.00	97.75	0.73
Co/SiO ₂ particle	0.86	97.91	0.42
SiO ₂ (fumed)	0.00	100.00	0.00
Co/SiO ₂	0.93	99.07	0.00

5.3. SWCNT synthesis in vertical reactor

5.3.1. Fluidized-bed reactor

The fluidized-bed reactors have been applied in many fields, including the circulating fluidized-bed boilers used for coal combustion,²²⁷ removal of CO₂ from gases after coal combustion in power plants²²⁸ and chemical waste incinerators.²²⁹ Fluidization is the operation by which fine solids are transformed into a fluid-like state through contact with a gas or liquid. At a low flow rate, the fluid just percolates through the void spaces of the particles while when the superficial velocity, denoted as u_0 , reaches a point where all the

particles are just suspended by the upward-flowing fluid, the bed is considered to be just fluidized as shown in **Figure 5-2** and the superficial velocity is defined as the minimum fluidization velocity, denoted as u_{mf} .

Figure 5-2. Schematic diagram of the fluidization.

Advantages of fluidized-bed reactor

The most noticeable advantage of the fluidized-bed reactor is their good heat and mass transfer for the gas-solid reactions. Because of its vigorous mixing, a uniform and controlled temperature profile is achieved through the bed. The same is valid for mass transfer considerations as well. For SWCNT synthesis in a well-designed fluidized bed system, all the particles are mixed homogeneously with no stagnant areas, allowing all the catalysts to be exposed to the carbon source and react with it. As a result, one may expect to achieve a higher efficiency and carbon yield.

The advantages of the fluidized-bed reactor for CNTs growth compared to the fixed-bed reactor are summarized in **Table 5-4**.

Table 5-4. Comparison between fluidized-bed and fixed-bed reactor for CNT synthesis.⁶⁷

	Fluidized-bed reactor	Fixed-bed reactor
Influence on CNT growth	-	--
Heat transfer	+++++	---
Mass transfer	+++++	--
Flow pattern	Well-mixed	Piston flow
Temperature control	+++++	----
Scale-up	++++	----
Achievable capacity	+++++	---
Continuous production	+++++	----

5.3.2. Fluidization of catalysts

Although the fluidized-bed technique seems a promising route for the scalable synthesis of SWCNTs, it brings some challenges such as the fluidization of nanoparticles. Usually, transition metals such as Fe, Co, Ni and their compounds are chosen as the catalysts in CVD process for SWCNT synthesis²³⁰ and these catalysts are dispersed on the supported materials, which are usually Al₂O₃, SiO₂, MgO nanoparticles, with a diameter less than 50 nm. According to Geldart's²³¹ research, particles can be divided into four groups, as shown in **Figure 5-3**. The nanoparticles in the catalysts for CNT synthesis belong to the Group C powder, which are difficult to be fluidized. The characteristic of this group of particles is that they have strong interparticle forces, including van der Waals interactions, electrostatic interactions and liquid bridging.²³² Liquid bridges are formed due to liquid adsorbed on the particle surface, and it can be eliminated by drying the particles. The electrostatic charge mainly depends on the tribocharging which is less important for nanoparticles.²³² Thus, the van der Waals forces remains the most important interparticle forces, which are practically

unavoidable. Therefore, I first studied suitable methods to enable the fluidization of catalysts.

Figure 5-3. Powder classification diagram for fluidization.²³³

Various methods have been applied to promote the fluidization of nanoparticles, including vibration agitation,²³⁴ sound field assisted fluidization,²³⁵⁻²³⁶ magnetic fields assisted fluidization,²³⁷⁻²³⁹ surface modification,²⁴⁰⁻²⁴¹ pulsed gas flow,²⁴² and mixing of fluidized particles.²⁴³⁻²⁴⁶ The reason behind the addition of fluidized particles is to break or reduce the interparticle forces. Compared with the other methods, it is easier to be implemented in a practical CNT synthesis process without the need for additional equipment. Therefore, this method was the method of choice in this study.

The onset of fluidization occurs when the drag force by upward moving fluid equals to the weight of the particles. The occurrence of fluidization can be visualized by measuring the correction between the pressure drop (Δp) of in the fluidized bed and the fluid's superficial velocity (u_0), which is the hypothetical (artificial) fluid velocity calculated as if the given phase or fluid were the only one flowing or present in the given cross sectional

area of the fluidized bed. As illustrated in **Figure 5-4**, under a typical fluidization condition, with the increase of u_0 , the Δp increases linearly until it reaches a maximum value. Afterwards, Δp remains unchanged even through u_0 continues increasing. The u_0 , at which Δp reaches the maximum is considered as u_{mf} .

It should be noted that the Δp - versus - u_0 diagram is usually measured at room temperature and atmospheric pressure. However, the synthesis conditions for SWCNTs are often at high temperature and pressure. u_{mf} would change at different temperatures and pressures.

Figure 5-4. Pressure drop versus gas velocity for a fluidized bed system.

A common model developed by Wen and Yu²⁴⁷ was used to predict the u_{mf} at SWCNT synthesis conditions. It should be noted that compared with other models, this model is easier to apply because it does not require the information of the detailed information about the shape of particles. u_{mf} at room temperature and pressure was first obtained from the Δp - versus - u_0 diagram. From the Equation 5-1 and 5-2, the average diameter of particles in the fluidized bed d_p can be calculated. Then, the fluid properties ρ_g , ρ_s , μ at SWCNT synthesis temperature and pressure can be found from Matheson Gas Data

Book.²⁴⁸ Finally, the u_{mf} at these conditions can be calculated from the Equation 5-2.

Equation 5-1.

$$N_{Ga} = \frac{d_p^3 \rho_g (\rho_s - \rho_g) g}{\mu^2}$$

Equation 5-2.

$$(N_{Re})_{mf} = \frac{\rho_g u_{mf} d_p}{\mu} = \sqrt{33.7^2 + 0.0408 N_{Ga}} - 33.7$$

where

N_{Ga} is Galileo number,

N_{Re} is Reynolds number,

$(N_{Re})_{mf}$ is Reynolds number under minimum fluidization,

$g = 980 \text{ cm/s}^2$ is acceleration of gravity,

μ is viscosity of gas ($\text{g/cm} \cdot \text{s}$),

u_0 is gas superficial velocity (cm/s),

d_p is particle diameter (cm),

and ρ_g is gas density, (g/cm^3).

(It should be noted that the Equations 5-1 and 5-2 should be applied when $0.001 \leq N_{Re} \leq 4000$.)

In a fluidized-bed reactor, when u_0 is increased to a certain value, the formation of gas bubbles may cause the inhomogeneity of the fluidized bed.²⁴⁹ Thus, it is necessary to control u_0 . In a typical fluidized-bed reactor, heat and mass transfer usually reach their maximum when the flow rate is around 3-6 times of u_{mf} .¹⁷⁰ In Liu *et al.*'s research,²⁵⁰ they

produced SWCNTs with ethanol that was introduced into the reactor by argon. With the increasing argon flow rate, the SWCNT yield reaches a maximum at the flow rate of 150 sccm. In another research, by using an Fe/Al₂O₃ catalyst, Corrias *et al.*²⁵¹ found that carbon yield reaches maximum when $u_0/u_{mf} = 7$. In the experiment, the gas flow rate should be controlled according to the fluidization of samples, timescale of synthesis process, and the SWCNT yield observed.

5.3.3. Reactor design

I have designed a reactor with 25 mm in diameter and 1 m in height. The reactor has two layers, the inner layer is made of quartz, which can stand high reaction temperature, and at the same time, it would not affect the synthesis of SWCNTs. A porous quartz plate with uniformly distributed pores is used as the gas distributor to allow the gas into the bed with a uniform distribution. The outer layer is made of stainless steels, which can hold pressure up to 10 bar, so CNT synthesis can be carried out at high pressure. Gaskets for sealing and protecting the quartz tube are made of silicone.

5.3.4. Fluidization test

The fluidization behavior of the catalysts was studied in a model fluidized-bed reactor, similar to the SWCNT synthesis reactor. The schematic diagram of the fluidized-bed reactor model is shown in **Figure 5-5**. The fluidized-bed reactor model is made of transparent poly (methyl methacrylate) (PMMA), which allows easy inspection of fluidization conditions. At the gas inlet at the bottom, a porous plate with 10 μm of uniformly distributed pores was used as the gas distributor to allow the dry air into the bed with a uniform distribution. The pressure drop in the bed can be measured by a differential manometer located at 90 and 190 mm above the distributor, which provides the voltage value. Catalysts were loaded into the reactor with an initial static bed height of 210 mm, slightly higher than

the location where the manometer located. Compressed air was used as the fluidization gas and its flow rate was controlled using a flowmeter.

Figure 5-5. Schematic diagram for test setup used for determining the fluidization conditions.

5.3.5. SWCNT synthesis

In the vertical reactor, SWCNT synthesis was carried out in two different modes. (1) SWCNT synthesis was conducted in the vertical reactor in the fix-bed mode. Different amounts of catalysts, *i.e.* 1 g and 2 g, were loaded into the vertical reactor with a different catalyst bed depth, *i.e.* 20 mm and 40 mm. The catalysts loaded on top of the porous quartz plate. The gas flow was introduced from the top of the reactor, went through the catalyst bed, and went out from the outlet at the bottom. The gas flow was controlled at different rates, *i.e.* 100 and 400 sccm. (2) SWCNT synthesis was conducted in fluidized-bed mode. The catalysts were mixed with silica gel at the weight ratio of 1:1.5, loaded on the porous quartz plate. After the reduction of catalysts by H_2 , CO was introduced into the reactor from the top inlet, increasing the pressure to 2 bar in a short period of time. Afterwards, the gas flow direction was changed, and CO was introduced from the bottom inlet to fluidize the catalysts

at the flow rate of 50 sccm. The gas flow rate was decided on the basis of fluidization and synthesis conditions. The synthesis under CO typically lasted for around 0.5 hours.

5.3.6. Results and discussions

5.3.6.1. Fluidization of catalysts

The SEM images of the catalysts were shown in **Figure 5-6**. **Figure 5-6a&b** show that the diameters of the Co/SiO₂ particle catalyst are far less than 50 μm , indicating that it belongs to the group C particle category. **Figure 5-6c** shows that the average diameter of silica gel ($\sim 2.5 \text{ g/cm}^3$) is around 100 μm , which belongs to the group A particle category. They are particles with the ideal size to improve the fluidization behavior of Co/SiO₂ particle catalyst.

Figure 5-6. SEM images of catalysts (a-b) Co/SiO₂ particle catalysts at different magnifications, (c) silica gel particles, (d) the mixture of Co/SiO₂ particle and silica gel at 60 wt.%.

Figure 5-7 shows the correlation between the pressure drop in the model fluidized

bed reactor and the superficial gas velocity. The fluidization behavior of the catalysts was tested first. The catalysts showed a poor fluidization behavior, after u_0 reaches 0.1 cm/s, at which point it becomes a slugging bed and the fluctuation appears till $u_0 = 0.27$ cm/s. When u_0 is larger than 0.27 cm/s, some channels are formed and the pressure drop decreases to an abnormally low value. For the mixture containing 40 wt.% silica gel, the pressure drop increases with the increase of gas velocity until it reaches 0.75 cm/s. Afterwards, it drops quickly to a small value like that of catalysts, indicating the appearance of gas channels in the fluidized bed. For these two particle systems (0 wt.% and 40 wt.% silica gel), no typical fluidization behavior can be observed and the pressure drop is not monotonic. Thus, it can be concluded that the mixture is not suitable for fluidization. When the silica gel content is increased to 60 wt.%, the pressure drop shows similar trend with the increase of the gas velocity until u_0 reaches 0.12 cm/s. Then, it drops to a static pressure. There is no channel or bubble occurrence in the bed. This is a typical minimum fluidization behavior. It is proposed that the addition of silica gel breaks the strong interparticle forces among Co/SiO₂ particle catalysts, leading to efficient fluidization. For the mixture containing 60 wt.% silica gel, **Figure 5-7** indicates that the u_{mf} is 0.12 cm/s. Similarly, the mixture containing 80 wt.% silica gel can also be fluidized with the larger u_{mf} of 0.21 cm/s. In addition, when the whole bed system keeps the fluidization state, the pressure drop value increases with the rise of the silica gel proportion. Since efficient fluidization can be achieved with 60 wt.% silica gel addition, this condition was used for the synthesis of SWCNTs.

Figure 5-7. The pressure drop in the model fluidized bed reactor versus the superficial gas velocity.

Following the method described early, for the mixture with 60 wt.% silica gel, $u_{mf} = 0.12 \text{ cm/s}$, then $d_p = \frac{\mu(\sqrt{33.7^2 + 0.0408N_{Ga}} - 33.7)}{\rho_g u_{mf}} = 3.9 \times 10^{-5} \text{ cm} = 39 \mu\text{m}$. Following this, considering the changes of N_{Ga} , ρ_g and μ under the specific growth condition, it is possible to calculate the $u_{mf} = \frac{\mu(\sqrt{33.7^2 + 0.0408N_{Ga}} - 33.7)}{\rho_g d_p} = 0.05 \text{ cm/s}$, then the flow rate of gas is 48 sccm. The detailed parameters used during calculation were shown in **Table 5-5**.

Table 5-5. Parameters for the prediction of u_{mf} under SWCNTs growth temperature.²⁴⁸

Parameter	$\mu \text{ (Pa} \cdot \text{s)}$	$\rho_s \text{ (kg/m}^3\text{)}$	$\rho_g \text{ (kg/m}^3\text{)}$	$g \text{ (m/s}^2\text{)}$
20 °C	1.8×10^{-5}	2.4×10^3	1.21	9.8
780 °C	4.4×10^{-5}	2.4×10^3	0.34	9.8

5.3.6.2. SWCNT synthesis

In the fixed-bed mode, 1 g catalysts were first to be used in the synthesis process and the CO flow rate was 400 sccm. The UV-vis-NIR absorption spectra in **Figure 5-8a** suggest

that carbon yield increased notably. However, the selectivity towards (9,8) nanotubes deteriorates. Many (6,5) nanotubes were produced. When the flow rate was decreased to 100 sccm, similar chirality selectivity and carbon yield was obtained as that observed in the horizontal reactor. These results suggest that the growth of SWCNTs is a diffusion-controlled process. CO can be more efficiently delivered to catalyst surface using the vertical fixed bed mode than the horizontal reactor. Higher concentration of CO near Co catalyst surface is not beneficial for their selectivity towards (9,8) nanotubes.

Figure 5-8. UV-vis-NIR absorption spectra of Co/SiO₂ particle catalysts after SWCNT synthesis in different reactors with different CO flow rates.

As what I have introduced in the introduction section of this chapter, when the amount of the catalyst was increased to 2 g per batch, the depth of the catalyst bed increased from 20 mm to 40 mm correspondingly, the products again became inhomogeneous in the fixed-bed mode. Thus, I tested the fluidized-bed mode in an attempt to address this issue. Based on the results of fluidization test described early, the CO flow rate was first set under 50 sccm. After the CVD synthesis, the UV-vis-NIR absorption spectra in **Figure 5-8b** show that there was almost no SWCNTs grown on the catalysts. After the CO flow rate was changed to 200 sccm (4 times of the u_{mf}), the results did not become better. It indicates that under my

experimental conditions, the fluidized-bed mode is not successful. Several reasons should be responsible for this result. First, the dimension of the reactor might be too small which may end up with an unwanted wall effect. (Note that the wall effect is dominant in small reactors.²⁵²) In fact, although a variety of reactors with different diameters have been used in CNT synthesis processes so far, many researchers preferred using small reactors with the diameter less than 50 mm.²⁵³ Hernadi *et al.*²⁵⁴ used a 6.4 mm-diameter quartz tube to produce MWCNTs. Qian *et al.* produced MWCNTs in a fluidized-bed reactor with 40 mm of diameter. It was found that CNTs produced in larger reactors have less defects or breakage because larger reactors provided sufficient space for growth with a uniform temperature.²⁵⁵ The second reason might be the running off of the catalyst. Even through the mixture of the catalysts and silica gel can be fluidized well; the catalysts might be blown away because of their smaller size compared to that of silica gel particles. The third reason might be related to the diffusion-controlled SWCNT synthesis process. In fluidized bed, CO concentration near catalyst surface may be much higher than that in fixed bed. The high CO concentration could lead to fast Co cluster nucleation and/or saturation of carbon in Co clusters. Both are not beneficial for achieving SWCNT chirality control.

5.4. Conclusions

A commercially available low cost silica particle was used to prepare Co catalysts for the chirality-selective synthesis of SWCNTs. SWCNTs grown from this catalyst show a narrow diameter distribution around 1.2 nm. PL results indicate chirality selectivity toward (9,8) nanotubes with the abundance of 46% among semiconducting nanotubes. In combination with my previous findings, the characterization results of the catalyst by ICP and XRF suggest that the presence of S residues on silica supports is responsible for the observed chirality selectivity.

SWCNT synthesis in the vertical fixed-bed and fluidized-bed reactors was also studied. The vertical fixed-bed reactor can host up to 5 times more catalysts (1 g catalysts per batch) than the horizontal reactor with the same reactor size, and produces SWCNTs having similar carbon yield and chirality selectivity. In contrast, the fast mass transfer in the fluidized bed is not beneficial for achieving SWCNT chirality control. These results indicate that there is a plenty of room for further improving catalyst supports and reactor design to achieve high yield chirality selectivity production of SWCNTs.

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For **Figure 5-3**, reprinted from Powder Technology, Yang, Wen-Ching, Modification and re-interpretation of Geldart's classification of powders, 2007, 171, 69, with permission from Elsevier.)

Chapter 6: Conclusions and outlook

6.1. Conclusions

Chapter 3 and 4 show that sulfur can play an important role in the chirality selective synthesis of SWCNTs. First, sulfur-containing compounds can be directly added into the carbon feedstock. However, Co clusters are easily poisoned by sulfur, leading to a sharp decrease of the carbon yield. This finding led me to find a way to “smartly” poison the catalyst. The Co/SiO₂ catalyst was treated by H₂S before SWCNT synthesis. This sulfidized catalyst shows good chirality selectivity without significantly reducing carbon yield. For details, when ethanol was used as the carbon precursor, the ethanol was the most expensive consumable because of its purity, with a price of 649.9 SGD/L. After a typical growth process, at least 1 mL ethanol had gone and the cost was 0.65 SGD. Taking thiophene for example, when 0.1 wt.% thiophene was added into ethanol, the catalyst shows good chirality selectivity toward (9,8) nanotubes with their relative abundance of 43.1% among all semiconducting nanotubes, however, the carbon yield is just about 0.3 wt.%. Despite of all the other cost, 0.65 SGD should be cost with a carbon production of 0.15 mg. When CO was used as the carbon precursor, CO was the most expensive consumable with the price of 175 SGD/6.8 M³ in 175 bar. Even the price of H₂S is as high as 1000 SGD/7.5 M³ in 150 bar, the quantity used in the sulfidation process was too small (0.06L). In a typical process, about 12 L (2 bar) CO was consumed and the cost was about 0.0034 SGD with the carbon yield of 2.5 wt.%. Despite of all the other cost, 0.0034 SGD should be cost with a carbon production of 2.5 mg. Compared with these two methods, it is obvious that the second one should be more promising for industry. Chapter 5 explores several methods to achieve scalable SWCNT

synthesis at lower production cost. First, low cost silica particles were used to replace high purity fumed silica in catalyst preparation. The Co/SiO₂ particle catalyst also shows good selectivity towards (9,8) nanotubes. Catalyst composition analysis suggests that sulfur residues in silica particles are responsible for the chirality selectivity. Next, the vertical fixed-bed CVD reactor was used to increase the scalability from 200 mg to 1 g per batch under a low CO flow rate with a similar chirality selection. Last, the Co/SiO₂ particle catalyst was fluidized after adding additional silica gel particles to improve its fluidization property. However, SWCNT synthesis under fluidization conditions showed poor control of chirality selectivity. These results suggest that SWCNT growth on metal catalysts surfaces is a diffusion-controlled reaction. The catalyst reactor design needs to be further improved to achieve both good chirality selection and high carbon yield.

6.2. Outlook

A wide range of SWCNT synthesis conditions was studied in this thesis while investigating the effect of sulfur compounds either as a part of carbon feedstock or as a catalyst modifier. It is feasible to improve the chirality selectivity towards desired relatively larger diameter SWCNTs, *i.e.* (9,8) nanotubes. Combining with suitable purification and enrichment methods, it is now possible to obtain high purity (9,8) nanotubes at a few milligram quantities per day production yield. This production yield is sufficient for many laboratory scale studies or niche applications. Some of these cooperative works are listed in my co-authored publications. Looking forward, it is important to further increase the production scale while preserving the good chirality selectivity. In my view, three areas are important for future research: (1) conducting more fundamental investigation on the mechanisms of the CNT formation. (2) developing high activity catalysts for archiving both

high carbon yield and good chirality selectivity, and (3) innovating CVD reactors to realize high yield production.

In the first area, the fundamental investigation can be conducted from two aspects: (1) the growth kinetics, (2) the thermodynamics. How do these two aspects influence the growth of SWCNTs? More investigations on nucleation, growth, termination and reaction behavior on individual nanotube level are necessary to explain this question. Subsequently, some optimized reaction pathways should be designed on the basis of these investigations.

In the second area, the efficiency of catalysts can be improved from three aspects: (1) the dispersion homogeneity of metal clusters over large surface area catalyst support materials, (2) the size distribution control of metal clusters, and (3) the stability of metal clusters under SWCNT synthesis condition. It is expected if the metal clusters with suitable sizes can be stabilized on the catalyst support, there will be less random aggregation/nucleation during SWCNT synthesis. Thus, more active metal clusters will be available for SWCNT growth, leading to higher carbon yield. In my project, sulfur was used to tune the chirality selectivity of Co/SiO₂ catalyst. It may be also possible to use other metal or non-metal elements to modify the catalysts with better controls. Further, new organic or inorganic synthesis methods can be used to produce metal clusters with well-defined size control. In addition, the interactions between metal clusters and catalyst support materials can be improved to obtain more stable metal clusters.

In the third area, I managed to increase SWCNT production by using the vertical fixed-bed reactor. However, the results obtained by using fluidized-bed reactor are not satisfactory, even though fluidization of catalyst particles has been successfully achieved. The poor performance may be originated from the mass-transfer controlled SWCNT growth process. Too many carbon radicals available near metal surface are not beneficial for SWCNT chirality control. Reducing the velocity of gas near fluidized catalyst particles and

diluting the concentration of carbon feedstock in carrier gas may create better mass transfer conditions, which are more favorable for achieving chirality selective SWCNT synthesis. Novel designs of fluidized bed reactors and optimizing their operation conditions will be essential to realize large scale production.

The research of SWCNTs has progressed significantly over the last 20 years. Solving some of the critical technological challenges, including those listed above, will enable their applications in different fields. In my view, it won't be too far to eventually unleash the great potentials of SWCNTs.

APPENDICES

Appendix-A: List of related publications

Chapter 3

Yuan, Y; Wei, Li; Jiang, Wenchao; Goh, Kunli; Lau, Raymond; and Chen, Yuan*; Sulfur induced chirality changes in single-walled carbon nanotube synthesis by ethanol chemical vapor deposition on Co/SiO₂ catalyst, *Journal of Materials Chemistry A*, **2015**, 3, 3310–3319.

Chapter 4

Yang Y; Karahan, H. Enis; Yıldırım, Cansu; Birer, Özgür; Wei, Li; Lau, Raymond; and Chen, Yuan*; “Smart poisoning” of Co/SiO₂ catalysts by sulfidation for chirality-selective synthesis of (9,8) single-walled carbon nanotubes, *Nanoscale*, **2016**, 8, 17705-17713

Appendix-B: Other publications

Wang, H; **Yuan, Y**; Wei, L; Goh, K; Yu, DS; Chen, Y*; Catalysts for chirality selective synthesis of single-walled carbon nanotubes, *Carbon*, **2015**, 81, 1-19

Goh, K; Heising, JK; **Yuan, Y**; Karahan, HE; Wei, L; Zhai, S; Koh, JX; Htin, NM; Zhang, F; Wang, R; Fane, AG; Dekker, M; Dehghani, F; Chen, Y*; Sandwich-architected poly (lactic acid)-graphene composite food packaging films; *ACS Applied Materials & Interfaces*, **2016**, 8, 9994–10004

Wei, L; Jiang, W; **Yuan, Y**; Goh, K; Yu, DS; Wang, L; Chen, Y*; Synthesis of free-standing carbon nanohybrid by directly growing carbon nanotubes on air-sprayed graphene oxide paper and its application in supercapacitor, *Journal of Solid State Chemistry*, **2015**, 224, 45–51

Jiang, W; Zhai, S; Qian, Q; **Yuan, Y**; Karahan, HE; Wei, L; Goh, K; Ng, AK; Wei, J; Chen, Y*; Space-confined assembly of all-carbon hybrid fibers for capacitive energy storage: realizing a build-to-order concept for micro-supercapacitors; *Energy & Environmental Science*, **2016**, 9, 611-622

Wei, L; Karahan, HE; Zhai, S; **Yuan, Y**; Qian, Q; Goh, K; Ng, AK; Chen, Y*; Microbe-derived carbon materials for electrical energy storage and conversion; *Journal of Energy Chemistry*, **2016**, 25, 189-196

Jiang, W; Zhai, S; Wei, L; **Yuan, Y**; Yu, D; Wang, L; Wei, J; Chen, Y*; Nickel hydroxide-carbon nanotube nanocomposites as supercapacitor electrodes: crystallinity dependent performances, *Nanotechnology*, **2015**, 26, 314003

Wei, L; Bai, SH; Peng, WK; **Yuan, Y**; Si, RM; Goh, KL; Jiang, RR; Chen, Y*; Narrow-chirality distributed single-walled carbon nanotube synthesis by remote plasma enhanced ethanol deposition on cobalt incorporated MCM-41 catalyst, *Carbon*, **2014**, 66, 134-143

Wei, L; Liu, B; Wang, X; Gui, H; **Yuan, Y**; Zhai, S; Ng, AK; Zhou, C; Chen, Y*; (9,8) single walled carbon nanotubes enrichment via aqueous two-phase separation and their thin film transistor applications, *Advanced Electronic Materials*, **2015**, 1, 1500151

Zhai, S; Jiang, W; Wei, L; Karahan, H. E.; **Yuan, Y**; Ng, AK; Chen, Y*; All-carbon solid-state yarn supercapacitors from activated carbon and carbon fibers for smart textiles, *Materials Horizons*, **2015**, 2, 598

Wei, L; Yu, DS; Karahan, H. E.; Birer, O; Goh, K; **Yuan, Y**; Jiang, W; Chen, Y*; *E. coli*-derived carbon with nitrogen and phosphorus dual functionalities for oxygen reduction reaction, *Catalysis Today*, **2015**, 249 228-235

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