Purification and chiral selective enrichment of single-walled carbon nanotubes for macroelectronic applications

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Purification and Chiral Selective Enrichment of Single-Walled Carbon Nanotubes for Macroelectronic Applications

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List of Abbreviations

AFM	Atomic Force Microscope
BET	Brunauer-Emmett-Teller
BJH	Barret-Joyner-Halenda
CNT	Carbon Nanotube
Co-MCM-41	Cobalt Incorporated Mobil Composition of Matter 41
CVD	Chemical Vapor Deposition
DGU	Density Gradient Ultracentrifugation
DOC	Sodium Deoxycholate
DTG	Differential Thermogravimetric
DWCNT	Double-Walled Carbon Nanotube
EMI	Electron Magnetic Interference
FET	Field Effect Transistor
HiPco	High Pressure CO
HTAB	Hexadecyltrimethyl Ammonium Bromide
IGA	Indium-Gallium-Arsenium
MCM-41	Mobil Composition of Matter 41
MD	Molecular Dynamic
MWCNT	Multi-Walled Carbon Nanotube
NP	Nanoparticle
OD	Optical Density
PL	Photoluminescence
PLE	Photoluminescence Excitation/Emission
RBM	Radial Breathing Mode

SC	Sodium Cholate
SDBS	Sodium Dodecyl Benzene Sulfonate
SDS	Sodium Dodecyl Sulfate
SEM	Scanning Electron Microscope
STM	Scanning Tunneling Microscope
SWCNT	Single-Walled Carbon Nanotube
TCD	Thermal Conductivity Detector
TEM	Transmission Electron Microscope
TFT	Thin Film Transistor
TGA	Thermogravimetric Analysis
TPR	Temperature Programmed Reduction
UV-vis-NIR	Ultraviolet-visible-Near infrared
VHS	Van Hove Singularity
XPS	X-Ray Photoluminescence Spectra/Spectroscopy

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Abstract

Purification and Chiral Selective Enrichment of Single-Walled Carbon Nanotubes for Macroelectronic Applications

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This thesis focuses on the purification and chiral selective enrichment of single-walled carbon nanotubes (SWCNTs) obtained from cobalt incorporated MCM-41 catalyst (Co-MCM-41) and their potential applications as macroelectronic devices. The properties of SWCNTs are chiral (n,m) dependent, and are sensitive to various impurities in SWCNT samples. Monodisperse high purity SWCNT samples are desired for their potential applications. However, until now, no synthesis methods are able to selectively grow SWCNTs with specific (n,m) structures.

As-synthesized SWCNTs from Co-MCM-41 were first purified by a centrifugation based method. The optimal centrifugation force was found at 120,000 g, which led to very high purity SWCNTs. Due to the strong van der Waals forces among nanotubes, aggregation of SWCNTs is one of the major obstacles for their potential applications. SWCNT suspensions containing various fractions of bundles were obtained by ultracentrifugation. Dialysis was used to

achieve controlled nanotube rebundling. A clear correlation was found between SWCNT photoluminescence (PL) sidebands and nanotube aggregation status.

Next, highly selective enrichment of SWCNTs, having (6,5) and (8,3) structures, was achieved (above 85% of the semiconducting tubes) through multistep extraction by sodium dodecyl sulfate (SDS) and sodium cholate (SC) co-surfactant solution. A systematic change in the chirality selectivity was observed when the weight ratio between SDS and SC varied in co-surfactant solutions, with maximum selectivity for (6,5) tubes yielded at 1:4. The enriched samples were further sorted by a density gradient ultracentrifugation (DGU) method. Subsequently, SWCNT thin-film field effect transistors (FETs) were fabricated using enriched SWCNTs. The electrical transport measurement (through I_{on}/I_{off} ratio) of thin film FETs was found to be the most sensitive technique to evaluate the purity of semiconducting SWCNTs.

Lastly, SWCNT films were prepared, which contained a high density of semiconducting SWCNTs obtained by a gel-centrifugation method. The thickness and transmittance of the films can be controlled for photoelectrochemical devices fabrication. Photocurrents generated by the films are 15–35 % higher than those from unsorted SWCNT films. Developing more scalable and selective methods for high purity monodisperse SWCNTs is crucial to enable their application in macroelectronic devices.

Chapter 1

Introduction

The work of this thesis focused on the purification and chiral selective enrichment of single-walled carbon nanotubes (SWCNTs) for macroelectronic applications.

Half a century has passed since the term “nanotechnology” was firstly introduced by Dr. Richard Feynman in his famous 1959 lecture [1-2]. Accelerated by the fast development in both theoretical knowledge and experimental techniques, various nanoscale materials were synthesized. And they exhibit unique properties, which show increasing potentials to remake our world [3]. Among these novel nano materials, carbon nanotubes (CNTs) have become a focused subject since they were discovered in 1991 [4-5]. Their exceptional mechanical, thermal and electronic properties promote them as promising candidates for various applications, such as high performance composite materials, catalyst supports, and next generation medical devices, but in particular, for macroelectronic applications.

Opposite from microelectronic devices where everything is striving to be as small as possible, macroelectronic devices have their circuits distributed over large substrates which obey the criterion that the bigger the better [6]. Such devices have already changed our daily life, for example, flat-panel displays fabricated from thin film transistors (TFTs). The future macroelectronic devices, such as transparent flexible touch screens and foldable solar cells, require materials, which not only possess good electronic properties, but also exhibit excellent mechanical properties, as well as thermal stability. The unique mechanical and electronic properties of SWCNTs make them a strong candidate for such applications. In

general, SWCNTs with precisely controlled properties are required for macroelectronic device fabrication. Moreover, high purity SWCNT samples are also needed to study their intrinsic properties, before their application potentials can be realized.

However, properties of SWCNTs are structure-dependent. Current synthesis methods usually produce SWCNTs with mixed structures. Until now, no synthesis protocols are able to produce monodisperse SWCNT samples. This has become a major obstacle to their potential applications. This thesis is dedicated to develop purification and chiral selective enrichment methods in order to obtain SWCNT samples with desired properties. This thesis starts with a short introduction of SWCNTs and a brief literature review on the current progress towards obtaining monodisperse SWCNT samples.

1.1 SWCNT

Since the report by Iijima in 1991 [7], CNTs quickly attracted lots of attention around the world. Two years later, CNTs with their tube wall consisting of only one graphitic layer were synthesized. They were named as SWCNTs after their siblings, multi-walled carbon nanotubes (MWCNTs) [4-5]. SWCNT can be visualized as a seamless cylindrical structure formed by rolling up of a single layer of graphite sheet. The diameter of SWCNTs ranges from 0.4 to 2 nm and their length can reach centimetres. The high length/diameter aspect ratio makes them an ideal one-dimension nanoscale system.

The structure of SWCNTs can be described by a chiral vector: the helicity vector $\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \equiv (n, m)$, where $(\vec{a}_1, \vec{a}_2)$ is the real space basis vector of a graphite sheet as shown in Figure 1-1. By connecting two carbon atoms on the graphite sheet along the $\vec{C}_h$ direction, a unique nanotube structure can be formed. The angle between $\vec{C}_h$ and $\vec{a}_1$

is called the chiral angle (θ) of a SWCNT. Due to the symmetry of the graphite hexagonal network structure, the chiral angle varies from 0° to 30° . The diameter (d_t) and chiral angle (θ) of a nanotube can be calculated from its chiral vector by the following equations:

$$d_t = 0.0783\sqrt{(m^2 + mn + n^2)} \quad (1)$$

$$\theta = \tan^{-1}(\sqrt{3}m/(2n + m)) \quad (2)$$

Figure 1-1 Schematic representation of SWCNT structure, a) zig-zag ($n,0$) nanotube, b) arm-chair (n,n) nanotube and c) chiral (n,m) nanotube [8].

This unique structure of SWCNTs results in excellent and attractive properties. However, these properties are structure-dependent. For a nanotube with a given (n,m) structure, if the difference between n and m can be divided by 3, this nanotube is metallic; otherwise it behaves like semiconducting materials. Metallic nanotubes are excellent conductors with a current density as high as 4×10^9 A/cm² [9] and a mobility up to 10,000 cm²/V·s [10]. The high conductivity and mobility is due to the weak acoustic phonon

scattering, which allows ballistic conduction in the longitude direction of a nanotube [11]. Semiconducting SWCNTs exhibit structure dependent band gaps ranging from 0.4 to 0.7 eV, which are generally inversely proportional to their diameter d_t [12]. In the common SWCNT diameter range (0.4 – 2 nm), there are more than 200 different (n,m) chiral species. The diverse SWCNT properties have become an obstacle for their applications, for example, in SWCNT based electronic devices, pure metallic nanotubes are needed as interconnects, while semiconducting nanotubes with specific band gaps are required as active device channel components.

Thus, monodisperse SWCNT samples are desired for both better understanding of their structure dependent intrinsic properties and future applications in macroelectronics. Various synthesis, purification and enrichment methods have been proposed to address this issue; and they are briefly introduced in the following parts of this chapter.

1.2 Selective synthesis of SWCNT

The most widely used SWCNT synthesis techniques today include arc-discharge, laser ablation and chemical vapour deposition (CVD) [13-15]. The mechanisms of the arc discharge and laser ablation method are similar. High temperature arc between two carbon electrodes or high energy laser beam evaporates carbon atoms from a Y-Ni [16] or Co/Ni[17] graphite composite target. The vaporized carbon atoms would rapidly condense and form SWCNTs on small metal clusters. High quality SWCNT materials have been produced by these two methods. However, it is difficult to control the structure of SWCNTs by these two methods. Furthermore, they usually only produce SWCNTs in powder forms; and are not suitable to grow SWCNTs on planar substrates.

CVD method provides more parameters to manipulate the structure of SWCNTs than the above mentioned two methods. CVD method bases on the deposition of gaseous carbon precursors on catalytic clusters. There are two key components in the process: one is the carbon precursor, and the other is the catalyst. Carbon precursors can be carbon monoxide (CO) [18-19], methane (CH₄) [20], ethanol (C₂H₅OH) [15], acetylene (C₂H₂), methanol (CH₃OH) [21] and many other hydrocarbons. Experiment results have demonstrated that different carbon precursors would affect the structure of SWCNTs [21-22]. On the other hand, catalysts used for SWCNT growth are usually nanoparticles supported on different substrates. Different transition metal nanoparticles, such as Co, Fe, Ni, Mo and their alloys have been used. More recently, Au [23], Pt [24], Ag [25], and even SiO₂ particles [26-27] have been utilized to grow SWCNTs. Substrates are also important for catalyst performance. A good supporting substrate should have the following properties: (1) high thermal stability, which prevents it from decomposing at the high SWCNT growth temperature; (2) large surface area, which enables both a high nanoparticle loading and uniform nanoparticle distribution; (3) strong metal-support interactions, which stabilize metal nanoparticles during SWCNT growth [28]; and (4) solubility in acid or alkaline solution, which allows an easy substrate removal in the followed purification step. Amorphous SiO₂ [13], Al₂O₃ [29] and MgO [30] have been used as porous substrates, while crystalline Si [31], thermal grown SiO₂ films [32] and quartz [33] are applied as planar substrates. Different methods can be used to load nanoparticles on substrates. For porous substrates, the common methods include impregnation [34], incorporation [35], combustion [36], and sol-gel process [37]. For planar substrate, dip-casting [38], spinning

coating [39] and electron beam sputtering [40] are widely used to pattern metal nanoparticles or deposit uniform thin metal films.

By carefully tuning catalyst formation methods, carbon precursors and growth conditions, researchers have successfully obtained SWCNTs with controlled chirality distribution. For example, narrowly chiral distributed SWCNT samples have been produced from Co-Mo [34], Fe-Co [41], Fe-Ru [42], and Co-MCM-41 catalysts [43]. Some as-prepared samples have more than 60% of semiconducting nanotubes with (6,5) or (7,5) chiral structures [34, 43]. However, they are still not monodisperse SWCNT samples required by many macroelectronic applications. Nevertheless, these synthesis methods provide good starting materials for further post-synthesis enrichment studies.

1.3 Purification of SWCNTs and their purity evaluation

Three issues need to be considered in SWCNT purification studies: (1) what are the impurities existing in as-prepared SWCNT samples? (2) What are the most suitable techniques to remove these impurities? And (3) how can we accurately evaluate the purity of a SWCNT sample?

1.3.1 Impurities and their purification methods

Impurities in as-prepared SWCNT samples can be classified into three types: (1) catalyst supporting substrates, such as MgO, Al₂O₃ and SiO₂; (2) catalytic metal nanoparticles; and (3) various carbonaceous by-products, such as amorphous carbon, few-walled and MWCNTs, carbon nanoparticles, graphite and fullerenes.

Many methods have been developed to purify SWCNT samples. Catalyst substrates can be dissolved in strong acids, such as HF or HNO₃ [44-47], or strong alkaline solutions [48]. Metal nanoparticles would also dissolve in various acids. The structural differences among carbonaceous impurities result in varied physiochemical properties, such as oxidation temperature and density. Based on these differences, purification methods can be developed. For example, amorphous carbon can be removed by controlled oxidation [49-50] because their oxidation temperature is lower than that of other carbonaceous impurities. However, it is not feasible to remove MWCNTs and graphite by oxidation due to the fact that their oxidation temperatures are higher than that of SWCNTs. On the contrary, MWCNTs may be removed by centrifugation because their densities are higher than that of SWCNTs [51-52].

Furthermore, a good purification method should not only remove various impurities, but also maintain the intrinsic properties of SWCNTs. On this aspect, most of chemical methods using acid treatments would inevitably introduce many defects on nanotube sidewall or ends by carboxyl groups (–COOH) addition. SWCNTs may also be shortened by oxidation treatments [46]. From an economical viewpoint, purification methods should also have a high recovery rate to save the cost.

1.3.2 SWCNT purity evaluation

The purity of a SWCNT sample can be examined by various techniques. The ultimate goal is to accurately determine the concentration of different impurities, as well as the abundance of different chiral species. Direct microscopic observation, element and thermal

analysis, and spectroscopic analysis can provide abundant information for SWCNT purity assessment.

Microscopic techniques, such as transmission electron microscope (TEM) and scanning electron microscope (SEM) [47, 49-50, 53-54] provide direct visual evidences for purity assessment. They are generally accurate and straightforward. However, their drawbacks are limited resolution and low throughput. The resolution of SEM is usually at a few nanometres, and it is difficult to differentiate SWCNT bundles from small MWCNTs. For both SEM and TEM, only tiny amount of samples can be examined in each analysis, it makes the purity evaluation a tedious and time-consuming process. Moreover, the purity of SWCNT samples could also be altered during SEM and TEM sample preparation.

Energy dispersive spectroscopy (EDS) [48], inductively coupled plasma atomic emission spectrometry (ICP-AES) and X-ray photoluminescence spectroscopy (XPS) [55] have been used to characterize the element composition (by EDX or ICP-AES) and chemical state of elements (by XPS) in SWCNT samples. They are sensitive to examine metal or catalyst substrate impurities, but they cannot tell the differences between SWCNTs and other carbonaceous impurities.

An efficient method to differentiate carbonaceous materials is thermal gravimetric analysis (TGA) [47, 49-50, 53-54, 56]. Different carbonaceous species can be oxidized at different temperatures, thus they can be identified and quantified based on their temperature-weight profiles. The drawbacks of TGA include: (1) it is a destructive method. The samples cannot be recovered after analysis. (2) Significant amount of samples are required. In general, at least 5 mg of SWCNT samples are needed to obtain a well-resolved temperature-weight profile. (3) The oxidation temperature of different carbonaceous

species may be altered by other factors, such as metal nanoparticle residues, defect sites, and adsorbed molecules on nanotube surface.

Spectroscopic techniques, such as resonant Raman spectroscopy [47, 49-50, 53] and ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectroscopy [54, 57], have been utilized to evaluate the purity of SWCNTs. In Raman spectroscopy, when the excitation laser energy coincides with the bandgap energy of a nanotube, intense resonant Raman signals can be detected from various vibration modes of SWCNTs. Those Raman features provide abundant structure information of SWCNT samples. Three major Raman features have been used for purity evaluation, including the radial breathing mode (RBM, 100~300 cm^{-1}), disorder induced D-band ($\sim 1300 \text{ cm}^{-1}$) and graphitic G-band (1500~1600 cm^{-1}). The intensity ratio between G band and D band is commonly used to assess the content of amorphous carbon and defects on nanotubes, although it is difficult to accurately determine whether a strong D band may come from amorphous carbon or defects on nanotubes. Moreover, most SWCNT samples contain various chiral species, which require multi-wavelength excitation laser sources. Such laser sources are not widely available in most research labs. UV-vis-NIR absorption spectroscopy can characterize interband transitions of SWCNTs. UV-vis-NIR spectra of SWCNTs are sensitive to impurities [58-62]. Itkis *et al.* proposed a SWCNT purity index based on S_{22} interband transition spectroscopic areas of SWCNTs [57]. Overall, spectroscopic techniques usually only require small amount of SWCNT samples (less than 0.1 mg); and the experiments can be carried out easily. But careful sample preparation is still required to minimize any contamination because SWCNT interband transitions are very sensitive to defects, doping, and the environment of solvents.

All above mentioned methods have their own advantages and drawbacks. Results obtained from various techniques should be combined together to provide a comprehensive evaluation of SWCNT samples. In general, the following criteria can be used as a benchmark for high purity SWCNT samples: (1) a single and sharp differential thermogravimetric (DTG) peak in the range of 400 ~ 600 °C should be observed in TGA analysis. (2) No metals and supporting materials can be detected in element analysis. (3) Intense interband transition spectroscopic features can be obtained in absorption spectroscopy. And (4) microscopic investigation should show clear nanotube structures.

1.4 Post-synthetic sorting

Despite significant efforts have been put on selective synthesis, current synthetic methods are still incapable to obtain monodisperse SWCNTs required for macroelectronic applications. Post-synthetic sorting is promised to solve the SWCNT polydispersity problem. Any separation method is based on the differences in SWCNT structures, such as diameter, length, and chirality. However, such structure differences are usually not well-defined among different nanotube species. Thus, selective chemistry, such as functionalization, adsorption and encapsulation, is utilized to amplify these differences before SWCNTs can be sorted by various techniques, including electrophoresis, chromatography, and ultracentrifugation. Moreover, various selective chemical treatments and separation techniques are often combined together to improve the overall sorting efficiency [63-64].

1.4.1 Selective chemistry

Chemical properties of SWCNTs have been summarized in a recent review [65]. A variety of selective chemical reactions have been developed based on the structure dependent chemical properties of SWCNTs. The commonly used selective chemical reactions can be classified into three types as shown in Figure 1-2: (1) covalent functionalization on nanotube sidewalls, defect sites and/or open ends, (2) non-covalent surfactant encapsulation, and (3) polymer wrapping.

Figure 1-2 Three types of selective chemical reactions: (a) selective covalent functionalization, (b) selective surfactant encapsulation and (c) selective polymer wrapping. Modified from [63]. Adapted by permission from Macmillan Publishers Ltd: Nature Nanotechnology, copyright 2008

Covalent functionalization reactions are designed to discriminate nanotubes as a function of their electronic type or diameter. The first such sample is the selective diazonium salt reaction found in 2003. Diazonium salts can selectively react with metallic carbon nanotubes [66-69]. They can strongly perturb the electronic structures of metallic nanotubes, which would consequently deactivate conducting channels in a SWCNT network. The reaction can take place in both aqueous solutions and organic solvents, for

example, tetrahydrofuran (THF) [70]. After reacted with diazonium salts, dispersed SWCNTs can be further sorted by various techniques, such as electrophoresis [71] and density gradient ultracentrifugation (DGU) [72]. Another example is the dichlorocarbonene addition on nanotube sidewalls. This reaction would also deactivate metallic nanotubes by opening a small band gap at their Fermi levels [59, 61]. Furthermore, nanotube sidewall cycloaddition reactions show different selectivities towards metallic and semiconducting nanotubes. For example, metallic SWCNTs can be suppressed by fluorinated olefins addition [73], while polycyclic aromatic labelled trialkylamine-N-oxide derivate azomethine ylides would preferentially react with semiconducting SWCNTs [74]. In addition, UV light assisted Os^{8+} reduction would selectively form OsO_2 nanoparticles on the surfaces of metallic nanotubes. The resulting nanotube-nanoparticle complex can be further sorted by DGU [75].

Other than the selectivity towards the metallicity of SWCNTs, diameter selective reactions have also been investigated. Nitronium ions would selectively deteriorate small diameter metallic nanotubes into amorphous carbon [76-78]. Solution phase selective ozonolysis of smaller diameter nanotubes is also possible due to the diameter-dependent pyramidalization activity and π -orbital misalignment [79]. Dissolution of SWCNTs in a sulphonic acid mixture by direct protonation is sensitive to their geometric strain, which can be utilized to achieve diameter selective sorting [80].

Although good separation results have been obtained by selective covalent functionalization reactions, these reactions would inevitably damage SWCNT structures and disturb their intrinsic properties. Non-covalent surfactant encapsulation uses small molecules to selectively encapsulate nanotubes with different structures. Their selectivities

are contributed by different physisorption strengths between various functional groups and nanotubes [81]. Common examples include molecules with amine ($-\text{NH}_2$) groups and large planar aromatic rings. Propylamine and isopropylamine show a strong affinity to metallic nanotubes in THF [82-83], while octadecylamine would selectively interact with acidified (*p*-doped) semiconducting nanotubes in dimethylformamide (DMF) [46, 84] or THF [81, 85]. Planar diporphyrins and monoporphyrins have strong affinity to semiconducting nanotubes [86]. Chirality selective encapsulation can be achieved by biomolecules, such as helical flavin mononucleotide assemblies [87] and oligo-acene [88]. Furthermore, bromine [89-90] and charge-transfer aromatics [91] bind strongly with metallic nanotubes, resulting in the formation of charge-transfer complexes. Even common surfactants, such as sodium dodecyl sulfate (SDS) and sodium cholate (SC), possess some minor selectivity to smaller diameter nanotubes compared to larger diameter nanotubes [92-93].

Comparable to surfactant encapsulation, some polymers can also efficiently wrap nanotubes with specific structures. Several fluorine-based polymers and polyaromatic amphiphiles [94] are found to be able to enrich SWCNTs by their chirality [95-96] or metallicity [97]. Heparin sodium salt can selectively enrich (8,4) nanotubes [98]. Single strand DNA shows strong affinity towards semiconducting nanotubes [99].

1.4.2 Separation techniques

A variety of separation techniques have been applied for SWCNT separation. The most commonly used techniques include electrophoresis, chromatography, and ultracentrifugation. These techniques usually do not introduce damages to nanotubes during

separation. They also provide many controllable process parameters. Thus, the process optimization becomes important in obtaining monodisperse SWCNT samples.

Electrophoresis is based on the motion differences among dispersed nanotubes under the influence of an electric field. Three types of electrophoresis methods have been investigated for SWCNT separation. The first method is the direct current (DC) electrophoresis. Covalently functionalized SWCNTs can be separated in an aqueous solution [71], and better separation results have been achieved in capillary tubes [100]. The second method is the high frequency alternative current (AC) dielectrophoresis. Unlike DC electrophoresis, where the separation is achieved by the motion of charged particles, dielectrophoresis uses the differences of the relative dielectric constants of metallic and semiconducting SWCNTs. Metallic nanotubes would be attracted to electrodes, while semiconducting nanotubes remain in the solvent [101]. The separation efficiency can be further improved by either increasing the AC field frequency [102-103] or neutralizing the charge on nanotube surfaces [104]. However, the overall throughput of the dielectrophoresis method is very limited [101]. Large electrodes [105] and microfluidic dielectrophoretic cells [106] may further improve the separation throughput. The third method is the agarose gel electrophoresis [107]. Semiconducting-metallic nanotube separation has been achieved by agarose gel electrophoresis [108-110]. The stronger interactions between semiconducting nanotubes and the agarose gel matrix enable the separation by expelling metallic SWCNTs from the gel.

Ion exchange chromatography has been successfully applied to separate SWCNTs suspended by single strand DNAs. This method has achieved one of the best chirality selective separation of SWCNTs [111-113], and 20 DNA sequences that each selectively

binds to a specific SWCNT chirality have been identified [114]. Theoretical models have also been developed to improve the sorting efficiency [112, 115-116].

DGU method developed by Arnold *et al.* in 2005 [117] offers a new route for nanotube separation. SWCNTs encapsulated in surfactant molecules can be sorted according to their densities [117-118]. Dispersed SWCNTs are loaded into a density gradient. In the presence of a centrifugal field, SWCNTs would be forced to travel through the density gradient until their densities equals to the local solution density. The density of the SWCNT-surfactant complex is highly sensitive to the diameter and chirality of SWCNTs as well as the structure of surfactants. SDS, SC and sodium deoxycholate (DOC) co-surfactant assisted DGU is able to separate nanotubes by their electronic types [118-121]. SWCNTs can also be decorated with metal nanoparticles to enhance their separation efficiency under DGU [122]. Moreover, the electrolyte concentration and solution pH can also influence the separation [123]. DGU can also be applied for length fractionation [124] and separation of double-walled carbon nanotubes (DWCNTs) [125]. In addition to experimental studies, theoretical studies have also been conducted to understand the surfactant-nanotube interactions [126-128].

1.4.3 Structural selective destruction

Other than separate SWCNTs with different structures, another approach is to selectively destroy nanotubes with specific structures in a sample. Research has shown that small diameter and high chiral angle SWCNTs can be selectively oxidized in an oxygen-rich atmosphere [129-130]. Additional laser or xenon-lamp irradiations can improve the oxidation selectivity towards metallic nanotubes in air [131-132]. Furthermore, metallic

SWCNTs can be etched by fluorine gas ($d_t < 1.1$ nm) [133] or hydrocarbon plasma ($d_t \sim 1.4\text{--}2$ nm) [134]. Electrical breakdown of metallic nanotubes in a nanotube network can also be achieved by applying high currents through conductive metallic nanotubes, while semiconducting nanotubes are survived by applying a gate bias voltage [135]. It should be noted that these destructive methods are typically irreversible process. Moreover, collateral damages may be introduced to adjacent nanotubes during the treatment.

1.5 Scope of this thesis

Solving the polydispersity problem of SWCNTs is essential for future SWCNT applications. This thesis will focus on SWCNT purification and post synthesis chiral selective enrichment methods towards obtaining monodisperse SWCNT samples. It is aimed to develop economical methods, which can be easily scaled up for industrial process.

General experiment minutiae and characterization methods of this study are discussed in Chapter 2. Chapter 3 describes the detail of a SWCNT purification method based on high speed ultracentrifugation. Since individualized SWCNTs are usually required for investigating their intrinsic properties and further separation processing, the correlation between the nanotube aggregation states in liquid suspensions and their photoluminescence sidebands is established in Chapter 4. Chiral selective enrichment by co-surfactant extraction is studied in Chapter 5. Combining DGU with the co-surfactant extraction method, Chapter 6 evaluates SWCNT samples enriched with different chiral species by different characterization methods to demonstrate their potentials for macroelectronic applications. Chapter 7 provides direct experimental evidences that the photocurrent generation can be improved by using SWCNT samples enriched with semiconducting

nanotubes. Chapter 8 summarizes the work of this thesis and provides a brief discussion of the future research directions.

1.6 Reference

1. Feynman, R.P., *There's Plenty of Room at the Bottom*. Engineering and Science 1960: p. 22-36.
2. Toumey, C., *Plenty of room, plenty of history*. Nat Nano, 2009. **4**(12): p. 783-784.
3. Drexler, K.E., *Engines of creation*. 1986: Anchor Press/Doubleday. 298.
4. Bethune, D.S., C.H. Klang, M.S. de Vries, G. Gorman, R. Savoy, J. Vazquez, and R. Beyers, *Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls*. Nature, 1993. **363**(6430): p. 605-607.
5. Iijima, S. and T. Ichihashi, *Single-shell carbon nanotubes of 1-nm diameter*. Nature, 1993. **363**(6430): p. 603-605.
6. Robert, H.R., G.H. Darrel, and P. Jae-Geun, *Macroelectronics* MRS Bulletin, 2006. **31**(6): p. 447-454.
7. Iijima, S., *Helical microtubules of graphitic carbon*. Nature, 1991. **354**(6348): p. 56-58.
8. Monthieux, M.S., P.; Flahaut, E.; Razafinimanana, M.; Laurent, C.; Peigney, A.; Bacsá, W.; Broto, J.-M., *Introduction to Carbon Nanotubes*, in *Springer Handbook of Nanotechnology*. 2004. p. 39.
9. Mintmire, J.W., B.I. Dunlap, and C.T. White, *Are fullerene tubules metallic?* Physical Review Letters, 1992. **68**(5): p. 631.
10. Hong, S. and S. Myung, *Nanotube Electronics: A flexible approach to mobility*. Nat Nano, 2007. **2**(4): p. 207-208.
11. O'Connell, M.J., *Carbon Nanotubes: Properties and Applications*. 2006: Taylor & Francis Group.
12. Dai, H., *Carbon Nanotubes: Synthesis, Integration, and Properties*. Accounts of Chemical Research, 2002. **35**(12): p. 1035-1044.

13. Engel-Herbert, R., H. Pforte, and T. Hesjedal, *CVD synthesis and purification of single-walled carbon nanotubes using silica-supported metal catalyst*. Materials Letters, 2007. **61**(11-12): p. 2589-2593.
14. Hiramatsu, M., T. Deguchi, H. Nagao, and M. Hori, *Area-selective growth of aligned single-walled carbon nanotube films using microwave plasma-enhanced CVD*. Diamond and Related Materials, 2007. **16**(4-7): p. 1126-1130.
15. Murakami, Y., S. Chiashi, Y. Miyauchi, M.H. Hu, M. Ogura, T. Okubo, and S. Maruyama, *Growth of vertically aligned single-walled carbon nanotube films on quartz substrates and their optical anisotropy*. Chemical Physics Letters, 2004. **385**(3-4): p. 298-303.
16. Journet, C., W.K. Maser, P. Bernier, A. Loiseau, M.L. de la Chapelle, S. Lefrant, P. Deniard, R. Lee, and J.E. Fischer, *Large-scale production of single-walled carbon nanotubes by the electric-arc technique*. Nature, 1997. **388**(6644): p. 756-758.
17. Guo, T., P. Nikolaev, A. Thess, D.T. Colbert, and R.E. Smalley, *Catalytic growth of single-walled nanotubes by laser vaporization*. Chemical Physics Letters, 1995. **243**(1-2): p. 49-54.
18. Chen, Y., D. Ciuparu, S. Lim, G.L. Haller, and L.D. Pfefferle, *The effect of the cobalt loading on the growth of single wall carbon nanotubes by CO disproportionation on Co-MCM-41 catalysts*. Carbon, 2006. **44**(1): p. 67-78.
19. Chen, Y., D. Ciuparu, S. Lim, Y. Yang, G.L. Haller, and L. Pfefferle, *Synthesis of uniform diameter single wall carbon nanotubes in Co-MCM-41: effects of CO pressure and reaction time*. Journal of Catalysis, 2004. **226**(2): p. 351-362.
20. Seifi, M., D.K. Ross, and A. Giannasi, *Raman characterisation of single-walled carbon nanotubes produced by the catalytic pyrolysis of methane*. Carbon, 2007. **45**(9): p. 1871-1879.
21. Wang, B., C.H.P. Poa, L. Wei, L.-J. Li, Y. Yang, and Y. Chen, *(n,m) Selectivity of Single-Walled Carbon Nanotubes by Different Carbon Precursors on Co-Mo Catalysts*. Journal of the American Chemical Society, 2007. **129**(29): p. 9014-9019.
22. Maruyama, S., R. Kojima, Y. Miyauchi, S. Chiashi, and M. Kohno, *Low-temperature synthesis of high-purity single-walled carbon nanotubes from alcohol*. Chemical Physics Letters, 2002. **360**(3-4): p. 229-234.

23. Takagi, D., Y. Kobayashi, H. Hibino, S. Suzuki, and Y. Homma, *Mechanism of Gold-Catalyzed Carbon Material Growth*. Nano Letters, 2008. **8**(3): p. 832-835.
24. Yuan, D., L. Ding, H. Chu, Y. Feng, T.P. McNicholas, and J. Liu, *Horizontally Aligned Single-Walled Carbon Nanotube on Quartz from a Large Variety of Metal Catalysts*. Nano Letters, 2008. **8**(8): p. 2576-2579.
25. Takagi, D., Y. Homma, H. Hibino, S. Suzuki, and Y. Kobayashi, *Single-Walled Carbon Nanotube Growth from Highly Activated Metal Nanoparticles*. Nano Letters, 2006. **6**(12): p. 2642-2645.
26. Liu, B., W. Ren, L. Gao, S. Li, S. Pei, C. Liu, C. Jiang, and H.-M. Cheng, *Metal-Catalyst-Free Growth of Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2009. **131**(6): p. 2082-2083.
27. Huang, S., Q. Cai, J. Chen, Y. Qian, and L. Zhang, *Metal-Catalyst-Free Growth of Single-Walled Carbon Nanotubes on Substrates*. Journal of the American Chemical Society, 2009. **131**(6): p. 2094-2095.
28. Lamouroux, E., P. Serp, and P. Kalck, *Catalytic Routes Towards Single Wall Carbon Nanotubes*. Catalysis Reviews: Science & Engineering, 2007. **49**(3): p. 341-405.
29. Hongo, H., F. Nihey, T. Ichihashi, Y. Ochiai, M. Yudasaka, and S. Iijima, *Support materials based on converted aluminum films for chemical vapor deposition growth of single-wall carbon nanotubes*. Chemical Physics Letters, 2003. **380**(1-2): p. 158-164.
30. Kang, S.J., C. Kocabas, T. Ozel, M. Shim, N. Pimparkar, M.A. Alam, S.V. Rotkin, and J.A. Rogers, *High-performance electronics using dense, perfectly aligned arrays of single-walled carbon nanotubes*. Nat Nano, 2007. **2**(4): p. 230-236.
31. Homma, Y., T. Yamashita, P. Finnie, M. Tomita, and T. Ogino, *Single-Walled Carbon Nanotube Growth on Silicon Substrates Using Nanoparticle Catalysts*. Japanese Journal of Applied Physics, 2002. **41**(Copyright (C) 2002 The Japan Society of Applied Physics): p. L89.
32. Wako, I., T. Chokan, D. Takagi, S. Chiashi, and Y. Homma, *Direct observation of single-walled carbon nanotube growth processes on SiO₂ substrate by in situ*

- scanning electron microscopy*. Chemical Physics Letters, 2007. **449**(4-6): p. 309-313.
33. Ding, L., D.N. Yuan, and J. Liu, *Growth of high-density parallel arrays of long single-walled carbon nanotubes on quartz substrates*. Journal of the American Chemical Society, 2008. **130**(16): p. 5428-+.
 34. Alvarez, W.E., B. Kitiyanan, A. Borgna, and D.E. Resasco, *Synergism of Co and Mo in the catalytic production of single-wall carbon nanotubes by decomposition of CO*. Carbon, 2001. **39**(4): p. 547-558.
 35. Yuan Chen , D.C., Yanhui Yang , Sangyun Lim , Chuan Wang , Gary L Haller and Lisa D Pfefferle *Single-wall carbon nanotube synthesis by CO disproportionation on nickel-incorporated MCM-41* Nanotechnology, 2005. **16**(7): p. S476.
 36. Flahaut, E., A. Govindaraj, A. Peigney, C. Laurent, A. Rousset, and C.N.R. Rao, *Synthesis of single-walled carbon nanotubes using binary (Fe, Co, Ni) alloy nanoparticles prepared in situ by the reduction of oxide solid solutions*. Chemical Physics Letters, 1999. **300**(1-2): p. 236-242.
 37. Zheng, B., Y. Li, and J. Liu, *CVD synthesis and purification of single-walled carbon nanotubes on aerogel-supported catalyst*. Applied Physics A: Materials Science & Processing, 2002. **74**(3): p. 345.
 38. Einarsson, E., H. Shiozawa, C. Kramberger, M.H. Rummeli, A. Gruneis, T. Pichler, and S. Maruyama, *Revealing the Small-Bundle Internal Structure of Vertically Aligned Single-Walled Carbon Nanotube Films*. The Journal of Physical Chemistry C, 2007. **111**(48): p. 17861-17864.
 39. Paillet, M., V. Jourdain, P. Poncharal, J.-L. Sauvajol, A. Zahab, J.C. Meyer, S. Roth, N. Cordente, C. Amiens, and B. Chaudret, *Versatile Synthesis of Individual Single-Walled Carbon Nanotubes from Nickel Nanoparticles for the Study of Their Physical Properties*. The Journal of Physical Chemistry B, 2004. **108**(44): p. 17112-17118.
 40. Sugime, H., S. Noda, S. Maruyama, and Y. Yamaguchi, *Multiple "optimum" conditions for Co-Mo catalyzed growth of vertically aligned single-walled carbon nanotube forests*. Carbon, 2009. **47**(1): p. 234-241.

41. Inoue, S., T. Nakajima, and Y. Kikuchi, *Trial for diameter-selective synthesis of single-walled carbon nanotubes*. Carbon, 2006. **44**(7): p. 1287-1291.
42. Li, X., X. Tu, S. Zaric, K. Welsher, W.S. Seo, W. Zhao, and H. Dai, *Selective Synthesis Combined with Chemical Separation of Single-Walled Carbon Nanotubes for Chirality Selection*. Journal of the American Chemical Society, 2007. **129**(51): p. 15770-15771.
43. Lim, S., D. Ciuparu, C. Pak, F. Dobek, Y. Chen, D. Harding, L. Pfefferle, and G. Haller, *Synthesis and Characterization of Highly Ordered Co-MCM-41 for Production of Aligned Single Walled Carbon Nanotubes (SWNT)*. The Journal of Physical Chemistry B, 2003. **107**(40): p. 11048-11056.
44. Chattopadhyay, D., I. Galeska, and F. Papadimitrakopoulos, *Complete elimination of metal catalysts from single wall carbon nanotubes*. Carbon, 2002. **40**(7): p. 985-988.
45. Igarashi, H., H. Murakami, Y. Murakami, S. Maruyama, and N. Nakashima, *Purification and characterization of zeolite-supported single-walled carbon nanotubes catalytically synthesized from ethanol*. Chemical Physics Letters, 2004. **392**(4-6): p. 529-532.
46. Liu, J., A.G. Rinzler, H. Dai, J.H. Hafner, R.K. Bradley, P.J. Boul, A. Lu, T. Iverson, K. Shelimov, C.B. Huffman, F. Rodriguez-Macias, Y.-S. Shon, T.R. Lee, D.T. Colbert, and R.E. Smalley, *Fullerene Pipes*. Science, 1998. **280**(5367): p. 1253-1256.
47. Rinzler, A.G., J. Liu, H. Dai, P. Nikolaev, C.B. Huffman, F.J. Rodríguez-Macías, P.J. Boul, A.H. Lu, D. Heymann, D.T. Colbert, R.S. Lee, J.E. Fischer, A.M. Rao, P.C. Eklund, and R.E. Smalley, *Large-scale purification of single-wall carbon nanotubes: process, product, and characterization*. Applied Physics A: Materials Science & Processing, 1998. **67**(1): p. 29-37.
48. Chen, Y., L. Wei, B. Wang, S. Lim, D. Ciuparu, M. Zheng, J. Chen, C. Zoican, Y. Yang, G.L. Haller, and L.D. Pfefferle, *Low-Defect, Purified, Narrowly (n,m)-Dispersed Single-Walled Carbon Nanotubes Grown from Cobalt-Incorporated MCM-41*. ACS Nano, 2007. **1**(4): p. 327-336.

49. Dillon, A.C., T. Gennett, K.M. Jones, J.L. Alleman, P.A. Parilla, and M.J. Heben, *A Simple and Complete Purification of Single-Walled Carbon Nanotube Materials*. Advanced Materials, 1999. **11**(16): p. 1354-1358.
50. Chiang, I.W., B.E. Brinson, R.E. Smalley, J.L. Margrave, and R.H. Hauge, *Purification and Characterization of Single-Wall Carbon Nanotubes*. The Journal of Physical Chemistry B, 2001. **105**(6): p. 1157-1161.
51. Nepal, D., D.S. Kim, and K.E. Geckeler, *A facile and rapid purification method for single-walled carbon nanotubes*. Carbon, 2005. **43**(3): p. 660-662.
52. Yu, A., E. Bekyarova, M.E. Itkis, D. Fakhruddinov, R. Webster, and R.C. Haddon, *Application of Centrifugation to the Large-Scale Purification of Electric Arc-Produced Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2006. **128**(30): p. 9902-9908.
53. Chiang, I.W., B.E. Brinson, A.Y. Huang, P.A. Willis, M.J. Bronikowski, J.L. Margrave, R.E. Smalley, and R.H. Hauge, *Purification and Characterization of Single-Wall Carbon Nanotubes (SWNTs) Obtained from the Gas-Phase Decomposition of CO (HiPco Process)*. The Journal of Physical Chemistry B, 2001. **105**(35): p. 8297-8301.
54. Itkis, M.E., D.E. Perea, R. Jung, S. Niyogi, and R.C. Haddon, *Comparison of Analytical Techniques for Purity Evaluation of Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2005. **127**(10): p. 3439-3448.
55. Mackeyev, Y., S. Bachilo, K.B. Hartman, and L.J. Wilson, *The purification of HiPco SWCNTs with liquid bromine at room temperature*. Carbon, 2007. **45**(5): p. 1013-1017.
56. Zhang, M., M. Yudasaka, A. Koshio, and S. Iijima, *Thermogravimetric analysis of single-wall carbon nanotubes ultrasonicated in monochlorobenzene*. Chemical Physics Letters, 2002. **364**(3-4): p. 420-426.
57. Itkis, M.E., D.E. Perea, S. Niyogi, S.M. Rickard, M.A. Hamon, H. Hu, B. Zhao, and R.C. Haddon, *Purity Evaluation of As-Prepared Single-Walled Carbon Nanotube Soot by Use of Solution-Phase Near-IR Spectroscopy*. Nano Letters, 2003. **3**(3): p. 309-314.

58. Itkis, M.E., S. Niyogi, M.E. Meng, M.A. Hamon, H. Hu, and R.C. Haddon, *Spectroscopic Study of the Fermi Level Electronic Structure of Single-Walled Carbon Nanotubes*. Nano Letters, 2001. **2**(2): p. 155-159.
59. Hu, H., B. Zhao, M.A. Hamon, K. Kamaras, M.E. Itkis, and R.C. Haddon, *Sidewall Functionalization of Single-Walled Carbon Nanotubes by Addition of Dichlorocarbene*. Journal of the American Chemical Society, 2003. **125**(48): p. 14893-14900.
60. Wu, Z., Z. Chen, X. Du, J.M. Logan, J. Sippel, M. Nikolou, K. Kamaras, J.R. Reynolds, D.B. Tanner, A.F. Hebard, and A.G. Rinzler, *Transparent, Conductive Carbon Nanotube Films*. Science, 2004. **305**(5688): p. 1273-1276.
61. Kamaras, K., M.E. Itkis, H. Hu, B. Zhao, and R.C. Haddon, *Covalent Bond Formation to a Carbon Nanotube Metal*. Science, 2003. **301**(5639): p. 1501-.
62. Hamon, M.A., M.E. Itkis, S. Niyogi, T. Alvaraez, C. Kuper, M. Menon, and R.C. Haddon, *Effect of Rehybridization on the Electronic Structure of Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2001. **123**(45): p. 11292-11293.
63. Hersam, M.C., *Progress towards monodisperse single-walled carbon nanotubes*. Nat Nano, 2008. **3**(7): p. 387-394.
64. Liu, J. and M.C. Hersam, *Recent Developments in Carbon Nanotube Sorting and Selective Growth*. MRS Bulletin, 2010. **35**(4): p. 315-321.
65. Tasis, D., N. Tagmatarchis, A. Bianco, and M. Prato, *Chemistry of Carbon Nanotubes*. Chemical Reviews, 2006. **106**(3): p. 1105-1136.
66. Strano, M.S., *Probing Chiral Selective Reactions Using a Revised Kataura Plot for the Interpretation of Single-Walled Carbon Nanotube Spectroscopy*. Journal of the American Chemical Society, 2003. **125**(51): p. 16148-16153.
67. Strano, M.S., C.A. Dyke, M.L. Usrey, P.W. Barone, M.J. Allen, H. Shan, C. Kittrell, R.H. Hauge, J.M. Tour, and R.E. Smalley, *Electronic Structure Control of Single-Walled Carbon Nanotube Functionalization*. Science, 2003. **301**(5639): p. 1519-1522.

68. An, L., Q. Fu, C. Lu, and J. Liu, *A Simple Chemical Route To Selectively Eliminate Metallic Carbon Nanotubes in Nanotube Network Devices*. Journal of the American Chemical Society, 2004. **126**(34): p. 10520-10521.
69. Balasubramanian, K., R. Sordan, M. Burghard, and K. Kern, *A Selective Electrochemical Approach to Carbon Nanotube Field-Effect Transistors*. Nano Letters, 2004. **4**(5): p. 827-830.
70. Toyoda, S., Y. Yamaguchi, M. Hiwatashi, Y. Tomonari, H. Murakami, and N. Nakashima, *Separation of Semiconducting Single-Walled Carbon Nanotubes by Using a Long-Alkyl-Chain Benzenediazonium Compound*. Chemistry - An Asian Journal, 2007. **2**(1): p. 145-149.
71. Kim, W.-J., M.L. Usrey, and M.S. Strano, *Selective Functionalization and Free Solution Electrophoresis of Single-Walled Carbon Nanotubes: Separate Enrichment of Metallic and Semiconducting SWNT*. Chemistry of Materials, 2007. **19**(7): p. 1571-1576.
72. Lee, C.W., X. Han, F. Chen, J. Wei, Y. Chen, M.B. Chan-Park, and L.-J. Li, *Solution-Processable Carbon Nanotubes for Semiconducting Thin-Film Transistor Devices*. Advanced Materials, 2010. **22**(11): p. 1278-1282.
73. Kanungo, M., H. Lu, G.G. Malliaras, and G.B. Blanchet, *Suppression of Metallic Conductivity of Single-Walled Carbon Nanotubes by Cycloaddition Reactions*. Science, 2009. **323**(5911): p. 234-237.
74. Menard-Moyon, C., N. Izard, E. Doris, and C. Mioskowski, *Separation of Semiconducting from Metallic Carbon Nanotubes by Selective Functionalization with Azomethine Ylides*. Journal of the American Chemical Society, 2006. **128**(20): p. 6552-6553.
75. Banerjee, S. and S.S. Wong, *Selective^{†††} Metallic Tube Reactivity in the Solution-Phase Osmylation of Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2004. **126**(7): p. 2073-2081.
76. An, K.H., J.S. Park, C.-M. Yang, S.Y. Jeong, S.C. Lim, C. Kang, J.-H. Son, M.S. Jeong, and Y.H. Lee, *A Diameter-Selective Attack of Metallic Carbon Nanotubes by Nitronium Ions*. Journal of the American Chemical Society, 2005. **127**(14): p. 5196-5203.

77. Yang, C.-M., J.S. Park, K.H. An, S.C. Lim, K. Seo, B. Kim, K.A. Park, S. Han, C.Y. Park, and Y.H. Lee, *Selective Removal of Metallic Single-Walled Carbon Nanotubes with Small Diameters by Using Nitric and Sulfuric Acids*. The Journal of Physical Chemistry B, 2005. **109**(41): p. 19242-19248.
78. An, K., C.-M. Yang, J. Lee, S. Lim, C. Kang, J.-H. Son, M. Jeong, and Y. Lee, *A diameter-selective chiral separation of single-wall carbon nanotubes using nitronium ions*. Journal of Electronic Materials, 2006. **35**(2): p. 235-242.
79. Banerjee, S. and S.S. Wong, *Demonstration of Diameter-Selective Reactivity in the Sidewall Ozonation of SWNTs by Resonance Raman Spectroscopy*. Nano Letters, 2004. **4**(8): p. 1445-1450.
80. Ramesh, S., H. Shan, E. Haroz, W.E. Billups, R. Hauge, W.W. Adams, and R.E. Smalley, *Diameter Selection of Single-Walled Carbon Nanotubes through Programmable Solvation in Binary Sulfonic Acid Mixtures†*. The Journal of Physical Chemistry C, 2007. **111**(48): p. 17827-17834.
81. Chattopadhyay, D., I. Galeska, and F. Papadimitrakopoulos, *A Route for Bulk Separation of Semiconducting from Metallic Single-Wall Carbon Nanotubes*. Journal of the American Chemical Society, 2003. **125**(11): p. 3370-3375.
82. Maeda, Y., S.-i. Kimura, M. Kanda, Y. Hirashima, T. Hasegawa, T. Wakahara, Y. Lian, T. Nakahodo, T. Tsuchiya, T. Akasaka, J. Lu, X. Zhang, Y. Yu, S. Nagase, S. Kazaoui, N. Minami, T. Shimizu, H. Tokumoto, and R. Saito, *Large-Scale Separation of Metallic and Semiconducting Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2005. **127**(29): p. 10287-10290.
83. Maeda, Y., M. Kanda, M. Hashimoto, T. Hasegawa, S.-i. Kimura, Y. Lian, T. Wakahara, T. Akasaka, S. Kazaoui, N. Minami, T. Okazaki, Y. Hayamizu, K. Hata, J. Lu, and S. Nagase, *Dispersion and Separation of Small-Diameter Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2006. **128**(37): p. 12239-12242.
84. Ramesh, S., L.M. Ericson, V.A. Davis, R.K. Saini, C. Kittrell, M. Pasquali, W.E. Billups, W.W. Adams, R.H. Hauge, and R.E. Smalley, *Dissolution of Pristine Single Walled Carbon Nanotubes in Superacids by Direct Protonation*. The Journal of Physical Chemistry B, 2004. **108**(26): p. 8794-8798.

85. Kim, S.N., Z. Luo, and F. Papadimitrakopoulos, *Diameter and Metallicity Dependent Redox Influences on the Separation of Single-Wall Carbon Nanotubes*. Nano Letters, 2005. **5**(12): p. 2500-2504.
86. Li, H., B. Zhou, Y. Lin, L. Gu, W. Wang, K.A.S. Fernando, S. Kumar, L.F. Allard, and Y.-P. Sun, *Selective Interactions of Porphyrins with Semiconducting Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2004. **126**(4): p. 1014-1015.
87. Ju, S.-Y., J. Doll, I. Sharma, and F. Papadimitrakopoulos, *Selection of carbon nanotubes with specific chiralities using helical assemblies of flavin mononucleotide*. Nat Nano, 2008. **3**(6): p. 356-362.
88. Tromp, R.M., A. Afzali, M. Freitag, D.B. Mitzi, and Z. Chen, *Novel Strategy for Diameter-Selective Separation and Functionalization of Single-Wall Carbon Nanotubes*. Nano Letters, 2008. **8**(2): p. 469-472.
89. Chen, Z., X. Du, M.-H. Du, C.D. Rancken, H.-P. Cheng, and A.G. Rinzler, *Bulk Separative Enrichment in Metallic or Semiconducting Single-Walled Carbon Nanotubes*. Nano Letters, 2003. **3**(9): p. 1245-1249.
90. Park, N., Y. Miyamoto, K. Lee, W. Ih Choi, J. Ihm, J. Yu, and S. Han, *Band gap sensitivity of bromine adsorption at carbon nanotubes*. Chemical Physics Letters, 2005. **403**(1-3): p. 135-139.
91. Lu, J., S. Nagase, X. Zhang, D. Wang, M. Ni, Y. Maeda, T. Wakahara, T. Nakahodo, T. Tsuchiya, T. Akasaka, Z. Gao, D. Yu, H. Ye, W.N. Mei, and Y. Zhou, *Selective Interaction of Large or Charge-Transfer Aromatic Molecules with Metallic Single-Wall Carbon Nanotubes: Critical Role of the Molecular Size and Orientation*. Journal of the American Chemical Society, 2006. **128**(15): p. 5114-5118.
92. McDonald, T.J., C. Engtrakul, M. Jones, G. Rumbles, and M.J. Heben, *Kinetics of PL Quenching during Single-Walled Carbon Nanotube Rebundling and Diameter-Dependent Surfactant Interactions†*. The Journal of Physical Chemistry B, 2006. **110**(50): p. 25339-25346.
93. McDonald, T.J., J.L. Blackburn, W.K. Metzger, G. Rumbles, and M.J. Heben, *Chiral-Selective Protection of Single-walled Carbon Nanotube Photoluminescence*

- by *Surfactant Selection*. The Journal of Physical Chemistry C, 2007. **111**(48): p. 17894-17900.
94. Marquis, R., C. Greco, I. Sadokierska, S. Lebedkin, M.M. Kappes, T. Michel, L. Alvarez, J.-L. Sauvajol, S.p. Meunier, and C. Mioskowski, *Supramolecular Discrimination of Carbon Nanotubes According to Their Helicity*. Nano Letters, 2008. **8**(7): p. 1830-1835.
95. Chen, F., B. Wang, Y. Chen, and L.-J. Li, *Toward the Extraction of Single Species of Single-Walled Carbon Nanotubes Using Fluorene-Based Polymers*. Nano Letters, 2007. **7**(10): p. 3013-3017.
96. Nish, A., J.-Y. Hwang, J. Doig, and R.J. Nicholas, *Highly selective dispersion of single-walled carbon nanotubes using aromatic polymers*. Nat Nano, 2007. **2**(10): p. 640-646.
97. Izard, N., S. Kazaoui, K. Hata, T. Okazaki, T. Saito, S. Iijima, and N. Minami, *Semiconductor-enriched single wall carbon nanotube networks applied to field effect transistors*. Applied Physics Letters, 2008. **92**(24): p. 243112-3.
98. Yan, L.Y., W. Li, X.F. Fan, L. Wei, Y. Chen, J.-L. Kuo, L.-J. Li, S.K. Kwak, Y. Mu, and M.B. Chan-Park, *Enrichment of (8,4) Single-Walled Carbon Nanotubes Through Coextraction with Heparin*. Small, 2010. **6**(1): p. 110-118.
99. Fantini, C., A. Jorio, A.P. Santos, V.S.T. Peressinotto, and M.A. Pimenta, *Characterization of DNA-wrapped carbon nanotubes by resonance Raman and optical absorption spectroscopies*. Chemical Physics Letters, 2007. **439**(1-3): p. 138-142.
100. Doorn, S.K., R.E. Fields, H. Hu, M.A. Hamon, R.C. Haddon, J.P. Selegue, and V. Majidi, *High Resolution Capillary Electrophoresis of Carbon Nanotubes*. Journal of the American Chemical Society, 2002. **124**(12): p. 3169-3174.
101. Krupke, R., F. Hennrich, H.v. Lohneysen, and M.M. Kappes, *Separation of Metallic from Semiconducting Single-Walled Carbon Nanotubes*. Science, 2003. **301**(5631): p. 344-347.
102. Krupke, R., F. Hennrich, M.M. Kappes, and H. v. Lohneysen, *Surface Conductance Induced Dielectrophoresis of Semiconducting Single-Walled Carbon Nanotubes*. Nano Letters, 2004. **4**(8): p. 1395-1399.

103. Krupke, R., S. Linden, M. Rapp, and F. Hennrich, *Thin Films of Metallic Carbon Nanotubes Prepared by Dielectrophoresis*. Advanced Materials, 2006. **18**(11): p. 1468-1470.
104. Hong, S., S. Jung, J. Choi, Y. Kim, and S. Baik, *Electrical Transport Characteristics of Surface-Conductance-Controlled, Dielectrophoretically Separated Single-Walled Carbon Nanotubes*. Langmuir, 2007. **23**(9): p. 4749-4752.
105. Lutz, T. and K.J. Donovan, *Macroscopic scale separation of metallic and semiconducting nanotubes by dielectrophoresis*. Carbon, 2005. **43**(12): p. 2508-2513.
106. Peng, H., N.T. Alvarez, C. Kittrell, R.H. Hauge, and H.K. Schmidt, *Dielectrophoresis Field Flow Fractionation of Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2006. **128**(26): p. 8396-8397.
107. Heller, D.A., R.M. Mayrhofer, S. Baik, Y.V. Grinkova, M.L. Usrey, and M.S. Strano, *Concomitant Length and Diameter Separation of Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2004. **126**(44): p. 14567-14573.
108. Tanaka, T., H. Jin, Y. Miyata, S. Fujii, H. Suga, Y. Naitoh, T. Minari, T. Miyadera, K. Tsukagoshi, and H. Kataura, *Simple and Scalable Gel-Based Separation of Metallic and Semiconducting Carbon Nanotubes*. Nano Letters, 2009. **9**(4): p. 1497-1500.
109. Tanaka, T., Y. Urabe, D. Nishide, and H. Kataura, *Continuous Separation of Metallic and Semiconducting Carbon Nanotubes Using Agarose Gel*. Applied Physics Express, 2009. **2**(Copyright (c) 2009 The Japan Society of Applied Physics): p. 125002.
110. Tanaka, T., H. Jin, Y. Miyata, and H. Kataura, *High-Yield Separation of Metallic and Semiconducting Single-Wall Carbon Nanotubes by Agarose Gel Electrophoresis*. Applied Physics Express, 2008. **1**(Copyright (c) 2008 The Japan Society of Applied Physics): p. 114001.
111. Zheng, M., A. Jagota, E.D. Semke, B.A. Diner, R.S. McLean, S.R. Lustig, R.E. Richardson, and N.G. Tassi, *DNA-assisted dispersion and separation of carbon nanotubes*. Nat Mater, 2003. **2**(5): p. 338-342.

112. Zheng, M., A. Jagota, M.S. Strano, A.P. Santos, P. Barone, S.G. Chou, B.A. Diner, M.S. Dresselhaus, R.S. Mclean, G.B. Onoa, G.G. Samsonidze, E.D. Semke, M. Usrey, and D.J. Walls, *Structure-Based Carbon Nanotube Sorting by Sequence-Dependent DNA Assembly*. Science, 2003. **302**(5650): p. 1545-1548.
113. Strano, M.S., M. Zheng, A. Jagota, G.B. Onoa, D.A. Heller, P.W. Barone, and M.L. Usrey, *Understanding the Nature of the DNA-Assisted Separation of Single-Walled Carbon Nanotubes Using Fluorescence and Raman Spectroscopy*. Nano Letters, 2004. **4**(4): p. 543-550.
114. Zheng, M. and E.D. Semke, *Enrichment of Single Chirality Carbon Nanotubes*. Journal of the American Chemical Society, 2007. **129**(19): p. 6084-6085.
115. Lustig, S.R., A. Jagota, C. Khripin, and M. Zheng, *Theory of Structure-Based Carbon Nanotube Separations by Ion-Exchange Chromatography of DNA/CNT Hybrids*. The Journal of Physical Chemistry B, 2005. **109**(7): p. 2559-2566.
116. Tu, X.M., S. Manohar, A. Jagota, and M. Zheng, *DNA sequence motifs for structure-specific recognition and separation of carbon nanotubes*. Nature, 2009. **460**(7252): p. 250-253.
117. Arnold, M.S., S.I. Stupp, and M.C. Hersam, *Enrichment of Single-Walled Carbon Nanotubes by Diameter in Density Gradients*. Nano Letters, 2005. **5**(4): p. 713-718.
118. Arnold, M.S., A.A. Green, J.F. Hulvat, S.I. Stupp, and M.C. Hersam, *Sorting carbon nanotubes by electronic structure using density differentiation*. Nat Nano, 2006. **1**(1): p. 60-65.
119. Green, A.A. and M.C. Hersam, *Colored Semitransparent Conductive Coatings Consisting of Monodisperse Metallic Single-Walled Carbon Nanotubes*. Nano Letters, 2008. **8**(5): p. 1417-1422.
120. Yanagi, K., Y. Miyata, and H. Kataura, *Optical and Conductive Characteristics of Metallic Single-Wall Carbon Nanotubes with Three Basic Colors; Cyan, Magenta, and Yellow*. Applied Physics Express, 2008. **1**(Copyright (c) 2008 The Japan Society of Applied Physics): p. 034003.
121. Zhao, P., E. Einarsson, R. Xiang, Y. Murakami, and S. Maruyama, *Controllable Expansion of Single-Walled Carbon Nanotube Dispersions Using Density Gradient*

- Ultracentrifugation*. The Journal of Physical Chemistry C, 2010. **114**(11): p. 4831-4834.
122. Kato, Y., Y. Niidome, and N. Nakashima, *Efficient Separation of (6,5) Single-Walled Carbon Nanotubes Using a "Nanometal Sink"*. Angewandte Chemie International Edition, 2009. **48**(30): p. 5435-5438.
 123. Niyogi, S., C.G. Densmore, and S.K. Doorn, *Electrolyte Tuning of Surfactant Interfacial Behavior for Enhanced Density-Based Separations of Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2008. **131**(3): p. 1144-1153.
 124. Fagan, J.A., M.L. Becker, J. Chun, P. Nie, B.J. Bauer, J.R. Simpson, A. Hight-Walker, and E.K. Hobbie, *Centrifugal Length Separation of Carbon Nanotubes*. Langmuir, 2008. **24**(24): p. 13880-13889.
 125. Green, A.A. and M.C. Hersam, *Processing and properties of highly enriched double-wall carbon nanotubes*. Nat Nano, 2009. **4**(1): p. 64-70.
 126. Sato, Y., K. Yanagi, Y. Miyata, K. Suenaga, H. Kataura, and S. Iijima, *Chiral-Angle Distribution for Separated Single-Walled Carbon Nanotubes*. Nano Letters, 2008. **8**(10): p. 3151-3154.
 127. Arnold, M.S., J. Suntivich, S.I. Stupp, and M.C. Hersam, *Hydrodynamic Characterization of Surfactant Encapsulated Carbon Nanotubes Using an Analytical Ultracentrifuge*. ACS Nano, 2008. **2**(11): p. 2291-2300.
 128. Nair, N., W.-J. Kim, R.D. Braatz, and M.S. Strano, *Dynamics of Surfactant-Suspended Single-Walled Carbon Nanotubes in a Centrifugal Field*. Langmuir, 2008. **24**(5): p. 1790-1795.
 129. Nagasawa, S., M. Yudasaka, K. Hirahara, T. Ichihashi, and S. Iijima, *Effect of oxidation on single-wall carbon nanotubes*. Chemical Physics Letters, 2000. **328**(4-6): p. 374-380.
 130. Miyata, Y., T. Kawai, Y. Miyamoto, K. Yanagi, Y. Maniwa, and H. Kataura, *Chirality-Dependent Combustion of Single-Walled Carbon Nanotubes*. The Journal of Physical Chemistry C, 2007. **111**(27): p. 9671-9677.

131. Huang, H., R. Maruyama, K. Noda, H. Kajiura, and K. Kadono, *Preferential Destruction of Metallic Single-Walled Carbon Nanotubes by Laser Irradiation*. The Journal of Physical Chemistry B, 2006. **110**(14): p. 7316-7320.
132. Zhang, Y., Y. Zhang, X. Xian, J. Zhang, and Z. Liu, *Sorting out Semiconducting Single-Walled Carbon Nanotube Arrays by Preferential Destruction of Metallic Tubes Using Xenon-Lamp Irradiation*. The Journal of Physical Chemistry C, 2008. **112**(10): p. 3849-3856.
133. Yang, C.-M., K.H. An, J.S. Park, K.A. Park, S.C. Lim, S.-H. Cho, Y.S. Lee, W. Park, C.Y. Park, and Y.H. Lee, *Preferential etching of metallic single-walled carbon nanotubes with small diameter by fluorine gas*. Physical Review B (Condensed Matter and Materials Physics), 2006. **73**(7): p. 075419-7.
134. Zhang, G., P. Qi, X. Wang, Y. Lu, X. Li, R. Tu, S. Bangsaruntip, D. Mann, L. Zhang, and H. Dai, *Selective Etching of Metallic Carbon Nanotubes by Gas-Phase Reaction*. Science, 2006. **314**(5801): p. 974-977.
135. Collins, P.G., M.S. Arnold, and P. Avouris, *Engineering Carbon Nanotubes and Nanotube Circuits Using Electrical Breakdown*. Science, 2001. **292**(5517): p. 706-709.

Chapter 2

General Experimental Methods

Monodisperse SWCNTs are promising candidates for macroelectronic applications, such as field effect transistors (FETs) [1-2], optoelectronic devices [3], and electromagnetic interference shielding [4-5]. Various post-synthetic sorting methods have been developed to obtain monodisperse SWCNTs. Purification and chiral selective enrichment of SWCNTs obtained from Co-MCM-41 catalyst was studied in this thesis. In this chapter, catalyst and SWCNT synthesis methods and basic purification methods used in this thesis were introduced. Furthermore, the basic principles of different characterization techniques and their applications in this thesis were also discussed.

2.1 Catalyst and SWCNT synthesis

A novel catalyst, cobalt incorporated MCM-41 (Co-MCM-41), was synthesized to provide large quantity of high purity SWCNTs with narrow chirality distribution for further purification and enrichment studies. Catalyst was synthesized following a reported protocol [6-7]. Briefly, tetramethylammonium silicate aqueous solution ($((\text{CH}_3)_4\text{N}(\text{OH})\cdot 2\text{SiO}_2$, 10% as Si, Sigma-Aldrich) was mixed with Cabosil® M-5 (Riedel-de-Haen) aqueous solution as silica source. $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ (99%, Sigma-Aldrich) salt was used as metal precursor. Hexadecyltrimethylammonium bromide ($\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{Br})(\text{CH}_3)_3$, HTAB, 99%, Sigma-Aldrich) solution, pretreated using an ion-exchange resin (Ambersep® 900, Sigma-Aldrich), was added to the mixture; and the pH of the mixture was adjusted using acetic acid (Merck). Metal content (Co) was kept at 3 wt%. The solution was autoclaved at 120°C

for 6 days. Purple colored solids were recovered from the solution, and then washed with water and dried in oven. The resulting powders were calcined in air flow at 540°C to remove remaining organic compounds.

In general, the CVD SWCNT synthesis process used in this study contains three major steps: catalyst prereduction, nanotube growth and protected cooling. Firstly, about 200 mg of Co-MCM-41 catalyst was loaded into an alumina boat and placed at the center of a tube reactor in a furnace. The catalyst was then reduced in 1 bar hydrogen (H₂, 99.999%, Soxal) gas flow under a temperature ramp of 10 °C/min to desired temperatures. After catalyst reduction, the reactor was purged with argon gas (Ar, 99.99%, Soxal), while temperature was continually increased to 800 °C. After temperature was stabilized, carbon monoxide gas (CO, 99.99%, Soxal) of 6-bar was introduced into the reactor as carbon precursor at a flow rate of 100 sccm. The SWCNT growth time was set to 60 min under CO. Finally, the reactor was cooled down to room temperature under Ar gas protection before the catalyst was collected from the reactor.

2.2 SWCNT purification

As-synthesized SWCNTs from Co-MCM-41 catalysts were a mixture of SWCNTs together with different impurities, including amorphous carbon, graphite, MWCNTs (carbon impurities), catalyst support (amorphous silica) and metal particles. High purity SWCNTs are desired for their potential applications. Two different purification methods were utilized in this thesis: the first one is a previous developed 4-step purification method, including washing by NaOH solution twice, refluxing in HCl, oxidation by O₂, followed by refluxing in HCl for the second time [8]. The second one is a new ultracentrifugation based

purification method with assistance of surfactants [9]. The details of the second purification method will be further discussed in Chapter 3.

2.3 Characterization techniques

Various characterization techniques have been utilized in this thesis to investigate physicochemical properties of catalysts and SWCNT samples. The aims are to examine the quality of catalysts; observe the morphology of catalyst and nanotube samples; evaluate the purity of SWCNTs; and assess the (n,m) distribution of different SWCNT samples. The principles and experimental procedures of these techniques are briefly discussed in this Chapter.

2.3.1 N₂ physisorption

The pore structure of Co-MCM-41 catalyst is critical to its performance in SWCNT synthesis. N₂ physisorption is an effective tool to determine the pore structure of Co-MCM-41. In a typical experiment, liquid N₂ is adsorbed on the solid surface of catalyst at 77 K, while desorption would readily occur simultaneously. The correlation between the amount of N₂ adsorbed and the pressure of N₂ at equilibrium is called adsorption isotherm. Adsorption isotherms have been classified into several common types [10]. MCM-41 material has the type IV isotherm. At low pressure ($P/P_0 < 0.25$), monolayer N₂ molecules would adsorb on the surface. With the increase of N₂ partial pressure, N₂ would form multilayers until condensation happens. This phenomenon results in a sharp increase in N₂ intake, displaying as a sharp step on the physisorption isotherm [11]. The surface area of catalyst can be calculated from its N₂ physisorption isotherm by Brunauer-Emmett-Teller

(BET) method [12]; and the pore volume and pore size are obtained by Barret-Joyner-Halenda (BJH) method [13]. In this study, nitrogen adsorption-desorption isotherms were measured using a static volumetric instrument Quanta Chrome Autosorb-6B.

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2.3.2 Temperature programmed reduction (TPR)

TPR is commonly used to characterize the interaction between metal species and their catalyst supports, as well as the surface chemical environment of catalysts. It is important to ensure that each batch of synthesized Co-MCM-41 catalysts has similar chemical properties, so that the properties of produced SWCNTs can be well controlled. TPR experiments were performed on a customized TPR setup, the thermal conductivity detector (TCD) of a Techcomp® 7900 gas phase chromatograph was used to monitor the variation in the gas flow. For a typical test, 100 mg of catalyst was loaded into a customized quartz tube; and pre-calcined in air flow at 500 °C for 60 min. This step helps to obtain a clean catalyst surface. After the quartz tube was cooled down to room temperature, a H₂ (5 % in Ar, Soxal) gas flow was introduced at 30 sccm. When the TCD signal became stable, the sample was heated up to 950 °C at a ramp rate of 5 °C/min and soaked at 950 °C for 30 min. Different metal oxides can be reduced at different temperatures. Some H₂ would be consumed during the reduction and form water. The generated water was removed by an acetone-liquid nitrogen cold trap. The consumption of H₂ resulted in thermal conductivity changes of the H₂ flow, leading to observable peaks in their TCD signals. Thus, the reduction temperatures of different metal species on the catalyst could be monitored.

2.3.3 Atomic force microscope (AFM)

AFM is an efficient tool for surface science study with a resolution at nanometer scale. It controls a cantilever with a sharp tip to interact with samples located on a surface. The cantilever is typically made of silicon or silicon nitride with a tip radius or curvature at nanometer scale. During the measurement, such a tip is brought close to a surface. Forces between the tip and the surface lead to some deflection of the cantilever. The force may be originated from mechanical contact, van der Waals interaction, surface tension, chemical bonding, or electrostatic bonding, *etc.* The deflection of the cantilever is measured through a laser spot reflected from the top of the cantilever to a detector. In this study, AFM was used to characterize the morphology of SWCNTs deposited on flat substrates, for example, SWCNT networks found in various macroelectronic devices. A MPF3D microscope from Asylum Research, operating in tapping mode, was used in this thesis. Typically, a Si cantilever (Arrow™ NC, Nanoworld) was used. The resolution of all AFM images was set to 512 lines $\times$ 512 pixels, and imaging sizes were varied for different samples.

2.3.4 Thermogravimetric analysis (TGA)

TGA is used to determine phase change or reaction temperature of samples under certain environments. By monitoring the weight change of samples against precisely controlled temperature ramps, the reaction temperatures, *e.g.*, reduction, decomposition and oxidation, can be determined. Differential thermogravimetric (DTG) profiles derived from TGA data may be used to unveil the exact reaction temperatures of samples and their compositions. Deconvolution of DTG curves sometimes provides weight percentages of different species in samples. In this thesis, TGA was used to analyze different carbon species in SWCNT samples. Generally, various carbon species have different oxidization

temperatures, *e.g.*, amorphous carbon is oxidized in air around 250 ~ 350 °C. SWCNTs are at 420 ~ 550 °C, depending on their diameters and abundance of defects. The oxidation temperature of MWCNTs would be as high as 700 °C, and graphite is oxidized around 800 °C. Larger diameter carbon nanotubes with fewer defects would have higher oxidation temperature. Metal nanoparticles existing in CNT samples can significantly reduce their oxidation temperature [14-15]. TGA experiments in this thesis were conducted on a PerkinElmer Diamond TG/DTA equipment. A sample was first kept at 110 °C for 30 min to remove moisture. Then the sample was heated up to 1025 °C under high purity air flow (50 sccm) in a ramp of 10 °C/min while its weight was continually monitored. The same temperature ramp was repeated again after the instrument was cooled down to room temperature. The recorded data was used as a baseline to correct the initial weight profile.

2.3.5 Raman spectroscopy

The vibration energies in SWCNTs can be quantized as phonons. The unique 1-D physical structure of SWCNTs results in diversified phonon dispersions. Raman spectroscopy can be used to characterize the structure of SWCNTs by probing their phonon dispersions. Raman spectroscopy relies on Raman scattering, an incident photon would interact with phonons resulting in energy shifts in the scattered photon. Figure 2-1 shows a schematic illustration of this scattering process. First, an electron would be excited to a virtual excited state by absorbing an incident photon, and then it relaxes back to the ground state by emitting a scattered photon. Accurate phonon modes can be obtained by measuring the differences between incident and scattered photons. Raman signals are usually very weak because only small fraction of photons would undergo Raman scattering

(approximately 1 in 10 million incident photons) [16]. When the absorbed or emitted photon energies (E_L) are close to the electronic state energy gaps (ΔE) of the molecule, much stronger resonance Raman signals can be obtained. In order to characterize different chiral species in a SWCNT sample, an ideal solution would be incidentally exciting the electrons by a laser source with tunable continuous energies; however such a laser source is usually expensive and not widely available. Normally, laser sources with multiple lines, which match of main chiral species in SWCNT samples, are utilized in the Raman spectroscopy characterization of SWCNTs.

Figure 2-1 A schematic illustration of typical Raman scattering processes.

Figure 2-2 A typical Raman spectrum acquired from a SWCNT bundle.

Figure 2-2 shows a typical Raman spectrum obtained from a SWCNT sample. Three features can be identified in the spectrum, which provide abundant structural information of the sample. The RBM in the low frequency range ($100 \sim 500 \text{ cm}^{-1}$) is a unique phonon mode of SWCNTs. It comes from the coherent vibration of carbon atoms along the nanotube radial direction as if the nanotube is breathing. RBM feature can be used to not only identify the existence of SWCNTs in a sample, but also assess different nanotube chiral species and their abundance. In general, the frequency of a nanotube RBM peak is inversely proportional to the diameter of the nanotube, which can be calculated by the following equation:

$$\omega_{RBM} = A/d_t + B \quad (1)$$

where A and B are two constants [17-19]. This equation is applicable for SWCNTs with diameters ranging from $1 \sim 2 \text{ nm}$ [20]. Furthermore, Kataura plot has been developed, which shows the correlation between the diameter and chirality of SWCNTs and their RBM

frequency [17]. (n,m) structures of SWCNT samples can be assigned by using continuous energy laser sources. The D-band around 1350 cm^{-1} comes from defect sites in SWCNTs and/or impurities such as amorphous carbon. The intensity ratio between D-band and G-band is often used to evaluate the purity of SWCNT samples. The G-band of SWCNTs can be split into two parts, the G^+ ($\sim 1590\text{ cm}^{-1}$) and G^- ($\sim 1570\text{ cm}^{-1}$) peaks, compared to a single peak centered around 1582 cm^{-1} of graphite or MWCNTs. The G^+ and G^- peaks originate from electron vibrations along the nanotube axis and nanotube circumference direction, respectively [21]. The lineshape and intensity of the G^- peak are sensitive to the content of metallic nanotubes in SWCNT samples. The Breit-Wigner-Fano (BWF) lineshape is commonly used to simulate the G band of SWCNT samples containing a large fraction of metallic nanotubes, while Lorentzian lineshape is used for semiconducting nanotubes [22-23].

In this study, Raman spectroscopy has been utilized to evaluate SWCNT purity and assess their chiral and diameter distribution. Raman spectra were acquired on a Renishaw Ramanscope in backscattering configuration equipped with 514.5 nm (2.41 eV), 633 nm (1.96 eV) and 785 nm (1.58 eV) lasers. Spectra excited by 488 nm laser (2.54 eV) were recorded on an Alpha 300 micro Raman microscope by WITec. All spectra were averaged over at least five random spots over SWCNT samples.

2.3.6 Photoluminescence (PL) spectroscopy

Photoluminescence involves photon-electron interactions. SWCNTs have sharp van Hove singularities (VHSs) in their band structure. The energy levels of the VHSs are labeled as $v_1, v_2 \dots v_i$ for valence bands and $c_1, c_2 \dots c_i$ for conduction bands. E_{ij} denotes the

transition energy between the corresponding v_i and the c_j energy levels. A typical semiconducting SWCNT band structure and its PL process are shown in Figure 2-3. An electron is first excited to an excited electronic state by absorbing a photon (E_{22}). Then, the excited electron steps down to the lowest vibrational level of the excited state. Next, the excited electron relaxes back to a ground state by emitting a photon (E_{11}) [24]. For a metallic nanotube, the density of state is nonzero at its Fermi level, and the excited electron would decay through such a channel back to the valence band without emitting photons.

Figure 2-3 Typical band structure and photoluminescence of a semiconducting SWCNT [25].

PL spectroscopy is a powerful tool to access the (n,m) distribution of semiconducting SWCNT samples. The excitation (E_{22}) and emission (E_{11}) energy pairs are unique to

particular (n,m) nanotubes. Their values have been calculated using different theoretical models, such as the tight-binding model [26] and the zone folding approximation [27-28]. Thus, the (n,m) species in SWCNT samples can be identified on the 2D excitation-emission PL intensity contour plot as shown in Figure 2-4. It should be noted that excitons on semiconducting nanotubes are highly mobile. When a semiconducting nanotube contacts with a metallic one, its PL emission can be easily eliminated due to the existence of additional exciton relaxing pathways. Individualizing SWCNT samples are necessary for a successful PL characterization. Various methods have been developed to disperse SWCNTs for PL characterization. In this thesis, SWCNTs were dispersed in surfactant solutions by sonication. PL spectra were collected on a Jobin-Yvon Nanolog-3 spectrofluorometer, equipped with an IGA (InGaAs) near-infrared (NIR) detector (800~1700 nm) and a 450 W Xenon lamp as the excitation light source.

Figure 2-4 Typical PL spectra of SWCNTs obtained from Co-MCM-41 catalyst, (a) a 3-D plot and (b) a 2D contour plot.

2.3.7 UV-vis-NIR absorption spectroscopy

PL spectroscopy can only detect semiconducting SWCNTs. UV-vis-NIR absorption spectroscopy is used to characterize both metallic and semiconducting nanotubes. A typical absorption spectrum of SWCNTs is shown in Figure 2-5. Peaks on the absorption spectrum correlate with bandgaps of the corresponding v_i and the c_j energy levels. Absorption peaks may be overlapped because the bandgaps of nanotubes may be close to each other. The background of an absorption spectrum is contributed by the π -plasmon resonance of carbonaceous impurities; and it has been utilized to evaluate the purity of SWCNT samples [14, 29]. Absorption spectrum may also be used to assess the (n,m) distribution of SWCNT samples through spectrum deconvolution [30]. In this thesis, UV-vis-NIR absorption spectra were obtained on a Varian Cary 5000 UV-vis-NIR spectrophotometer.

Figure 2-5 A typical UV-vis-NIR absorption spectrum of SWCNTs.

2.4 (n,m) abundance evaluation

In order to develop efficient chiral selective enrichment methods, accurate and convenient (n,m) abundance evaluation is necessary. Raman[17], PL [31] and UV-vis-NIR absorption spectroscopy [30] are the commonly used characterization techniques to identify the (n,m) structures of SWCNT samples. Raman spectroscopy provides such information by the RBM shifts and G-band peak lineshape. However, lasers with multiple excitations or continuous tunable excitation energies are needed for SWCNT samples containing different chiral species. PL spectroscopy can only provide detailed (n,m) assignment for semiconducting nanotubes. Even though UV-vis-NIR absorption spectroscopy can detect both metallic and semiconducting nanotubes, their absorption peaks are highly overlapped for common SWCNT samples. And it is difficult to deconvolute such absorption spectra. All three techniques have some shortcomings in (n,m) abundance evaluation.

A fundamental challenge in (n,m) abundance evaluation is that the experimentally observed signal intensity (I^{exp}) depends on not only the SWCNT concentration but also the chiral dependent intrinsic property (I^{cal}) of SWCNTs. In general, the observed intensity can be expressed by the following simplified equation:

$$I^{exp} = \eta \cdot I^{cal} \cdot C \quad (2)$$

where η is the detection efficiency of the instrument, C is the concentration of SWCNTs, I^{cal} stands for the intrinsic Raman scattering efficiency [18], the PL quantum efficiency [32], or the absorption extinction coefficient [30]. Various theoretical models have been proposed to predict such intrinsic properties [33]. Popov *et al.* calculated the Raman scattering efficiency of 50 semiconducting nanotubes by a symmetry-adapted nonorthogonal tight-binding model [34]. Jiang *et al.* investigated various metallic

nanotubes [35]. Reich *et al.* proposed an exciton-exciton resonance mechanism to determine the PL quantum efficiency [36], and the results were used to explain the diameter and chiral angle dependence PL results observed by O'Connell *et al.* [37]. Oyama *et al.* developed a single particle tight-binding theory to calculate the PL quantum efficiency and the absorption extinction coefficient [32].

The calculated intrinsic properties of SWCNTs have been utilized in the (n,m) abundance evaluation. For example, the observed Raman intensity (I^{exp}) of different (n,m) species in CoMoCat SWCNT samples was divided by their predicted Raman scattering efficiency, I_{RBM}^{cal} , to determine their concentration [38]. Oyama *et al.* applied the similar strategy in PL spectroscopy [32]. Luo *et al.* evaluated the accuracy of the exciton-exciton resonance model and the electron-phonon model by reconstructing the absorption spectra of SWCNTs obtained from Co-MCM-41 catalyst [32, 36, 39]. Their results demonstrated that the electron-phonon model by Oyama *et al.* provides a more accurate (n,m) abundance evaluation. In this thesis, the I_{PL}^{cal} values proposed by Oyama *et al.* have been adopted to determine the semiconducting nanotube populations by PL spectroscopy.

It should be noted that, other than the intrinsic properties of different chiral species, many environmental factors could also influence the PL intensity of SWCNTs [40-42]. One method was proposed to limit such influences. As illustrated in Figure 2-6, the partial differentiation intensity instead of the direct PL emission intensity can be used to calculate the (n,m) population [2]. Both methods have been applied and compared in this thesis. Results of (n,m) abundance evaluation for different samples were discussed in following chapters.

Figure 2-6 (a) A 2D excitation-emission intensity PL map, (b) The partial deviation intensity map obtained from (a), (c) and (d) the measured emission intensity and its partial deviation vs. the emission wavelength.

2.5 Reference

1. An, K.H., J.S. Park, C.M. Yang, S.Y. Jeong, S.C. Lim, C. Kang, J.H. Son, M.S. Jeong, and Y.H. Lee, *A diameter-selective attack of metallic carbon nanotubes by nitronium ions*. Journal of the American Chemical Society, 2005. **127**(14): p. 5196-5203.
2. Arnold, M.S., A.A. Green, J.F. Hulvat, S.I. Stupp, and M.C. Hersam, *Sorting carbon nanotubes by electronic structure using density differentiation*. Nature Nanotechnology, 2006. **1**(1): p. 60-65.

3. Sakakibara, Y., A.G. Rozhin, H. Kataura, Y. Achiba, and M. Tokumoto, *Carbon nanotube-poly(vinylalcohol) nanocomposite film devices: Applications for femtosecond fiber laser mode lockers and optical amplifier noise suppressors*. Japanese Journal of Applied Physics Part 1-Regular Papers Short Notes & Review Papers, 2005. **44**(4A): p. 1621-1625.
4. Li, N., Y. Huang, F. Du, X.B. He, X. Lin, H.J. Gao, Y.F. Ma, F.F. Li, Y.S. Chen, and P.C. Eklund, *Electromagnetic interference (EMI) shielding of single-walled carbon nanotube epoxy composites*. Nano Letters, 2006. **6**(6): p. 1141-1145.
5. Yang, Y.L. and M.C. Gupta, *Novel carbon nanotube-polystyrene foam composites for electromagnetic interference shielding*. Nano Letters, 2005. **5**(11): p. 2131-2134.
6. Ciuparu, D., Y. Chen, Y. Yang, L. Pfefferle, and G.L. Haller, *Pore Curvature Effect on the Stability of Co-MCM-41 and the Formation of Size-Controllable Subnanometer Co Clusters*. The Journal of Physical Chemistry B, 2005. **109**(6): p. 2285-2294.
7. Lim, S., D. Ciuparu, C. Pak, F. Dobek, Y. Chen, D. Harding, L. Pfefferle, and G. Haller, *Synthesis and Characterization of Highly Ordered Co-MCM-41 for Production of Aligned Single Walled Carbon Nanotubes (SWNT)*. The Journal of Physical Chemistry B, 2003. **107**(40): p. 11048-11056.
8. Chen, Y., L. Wei, B. Wang, S. Lim, D. Ciuparu, M. Zheng, J. Chen, C. Zoican, Y. Yang, G.L. Haller, and L.D. Pfefferle, *Low-Defect, Purified, Narrowly (n,m)-Dispersed Single-Walled Carbon Nanotubes Grown from Cobalt-Incorporated MCM-41*. ACS Nano, 2007. **1**(4): p. 327-336.
9. Wei, L., B. Wang, Q. Wang, L.-J. Li, Y. Yang, and Y. Chen, *Effect of Centrifugation on the Purity of Single-Walled Carbon Nanotubes from MCM-41 Containing Cobalt*. The Journal of Physical Chemistry C, 2008. **112**(45): p. 17567-17575.
10. Sing, K.S.W., *Physisorption of nitrogen by porous materials*. Journal of Porous Materials, 1995. **2**(1): p. 5-8.
11. Selvam, P., S.K. Bhatia, and C.G. Sonwane, *Recent Advances in Processing and Characterization of Periodic Mesoporous MCM-41 Silicate Molecular Sieves*. Industrial & Engineering Chemistry Research, 2001. **40**(15): p. 3237-3261.

12. Brunauer, S., P.H. Emmett, and E. Teller, *Adsorption of Gases in Multimolecular Layers*. Journal of the American Chemical Society, 1938. **60**(2): p. 309-319.
13. Barrett, E.P., L.G. Joyner, and P.P. Halenda, *The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms*. Journal of the American Chemical Society, 1951. **73**(1): p. 373-380.
14. Itkis, M.E., D.E. Perea, R. Jung, S. Niyogi, and R.C. Haddon, *Comparison of Analytical Techniques for Purity Evaluation of Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2005. **127**(10): p. 3439-3448.
15. Shi, Z., Y. Lian, F. Liao, X. Zhou, Z. Gu, Y. Zhang, and S. Iijima, *Purification of single-wall carbon nanotubes*. Solid State Communications, 1999. **112**(1): p. 35-37.
16. Harris, D.C., *Symmetry and spectroscopy : an introduction to vibrational and electronic spectroscopy* 1989: Dover Publications.
17. Jorio, A., R. Saito, J.H. Hafner, C.M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, and M.S. Dresselhaus, *Structural (n,m) Determination of Isolated Single-Wall Carbon Nanotubes by Resonant Raman Scattering*. Physical Review Letters, 2001. **86**(6): p. 1118.
18. Milnera, M., J. Kürti, M. Hulman, and H. Kuzmany, *Periodic Resonance Excitation and Intertube Interaction from Quasicontinuous Distributed Helicities in Single-Wall Carbon Nanotubes*. Physical Review Letters, 2000. **84**(6): p. 1324.
19. Souza Filho, A.G., S.G. Chou, G.G. Samsonidze, G. Dresselhaus, M.S. Dresselhaus, L. An, J. Liu, A.K. Swan, M.S. Ünlü, B.B. Goldberg, A. Jorio, A. Grüneis, and R. Saito, *Stokes and anti-Stokes Raman spectra of small-diameter isolated carbon nanotubes*. Physical Review B, 2004. **69**(11): p. 115428.
20. Kurti, J., V. Zolyomi, M. Kertesz, and G. Sun, *The geometry and the radial breathing mode of carbon nanotubes: beyond the ideal behaviour*. New Journal of Physics, 2003. **5**: p. 1-21.
21. Rao, A.M., E. Richter, S. Bandow, B. Chase, P.C. Eklund, K.A. Williams, S. Fang, K.R. Subbaswamy, M. Menon, A. Thess, R.E. Smalley, G. Dresselhaus, and M.S. Dresselhaus, *Diameter-selective Raman scattering from vibrational modes in carbon nanotubes*. Science, 1997. **275**(5297): p. 187-191.

22. Brown, S.D.M., A. Jorio, P. Corio, M.S. Dresselhaus, G. Dresselhaus, R. Saito, and K. Kneipp, *Origin of the Breit-Wigner-Fano lineshape of the tangential G-band feature of metallic carbon nanotubes*. Physical Review B, 2001. **63**(15): p. 155414.
23. Pimenta, M.A., A. Marucci, S.A. Empedocles, M.G. Bawendi, E.B. Hanlon, A.M. Rao, P.C. Eklund, R.E. Smalley, G. Dresselhaus, and M.S. Dresselhaus, *Raman modes of metallic carbon nanotubes*. Physical Review B, 1998. **58**(24): p. R16016.
24. Weisman, R.B. and S.M. Bachilo, *Dependence of Optical Transition Energies on Structure for Single-Walled Carbon Nanotubes in Aqueous Suspension: An Empirical Kataura Plot*. Nano Lett., 2003. **3**(9): p. 1235-1238.
25. Weisman, R.B., *Fluorescence Spectroscopy of Single-Walled Carbon Nanotubes*, in *Applied Physics of Nanotubes: Fundamentals of Theory, Optics, and Transport Devices* 2005, Springer. p. 183-202.
26. Kataura, H., Y. Kumazawa, Y. Maniwa, I. Umez, S. Suzuki, Y. Ohtsuka, and Y. Achiba, *Optical properties of single-wall carbon nanotubes*. Synthetic Metals, 1999. **103**(1-3): p. 2555-2558.
27. Mintmire, J.W. and C.T. White, *Universal Density of States for Carbon Nanotubes*. Physical Review Letters, 1998. **81**(12): p. 2506.
28. Charlier, J.C. and P. Lambin, *Electronic structure of carbon nanotubes with chiral symmetry*. Physical Review B, 1998. **57**(24): p. R15037.
29. Itkis, M.E., D.E. Perea, S. Niyogi, S.M. Rickard, M.A. Hamon, H. Hu, B. Zhao, and R.C. Haddon, *Purity Evaluation of As-Prepared Single-Walled Carbon Nanotube Soot by Use of Solution-Phase Near-IR Spectroscopy*. Nano Letters, 2003. **3**(3): p. 309-314.
30. Hagen, A. and T. Hertel, *Quantitative Analysis of Optical Spectra from Individual Single-Wall Carbon Nanotubes*. Nano Letters, 2003. **3**(3): p. 383-388.
31. Bachilo, S.M., M.S. Strano, C. Kittrell, R.H. Hauge, R.E. Smalley, and R.B. Weisman, *Structure-Assigned Optical Spectra of Single-Walled Carbon Nanotubes*. Science, 2002. **298**(5602): p. 2361-2366.
32. Oyama, Y., R. Saito, K. Sato, J. Jiang, G.G. Samsonidze, A. Gruneis, Y. Miyauchi, S. Maruyama, A. Jorio, G. Dresselhaus, and M.S. Dresselhaus, *Photoluminescence intensity of single-wall carbon nanotubes*. Carbon, 2006. **44**(5): p. 873-879.

33. Dresselhaus, M.S., G. Dresselhaus, R. Saito, and A. Jorio, *Raman spectroscopy of carbon nanotubes*. Physics Reports, 2005. **409**(2): p. 47-99.
34. Popov, V.N., L. Henrard, and P. Lambin, *Resonant Raman Intensity of the Radial Breathing Mode of Single-Walled Carbon Nanotubes within a Nonorthogonal Tight-Binding Model*. Nano Letters, 2004. **4**(9): p. 1795-1799.
35. Jiang, J., R. Saito, A. Gruneis, S.G. Chou, G.S. Ge, A. Jorio, G. Dresselhaus, and M.S. Dresselhaus, *Intensity of the resonance Raman excitation spectra of single-wall carbon nanotubes*. Physical Review B (Condensed Matter and Materials Physics), 2005. **71**(20): p. 205420.
36. Reich, S., C. Thomsen, and J. Robertson, *Exciton Resonances Quench the Photoluminescence of Zigzag Carbon Nanotubes*. Physical Review Letters, 2005. **95**(7): p. 077402.
37. O'Connell, M.J., S.M. Bachilo, C.B. Huffman, V.C. Moore, M.S. Strano, E.H. Haroz, K.L. Rialon, P.J. Boul, W.H. Noon, C. Kittrell, J. Ma, R.H. Hauge, R.B. Weisman, and R.E. Smalley, *Band Gap Fluorescence from Individual Single-Walled Carbon Nanotubes*. Science, 2002. **297**(5581): p. 593-596.
38. Jorio, A., A.P. Santos, H.B. Ribeiro, C. Fantini, M. Souza, J.P.M. Vieira, C.A. Furtado, J. Jiang, R. Saito, L. Balzano, D.E. Resasco, and M.A. Pimenta, *Quantifying carbon-nanotube species with resonance Raman scattering*. Physical Review B (Condensed Matter and Materials Physics), 2005. **72**(7): p. 075207.
39. Luo, Z., L.D. Pfefferle, G.L. Haller, and F. Papadimitrakopoulos, *(n,m) Abundance Evaluation of Single-Walled Carbon Nanotubes by Fluorescence and Absorption Spectroscopy*. J. Am. Chem. Soc., 2006. **128**(48): p. 15511-15516.
40. Chou, S.G., F. Plentz, J. Jiang, R. Saito, D. Nezich, H.B. Ribeiro, A. Jorio, M.A. Pimenta, G.G. Samsonidze, A.P. Santos, M. Zheng, G.B. Onoa, E.D. Semke, G. Dresselhaus, and M.S. Dresselhaus, *Phonon-Assisted Excitonic Recombination Channels Observed in DNA-Wrapped Carbon Nanotubes Using Photoluminescence Spectroscopy*. Physical Review Letters, 2005. **94**(12): p. 127402.
41. Kiowski, O., K. Arnold, S. Lebedkin, F. Hennrich, and M.M. Kappes, *Direct observation of deep excitonic states in the photoluminescence spectra of single-walled carbon nanotubes*. Physical Review Letters, 2007. **99**(23).

42. Lebedkin, S., F. Hennrich, O. Kiowski, and M.M. Kappes, *Photophysics of carbon nanotubes in organic polymer-toluene dispersions: Emission and excitation satellites and relaxation pathways*. Physical Review B, 2008. 77(16).

Chapter 3

A Purification Method Based on Centrifugation

This chapter focuses on a purification method based on high-speed centrifugation, which enables the production of SWCNTs with one of the highest reported purity indices.

Centrifugation is an essential step in many nanotube purification methods [1-2]. Discovery of band gap luminescence from individual SWCNTs is made possible by centrifugation of SDS dispersed nanotubes after removing nanotube bundles [2]. Bulk purification methods using centrifugation was also found to be effective in removing amorphous carbon [3] and carbon nanoparticles [4]. Gradient ultracentrifugation has recently been intensively studied for selective enrichment of certain (n,m) SWCNTs [5]. Ideally, the subtle density difference among SWCNTs and various impurities (both non-nanotube impurities and undesired nanotubes) should enable a precise separation of different fractions in SWCNT samples.

A novel catalyst, Co-MCM-41 has been developed [6-8]. Through precise control of subnanometer scale metal clusters in MCM-41 template, this catalyst produces SWCNTs with very narrow diameter distribution containing ca. 20 different (n,m) nanotubes [9]. A mild, four-step purification procedure using NaOH reflux, HCl wash, and oxidation by 4 mol % molecular oxygen has been developed to purify SWCNTs from Co-MCM-41 [10]. However, acid treatments, including HF, HNO₃, H₂SO₄, and HCl, inevitably destroy some SWCNTs. Therefore, it is expected that by applying centrifugation-based purification methods, the nanotube purity can be further improved.

Apart from the purification methods, the evaluation of SWCNT purity relies on different analytical techniques, for example, optical absorption, photoluminescence, Raman spectroscopy, scanning probe microscopy (AFM), SEM, TEM, TGA, EDX, XPS, and ICP-AES. Widely accepted standards for establishing SWCNT purity levels from these techniques remain elusive, in part, also due to the lack of direct comparison among SWCNT samples from different sources. Comparison of analytical techniques for purity evaluation of SWCNTs has been reported [11]. However, impurities and structure diversities of SWCNTs complicate the interpretation of analytical results. Therefore, it is essential to further develop SWCNT purity standards.

3.1 SWCNT synthesis from Co-MCM-41

The Co-MCM-41 catalyst was synthesized following the method described in Chapter 2. To assure the quality, consistence and reproducibility of the catalyst synthesis, N₂ physisorption and TPR were used to examine catalysts prior to the SWCNT synthesis. Figure 3-1 shows a typical adsorption/desorption isotherm and pore size distribution of Co-MCM-41 catalyst synthesized using a 16 carbon chain surfactant, hexadecyl trimethyl ammonium bromide (HTAB) and a typical TPR result of the C16-Co-MCM-41 catalyst is shown in Figure 3-2.

Good quality catalyst is required to obtain high quality SWCNT samples for further purification and applications. Based on the N₂ physisorption and TPR result, four criteria based on Co-MCM-41 physical and chemical properties are established to evaluate the catalyst quality. (1) The surface area determined by N₂ adsorption-desorption isotherm should be larger than 1000 m²/g. (2) The full width at half-maximum (FWHM) of the pore

size distribution curve is less than 0.2 nm. (3) Only one major reduction peak centered around 850 °C can be obtained from the TPR profile. (4) Reduction peaks associated with Co_3O_4 and CoO below 500 °C are absent in the TPR profile. The surface area and pore size distribution results were used to evaluate the structure of the mesoporous MCM-41 silica template. The cobalt oxide state and species distribution inside the silica support can be determined by the TPR profile [6-8].

Figure 3-1 N_2 physisorption results of Co-MCM-41 catalysts: (a) adsorption/desorption isotherm; (b) pore size distributions calculated using BET method.

Figure 3-2 TPR profile obtained from a high quality C16-Co-MCM-41 catalyst sample.

3.2 Purification of SWCNTs obtained from Co-MCM-41 catalyst

The main impurities in the as-grown sample can be divided into 3 different types, (1) carbonaceous impurities like DWCNTs, MWCNTs, amorphous carbon and graphitic carbon nanoparticles; (2) catalyst template and (3) metallic nanoparticles formed during the reaction. Co-MCM-41 catalyst was developed to preferentially grow SWCNTs under specially designed synthesis environment. So the difficulties of DWCNT, MWCNT or graphitic nanoparticles removal can be neglected. The remaining impurities are the amorphous silica support, metal nanoparticles and amorphous carbon. Here, a purification protocol based on centrifugation method was proposed. First, the as-grown sample was reflux in 1M NaOH solution twice to remove the silica template. The removal efficiency of the mild basic solution wash has been demonstrated before [10]. Then the collected black

powder, which was a mixture of SWCNT, carbonaceous impurities and metals, was suspended in 2 wt% sodium cholate (SC) solution by sonication and centrifuged at different centrifugation forces. This step is designed to remove the carbonaceous impurities and metal nanoparticles but retain the SWCNTs into the suspensions. Finally, the nanotube obtained from the supernatant after centrifugation was annealed at 350 °C in air to remove the surfactant. Experiment results and details will be further discussed. Figure 3-3 illustrates the schematic diagram of the purification protocols described above.

Figure 3-3 Schematic diagram of the purification protocol

In this study, one of the major advantages of Co-MCM-41 catalyst is that the template, a mesoporous amorphous silicate, can be easily removed by mild base solution phase reaction following the equation shown below:

The template, consists of ultra-thin silica wall with thickness about 1 nm [12], was dissolved by 1 M NaOH solution reflux for twice and removed by vacuum filtration using a nylon membrane (0.2 µm pore size, 47 mm diameter, Whatman). Previous study showed that the silica can be successfully removed [10]. The black powders collected on the membrane were washed with DI water to remove adsorbed ions before they were put into an 80 °C oven and dried overnight.

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Without any further treatment, 1 mg of the dried black powder was suspended in 10 mL of 2 wt% sodium cholate hydrate (SC, SigmaUltra, Sigma-Aldrich) aqueous solution and sonicated in a cup-horn sonicator (SONICS, VCX-130) at 80% amplitude (~20W) for 60 min in ice-water bath. The suspension was centrifuged for 1 hour at different centrifugation forces ranging from 0 g to 180,000 g at 20,000 g interval in a micro-ultracentrifuge (CS150GXL, Hitachi-Koki) after sonication. The sonicated black solution was carefully put into 10 polycarbonate centrifugation tubes (1.1cm in diameter, 3.4 cm in length) in a S140AT fixed angle rotor. Figure 3-4 is a cross-section diagram of the rotor. After centrifugation, the upper 80% of the supernatant was carefully decanted and kept for further analysis.

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Figure 3-4 The cross-section diagram of the S140AT rotor [13]

In order to recover the nanotubes from the suspension, a mixed cellulose ester membrane (47 mm, Millipore) was used. The pore size is 0.025 μm , which would prevent the individualized SWCNTs or small bundles to penetrate. The SWCNT obtained on the membrane was washed with excess amount of water (200 mL DI water to ~10 mL SWCNT solution) to remove the surfactant molecules by vacuum filtration. Though people may

expect that this wash step might remove all the surfactant molecules from the nanotube surface, the TGA profiles obtained from the washed sample confirmed that there was still a layer of SC molecules adsorbed on the surface of the nanotubes.

TGA profiles demonstrated that the surfactant, SC, could not be removed thoroughly by simple solvent wash and further treatment was needed to get impurity free SWCNT samples. TGA results obtained from commercial available purified carbon nanotube samples show that single walled carbon nanotubes will start burning at 400 °C and burn out around 550~600 °C depending on their diameter and defect level while pure SC will start burning at 300 °C [14]. In order to remove the surfactant, 2 mg of dry SWCNT powder collected from the MCE membrane after been washed with excess amount of solvent was put into a clean and pre-calcined alumina boat. The boat was placed in the middle of the working tube and a thermal couple was attached to the boat to provide a precise temperature control. 100sccm air flow (99.9%, Soxal) controlled by a mass flow controller (Brooks, NY, US) was introduced into the tube and the sample was heated to 350 °C at a ramp of 10 °C/min and soaked at the temperature for 30 min. The sample was cooled down to room temperature in air flow until it was taken out from the furnace. After the calcination, the remaining black powder was collected and used for characterization.

3.3 Effects of centrifugation on the SWCNT purity

This section will discuss the characterization results of samples obtained from each purification step stated above. Various characterization methods, *e.g.* UV-vis-NIR absorption, PL, resonance Raman spectroscopy, TGA, TEM, SEM and EDX were adopted.

3.3.1 Purity analysis using spectroscopic characterization methods

Itkis *et al.* [11, 15] proposed an assessment method for bulk SWCNT samples by using solution-phase absorption spectroscopy. The UV-vis-NIR parts of SWCNT absorption spectra exhibit characteristic absorption features, originating from the interband transitions in semiconducting and metallic SWCNTs, which ride on the top of the absorption background. The ratio $AA(S)/AA(T)$ is defined as the SWCNT purity index, where $AA(S)$ is the area of the E_{22} interband transition after baseline subtraction and $AA(T)$ is the total area under the spectral curve [11, 15]. The concentration of the SWCNT dispersions obtained from different centrifugation force field was calibrated using 2 wt% SC water solution. The absorbance at 851 nm was used as a criterion. All the samples were adjusted to 0.2 ± 0.005 in a quartz cuvette with 10 mm optical path length. The purity indices of all the samples were extracted through the spectrum from 530 nm to 780 nm and this part is the S_{22} absorption range of SWCNTs produced from Co-MCM-41 catalyst. A straight line fitted from the absorbance at 530 nm and 780 nm was introduced and served as the background baseline by assuming that the baseline is a straight line with respect to the photon energy. Three to five samples were measured for each centrifugation speed and the purity indices were calculated to eliminate errors. The absorption spectrum and the purity index of each sample were shown in Figure 3-5.

From Figure 3-5B, after silica removal, the purity index was 0.129 (0 g centrifugation force). With the increase of the centrifugation force, the purity index increase steadily until it reaches the maximum of 0.268 at 120,000 g force, approaching the estimated value of 0.325 for an analytical pure SWCNT sample [11]. This is the highest purity index ever

reported in literatures so far. The previous highest value came from purified arc-discharged SWCNTs dispersed in DMF with a purity index to be 0.240 [4, 15].

Figure 3-5 (a) UV-vis-NIR spectra of SC dispersed SWCNTs after centrifugation at different forces. (b) Purity index (AA(S)/AA(T)) of SWCNTs.

Two commercial available high purity SWCNT samples, super purified HiPco® (Unidym) and SWeNT® SG 65 (SouthWest NanoTechnologies) were sonicated and centrifuged at 120,000 g following the same procedure and the purity index for these two samples was 0.087 and 0.194, respectively. The spectra of these two samples were shown in Figure 3-6. The background of absorption spectra has contributions from both carbonaceous impurities and SWCNT structure [15]. From Figure 3-5B, the centrifugation force applied to the sonicated SWCNT solution can be discussed in two parts. First, since centrifugation separation is based on the different density of each species in a sample, when centrifugation force was applied from 0 to 120,000 g, carbonaceous impurities (such as amorphous carbon) and metal nanoparticles with packed structures exhibiting higher density than SWCNTs with hollow structures would settle firstly. The removal of these carbonaceous impurities from the supernatant directly decreases their contribution to the background in the absorption spectra and therefore leading to a higher purity index. Second, when centrifugation force higher than 120,000 g was applied, the purity index began to decrease though a constant purity index was expected. No change was observed in the intensity of the absorption background but the intensity contributed from SWCNT on top of the background decreased continuously. Based on the Lambert-Beer's Law, the absorption intensity is proportional to the solute concentration in a solution. The decrease of the intensity contributed from SWCNTs indicates that the nanotubes begin to settle to the sediment part as well when the force is too strong. This phenomenon suggests that the intensity of absorption background contributed from SWCNTs is not directly related to the concentration of suspended SWCNTs and further study on the origin of the absorption

background and its correlation with SWCNT concentration is needed to clarify this problem.

Figure 3-6 Absorption spectrum of SC dispersed (a) Super purified HiPco®; (b) SWeNT® SG 65 SWCNT after 120,000 g centrifugation. Purity indices were extracted in the range of SWCNT S_{22} transition.

Previous study demonstrated that purified SWCNT samples following a four-step purification method could reach a purity index at 0.105 in a 1 wt% SDS (99%, Sigma-Aldrich) suspension [10]. Those nanotubes were acid treated. For further comparison, the account of surfactant resonance ratios should be taken into consideration. Tan *et al.* have collected the resonance ratios of more than 10 surfactants and some of their combinations [16]. The resonance ratio of SC and SDS is 0.147 and 0.084, respectively, which is about 1.75 times higher. If this ratio was considered, the purity index for the SWCNTs purified following the four-step should be:

$$0.105 \times 1.75 = 0.184,$$

which is still an improvement of ~146% in the purity index.

Figure 3-7 2D PLE maps of SWCNT suspensions obtained from different centrifugation forces.

The absorption spectroscopy has demonstrated that with the assistance of centrifugation at 120,000 g, the purity index of nanotube samples can reach a maximum. The second task is to investigate whether the centrifugation method would alter the chirality distribution of SWCNT samples. PL maps of SWCNT dispersions obtained from different centrifugation forces were collected and shown in Figure 3-7. The abundance of each chiral type was evaluated as well. To evaluate the abundance from PL maps, the theoretical quantum efficiency should be considered [17]. Recent results demonstrated that the difference of PL efficiencies among various (n,m) species may not be as large as the theoretical estimations [18]. The abundance was calculated both using and not using the theoretical value following the method discussed in Chapter 2. The results were listed in Table 3-1 and plotted in Figure 3-8. As illustrated in Figure 3-8, the variation in the abundance of dominating (7,5) species is between 7% and 10% with or without the consideration of the I^{cal} . This suggests that no specific (n,m) enrichment happened during the centrifugation process.

In Figure 3-7, additional peaks known as sideband other than the bright PLE peaks resulted from major interband transitions assigned to particular nanotube species can be found. The PLE maps in Figure 3-7 tend to become “cleaner” with increasing centrifugal forces. Previous observations [19-21] of PLE sideband peaks have been attributed to excitation to the exciton-phonon bound state [22-24]. Maruyama *et al.* further categorize the origins for these sidebands into “excitonic-phonon” or “pure electronic” excitation using single-walled carbon-13 nanotubes [24]. To better understand the impact of SWCNT purity on their PLE spectroscopy, the investigation of the PLE spectrum is focused on one specific (n,m) type, $(7,5)$ nanotubes, which have the strongest PLE intensity in our samples. PLE spectrum in panel (a) of Figure 3-9 correspond to vertical cuts of PLE maps at the emission energy of $(7,5)$ nanotubes represented by the solid white line in Figure 3-7. Each PLE spectra is normalized by the $E_{22}-E_{11}$ transition peak intensity for comparison. PLE spectra reveal three sideband peaks similar to those observed previously [24]. The three sidebands are located at 828 ± 2 nm (A), 694 ± 2 nm (B) and 578 ± 2 nm (C) respectively.

Figure 3-8 Abundance of semiconducting nanotubes in SWCNT samples obtained after centrifugation at different forces. (a) Abundance calculated using I^{cal} [17] and (b) Abundance calculated without I^{cal} .

Table 3-1 Properties and calculated abundance of different (n,m) species in samples obtained after centrifugation at different forces.

Properties	(n,m)								
	(6,5)	(7,5)	(7,6)	(8,3)	(8,4)	(8,6)	(9,2)	(9,4)	(10,2)
d_t, nm	0.76	0.83	0.90	0.78	0.84	0.97	0.81	0.92	0.88
θ	27.00	24.50	27.46	15.30	19.11	25.28	9.53	17.48	8.95
I^{cal} [17]	0.67	0.71	0.47	2.13	0.46	0.49	0.40	0.70	2.38
Centrifugal forces, g	Abundance calculated with the I^{cal}								
	0	12.73	44.23	7.41	4.79	14.52	5.38	5.11	3.11
	20,000	13.58	42.63	7.61	6.00	14.10	5.47	5.05	4.11
	40,000	12.79	43.41	8.11	5.51	12.79	5.90	5.31	5.08
	60,000	13.33	44.32	10.34	5.55	12.93	3.93	2.67	5.81
	80,000	11.78	45.85	11.91	5.04	13.26	4.63	0.00	5.51
	100,000	16.20	43.30	7.41	5.36	16.61	3.67	0.00	5.06
	120,000	13.88	45.51	7.47	5.08	14.28	3.71	3.25	5.03
	140,000	15.23	43.08	7.15	5.91	14.65	4.07	2.62	4.88
	160,000	11.66	43.26	11.59	3.99	14.10	5.31	3.76	4.73
	180,000	12.73	44.60	12.13	3.95	12.56	3.53	5.03	4.09
	Abundance calculated without the I^{cal}								
	0	14.70	39.35	6.80	9.07	11.47	5.50	4.08	4.93
	20,000	14.21	35.94	6.64	9.61	14.05	5.46	2.27	5.21
	40,000	12.31	41.14	7.29	7.25	14.09	6.00	3.35	5.90
	60,000	11.92	38.15	9.17	11.64	9.38	3.45	2.50	6.93
	80,000	11.14	41.76	9.90	11.71	9.32	3.10	0.00	6.87
	100,000	14.11	38.82	7.78	11.54	11.94	2.78	0.00	6.15
	120,000	13.08	41.17	7.37	10.51	10.76	2.19	3.71	5.61
	140,000	13.49	38.79	7.18	12.11	10.08	2.87	2.46	6.01
	160,000	11.47	40.26	9.91	9.68	10.21	3.18	2.89	6.79
	180,000	12.19	42.25	8.14	12.03	8.26	3.47	2.88	5.09

Figure 3-9 (a) PL emission spectra of SWCNT suspensions after centrifugation at different forces. Each emission spectrum was extracted along S_{11} emission energy of (7,5) nanotubes from Figure 3-7. (b) Correlations between spectra features shown in Figure 3-9A with centrifugation forces. Linewidth for (7,5) E_{11} emission peaks at E_{22} excitation energy. (c)-(f) Intensity ratio between E_{11} emission peaks at S_{33} excitation energy, sideband C, B, A and E_{11} emission peaks at E_{22} excitation energy.

The sideband intensities show systematic changes with centrifugal forces. The intensity ratios of sidebands over E_{11} excitation peaks excited at E_{22} energy were further calculated, using the intensities of peaks determined from the amplitude of their partial derivatives. Panel (d) through (f) of Figure 3-9 illustrate the correlation between sideband intensity ratios and centrifugal forces. SWCNT dispersions obtained at lower centrifugation forces have stronger sidebands, resulting in higher intensity ratios. However, the intensity ratios

decline when the centrifugal forces increases and the intensities become nearly constant when the forces are larger than 100,000 g. The results here suggest that the impurity is associated with the sideband. However, previous studies [24] have proposed that the side band is purely intrinsic from carbon nanotubes. There are several possibilities: either the side bands are from the impurities or the impurities (including the bundling of nanotubes) assist the excitonic-phonon interaction. Regardless of origin of PLE sidebands, it is apparent that the increase of centrifugal forces can lower the sideband intensities for our samples. There is another peak on panel (a) of Figure 3-9 at 338 ± 2 nm, which can be assigned to $E_{33}-E_{11}$ interband transition. The intensity ratios between $E_{33}-E_{11}$ over $E_{22}-E_{11}$ also show an interesting trend. As rendered in panel (c) of Figure 3-9, without centrifugation, the $E_{33}-E_{11} / E_{22}-E_{11}$ ratio is less than 0.1. This ratio increases and settles between 0.6 and 0.8 after centrifugation. For $E_{22}-E_{11}$ peaks, no significant peak shift was observed but the linewidths of $E_{11}-E_{22}$ peaks decrease with the increase of centrifugal forces.

It can be speculated that metallic nanotubes in small SWCNT bundles and carbonaceous impurities may affect the intensities of sidebands and $E_{33}-E_{11}$ peaks, as well as linewidths of $E_{22}-E_{11}$ peaks. With the increase of centrifugal forces (from 0 to 100,000 g), most SWCNT bundles and carbonaceous impurities are removed from SWCNT supernatants, leaving behind individual dispersed SWCNTs that lead to higher $E_{33}-E_{11}$ peak intensities, less sideband peak intensities, and narrower $E_{22}-E_{11}$ peaks. These changes in PLE spectra are correlated with SWCNT purity index based on absorption spectroscopy, which provide new tools for SWCNT purity evaluation. However, it should be noted that when centrifugal forces are larger than 100,000 g, these features in PLE spectra become nearly constant, even though purity indexes based on absorption spectroscopy decrease at

very high centrifugal forces as shown in Figure 3-5. Further studies of these features will be discussed in later chapters.

Figure 3-10 Raman spectra of SWCNT solid samples: (a) after centrifugation at 20,000 g; (b) after centrifugation at 120,000 g; (c) after heating at 350 °C to remove SC.

Due to the resonance Raman effect of SWCNTs, 633 nm laser which is closer to the major semiconducting nanotubes ((7,5) nanotubes, $E_{22} = 1.923$ eV, $\lambda_{22}=645$ nm) in the samples was selected for Raman spectroscopy characterization. Figure 3-10 shows the Raman spectra of SWCNT films on filter membranes after centrifugation at 20,000 and 120,000 g. Three typical bands (RBM, D band and G band) associated with SWCNT samples can be easily identified. An important feature related to SWCNT purity is the D band that is correlated with either the presence of defects in the nanotube walls or the presence of amorphous carbon material in the sample [6]. D band intensity is very weak

(ratio of D band intensity to G band intensity is less than 0.0024) in the centrifuged sample, indicating very high quality SWCNTs obtained after centrifugation.

Furthermore, SWCNTs under different centrifugal forces were tested. There is no change in the D band to G band ratios, which are commonly used for SWCNT purity evaluation. This is probably because the solid phase Raman spectroscopy is not as sensitive as solution phase absorption spectroscopy and PLE spectroscopy in detecting the changes in SWCNT purity. From above discussion, it can be found that absorption spectroscopy, PLE mapping and Raman spectroscopy are sensitive to carbon nanotube purity and quality.

3.3.2 Thermal gravimetric analysis

TGA has been used to distinguish different carbon species in SWCNT samples [25]. However, oxidation temperatures of SWCNTs have been observed to vary considerably in a rather wide temperature range [25-27] because of the influences from metallic residues, DWCNTs and MWCNTs. SWCNT samples at different purification stage were measured and their TGA and DTG profiles are shown in Figure 3-11.

Three distinctive features can be identified from Figure 3-11A. The peak at 220 °C is attributed to oxygen uptake by oxidation of cobalt nanoparticles (a positive peak shows gaining weight), while the single peak at relatively lower temperature of 360 °C is due to the SWCNT catalytic oxidation assisted by metallic residues. Conversely, the high temperature peak at 930 °C is related to graphite and/or thick carbon layers covering small Co clusters, with a nearby positive peak that can be caused by the oxidation of cobalt clusters after their carbon shells are destroyed. The residual materials at 1025 °C are at 7.17 wt%. Also the lack of any features in the range of 600 to 700 °C indicates that the Co-

MCM-41 would preferentially produce SWCNTs but not MWNTs. After centrifugation at 20,000 g, several changes can be observed in Figure 3-11B: (1) the oxygen uptake peak by cobalt oxidation disappears, (2) the graphite peak is gone, (3) a new peak at 420 °C appears, and (4) the residual materials at 1025 °C decrease to 0.34 wt%. These results suggest that centrifugation can efficiently remove metallic residues, graphite and carbon nanoparticles. The new peak at 420 °C should belong to SWCNTs with diameter around 0.7-1.0 nm. The same measurement was also performed on commercial purified nanotube samples. As shown in Figure 3-12, both Super purified HiPco and CoMoCAT SG 65 SWCNTs have peaks at the same temperature.

An intriguing question is what contributes to the peak at 335 °C in the DTG profiles? Low-temperature peaks may be contributed by either the catalytic oxidation of carbon species when metallic residues are attached to carbon materials or amorphous carbon. However, with the increasing centrifugal forces, both metallic residues and amorphous carbon should be completely removed. The 335 °C peak is also noted in part C of Figure 3-11 for SWCNTs obtained after centrifugation at 120 000 g. The DTG profile is fitted by two Gaussian lines. It is found that the peak at 335 °C accounts for more than 40 wt % of total weight loss in TGA. It is proposed that this peak comes from SC molecules adsorbed on the surface of SWCNTs. Both theoretical calculations and experimental studies were carried out to verify this hypothesis. To have a simplified model, it is assumed that all the nanotubes in the SWCNTs samples are (7,5) nanotubes with open ends and a length of 1 μm . There is no doubt that multilayer of SC molecules adsorption on the surface may be also possible. After excess amount of water is used to wash SC molecules under vacuum

filtration, it can simply assumed that there is still one layer of SC molecules covering the whole surface of SWCNTs.

Figure 3-11 TGA and DTG profiles of SWCNT samples at different purification stages. (a) as-synthesized SWCNTs from Co-MCM-41 after silica support removal. (b) and (c) Filtered and washed SWCNT supernatants obtained after centrifugation at 20,000 g and 120,000 g respectively. Red lines are two Gaussian lines used in curve fitting. (d) Samples of (c) were further heated in air flow at 350 °C for 30 min.

Figure 3-12 TGA and DTG profiles of commercial SWCNT samples. (a) CoMoCAT SG 65 as received. (b) Filtered and washed SWCNT supernatants obtained from (a) after SC dispersion and centrifugation at 120,000 g. (c) super purified HiPco® as received. (d) Filtered and washed SWCNT supernatant obtained from (c) after SC dispersion and centrifugation at 120,000 g.

Calculation of SWCNT structure follows the standard definition as described below [28]. The diameter of SWCNT is calculated using equation (1), where a_{CC} is the nearest neighbor C-C distance, and $a_{CC} = 1.421 \text{ \AA}$ (in graphite).

$$d_t = \frac{c_h}{\pi} = \sqrt{3}a_{CC}(m^2 + mn + n^2)^{\frac{1}{2}}/\pi \quad (1)$$

The number of carbon hexagons, N , contained within the 1D unit cell is determined by equation (2), where d_R is the greatest common divisor of $(2n+m, 2m+n)$ as equated in equation (3), with d representing the greatest common divisor of (n, m) .

$$N = 2(m^2 + mn + n^2)/d_R \quad (2)$$

$$d_R = \begin{cases} d & \text{if } n - m \text{ is not a multiple of } 3d \\ 3d & \text{if } n - m \text{ is a multiple of } 3d \end{cases} \quad (3)$$

Thus, the carbon atom number in one unit cell n_{cu} can be calculated by:

$$n_{cu} = 2N \quad (4)$$

The length of a unit cell along the nanotube axis direction is derived from the magnitude of the translation vector $\mathbf{T}$, which is the linear combination based on the basis vectors $(\mathbf{a}_1, \mathbf{a}_2)$ in real space of the hexagon structure of graphite.

$$\mathbf{T} = t_1\mathbf{a}_1 + t_2\mathbf{a}_2 \equiv (t_1, t_2) \quad (5)$$

Where coefficient t_1 and t_2 are given by:

$$\begin{cases} t_1 = (2m + n)/d_R \\ t_2 = -(2n + m)/d_R \end{cases} \quad (6)$$

The length of the translation vector T is:

$$T = |T| = \frac{\sqrt{3}|C_h|}{d_R} = 3a_{CC}(m^2 + mn + n^2)^{\frac{1}{2}}/d_R \quad (7)$$

The size of SC molecule is 0.6 nm in width and 1.32 nm in length as shown in Figure 3-13. [29]. Furthermore, it is assumed that SC molecules are roughly in a rectangular shape to cover the nanotube surface, neglecting the stacking of SC molecules on the nanotube surface due to the curvature effect.

Figure 3-13 Molecular structure of sodium cholate.

The molecule weight of SC is 438.7 g/mol. The calculated results indicate that for 1 mg of (7,5) nanotubes, the total adsorbed SC are 1.71 mg, which account for 63 wt % of SWCNT samples obtained after filtration and wash. Alternatively, Nair *et al.* [29] have proposed a dynamic model to study surfactant-suspended SWCNTs in a centrifugal field. The average number of SC molecule adsorbed on the (7,5) nanotube surface is estimated to

be 2.1382 per nm. Based on such an estimation, for 1 mg of (7,5) nanotubes, the adsorbed SC would be 0.749 mg, which is less than half of the calculated result based on the previous fully covered model. If the peak at 335 °C in panel (c) of Figure 3-11 comes from adsorbed SC molecules, the weight of SC is between the two predicted values.

Figure 3-14 TGA and DTG profile of pure SC surfactant.

As shown in Figure 3-12, TGA results of both super purified HiPco and SWeNT SG 65 do not have peaks at 335 °C. However, when these two commercial samples were dispersed in 2 wt % SC solution followed by filtration and wash (*i.e.*, the same procedure as performed on SWCNTs from Co-MCM-41), the additional peak at 335 °C appears. To rule out the possibility that the peak at 335 °C may come from damaged SWCNTs caused by sonication, commercial samples were sonicated in pure deionized water, rather than 2 wt % SC solution, under the same sonication condition. No additional peak at 335 °C was

observed in their TGA profiles, confirming that no significant damages are induced to SWCNTs. Overall, both theoretical calculations and experimental studies strongly support that SC adsorbed on SWCNT surfaces cause the observed low temperature peak in TGA. Furthermore, TGA profile demonstrated that SC would start burning at 330 °C as shown in Figure 3-14.

Surfactant removal is also an important issue for many SWCNT potential applications. The first attempt to remove SC molecules was performed by washing SWCNT samples with various solvents, including bath sonication in glacial acetic acid and methanol. However, the low-temperature peak at 335 °C appears persistently in TGA. No common solvents were found to be capable of removing the adsorbed SC efficiently. It is reasonable that heating up SWCNT samples may be more effective to disturb the interaction between SC and SWCNT surfaces. SWCNT samples were heated in air flow at 350 °C for 30 min. The TGA results of the heated samples are shown in panel (d) of Figure 3-11, indicating the successful removal of adsorbed SC molecules. This sample was also characterized by Raman, UV-vis-NIR and PL spectroscopy, as shown in part (c) of Figure 3-10 and in Figures 3-15.

No changes are observed in the D to G ratio of the Raman spectrum in part (c) of Figure 3-10. Purity index and PL spectra features also have no changes compared to those from SWCNT samples before heating treatment. These indicate that no damage was introduced to the SWCNTs during the heat treatment. The success of surfactant removal using heating in air at 350 °C relies on the removal of metallic residues. If a significant amount of metallic residues are still attached to SWCNTs, heating in air can initiate the oxidation of SWCNTs as the metallic residues act as catalysts. The same heating

experiment was performed on a SC dispersed SWCNT sample before any centrifugation, and the outcome showed that a significant amounts of SWCNTs were burnt off. It should also be noted that adsorbed SC molecules are likely to be desorbed from SWCNT surface due to the heating and carrying away by air flow, rather than oxidizing at 350 °C.

Figure 3-15 (a) Absorption spectra and (b) PLE map of 350 °C heated samples resuspended in 2 wt% SC solution by sonication and 120,000g centrifugation.

3.3.3 Electron microscope study and element analysis

Furthermore, both FESEM and TEM were applied to characterize SWCNT samples. EDS spectra displayed in Figure 3-16 indicate the decrease of cobalt concentration with the increase of centrifugal force. The detailed composition data are presented in Table 3-2. The results confirmed that cobalt residues were successfully removed from SWCNTs after centrifugation at 120,000 g. Figure 3-17 shows the TEM micrographs of SWCNTs under different purification conditions. Metal residues and amorphous carbon attached to

SWCNT bundles are observed in the starting material. With an increase of centrifugal forces, less metallic residues are observed.

Figure 3-16 Compositional changes after centrifugation at different forces characterized by EDS. The inserts show SEM images of SWCNT films. The black scale bars in SEM images are at 1 μm .

Table 3-2 Composition change of SWCNT samples centrifuged at different forces

	Raw		20,000g		120,000g	
	mass%	At%	mass%	At%	mass%	At%
C K α	23.28	44.72	71.43	87.86	91.75	94.13
O K α	21.51	31.02	7.26	6.7	7.39	5.69
Na K α	0.51	0.52	--	--	--	--
Si K α	5.44	4.47	0.35	0.18	0.03	0.01
Co L α	49.26	19.28	20.96	5.25	0.83	0.17

Figure 3-17 TEM images of SWCNTs. (a) and (d) as-synthesized SWCNTs after MCM-41 support removal by NaOH reflux; (b) and (e) after centrifugation at 20,000 g. (c) and (f) after centrifugation at 120,000 g.

3.4 Comparison of the different purity evaluation and purification methods

There are still no standardized analytical techniques for purity evaluation of SWCNTs. TGA is capable of measuring the metallic residue content. Solution-phase absorption and Raman spectroscopy are more sensitive in differentiating SWCNTs and carbonaceous impurities [11]. In this study, it has been demonstrated that the sideband features in PLE spectra are also sensitive tools for evaluating the purity of surfactant dispersed SWCNTs. As shown in Table 3-3, combining these analytical techniques, it is feasible to have a reliable quality control of SWCNT products. SWCNTs from Co-MCM-41 catalyst after centrifugation at 120,000 g show the highest purity index reported so far. The efficiency of this purification procedure is summarized in Table 3-4. Approximately 10 mg of SWCNTs after silica removal were used as starting materials. SWCNTs obtained after centrifugation and heating in air are denoted as products. Under the optimized condition, that is centrifugation at 120,000 g, 12.9 wt% of starting materials was recovered, with doubling of SWCNT purity.

Table 3-3 Parameters from various techniques for evaluating SWCNT purity.

Centrifugation force, g	Parameters			
	Purity index ^a	$A/E_{11}-E_{22}$ ^b	Residues ^c , wt %	Co composition ^d , at. %
0	0.129	1.78	7.17	19.28
20,000	0.224	1.72	0.34	5.25
120,000	0.268	0.04	0.15	0.17

^a Purity index determined from UV-vis-NIR absorption spectroscopy. ^b The intensity ratio between sideband A and PLE $E_{22}-E_{11}$ transition peaks of (7,5) nanotubes from PLE spectra. ^c The weight of residues at 1025 °C after TGA. ^d Co composition determined from FESEM-EDS.

Table 3-4 Relative purity index, and recovery efficiency at various centrifugal forces

Centrifugation forces, g	weight of starting materials, mg	Weight of product, mg	Purity index ^a	Recovery efficiency ^b , %	Relative purity ^c , %
20,000	10.51	2.43	0.224	23.1	173.6
120,000	10.95	1.41	0.268	12.9	207.8
180,000	10.48	0.96	0.160	9.2	124.0

^a Purity index determined from UV-vis-NIR absorption spectroscopy. ^b Recovery efficiency is defined as $W_{(\text{products})}/W_{(\text{starting materials})}$. ^c Relative purity is obtained by using purity index of starting material as reference of 1.

From the studies of DMF dispersed electric arc-discharge grown SWCNTs, Haddon *et al.* estimated the analytically pure SWCNT samples, which cannot be further purified, the purity can be characterized by the purity index obtained from the AA(S)/AA(T) value which would be ~ 0.325 [11]. It should be noted that there are still no samples available which can be considered as “real” analytically pure SWCNTs to verify such estimation. In this study, measurements by using various analytical techniques demonstrate a SWCNT sample approaching analytically pure. The improved purity level may come from two aspects. Firstly, good quality Co-MCM-41 catalysts provide well controlled metallic particles which minimize the production of various carbonaceous impurities while ultrathin silica walls are soluble in dilute NaOH aqueous solution that the silica catalyst support can be removed without destroying SWCNTs. Secondly, the centrifugation purification procedure without any acid treatment would introduce less defects to SWCNTs. It is found that common acid treatments (using HF, HNO₃, H₂SO₄, or even HCl) would damage SWCNTs, which lower their purity indices. It should also be noted that sonication in this study is controlled at low amplitude for 30 min, which does no significant harm to SWCNT

structures. No significant changes in the purity index were observed when we varied the sonication time from 10 min to 2 hours.

The protocol developed in this study towards analytically pure SWCNTs is especially relevant to two research areas for further exploration. (1) It is increasingly recognized that applications of SWCNTs would cause potential health and environmental risks. Though the potential toxicity of carbon nanotubes is still debatable and showing apparently conflicting results [30-32]. Various principal cytotoxic mechanisms have been proposed including oxidative stress [33], metal toxicity [34], and physical piercing [35-36]. It should be noticed that many toxicity studies have used SWCNT samples with significant amount of impurities. It has been hypothesized that the metal residues such as Ni, Co and Fe other than carbon nanotubes themselves are the main reasons for the observed toxicity. Some pioneering work on bioavailability of metals from carbon nanotubes has been reported [37-38]. In this study, SWCNTs with very low metallic residues at 0.15 wt% have been obtained. Hence, the improved purity in SWCNTs can play an important role in evaluating the potential health and environmental risks of this material. (2) The properties of SWCNTs depend on their atomic structure denoted by the chiral index (n,m) . To achieve optimal performance in applications, except for the purity of SWCNTs, populations of SWCNTs should be monodisperse with respect to electronic type, diameter, length and helicity. Hersam summarized the progress towards monodisperse SWCNTs in a recent review, which includes strategies on enrichment by selective chemistry, electrical breakdown, electrophoretic separation, chromatography, and ultracentrifugation [39]. Enrichment efficiencies in many of those strategies depend on the starting purity of SWCNTs. High

purity SWCNTs with narrow chirality distribution may potentially help to improve current enrichment efforts.

3.5 Conclusion

Centrifugation has been applied to purify SWCNTs grown from Co-MCM-41 catalyst by CO disproportionation. After centrifugation at 120,000 g, SWCNT purity index based on absorption spectra of SC dispersed SWCNTs is 0.268. It is the highest value reported so far approaching the previously estimated value of ~ 0.325 for analytically pure SWCNTs [11]. From PLE study, (1) linewidth for $E_{22}-E_{11}$ transition, (2) intensities of three sidebands, and (3) intensities of $E_{33}-E_{11}$ transition are related to SWCNT purity. These criteria can be used to evaluate the purity of SWCNT samples. Both TGA results and theoretical models demonstrated that SC molecules adsorbed on the SWCNT surface cannot be easily washed away by water or other solvent. After removal of metallic residues, adsorbed SC molecules can be eliminated by heating in air flow at 350 °C for 30 min. Combining UV-vis-NIR absorption, PL spectroscopy, SEM, TEM and TGA, it is feasible to have a reliable quality control of SWCNT products. Purification protocol towards analytically pure SWCNTs in this study may prove useful for evaluating health and environmental effects of SWCNT material and improving separation efficiencies of nanotube species in accordance to electronic type, diameter, length and helicity.

3.6 Reference

1. Nepal, D., D.S. Kim, and K.E. Geckeler, *A facile and rapid purification method for single-walled carbon nanotubes*. Carbon, 2005. **43**(3): p. 660-662.

2. O'Connell, M.J., S.M. Bachilo, C.B. Huffman, V.C. Moore, M.S. Strano, E.H. Haroz, K.L. Rialon, P.J. Boul, W.H. Noon, C. Kittrell, J. Ma, R.H. Hauge, R.B. Weisman, and R.E. Smalley, *Band Gap Fluorescence from Individual Single-Walled Carbon Nanotubes*. Science, 2002. **297**(5581): p. 593-596.
3. Shen, K., S. Curran, H. Xu, S. Rogelj, Y. Jiang, J. Dewald, and T. Pietrass, *Single-Walled Carbon Nanotube Purification, Pelletization, and Surfactant-Assisted Dispersion: A Combined TEM and Resonant Micro-Raman Spectroscopy Study*. The Journal of Physical Chemistry B, 2005. **109**(10): p. 4455-4463.
4. Yu, A., E. Bekyarova, M.E. Itkis, D. Fakhrutdinov, R. Webster, and R.C. Haddon, *Application of Centrifugation to the Large-Scale Purification of Electric Arc-Produced Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2006. **128**(30): p. 9902-9908.
5. Arnold, M.S., A.A. Green, J.F. Hulvat, S.I. Stupp, and M.C. Hersam, *Sorting carbon nanotubes by electronic structure using density differentiation*. Nat Nano, 2006. **1**(1): p. 60-65.
6. Ciuparu, D., Y. Chen, S. Lim, G.L. Haller, and L. Pfefferle, *Uniform-Diameter Single-Walled Carbon Nanotubes Catalytically Grown in Cobalt-Incorporated MCM-41*. The Journal of Physical Chemistry B, 2003. **108**(2): p. 503-507.
7. Ciuparu, D., Y. Chen, S. Lim, Y. Yang, G.L. Haller, and L. Pfefferle, *Mechanism of Cobalt Cluster Size Control in Co-MCM-41 during Single-Wall Carbon Nanotubes Synthesis by CO Disproportionation*. The Journal of Physical Chemistry B, 2004. **108**(40): p. 15565-15571.
8. Ciuparu, D., Y. Chen, Y. Yang, L. Pfefferle, and G.L. Haller, *Pore Curvature Effect on the Stability of Co-MCM-41 and the Formation of Size-Controllable Subnanometer Co Clusters*. The Journal of Physical Chemistry B, 2004. **109**(6): p. 2285-2294.
9. Luo, Z., L.D. Pfefferle, G.L. Haller, and F. Papadimitrakopoulos, *(n,m) Abundance Evaluation of Single-Walled Carbon Nanotubes by Fluorescence and Absorption Spectroscopy*. Journal of the American Chemical Society, 2006. **128**(48): p. 15511-15516.

10. Chen, Y., L. Wei, B. Wang, S. Lim, D. Ciuparu, M. Zheng, J. Chen, C. Zoican, Y. Yang, G.L. Haller, and L.D. Pfefferle, *Low-Defect, Purified, Narrowly (n,m)-Dispersed Single-Walled Carbon Nanotubes Grown from Cobalt-Incorporated MCM-41*. ACS Nano, 2007. **1**(4): p. 327-336.
11. Itkis, M.E., D.E. Perea, R. Jung, S. Niyogi, and R.C. Haddon, *Comparison of Analytical Techniques for Purity Evaluation of Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2005. **127**(10): p. 3439-3448.
12. Lim, S., D. Ciuparu, Y. Chen, Y. Yang, L. Pfefferle, and G.L. Haller, *Pore Curvature Effect on the Stability of Co-MCM-41 and the Formation of Size-Controllable Subnanometer Co Clusters†*. The Journal of Physical Chemistry B, 2004. **109**(6): p. 2285-2294.
13. Zhang, Y. and S. Iijima, *Elastic Response of Carbon Nanotube Bundles to Visible Light*. Physical Review Letters, 1999. **82**(Copyright (C) 2009 The American Physical Society): p. 3472.
14. Tomassetti, M., L. Campanella, and G. D'Ascenzo, *Thermogravimetric analysis of conjugated and unconjugated sodium cholates*. Thermochimica Acta, 1984. **78**(1-3): p. 235-249.
15. Itkis, M.E., D.E. Perea, S. Niyogi, S.M. Rickard, M.A. Hamon, H. Hu, B. Zhao, and R.C. Haddon, *Purity Evaluation of As-Prepared Single-Walled Carbon Nanotube Soot by Use of Solution-Phase Near-IR Spectroscopy*. Nano Letters, 2003. **3**(3): p. 309-314.
16. Tan, Y. and D.E. Resasco, *Dispersion of Single-Walled Carbon Nanotubes of Narrow Diameter Distribution*. The Journal of Physical Chemistry B, 2005. **109**(30): p. 14454-14460.
17. Oyama, Y., R. Saito, K. Sato, J. Jiang, G.G. Samsonidze, A. Gruneis, Y. Miyauchi, S. Maruyama, A. Jorio, G. Dresselhaus, and M.S. Dresselhaus, *Photoluminescence intensity of single-wall carbon nanotubes*. Carbon, 2006. **44**(5): p. 873-879.
18. Tsyboulski, D.A., J.-D.R. Rocha, S.M. Bachilo, L. Cognet, and R.B. Weisman, *Structure-Dependent Fluorescence Efficiencies of Individual Single-Walled Carbon Nanotubes*. Nano Letters, 2007. **7**(10): p. 3080-3085.

19. Chou, S.G., F. Plentz, J. Jiang, R. Saito, D. Nezich, H.B. Ribeiro, A. Jorio, M.A. Pimenta, G.G. Samsonidze, A.P. Santos, M. Zheng, G.B. Onoa, E.D. Semke, G. Dresselhaus, and M.S. Dresselhaus, *Phonon-Assisted Excitonic Recombination Channels Observed in DNA-Wrapped Carbon Nanotubes Using Photoluminescence Spectroscopy*. Physical Review Letters, 2005. **94**(12): p. 127402.
20. Plentz, F., H.B. Ribeiro, A. Jorio, M.S. Strano, and M.A. Pimenta, *Direct Experimental Evidence of Exciton-Phonon Bound States in Carbon Nanotubes*. Physical Review Letters, 2005. **95**(24): p. 247401.
21. Htoon, H., O.C. M. J., S.K. Doorn, and V.I. Klimov, *Single Carbon Nanotubes Probed by Photoluminescence Excitation Spectroscopy: The Role of Phonon-Assisted Transitions*. Physical Review Letters, 2005. **94**(12): p. 127403.
22. Perebeinos, V., J. Tersoff, and P. Avouris, *Scaling of Excitons in Carbon Nanotubes*. Physical Review Letters, 2004. **92**(25): p. 257402.
23. Jiang, J., R. Saito, A. Grüneis, S.G. Chou, G.G. Samsonidze, A. Jorio, G. Dresselhaus, and M.S. Dresselhaus, *Photoexcited electron relaxation processes in single-wall carbon nanotubes*. Physical Review B, 2005. **71**(4): p. 045417.
24. Miyauchi, Y. and S. Maruyama, *Identification of an excitonic phonon sideband by photoluminescence spectroscopy of single-walled carbon-13 nanotubes*. Physical Review B (Condensed Matter and Materials Physics), 2006. **74**(3): p. 035415-7.
25. Alvarez, W.E., F. Pompeo, J.E. Herrera, L. Balzano, and D.E. Resasco, *Characterization of single-walled carbon nanotubes (SWNTs) produced by CO disproportionation on Co-Mo catalysts*. Chemistry of Materials, 2002. **14**(4): p. 1853-1858.
26. Chen, Y., D. Ciuparu, S. Lim, G.L. Haller, and L.D. Pfefferle, *The effect of the cobalt loading on the growth of single wall carbon nanotubes by CO disproportionation on Co-MCM-41 catalysts*. Carbon, 2006. **44**(1): p. 67-78.
27. Rinzler, A.G., J. Liu, H. Dai, P. Nikolaev, C.B. Huffman, F.J. Rodríguez-Macías, P.J. Boul, A.H. Lu, D. Heymann, D.T. Colbert, R.S. Lee, J.E. Fischer, A.M. Rao, P.C. Eklund, and R.E. Smalley, *Large-scale purification of single-wall carbon nanotubes: process, product, and characterization*. Applied Physics A: Materials Science & Processing, 1998. **67**(1): p. 29.

28. Dresselhaus, M.S., G. Dresselhaus, and P. Avouris, *Carbon Nanotubes Synthesis, Structure, Properties, and Applications*. 2001: Springer: Berlin.
29. Nair, N., W.-J. Kim, R.D. Braatz, and M.S. Strano, *Dynamics of Surfactant-Suspended Single-Walled Carbon Nanotubes in a Centrifugal Field*. *Langmuir*, 2008. **24**(5): p. 1790-1795.
30. Worle-Knirsch, J.M., K. Pulskamp, and H.F. Krug, *Oops They Did It Again! Carbon Nanotubes Hoax Scientists in Viability Assays*. *Nano Letters*, 2006. **6**(6): p. 1261-1268.
31. Hurt, R.H., M. Monthieux, and A. Kane, *Toxicology of carbon nanomaterials: Status, trends, and perspectives on the special issue*. *Carbon*, 2006. **44**(6): p. 1028-1033.
32. Poland, C.A., R. Duffin, I. Kinloch, A. Maynard, W.A.H. Wallace, A. Seaton, V. Stone, S. Brown, W. MacNee, and K. Donaldson, *Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study*. *Nat Nano*, 2008. **3**(7): p. 423-428.
33. Manna, S.K., S. Sarkar, J. Barr, K. Wise, E.V. Barrera, O. Jejelowo, A.C. Rice-Ficht, and G.T. Ramesh, *Single-Walled Carbon Nanotube Induces Oxidative Stress and Activates Nuclear Transcription Factor-kappaB in Human Keratinocytes*. *Nano Letters*, 2005. **5**(9): p. 1676-1684.
34. Shvedova, A.A., E.R. Kisin, R. Mercer, A.R. Murray, V.J. Johnson, A.I. Potapovich, Y.Y. Tyurina, O. Gorelik, S. Arepalli, D. Schwegler-Berry, A.F. Hubbs, J. Antonini, D.E. Evans, B.-K. Ku, D. Ramsey, A. Maynard, V.E. Kagan, V. Castranova, and P. Baron, *Unusual inflammatory and fibrogenic pulmonary responses to single-walled carbon nanotubes in mice*. *Am J Physiol Lung Cell Mol Physiol*, 2005. **289**(5): p. L698-708.
35. Kang, S., M. Pinault, L.D. Pfefferle, and M. Elimelech, *Single-Walled Carbon Nanotubes Exhibit Strong Antimicrobial Activity*. *Langmuir*, 2007. **23**(17): p. 8670-8673.
36. Narayan, R.J., C.J. Berry, and R.L. Brigmon, *Structural and biological properties of carbon nanotube composite films*. *Materials Science and Engineering: B*, 2005. **123**(2): p. 123-129.

37. Guo, L., D.G. Morris, X. Liu, C. Vaslet, R.H. Hurt, and A.B. Kane, *Iron Bioavailability and Redox Activity in Diverse Carbon Nanotube Samples*. Chemistry of Materials, 2007. **19**(14): p. 3472-3478.
38. Liu, X., V. Gurel, D. Morris, D.W. Murray, A. Zhitkovich, A.B. Kane, and R.H. Hurt, *Bioavailability of Nickel in Single-Wall Carbon Nanotubes*. Advanced Materials, 2007. **19**(19): p. 2790-2796.
39. Hersam, M.C., *Progress towards monodisperse single-walled carbon nanotubes*. Nat Nano, 2008. **3**(7): p. 387-394.

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Chapter 4

Aggregation-dependent Photoluminescence Sidebands in SWCNT

Aggregation of SWCNTs is one of the major obstacles for many nanotube fundamental studies and their practical applications in macroelectronics. Strong van der Waals forces, approximate 500 eV/ μm , exist among nanotubes [1-2], which result in substantial SWCNT aggregation in either aqueous or organic solvents. The aggregation state of SWCNTs has a profound impact on their observed optical properties; in particular, PL spectroscopy has been adopted to demonstrate the individualization of nanotubes in dispersions [3-5]. The PL phenomenon of SWCNTs was firstly observed on the individually dispersed nanotubes in SDS surfactant aqueous solution [6]. PL was also observed within small nanotube bundles, while the formation of large bundles resulted in quenching of nanotube PL [7-9]. The optically excited electron-hole pairs in SWCNTs are highly mobile. With the diffusional range of 90 nanometers, an exciton may visit over 10,000 atomic sites during its life span [10]. As a result, the intensity of PL spectrum is found to be strongly influenced by not only the nanotube aggregation, but also many other factors such as the local environment created by solvents and adsorbed molecules [3, 10-17], structural defects on nanotubes [10-13], and the length of nanotubes [18-19].

In addition to the primary PL excitation-emission transitions at $E_{22}-E_{11}$ (emission from the first van Hove band gap E_{11} caused by excitation of the second van Hove band gap E_{22}), several well-resolved sidebands can also be observed in PL spectra from well-dispersed SWCNTs, though the intensity is rather low [2, 20-21]. The origin of these sidebands has

been being extensively studied and debated both theoretically and experimentally [5, 22-27]. The sidebands neighboring to the primary PL peaks are assigned to transverse excitation induced emissions ($E_{12,21}$), emissions from exciton–phonon interactions (G – and G' –phonon-coupled processes), emissions contributed by dark excitonic state pathways, and exciton energy transfers among nanotubes with different structures [defined by chiral indices (n,m)] [28-29]. Some of these PL sidebands are found to be strongly correlated with intertube interactions in SWCNT bundles [30-31]. It is both fundamentally interesting and practically useful to understand how the aggregation of SWCNTs affects the intensities of the PL sidebands. The correlation between PL sidebands and the aggregation of SWCNTs may also offer a sensitive means to monitor the aggregation of SWCNTs. However, such correlation has not been systematically studied so far.

The goals of this Chapter are (1) to obtain well defined SWCNT samples containing different fractions of nanotube bundles; (2) to establish a reliable correlation between PL sideband intensities and nanotube aggregation; (3) to verify the correlation under diverse dispersion conditions involving various surfactants and solvents; (4) to compare the sensitivity of PL sidebands toward the aggregation of SWCNTs with several other commonly adopted characterization methods, such as absorption spectroscopy and atomic force microscope (AFM).

4.1 Sample preparation

Nanotubes with different (n,m) structures would bundle together and induce various tube-tube energy transitions. The complexity of PL sidebands on SWCNT PL maps increases exponentially with the increase of (n,m) species. Two SWCNT samples with

narrow (n,m) distribution, enriched in (6,5) and (7,5) species, respectively, were employed in this study. (6,5) enriched SWCNTs obtained from CoMoCAT process were purchased from SouthWest NanoTechnologies (SWeNT SG 65). 50% of semiconducting nanotubes have the (6,5) structure. (7,5) enriched SWCNTs were produced from Co-MCM-41 catalyst [32-33], which was synthesized following the protocol described in Chapter 2. The dominant (7,5) nanotube accounts for about 45% of semiconducting species. SWCNTs were purified by using a centrifugation based method as discussed in Chapter 3 [34]. This purification procedure helps to eliminate the influences of impurities such as catalyst residues, amorphous carbon, multi-walled carbon nanotubes (MWCNTs), nanoparticles, and graphite as demonstrated by their TGA profiles shown in Figure 4-1.

After purification, purified SWCNTs were then suspended in 2 wt % SC aqueous solution by sonication for 60 min in an ice-water bath. Subsequently, the SWCNT dispersions were centrifuged in a fixed angle rotor (S140AT, Hitachi-Koki) for 1 hour at different centrifugation forces varying from 20,000 g to 180,000 g at an interval of 20,000 g. The upper 80% of the supernatant was decanted from centrifugation tubes. The concentration of collected SWCNT dispersions was adjusted with 2 wt % SC solution so that their optical absorbance at 800 nm after passing through a quartz cell with 10 mm light pathlength was 0.2 on a Varian Cary 5000 UV-vis-NIR absorption spectrometer. The concentration calibrated SWCNT suspensions were further bath sonicated for 10 min to ensure efficient mixing. Similar sample preparation procedures were repeated on SDS and SDBS dispersed SWCNTs in aqueous solvents, as well as fluorine-based organic polymer (poly(9,9-dioctylfluorenyl-2,7-diyl), PFO) dispersed SWCNTs in toluene. SWCNTs were also dispersed in pure organic solvents such as N-methylpyrrolidone (NMP) and DMF;

nevertheless, most of the nanotubes would precipitate in organic solvents when large centrifugation forces were applied.

Figure 4-1 TGA and DTG profiles of the samples used in this study. (a) (7,5) enriched sample obtained from Co-MCM-41 catalyst; (b) (6,5) enriched sample from CoMoCAT catalyst.

Controlled rebundling of nanotubes in suspensions was achieved by modulating the surfactant concentration in SWCNT dispersions through dialysis. A cup formed by 50 kDa semipermeable cellulose membrane (Spectra/Por, USA) containing 5 mL of SWCNT dispersions was placed in a deionized water bath at room temperature. SWCNT suspensions were dialyzed for 3, 6, 12, 18, and 24 h. PL measurements were performed on those dialyzed SWCNT suspensions following the prescribed method above.

2D PL maps were recorded on a Jobin-Yvon Nanolog-3 spectrofluorometer equipped with an InGaAs CCD detector and a monochromatized excitation light source (a 450 W xenon lamp). The excitation and emission slits were set to 5 nm. PL maps were acquired by scanning the excitation wavelength from 300 to 850 nm (4.14 to 1.46 eV) in a step increase

of 0.5-2 nm. The emission wavelength ranged from 835 to 1360 nm (1.49 to 0.91 eV). The spectral resolution in the measured emission range is about 0.15 nm. The instrument was calibrated and aligned before conducting each experiment. All measurements were done at ambient conditions.

AFM measurements were conducted on a MFP3D microscope with a cantilever (Arrow NC, Nanoworld) operating in tapping mode. The scan rate was set to 1 Hz at various scan sizes, while the resolution was set to 512 pixels $\times$ 512 lines. SWCNT dispersions ($\sim 5 \mu\text{L}$) were dropcasted on $1 \text{ cm} \times 1 \text{ cm}$ Si wafers with a 200 nm thick SiO_2 top layer. A self-assembled monolayer of 3-aminopropyl triethoxysilane (APTES, Sigma-Aldrich) was formed on the SiO_2 before nanotube suspensions were deposited [35]. The SWCNT coated wafers were dried and washed with methanol to remove the excess surfactant molecules. The wafers were then blown dry in N_2 and baked at 80°C overnight to remove any remaining moisture before the AFM measurement.

Raman spectra of SWCNT suspensions obtained from Co-MCM-41 catalyst and CoMoCAT process. Raman spectra of nanotube suspensions were obtained on a Renishaw Raman spectrometer using 633 nm laser (1.96 eV). The laser spot was focused on the suspension at $\sim 10 \mu\text{m}$ spot. Laser energies of 2.5-5 mW were used. Integration times of 20 seconds were adapted.

4.2 Analysis of photoluminescence features

SWCNTs with narrow (n,m) distribution were employed to simplify the interpretation of PL sideband peaks, due to the fact that the number of possible exciton relaxation pathways increases exponentially with the increase of (n,m) species in a SWCNT sample.

In agreement with previous studies on SWCNTs obtained from the CoMoCAT process [36] and Co-MCM-41 catalysts [37], the PL results showed that SWCNT dispersions contain mainly five small diameter and large chiral angle nanotubes including (8,3), (6,5), (7,5), (8,4), and (7,6). SWCNTs from Co-MCM-41 are enriched with (7,5) nanotubes; and most CoMoCAT nanotubes have the (6,5) structure. As shown in Figure 4-2, PL peaks from the primary excitation-emission transitions, as well as the emission and excitation satellites resulting from other relaxation pathways, can be clearly identified. According to the PL map shown in panel (a) of Figure 4-2, the (n,m) species were assigned based on $E_{22}-E_{11}$ optical transitions of the main PL peaks by their E_{22} excitation and E_{11} emission energies. The observed peak positions and emission line widths (20-60 meV) are consistent with the results obtained for SWCNTs in aqueous dispersions [38]. The brightest $E_{11}-E_{11}$ peaks shown in Figure 4-2 come from the direct photoexcitation of the E_{11} states of (n,m) nanotubes followed by the radiative recombination of excitons. $E_{11}-E_{11}$ peaks overlap with the Rayleigh scattering line by a small Stokes shift [39]. $E_{33}-E_{11}$ transitions (emission from the first van Hove band gap E_{11} caused by excitation to the third van Hove band gap E_{33}) can also be clearly identified in Figure 4-2, which is consistent with the theoretical values predicted by Haroz *et al.* [40]. Along the emission wavelength of (7,5) nanotubes at 1026 nm (the white line in Figure 4-2), several low-intensity but well-resolved PL features can be identified. First, the peaks ($E_{11} + G$ and $E_{11} + G'$) right below the $E_{11}-E_{11}$ peak are contributed by the phonon-coupled $E_{11}-E_{11}$ photoexcitation-emissions, whereas G and G' represent SWCNT Raman-active normal and overtone vibrational modes, respectively [39]. The exciton-phonon coupling (the energy coupling between electron transitions and vibrations) is more pronounced in dispersed nanotubes as well as in substrate-deposited or

freely suspended individual nanotubes [39]. Similarly, the exciton-phonon coupling satellite peaks ($E_{22} + G$ and $E_{22} + G'$) can be observed below the $E_{22}-E_{11}$ peaks in Figure 4-2. Second, along the white line in panel (a) of Figure 4-3, the PL features locating above the $E_{22}-E_{11}$ optical transition peaks have been correlated with the cross-interband degenerate E_{12} and E_{21} photoexcitations, which correspond to interband transitions between symmetric pairs of the van Hove singularities in the valence and conduction bands of SWCNTs. Similar peaks have been previously observed in both a water-surfactant dispersion [41] and an organic solvent-polymer dispersion [39]. They are usually 140-200 meV blue-shifted from the simple calculated $(E_{22} + E_{11})/2$ transition energies depending on the strength of the coulomb interaction in SWCNTs [41]. Their intensities are about ten times weaker compared to the primary $E_{22}-E_{11}$ optical transitions [41]. Lastly, peaks from cross-interband E_{13} and E_{31} photoexcitations are also identified above the $E_{33}-E_{11}$ optical transition peaks, although their energies spread over a wide energy range. Exciton energy transfer (EET) among different (n,m) nanotubes resulting from direct physical contacts in SWCNT bundles has been previously reported [42-44], where photoexcited carriers migrate from large band gap SWCNTs into smaller band gap SWCNTs, leading to an enhanced emission from the latter. This EET phenomenon is noticeable between (6,5) and (7,5) nanotubes, two of the most populous (n,m) species in the two nanotube samples used in this study. As illustrated in Figure 4-2, the PL peaks caused by EET from (6,5) to (7,5) nanotubes partially overlap with the electron-phonon coupling satellite peaks ($E_{22} + G$ and $E_{22} + G'$) of (7,5) species. The emission intensities of $E_{11}-E_{11}$ peaks, $E_{22}-E_{11}$ peaks, and sidebands differed significantly. Especially, the $E_{11}-E_{11}$ peaks are overlapped with the strong scattering light line, and they are 10-20 times more intense than the $E_{22}-E_{11}$ peaks.

The 2D PLE map shown in Figure 4-2 was logarithmically scaled to evade any PL peak information loss.

Figure 4-2 (a) PL map (emission intensity vs excitation and emission wavelength) of (7,5) enriched SWCNTs obtained from Co-MCM-41 in aqueous SC dispersion after centrifugation at 120,000 g. PL intensity is logarithmically scaled. (b) PLE spectrum of (7,5) nanotube at its E_{11} emission wavelength (1026 nm, indicated by the white line in panel (a)).

To further consolidate the assignment of different peaks observed in panel (a) of Figure 4-2, the PL excitation (PLE) spectrum of (7,5) nanotube at its E_{11} emission wavelength (1026 nm) is presented in panel (b) of Figure 4-2. The intensity of scattered light at the $E_{11}-E_{11}$ transition is 15 times higher compared to that of the PL $E_{22}-E_{11}$ optical transition. Other

minor PL sidebands, such as emissions peaks contributed by dark excitonic state pathways, have been omitted because of their extremely low intensity. Possible sideband origins along the excitation directions are schematically illustrated in Figure 4-3.

Figure 4-3 Schematic diagram of experimentally observed emission peaks on 2D PL maps. Different exciton recombination pathways are labeled accordingly to the above discussion. Other PL sidebands are omitted.

Separately, the energies of G and G' vibrational modes for both (7,5) and (6,5) enriched SWCNT dispersions were measured by Raman spectroscopy, as shown in Figure 4-4. The positions of all experimentally identified PL peaks in this study along with the theoretically derived values are listed in Table 4-1 to Table 4-4. In general, the experimental results are in good agreement with theoretically derived values

Figure 4-4 Raman spectra of the samples used in this study. (a) (7,5) enriched sample obtained from Co-MCM-41 catalyst; (b) (6,5) enriched sample from CoMoCAT nanotubes.

An individual nanotube in a close packed surfactant micelle has a specific gravity of approximately 1.0, whereas that of a nanotube bundle is larger than unity [45]. To ensure the initial starting points used for centrifuged samples are similar, the same batch of

purified SWCNTs was suspended in the same surfactant solution by sonication for 60 min before being evenly divided into different parts for centrifugation. By tuning the centrifugation speed from 20,000 to 180,000 g, SWCNT dispersions containing different amounts of bundles were obtained. The PLE spectra of those samples were measured to establish a correlation between PL sideband and nanotube aggregation. Figure 4-5 shows PL maps of SWCNT dispersions from CoMoCAT process and Co-MCM-41 catalysts. The maximum intensity of main PL $E_{22}-E_{11}$ peaks increases with the increase of centrifugation force, which agrees with previous studies that bundling is a major factor in PL $E_{22}-E_{11}$ emission quenching [46]. It is difficult to completely remove the excitation light from intense scattered lights at $E_{11}-E_{11}$, which may cause uncertainty in the measured results; therefore, all PL peaks related to the $E_{11}-E_{11}$ transition have been excluded in this study.

Table 4-1 PL peak positions and phonon energies of (6,5) and (7,5) SWCNTs

Helicity	Band gap	Wavelength, nm	Energy, eV		Raman Shift, cm^{-1} ^a	Phonon Energy, eV
(7,5)	E_{11}	1026.00	1.209	G	1591.07	0.197
	E_{22}	646.00	1.921	G'	2597.00	0.322
	E_{33}	336.00	3.693	D	1312.00	0.163
(6,5)	E_{11}	985.13	1.259	G	1593.30	0.198
	E_{22}	568.00	2.184	G'	2600.61	0.323
	E_{33}	344.00	3.607	D	1313.88	0.163

Table 4-2 G and G' phonon coupled emission peak positions of (6,5) and (7,5) SWCNT

	(7,5)				(6,5)			
	Wavelength, nm		Energy, eV		Wavelength, nm		Energy, eV	
	Experiment	Derived	Experiment	Derived	Experiment	Derived	Experiment	Derived
E ₁₁ +G	882	882.02	1.407	1.407	846	851.48	1.467	1.457
E ₂₂ +G	576	585.79	2.154	2.118	518	520.86	2.395	2.382
E ₃₃ +G	N/A	318.95	N/A	3.890	N/A	326.13	N/A	3.804
E ₁₁ +G'	812	810.14	1.528	1.531	782	784.22	1.587	1.582
E ₂₂ +G'	554	553.19	2.240	2.243	492	494.90	2.522	2.507
E ₃₃ +G'	N/A	309.03	N/A	4.015	N/A	315.75	N/A	3.929
E ₁₁ +D	N/A	904.27	N/A	1.372	N/A	872.23	N/A	1.422
E ₂₂ +D	N/A	595.53	N/A	2.083	N/A	528.55	N/A	2.347
E ₃₃ +D	N/A	321.81	N/A	3.855	N/A	329.12	N/A	3.770

Table 4-3 Exciton energy transfer emission peak positions of (6,5) and (7,5) SWCNT

	Helicity	Band gap	Wavelength, nm	Energy, eV
excitation	(6,5)	E ₂₂	568.00	2.184
emission	(7,5)	E ₁₁	985.13	1.259

Table 4-4 Transverse exciton emission peak positions of (6,5) and (7,5) SWCNT

(7,5) nanotubes					
	Wavelength, nm		Energy, eV		ΔE , meV
	Experiment	Derived	Experiment	Derived	
E ₁₂	698	792.82	1.778	1.565	212.585
E _{13,31}	N/A	506.22	N/A	2.451	N/A
(6,5) nanotubes					
	Wavelength, nm		Energy, eV		ΔE , meV
	Experiment	Derived	Experiment	Derived	
E ₁₂	642	720.55	1.933	1.722	210.677
E _{13,31}	N/A	509.93	N/A	2.433	N/A

Figure 4-5 2D PLE maps of the nanotube suspensions obtained from different centrifugation speed. (a) (7,5) enriched Co-MCM-41 sample and (b) (6,5) enriched CoMoCAT sample.

Compared with Figure 4-3, Figures 4-5 does not include the intense $E_{11}-E_{11}$ peaks near the strong scattering lights. Shown in panel (a) and (c) in Figure 4-6, at the maximum emission wavelengths of (6,5) and (7,5) nanotubes, five PL peak features were selected for evaluation, including two peaks directly related to the main PL $E_{22}-E_{11}$ emissions and three PL sideband features. Several quantitative factors were adopted for the evaluation: (1) the PL FWHM of dominating (n,m) species, (2) the peak positions of $E_{22}-E_{11}$ PL emissions, (3) the intensity ratios between transverse $E_{12,21}$ sidebands and $E_{22}-E_{11}$ peaks, (4) the intensity ratios between phonon coupled $E_{22} + G$, G' sidebands and $E_{22}-E_{11}$ peaks, and (5) the

intensity ratios between $E_{33}-E_{11}$ and $E_{22}-E_{11}$ peaks. The easily determined overall intensity was measured other than peak deconvolution due to the fact that the PL peak from (7,5) nanotube emission caused by EET from (6,5) nanotubes is overlapped with its phonon coupled $E_{22} + G'$ sidebands.

Figures 4-6 and Figure 4-7 clearly demonstrate the correlations between these PL features and the centrifugation force applied to the SWCNT dispersions. Previous studies showed that small bundles exhibited larger FWHM values and a progressively shifted PL peak relative to individualized SWCNTs [46]. Similar trends in FWHM values and the PL peak position shifts were observed in this study. The FWHM values illustrated in panel (b) and (d) of Figure 4-6 decrease from 28-30 nm to 16-18 nm with the centrifugation force increasing from 20,000 to 180,000 g. Aggregation causes systematic changes in the PL sidebands. Shown in panel (b) and (d) of Figure 4-6, the intensity ratio of the transverse sideband to the main PL emission peak ($I(E_{12,21})/I(E_{22}-E_{11})$) of (7,5) nanotubes decreases from 0.4 to 0.2 with the increase of the centrifugation force. The same ratio of (6,5) nanotubes declines from 0.28 to 0.18. The intensity ratios of phonon coupled sidebands to the main PL emission peaks also decrease with the increase of the centrifugation force. On the contrary, the intensity ratios of $E_{33}-E_{11}$ peaks to the main PL emission peaks after centrifugation at 180,000 g are about 2-3 times higher than those observed after centrifugation at 20,000 g.

Figure 4-6 (a) and (c) PL spectra of the (7,5) and (6,5) enriched samples picked out at their emission wavelengths respectively; (b) and (d) correlation between the FWHM, the peak intensities and the centrifugation speed of the two sets of samples.

Figure 4-7 $E_{22}-E_{11}$ excitation and emission peaks shift with the increase of centrifugation force. (a) and (b), (7,5) enriched samples along the excitation and emission wavelength directions respectively; (c) and (d) (6,5) enriched samples along the excitation and emission wavelength directions respectively.

Figure 4-7 shows the peak shifts of the (6,5) and (7,5) nanotubes. The emission peaks blue-shifted about 15.3 and 11.9 meV, while the excitation peaks red-shifted about 9.9 and 7.2 meV, respectively. The red-shift of excitation peaks suggests that lower excitation energies are needed for individual nanotubes compared to those required by nanotube bundles, while the blue-shift of emission peaks indicates that individual nanotubes would emit at higher emission energies. These results confirmed that the SWCNT dispersions obtained after centrifugation at different forces contained various fractions of individualized and bundled nanotubes.

It is necessary to verify whether the observed correlations between PL sidebands and centrifugation forces are mainly contributed by the SWCNT aggregation, because PLE of SWCNTs could be sensitive to many factors [47-60]. It should be noted that SWCNT samples employed in this study were purified by using the centrifugation based method to efficiently remove impurities [34]; the influence of impurities on the observed PL results can be ruled out. To further control the aggregation of SWCNTs, dialysis was applied to vary the surfactant concentrations in the suspensions. Small surfactant molecules can pass through the semipermeable cellulose membrane when the surfactant concentrations differ on two sides of the membrane, while SWCNTs cannot penetrate due to their relatively bigger sizes. Individually dispersed nanotubes would rebundle back together and result in higher nanotube bundle fractions if the surfactant concentration in a SWCNT dispersion decreases [61]. Figure 4-8 and Figure 4-9 illustrate the PL maps of the 120,000 g centrifuged (7,5) and (6,5) enriched SWCNTs after dialysis for different periods of time. Extended dialysis led to more nanotube bundles; consequently, more pronounced PL sideband features were observed. Panel (b) of Figure 4-8 and Figure 4-9 show the emission

spectra of the dialyzed samples. The summary of intensity changes from PL sideband features is illustrated in Panel (c) of Figure 4-8 and Figure 4-9. The results suggested an enhanced nanotube aggregation upon dialysis. The dialysis time further extended up to 48 h, but no clear luminescence signals can be detected due to the severe rebundling of nanotubes. These results confirm that the intensity changes of PL sideband features are mainly contributed by the aggregation of SWCNTs.

Figure 4-8 PLE features of (7, 5) enriched nanotube samples after dialysis. (a), PLE maps, (b), spectra taken at the E_{11} emission wavelength and (c), intensity ratios of the SWCNT suspensions after dialyzed 3, 6, 12, 18 and 24 hours.

Figure 4-9 PLE features of (6, 5) enriched nanotube samples after dialysis. (a), PLE maps, (b), spectra taken at the E_{11} emission wavelength and (c), intensity ratios of the SWCNT suspensions after dialyzed 3, 6, 12, 18 and 24 hours.

It can be interpreted that the observed enhancement of PL sidebands is contributed by the changes in the exciton relaxation routes in SWCNTs. If a nanotube is well isolated from others, the preferred exciton relaxation route is the $E_{22}-E_{11}$, leading to an intense primary PL peak ($E_{22}-E_{11}$). When several nanotubes are closely bundled, fewer excitons would relax through the $E_{22}-E_{11}$ route because of the existence of additional relaxation routes. This results in the suppression of the primary PL peak. As shown in Figure 4-8 and Figure 4-9, the intensity of the primary PL peak decreases significantly from 6390 to 395 counts

and 5970 to 327 counts. The bundle formation would also suppress the $E_{33}-E_{11}$ relaxation route, leading to weaker $E_{33}-E_{11}$ sidebands. The tube-tube interactions may enhance the exciton relaxation through phonon assisted routes ($E_{22} + G$ and $E_{22} + G'$). The EETs can also be enhanced due to close contacts among nanotubes in bundles. Furthermore, the optical transition selection rules for $E_{12,21}$ shall be changed because of the changes in symmetry of electronic bands [62], which may contribute to the observed intensity increases in the $E_{12,21}$ sidebands as well.

4.3 Effect of solution environment

Different surfactants or solvents may also affect the PL process. It raises the question over whether the aggregation dependent photoluminescence sidebands can be observed in conditions other than in the SC dispersed aqueous solution. Two other commonly used surfactants: SDS and SDBS were tested in aqueous solutions. Figure 4-10 illustrates PL maps of SDS dispersed purified SWCNTs from Co-MCM-41 catalysts after centrifugation at 0, 60,000, 120,000, and 180,000 g. PL sideband intensities remarkably change on these PL maps. The intensity ratios of the three sidebands to the main PL $E_{22}-E_{11}$ peak are plotted in panel (b) of Figure 4-10. The intensity ratios obtained on SDS dispersed SWCNTs agree well with those on SC dispersed SWCNTs. Similar results were also found on SDBS dispersed SWCNTs. SWCNTs dispersed by a fluorine-based organic polymer (poly(9,9-dioctylfluorenyl-2,7-diyl), PFO) in toluene were also tested. This dispersion agent was previously used to achieve chirality selection extraction of SWCNTs [63]. Similarly, clear correlations between SWCNT PL sidebands and nanotube aggregation states were established, although the exact values of intensity ratios are different from those obtained in

aqueous solvents. Pure organic solvents, such as NMP and DMF, were also tested to disperse SWCNTs. However, with the increase of centrifugation force, most of the SWCNTs would precipitate in organic solvents. The overall PL intensities of SWCNTs dispersed in NMP or DMF are extremely weak (less than 60 counts). This suggests that SWCNT suspensions in organic solvents either contain a very small fraction of individual nanotubes or have strong solvent-nanotube interactions which may quench the PL emissions from SWCNTs [64].

Figure 4-10 (a) 2D PLE map of SDS suspended (6,5) enriched nanotube samples prepared at different centrifugation force. (b) Linewidth of the $E_{22} \rightarrow E_{11}$ singlet emission peaks and the three major sideband intensity ratios obtained from the PLE maps.

4.4 Comparison of evaluation methods for nanotube aggregation

Individually dispersing SWCNTs is one of the major obstacles to many fundamental studies and applications. The strategies to individualize nanotubes include the following:

(1) chemically functionalizing nanotubes by introducing hydrophilic functional groups on nanotube surfaces [65-66]; (2) coating nanotubes with surfactants, biomolecules, or polymers [63, 67-68]; and (3) dispersing nanotubes in specific solvents such as NMP [69]. The evaluation of various proposed dispersion methods relies on the efficiency and sensitivity of the methodology characterizing the aggregation of SWCNTs. Commonly applied methods for evaluating SWCNT aggregation include the following: microscopes, such as scanning electron microscope (SEM), transmission electron microscope (TEM), and atomic force microscope (AFM); and spectroscopic techniques, such as absorption, Raman, and PL. SEM has difficulty in characterizing individual SWCNTs with the diameter at 1 nm. The sample preparation procedures required for TEM measurement usually involve the deposition of nanotubes on TEM grids, washing, and drying. The aggregation of nanotubes may change during the sample preparation. All microscope based methods have the same disadvantage that only a small fraction of samples can be evaluated. Spectroscopic methods can directly probe the aggregation of SWCNTs in bulk suspensions. Due to the resonance enhancement effect of SWCNT, multiple laser excitations are required to characterize SWCNTs containing different (n,m) species by using Raman spectroscopy. It is proposed here that the well-resolved PL sideband features can be adopted as a highly sensitive tool to evaluate the aggregation of SWCNTs. In particular, the intensity ratios of three PL sideband features (the transverse sideband $E_{12,21}$, the phonon coupled sidebands $E_{22} + G, G'$, and the $E_{33}-E_{11}$ emission) to the main $E_{22}-E_{11}$ peak can be used. As shown in Figure 4-11, the comparative UV-vis-NIR absorption spectroscopy study was carried out to characterize the SWCNT suspensions obtained after centrifugation at different forces.

Figure 4-11 (a) UV-vis-NIR absorption spectroscopy of (7,5) enriched SWCNTs after centrifuge at different centrifugation forces. The spectra were shifted in y-axis to better illustrate the possible changes in absorption peaks of different (n,m) species. (b) Unshifted absorption spectra obtained from SWCNT dispersions after centrifugation at different forces.

Figure 4-12 Typical AFM images for SWCNT dispersion obtained after (a) 20,000 g, (b) 60,000 g, (c) 120,000 g and (d) 180,000 g force centrifugation. (e) and (f) show the height profiles of black line in (c) and (d).

Absorption spectra of different SWCNT suspensions demonstrate similar absorption spectroscopic patterns. Although the FWHM of absorption peaks and the absorption peak shifts were previously linked to the aggregation of nanotubes, only minor changes can be observed in Figure 4-11. On the contrary, aggregation-dependent PL sideband features are much more pronounced.

AFM has also been widely applied to demonstrate the individualized dispersion of SWCNTs [64, 69]. Panels (a) ~ panel (d) of Figure 4-12 show the AFM images of (7,5) enriched SWCNT dispersions. Nanotubes were deposited on 1 cm × 1 cm Si wafers with a 200 nm thick SiO₂ top layer. The SiO₂ surface was pretreated with 3-aminopropyltriethoxysilane (APTES) to enhance the nanotube-surface interaction [35]. The height scale of these images was set to the same value for direct comparison. Figure 4-12 supports the claim that the SWCNT samples used in this study are free of impurities. (Note that bright dots are due to surfactant residues.) The AFM image obtained from nanotube dispersion centrifuged at 20,000 g clearly shows some nanotube bundles, while most of the nanotube bundles can be removed upon the increase of centrifugation force to 60,000 g. Panels e and f of Figure 4-12 illustrate the height profiles for dispersions centrifuged at 120,000 and 180,000 g, respectively. They verify that the samples used in this study contained different amounts of bundles. The height of most peaks is at 0.9-1.5 nm, which is coincident with the height of individualized nanotubes. The peak with the height of ~2.7 nm in panel (e) of Figure 4-12 is likely attributed to a cross point of two overlapping nanotubes, while the peak with the height of ~3.1 nm is from a small bundle consisting of two or three individual nanotubes. About 8-9% of the observed nanotube like structures (around 10 out of the total 110-120 counted nanotubes in the measured area) has a height higher than that of an individual nanotube. However, it is difficult to determine whether they are originally bundled in SWCNT suspensions or rebundled on substrate during the drying and washing process. The root-mean-square (RMS) of an AFM height profile is often used to quantify the aggregation of SWCNTs. The RMS value of height profiles for

panel (a) through panel (d) in Figure 4-12 is 2.627, 1.332, 1.319, and 1.307 nm, respectively, with less than 2% difference among the values of the latter three.

To make a more explicit comparison, we also compiled the results of UV-vis absorption, AFM, and PL maps together in Figure 4-13. Exponential curves were fitted to subtract absorbance background from UV-vis absorption spectra. The ratios between background areas and the total integrated areas under absorption spectra were plotted against centrifugation speed in panel (d) of Figure 4-13.

Figure 4-13 Comparison of the different evaluation methods applied to nanotube dispersions after centrifugation at different forces. (a) UV-vis-NIR absorption spectra; (b) tapping mode AFM height profiles; (c) 2D PL maps and (d) comparison of the representative criteria extracted from different characterization methods.

The root-mean-square of AFM height profiles was also plotted. For PL maps, the intensity ratios of the three sideband features to the major $E_{22}-E_{11}$ emission peak were used for comparison. The absorbance background ratios of the four samples range from 72.9% (20,000 g) to 63.6% (120,000 g). The differences among the latter three samples at higher centrifuge speeds were within 5%. Similarly, the RMS values were almost the same for the suspensions obtained after centrifugation at 60,000, 120,000, and 180,000 g. However, all three PL sidebands from the same set of samples exhibit clear and significant changes. It can be concluded that PL sideband features are more sensitive to monitor the aggregation of SWCNTs than UV-vis absorption and AFM. Overall, in potential applications, a standard calibration curve to correlate the aggregation of SWCNTs and their PL sideband features in a specific surfactant and solvent mixture should be constructed first. Subsequently, the aggregation of nanotubes can be easily monitored by referring to the standard curve. This proposed method may be applied under various dispersion mixtures, as long as the dispersion agents or solvents do not have a strong PL interference with that of SWCNTs.

4.5 Conclusion

The correlation between nanotube PLE sideband intensities (the transverse $E_{12,21}-E_{11}$ emission, the phonon coupled $E_{22} + G, G'-E_{11}$ emission and the $E_{33}-E_{11}$ emission band) and the nanotube aggregation status in a suspension was obtained from two purified nanotube samples enriched with (6,5) and (7,5) nanotubes respectively. SWCNT suspensions containing different bundle fractions were prepared via centrifugation of surfactant dispersed nanotube dispersions at different centrifugal forces ranging from 20,000 to 180,000 g. The aggregation of nanotubes can be further tuned by the controlled rebundling

through dialysis. The intensity ratios between $E_{12,21}$ or $E_{22} + G, G'$ and the primary $E_{22}-E_{11}$ PL peak decreased with the removal of nanotube bundles. On the contrary, the intensity ratio between $E_{33}-E_{11}$ and $E_{22}-E_{11}$ PL peaks increased when fewer nanotube bundles existed in suspensions. These aggregation-dependent PL sidebands can also be observed under different dispersion conditions, such as SDS, SDBS aqueous solutions, and PFO in toluene. They are more sensitive toward characterizing the aggregation of SWCNTs than absorption spectroscopy and AFM.

4.6 Reference

1. Girifalco, L.A., M. Hodak, and R.S. Lee, *Carbon nanotubes, buckyballs, ropes, and a universal graphitic potential*. Phys. Rev. B: Condens. Matter, 2000. **62**(19): p. 13104 - 13110
2. Wang, F., G. Dukovic, L.E. Brus, and T.F. Heinz, *The optical resonances in carbon nanotubes arise from excitons*. Science, 2005. **308**(5723): p. 838-841.
3. Wang, R.K., H.O. Park, W.C. Chen, C. Silvera-Batista, R.D. Reeves, J.E. Butler, and K.J. Ziegler, *Improving the Effectiveness of Interfacial Trapping in Removing Single-Walled Carbon Nanotube Bundles*. J. Am. Chem. Soc., 2008. **130**(44): p. 14721-14728.
4. Giordani, S., S.D. Bergin, V. Nicolosi, S. Lebedkin, M.M. Kappes, W.J. Blau, and J.N. Coleman, *Debundling of single-walled nanotubes by dilution: Observation of large populations of individual nanotubes in amide solvent dispersions*. J. Phys. Chem. B, 2006. **110**(32): p. 15708-15718.
5. Silvera-Batista, C.A., P. Weinberg, J.E. Butler, and K.J. Ziegler, *Long-Term Improvements to Photoluminescence and Dispersion Stability by Flowing SDS-SWNT Suspensions through Microfluidic Channels*. J. Am. Chem. Soc., 2009. **131**(35): p. 12721-12728.
6. O'Connell, M.J., S.M. Bachilo, C.B. Huffman, V.C. Moore, M.S. Strano, E.H. Haroz, K.L. Rialon, P.J. Boul, W.H. Noon, C. Kittrell, J.P. Ma, R.H. Hauge, R.B.

- Weisman, and R.E. Smalley, *Band gap fluorescence from individual single-walled carbon nanotubes*. Science, 2002. **297**(5581): p. 593-596.
7. Crochet, J., M. Clemens, and T. Hertel, *Quantum yield heterogeneities of aqueous single-wall carbon nanotube suspensions*. J. Am. Chem. Soc., 2007. **129**(26): p. 8058-8059.
8. Niyogi, S., S. Boukhalfa, S.B. Chikkannanavar, T.J. McDonald, M.J. Heben, and S.K. Doorn, *Selective Aggregation of Single-Walled Carbon Nanotubes via Salt Addition*. J. Am. Chem. Soc., 2007. **129**(7): p. 1898-1899.
9. Torrens, O.N., D.E. Milkie, M. Zheng, and J.M. Kikkawa, *Photoluminescence from intertube carrier migration in single-walled carbon nanotube bundles*. Nano Lett., 2006. **6**(12): p. 2864-2867.
10. Cognet, L., D.A. Tsyboulski, J.D.R. Rocha, C.D. Doyle, J.M. Tour, and R.B. Weisman, *Stepwise quenching of exciton fluorescence in carbon nanotubes by single-molecule reactions*. Science, 2007. **316**(5830): p. 1465-1468.
11. Gokus, T., A. Hartschuh, H. Harutyunyan, M. Allegrini, F. Hennrich, M. Kappes, A.A. Green, M.C. Hersam, P.T. Araujo, and A. Jorio, *Exciton decay dynamics in individual carbon nanotubes at room temperature*. Appl. Phys. Lett., 2008. **92**(15): p. 153116.
12. Qian, H., P.T. Araujo, C. Georgi, T. Gokus, N. Hartmann, A.A. Green, A. Jorio, M.C. Hersam, L. Novotny, and A. Hartschuh, *Visualizing the local optical response of semiconducting carbon nanotubes to DNA-wrapping*. Nano Lett., 2008. **8**(9): p. 2706-2711.
13. Tsyboulski, D.A., J.D.R. Rocha, S.M. Bachilo, L. Cognet, and R.B. Weisman, *Structure-dependent fluorescence efficiencies of individual single-walled carbon nanotubes*. Nano Lett., 2007. **7**(10): p. 3080-3085.
14. Doyle, C.D., J.D.R. Rocha, R.B. Weisman, and J.M. Tour, *Structure-dependent reactivity of semiconducting single-walled carbon nanotubes with benzenediazonium salts*. J. Am. Chem. Soc., 2008. **130**(21): p. 6795-6800.
15. Strano, M.S., C.B. Huffman, V.C. Moore, M.J. O'Connell, E.H. Haroz, J. Hubbard, M. Miller, K. Rialon, C. Kittrell, S. Ramesh, R.H. Hauge, and R.E. Smalley,

- Reversible, band-gap-selective protonation of single-walled carbon nanotubes in solution.* J. Phys. Chem. B, 2003. **107**(29): p. 6979-6985.
16. Choi, J.H. and M.S. Strano, *Solvatochromism in single-walled carbon nanotubes.* Appl. Phys. Lett., 2007. **90**(22): p. 223114.
 17. Blackburn, J.L., T.J. McDonald, W.K. Metzger, C. Engtrakul, G. Rumbles, and M.J. Heben, *Protonation effects on the branching ratio in photoexcited single-walled carbon nanotube dispersions.* Nano Lett., 2008. **8**(4): p. 1047-1054.
 18. Fagan, J.A., J.R. Simpson, B.J. Bauer, S.H.D. Lacerda, M.L. Becker, J. Chun, K.B. Migler, A.R.H. Walker, and E.K. Hobbie, *Length-dependent optical effects in single-wall carbon nanotubes.* J. Am. Chem. Soc., 2007. **129**(34): p. 10607-10612.
 19. Heller, D.A., R.M. Mayrhofer, S. Baik, Y.V. Grinkova, M.L. Usrey, and M.S. Strano, *Concomitant length and diameter separation of single-walled carbon nanotubes.* J. Am. Chem. Soc., 2004. **126**(44): p. 14567-14573.
 20. Dresselhaus, M.S., G. Dresselhaus, R. Saito, and A. Jorio, *Exciton Photophysics of Carbon Nanotubes.* Annu. Rev. Phys. Chem. , 2007. **58**(1): p. 719-747.
 21. Matsuda, K., T. Inoue, Y. Murakami, S. Maruyama, and Y. Kanemitsu, *Exciton fine structure in a single carbon nanotube revealed through spectral diffusion.* Phys. Rev. B: Condens. Matter, 2008. **77**(19): p. 193405.
 22. Chou, S.G., F. Plentz, J. Jiang, R. Saito, D. Nezich, H.B. Ribeiro, A. Jorio, M.A. Pimenta, G.G. Samsonidze, A.P. Santos, M. Zheng, G.B. Onoa, E.D. Semke, G. Dresselhaus, and M.S. Dresselhaus, *Phonon-assisted excitonic recombination channels observed in DNA-wrapped carbon nanotubes using photoluminescence spectroscopy.* Phys. Rev. Lett., 2005. **94**(12): p. 127402.
 23. Hertel, T., V. Perebeinos, J. Crochet, K. Arnold, M. Kappes, and P. Avouris, *Intersubband Decay of 1-D Exciton Resonances in Carbon Nanotubes.* Nano Lett., 2008. **8**(1): p. 87-91.
 24. Miyauchi, Y. and S. Maruyama, *Identification of an excitonic phonon sideband by photoluminescence spectroscopy of single-walled carbon-13 nanotubes.* Phys. Rev. B: Condens. Matter, 2006. **74**(3): p. 035415.

25. Murakami, Y. and J. Kono, *Existence of an upper limit on the density of excitons in carbon nanotubes by diffusion-limited exciton-exciton annihilation: Experiment and theory*. Phys. Rev. B: Condens. Matter, 2009. **80**(3): p. 035432.
26. Murakami, Y., B. Lu, S. Kazaoui, N. Minami, T. Okubo, and S. Maruyama, *Photoluminescence sidebands of carbon nanotubes below the bright singlet excitonic levels*. Phys. Rev. B: Condens. Matter, 2009. **79**(19): p. 195407.
27. Zhao, H. and S. Mazumdar, *Electron-Electron Interaction Effects on the Optical Excitations of Semiconducting Single-Walled Carbon Nanotubes*. Phys. Rev. Lett., 2004. **93**(15): p. 157402.
28. Kiowski, O., K. Arnold, S. Lebedkin, F. Hennrich, and M.M. Kappes, *Direct observation of deep excitonic states in the photoluminescence spectra of single-walled carbon nanotubes*. Phys. Rev. Lett., 2007. **99**(23): p. 237402.
29. Lebedkin, S., F. Hennrich, O. Kiowski, and M.M. Kappes, *Photophysics of carbon nanotubes in organic polymer-toluene dispersions: Emission and excitation satellites and relaxation pathways*. Phys. Rev. B: Condens. Matter, 2008. **77**(16): p. 165429.
30. Tan, P.H., A.G. Rozhin, T. Hasan, P. Hu, V. Scardaci, W.I. Milne, and A.C. Ferrari, *Photoluminescence spectroscopy of carbon nanotube bundles: Evidence for exciton energy transfer*. Phys. Rev. Lett., 2007. **99**(13): p. 137402.
31. Chen, F.M., W.J. Zhang, M.L. Jia, L. Wei, X.F. Fan, J.L. Kuo, Y. Chen, M.B. Chan-Park, A.D. Xia, and L.J. Li, *Energy Transfer from Photo-Excited Fluorene Polymers to Single-Walled Carbon Nanotubes*. J. Phys. Chem. C, 2009. **113**(33): p. 14946-14952.
32. Chen, Y., D. Ciuparu, S. Lim, G.L. Haller, and L.D. Pfefferle, *The effect of the cobalt loading on the growth of single wall carbon nanotubes by CO disproportionation on Co-MCM-41 catalysts*. Carbon, 2006. **44**(1): p. 67-78.
33. Ciuparu, D., Y. Chen, S. Lim, G.L. Haller, and L. Pfefferle, *Uniform-Diameter Single-Walled Carbon Nanotubes Catalytically Grown in Cobalt-Incorporated MCM-41*. The Journal of Physical Chemistry B, 2003. **108**(2): p. 503-507.
34. Wei, L., B. Wang, Q. Wang, L.-J. Li, Y. Yang, and Y. Chen, *Effect of Centrifugation on the Purity of Single-Walled Carbon Nanotubes from MCM-41*

- Containing Cobalt*. The Journal of Physical Chemistry C, 2008. **112**(45): p. 17567-17575.
35. Liu, J., M.J. Casavant, M. Cox, D.A. Walters, P. Boul, W. Lu, A.J. Rimberg, K.A. Smith, D.T. Colbert, and R.E. Smalley, *Controlled deposition of individual single-walled carbon nanotubes on chemically functionalized templates*. Chemical Physics Letters, 1999. **303**(1-2): p. 125-129.
 36. Bachilo, S.M., L. Balzano, J.E. Herrera, F. Pompeo, D.E. Resasco, and R.B. Weisman, *Narrow (n,m)-Distribution of Single-Walled Carbon Nanotubes Grown Using a Solid Supported Catalyst*. Journal of the American Chemical Society, 2003. **125**(37): p. 11186-11187.
 37. Chen, Y., L. Wei, B. Wang, S. Lim, D. Ciuparu, M. Zheng, J. Chen, C. Zoican, Y. Yang, G.L. Haller, and L.D. Pfefferle, *Low-Defect, Purified, Narrowly (n,m)-Dispersed Single-Walled Carbon Nanotubes Grown from Cobalt-Incorporated MCM-41*. ACS Nano, 2007. **1**(4): p. 327-336.
 38. Weisman, R.B. and S.M. Bachilo, *Dependence of Optical Transition Energies on Structure for Single-Walled Carbon Nanotubes in Aqueous Suspension: An Empirical Kataura Plot*. Nano Letters, 2003. **3**(9): p. 1235-1238.
 39. Lebedkin, S., F. Hennrich, O. Kiowski, and M.M. Kappes, *Photophysics of carbon nanotubes in organic polymer-toluene dispersions: Emission and excitation satellites and relaxation pathways*. Physical Review B (Condensed Matter and Materials Physics), 2008. **77**(16): p. 165429-8.
 40. Haroz, E.H., S.M. Bachilo, R.B. Weisman, and S.K. Doorn, *Curvature effects on the E_{33} and E_{44} exciton transitions in semiconducting single-walled carbon nanotubes*. Physical Review B (Condensed Matter and Materials Physics), 2008. **77**(12): p. 125405-9.
 41. Miyauchi, Y. and S. Maruyama, *Identification of an excitonic phonon sideband by photoluminescence spectroscopy of single-walled carbon-13 nanotubes*. Physical Review B (Condensed Matter and Materials Physics), 2006. **74**(3): p. 035415-7.
 42. Chen, F., W. Zhang, M. Jia, L. Wei, X.-F. Fan, J.-L. Kuo, Y. Chen, M.B. Chan-Park, A. Xia, and L.-J. Li, *Energy Transfer from Photo-Excited Fluorene Polymers*

- to *Single-Walled Carbon Nanotubes*. The Journal of Physical Chemistry C, 2009. **113**(33): p. 14946-14952.
43. Tan, P.H., T. Hasan, F. Bonaccorso, V. Scardaci, A.G. Rozhin, W.I. Milne, and A.C. Ferrari. *Optical properties of nanotube bundles by photoluminescence excitation and absorption spectroscopy*. in *Symposium on Electron Transport in Low-Dimensional Carbon Structures/Science and Technology of Nanotubes and Nanowires*. 2007. Strasbourg, FRANCE.
 44. Torrens, O.N., D.E. Milkie, M. Zheng, and J.M. Kikkawa, *Photoluminescence from Intertube Carrier Migration in Single-Walled Carbon Nanotube Bundles*. Nano Letters, 2006. **6**(12): p. 2864-2867.
 45. O'Connell, M.J., S.M. Bachilo, C.B. Huffman, V.C. Moore, M.S. Strano, E.H. Haroz, K.L. Rialon, P.J. Boul, W.H. Noon, C. Kittrell, J. Ma, R.H. Hauge, R.B. Weisman, and R.E. Smalley, *Band Gap Fluorescence from Individual Single-Walled Carbon Nanotubes*. Science, 2002. **297**(5581): p. 593-596.
 46. Ju, S.-Y., W.P. Kopcha, and F. Papadimitrakopoulos, *Brightly Fluorescent Single-Walled Carbon Nanotubes via an Oxygen-Excluding Surfactant Organization*. Science, 2009. **323**(5919): p. 1319-1323.
 47. Blackburn, J.L., T.J. McDonald, W.K. Metzger, C. Engtrakul, G. Rumbles, and M.J. Heben, *Protonation Effects on the Branching Ratio in Photoexcited Single-Walled Carbon Nanotube Dispersions*. Nano Letters, 2008. **8**(4): p. 1047-1054.
 48. Choi, J.H. and M.S. Strano, *Solvatochromism in single-walled carbon nanotubes*. Applied Physics Letters, 2007. **90**(22): p. 223114-3.
 49. Cognet, L., D.A. Tsyboulski, J.-D.R. Rocha, C.D. Doyle, J.M. Tour, and R.B. Weisman, *Stepwise Quenching of Exciton Fluorescence in Carbon Nanotubes by Single-Molecule Reactions*. Science, 2007. **316**(5830): p. 1465-1468.
 50. Doyle, C.D., J.-D.R. Rocha, R.B. Weisman, and J.M. Tour, *Structure-Dependent Reactivity of Semiconducting Single-Walled Carbon Nanotubes with Benzenediazonium Salts*. Journal of the American Chemical Society, 2008. **130**(21): p. 6795-6800.
 51. Duque, J.G., L. Cognet, A.N.G. Parra-Vasquez, N. Nicholas, H.K. Schmidt, and M. Pasquali, *Stable Luminescence from Individual Carbon Nanotubes in Acidic, Basic,*

- and Biological Environments*. Journal of the American Chemical Society, 2008. **130**(8): p. 2626-2633.
52. Fagan, J.A., J.R. Simpson, B.J. Bauer, S.H. De Paoli Lacerda, M.L. Becker, J. Chun, K.B. Migler, A.R. Hight Walker, and E.K. Hobbie, *Length-Dependent Optical Effects in Single-Wall Carbon Nanotubes*. Journal of the American Chemical Society, 2007. **129**(34): p. 10607-10612.
 53. Harutyunyan, H., T. Gokus, A.A. Green, M.C. Hersam, M. Allegrini, and A. Hartschuh, *Defect-Induced Photoluminescence from Dark Excitonic States in Individual Single-Walled Carbon Nanotubes*. Nano Letters, 2009. **9**(5): p. 2010-2014.
 54. Heller, D.A., R.M. Mayrhofer, S. Baik, Y.V. Grinkova, M.L. Usrey, and M.S. Strano, *Concomitant Length and Diameter Separation of Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2004. **126**(44): p. 14567-14573.
 55. Naumov, A.V., S.M. Bachilo, D.A. Tsyboulski, and R.B. Weisman, *Electric Field Quenching of Carbon Nanotube Photoluminescence*. Nano Letters, 2008. **8**(5): p. 1527-1531.
 56. Qian, H., P.T. Araujo, C. Georgi, T. Gokus, N. Hartmann, A.A. Green, A. Jorio, M.C. Hersam, L. Novotny, and A. Hartschuh, *Visualizing the Local Optical Response of Semiconducting Carbon Nanotubes to DNA-Wrapping*. Nano Letters, 2008. **8**(9): p. 2706-2711.
 57. Silvera-Batista, C.A., P. Weinberg, J.E. Butler, and K.J. Ziegler, *Long-Term Improvements to Photoluminescence and Dispersion Stability by Flowing SDS-SWNT Suspensions through Microfluidic Channels*. Journal of the American Chemical Society, 2009. **131**(35): p. 12721-12728.
 58. Strano, M.S., C.B. Huffman, V.C. Moore, M.J. O'Connell, E.H. Haroz, J. Hubbard, M. Miller, K. Rialon, C. Kittrell, S. Ramesh, R.H. Hauge, and R.E. Smalley, *Reversible, Band-Gap-Selective Protonation of Single-Walled Carbon Nanotubes in Solution*. The Journal of Physical Chemistry B, 2003. **107**(29): p. 6979-6985.

59. Tsyboulski, D.A., J.-D.R. Rocha, S.M. Bachilo, L. Cognet, and R.B. Weisman, *Structure-Dependent Fluorescence Efficiencies of Individual Single-Walled Carbon Nanotubes*. Nano Letters, 2007. **7**(10): p. 3080-3085.
60. Wang, R.K., H.-O. Park, W.-C. Chen, C. Silvera-Batista, R.D. Reeves, J.E. Butler, and K.J. Ziegler, *Improving the Effectiveness of Interfacial Trapping in Removing Single-Walled Carbon Nanotube Bundles*. Journal of the American Chemical Society, 2008. **130**(44): p. 14721-14728.
61. Richard, C., F. Balavoine, P. Schultz, T.W. Ebbesen, and C. Mioskowski, *Supramolecular Self-Assembly of Lipid Derivatives on Carbon Nanotubes*. Science, 2003. **300**(5620): p. 775-778.
62. Miyauchi, Y., M. Oba, and S. Maruyama, *Cross-polarized optical absorption of single-walled nanotubes by polarized photoluminescence excitation spectroscopy*. Physical Review B (Condensed Matter and Materials Physics), 2006. **74**(20): p. 205440-6.
63. Chen, F., B. Wang, Y. Chen, and L.-J. Li, *Toward the Extraction of Single Species of Single-Walled Carbon Nanotubes Using Fluorene-Based Polymers*. Nano Letters, 2007. **7**(10): p. 3013-3017.
64. Giordani, S., S.D. Bergin, V. Nicolosi, S. Lebedkin, M.M. Kappes, W.J. Blau, and J.N. Coleman, *Debundling of Single-Walled Nanotubes by Dilution: Observation of Large Populations of Individual Nanotubes in Amide Solvent Dispersions*. The Journal of Physical Chemistry B, 2006. **110**(32): p. 15708-15718.
65. Banerjee, S., T. Hemraj-Benny, and S.S. Wong, *Covalent Surface Chemistry of Single-Walled Carbon Nanotubes*. Advanced Materials, 2005. **17**(1): p. 17-29.
66. Niyogi, S., M.A. Hamon, H. Hu, B. Zhao, P. Bhowmik, R. Sen, M.E. Itkis, and R.C. Haddon, *Chemistry of Single-Walled Carbon Nanotubes*. Accounts of Chemical Research, 2002. **35**(12): p. 1105-1113.
67. Wenseleers, W., I.I. Vlasov, E. Goovaerts, E.D. Obraztsova, A.S. Lobach, and A. Bouwen, *Efficient Isolation and Solubilization of Pristine Single-Walled Nanotubes in Bile Salt Micelles*. Advanced Functional Materials, 2004. **14**(11): p. 1105-1112.
68. Yan, L.Y., Y.F. Poon, M.B. Chan-Park, Y. Chen, and Q. Zhang, *Individually Dispersing Single-Walled Carbon Nanotubes with Novel Neutral pH Water-Soluble*

- Chitosan Derivatives*. The Journal of Physical Chemistry C, 2008. **112**(20): p. 7579-7587.
69. Bergin, S.D., V. Nicolosi, P.V. Streich, S. Giordani, Z. Sun, A.H. Windle, P. Ryan, N.P.P. Niraj, Z.-T.T. Wang, L. Carpenter, W.J. Blau, J.J. Boland, J.P. Hamilton, and J.N. Coleman, *Towards Solutions of Single-Walled Carbon Nanotubes in Common Solvents*. Advanced Materials, 2008. **20**(10): p. 1876-1881.

Chapter 5

(n,m) Selective Enrichment of SWCNTs via Co-Surfactant Extraction

Mono-dispersed SWCNT sample is crucial to many SWCNT applications as well as the investigation of SWCNT intrinsic properties. As discussed in Chapter 2, efforts have been made to improve the bulk sample chiral distribution. Recent progress of post-synthetic approaches indicates that the interaction between the suspension molecules and the nanotubes may play an important role during the separation process as the evidences from DNA assisted separation [1-2], fluorine polymer selective wrapping [3-4] and SC assisted separation using density gradient ultracentrifugation[5]. Chiral selective sedimentation by salt addition further hints that such interaction should be detailed studied [6-7]. Semiconducting-metallic (S-M) separation of large diameter SWCNT can be achieved by DGU in an as-prepared gradient contains co-surfactant with an optimized concentration ratio [5]. More recently, co-surfactant separation based on other surfactant molecules and combinations have been reported [8-9]. Prior to these reports, it is found that small diameter nanotubes can be selectively enriched by a SDS-SC co-surfactant extraction.

5.1 Sodium dodecyl sulfate-sodium cholate co-surfactant extraction of SWCNT

Narrowly (n,m) -distributed SWCNTs were obtained from Co-MCM-41 catalysts. The catalyst and SWCNTs were synthesized following the protocol described in Chapter 2 [10-12]. The as-synthesized nanotubes were purified before dispersion by the ultracentrifugation based method discussed in Chapter 3 [13]. SDS (MP Biomedicals), SC

(Sigma, SigmaUltra), and sodium dodecyl benzene sulfonate (SDBS) (Sigma-Aldrich, 99%) were used as received. Co-surfactant solutions were prepared by dissolving specific weight ratios of surfactants in 10% (w/v) iodixanol (60% (w/v), OptiPrep[®], Sigma) water solutions (which show better (n, m) selectivity than pure water). The weight and molar ratios of co-surfactant solutions used are listed in Table 5-1.

Table 5-1 Concentration of SDS-SC co-surfactant solutions

Surfactant	CMC (25 °C), mM[14]	weight ratio of 2 wt% SC	SC conc., mM	SDS conc., mM	SC/SDS molar ratio
SDS (1 wt%)	8.35	0	0	34.72	N/A
		0.1	4.65	62.50	0.07
		0.2	9.29	55.56	0.17
		0.3	13.94	48.61	0.29
		0.4	18.58	41.67	0.45
SDS/SC (2 wt%)		0.5	23.23	34.72	0.67
		0.6	27.87	27.78	1.00
		0.7	32.52	20.83	1.56
		0.8	37.16	13.89	2.68
		0.85	39.48	10.42	3.79
		0.9	41.81	6.94	6.02
SC (2 wt%)	~6	1	46.45	0.00	N/A

10.0 mg of SWCNTs were dispersed in 10 mL of surfactant solution by sonication using an ultrasonicator (SONICS, VCX-130) at 20 W for 30 min in an ice bath. The suspension was centrifuged for 1 h at 50,000 g (Hitachi-Koki, CS150GXL) to remove nanotube bundles and other impurities. Subsequently, homogeneous supernatants were collected for spectroscopic measurement (upper 80% supernatant). PLE characterization and UV-vis-NIR absorption was also performed. Multiple parallel experiments (dispersions and spectroscopic measurements) were carried out, and no significant difference was observed among parallel experiments.

Systematic changes in the fluorescence and absorption spectra are observed when the weight ratio between SDS and SC varies in co-surfactant solutions, as shown in Figure 5-1 and Figures 5-2. (7,5) is the most dominate semiconducting chirality in the bulk samples obtained from Co-MCM-41 catalyst, which consists about 45~48% of total semiconducting nanotubes. No obvious difference in (*n,m*) selectivity was found for individual SDS and SC solutions. However, with increasing SC concentration in co-surfactant solutions, the intensity of the (6,5) nanotubes increases while that of the (7,5) nanotubes decreases. When SDS to SC weight ratio is 1:4, the intensity of the (6,5) nanotubes reaches the maximum. However, when the SC concentration is further increased, the (6,5) intensity drops back to the level observed in individual surfactant solutions. Taking into account the relative fluorescence efficiency, the abundance of different semiconducting SWCNTs were evaluated by the method proposed in Chapter 2 based on the single-particle tight binding theory model. The results are depicted in Figure 5-3 and summarized in Table A I-1 to Table A I-12 (Appendix I).

Figure 5-1 Optical absorption spectra of SWCNTs in SDS-SC co-surfactant solutions. (A) SDS (1 wt %), (B) total 2 wt % and SDS:SC = 90:10, (C) total 2 wt % and SDS:SC = 80:20, (D) total 2 wt % and SDS:SC = 70:30, (E) total 2 wt % and SDS:SC = 60:40, (F) total 2 wt % and SDS:SC = 50:50, (G) total 2 wt % and SDS:SC = 40:60, (H) total 2 wt % and SDS:SC = 30:70, (I) total 2 wt % and SDS:SC = 20:80, (J) total 2 wt % and SDS:SC = 15:85, (K) total 2 wt % and SDS:SC = 10:90, (L) SC (2 wt %).

Figure 5-2 2D PLE maps of SWCNTs in SDS-SC co-surfactant solutions. A to L correspond to sample codes in Figure 5-1. Each bright spot corresponds to one SWCNT chiral type as labeled.

Abundance evaluation from PL spectroscopy clearly demonstrated that small diameter nanotubes become most dominant chiral species when the weight ratio of SDS to SC is 1:4. The abundance of the smallest (6,5) nanotubes increased from 13% to 47% while the abundance of the larger (7,5) nanotubes decreased to less than 15% comparing to the value which is about 45% in both pure SDS or SC dispersions.

Figure 5-3 Abundance change of (6,5) and (7,5) nanotubes. A. pure SDS solution; B. SDS : SC = 2 : 3; C. SDS : SC = 1 : 4 and D. pure SC solution.

5.2 Origin of the selectivity

The optical characteristics of SWCNTs depend on nanotube chirality, diameter, length, and solution environment [15-17]. Owing to the fact that the sonication processes were kept the same and no obvious difference in nanotube length (by AFM) was found for all samples, the influence of length was ruled out. It is known that the fluorescence intensity is sensitive

to the environment, for instance, the ionic strength of solutions. Hence, a resuspension experiment was designed and carried out to clarify that the observed fluorescence intensity alterations were due to the difference in relative content of SWCNT species. 10 mL of the SWCNT suspended in 1:4 SDS-SC co-surfactant solutions were filtered on a mixed cellulose ester membrane (25nm, Millipore) using vacuum filtration. Water (a total of 1 L) was used to repeatedly wash away surfactants. Next, “clean” SWCNTs on the membrane filter were divided into two fractions and resuspended in SDS (1 wt %) and SC (2 wt %) surfactant solutions separately. PL measurements were performed on these two resuspended samples. Figure 5-4 confirms that no difference is observed among these three dispersions, indicating that the remarkable nanotube enrichment using co-surfactant suggested in Figure 5-2 is strongly corroborated.

Figure 5-4 2D PLE map for SWCNTs suspended in (a) total 2 wt % SDS:SC = 1:4, resuspended in (b) 1 wt% SDS and (c) 2 wt% SC.

In the current work, even though the density gradient was not used, a centrifugation step was nevertheless employed prior to spectroscopic analysis. The observed chirality

selectivity could be due to the density difference amplified by centrifugation instead of binding electivity induced by different co-surfactant solutions. To address this issue, fluorescence and UV-vis-NIR measurement were performed on the as-dispersed samples without the centrifugation step. After sonication in the SC and SC/SDS co-surfactant solutions, the solutions were poured into two capped glass vials and sealed up with Parafilm[®]. The solutions were kept still for 24 hours so that the undispersed SWCNTs settled at the bottom of the vials. Clear SWCNT dispersions were observed. The whole supernatants were carefully collected and used for spectroscopic analysis. As shown in Figure 5-5, significant differences between these two samples are noted. These differences are similar to those observed after the centrifugation step. Therefore, we conclude that selective binding and solubilization induced by co-surfactants indeed take place, and centrifugation can help the undispersed SWCNTs settle quickly.

Arnold *et al.* reported the separation of metallic and semiconducting nanotubes using density gradient together with 1:4 SDS/SC mixtures [5]. They observed such separation using laser ablation-grown SWCNTs. However, we do not observe metallic and semiconducting nanotube separation via the co-surfactant extraction using Co-MCM-41-grown SWCNTs in this study. As shown in Figure 5-1, the optical absorption spectra are similar in the 400-500 nm region, which includes the M_{11} peaks that belong to metallic nanotubes in the diameter range of 0.7-0.8 nm. It is reasonable that the reported metallic and semiconducting separation using 1:4 SDS/SC co-surfactant could be only effective for a specific type of nanotubes. The co-surfactant extraction process discussed in this chapter has several advantages over gradient separation, for instance, a lower centrifugation speed

and no solution fractionation, which may lead to a more scalable process for a large quantity of (n,m) - specific SWCNTs.

Figure 5-5 2D PLE map for SWCNTs suspended in (a) 2 wt% SC and (b) total 2 wt % SDS:SC = 1:4, (c) UV-vis-NIR absorption spectra of the 2 sample.

The selective enrichment of specific (n,m) SWCNTs using co-surfactant extraction has not been reported previously. It may be due to the lack of starting samples with narrow chiral distribution. For comparisons, the co-surfactant extraction process was applied on HiPco samples (with a larger average diameter and wider chirality distribution relative to our nanotubes), and no clear selectivity to specific (n,m) nanotubes was observed. This

outcome probably suggests that the SDS/SC co-surfactant are more efficient for smaller-diameter nanotubes with a narrow (n,m) distribution. It also indicates the importance of a narrowly distributed starting sample in obtaining single (n,m) nanotubes in large quantities.

Table 5-2 Concentration of SDS-SC co-surfactant solutions

Surfactant	Sample Name	CMC (25 °C), mM [14]	weight ratio of 2 wt% SC	C_{SC} , mM	C_{SDBS} , mM	SC/SDBS molar ratio
SC (2 wt%)		~6	1	46.45		N/A
SDBS/SC (2 wt%)	(b)		0.8	37.16	11.49	3.23
	(c)		0.95	37.16	2.66	13.97
	(d)		0.77	7.12	2.66	2.68
SDBS (1 wt%)	(a)	1.6	0	0	28.74	N/A

Furthermore, it is found that such selectivity only exists with specific surfactant combinations. Different SDBS/SC co-surfactant combinations (Table 5-2) were also studied. Firstly, the ratio of SDBS/ SC = 1:4, which is the weight ratio at the ‘turning point’ of SDS/SC combination is tested while the total surfactant concentration was still kept at 2 wt%. Then the significant difference between the two CMCs (8.35 mM for SDS and 1.6 mM for SDBS, both at 25 °C [14]) is taken into consideration. Therefore, the molar concentration of SDBS in the SDBS-SC co-surfactant solution is determined by the equation below:

$$C_{SDBS} = \frac{C_{SDS}}{CMC_{SDS}/CMC_{SDBS}} = \frac{13.89}{8.35/1.6} = 2.66 \text{ mM} \quad (1)$$

where C_{SDS} is the molecular concentration of SDS in the most chiral selective SDS/SC solution (SDS/ SC = 1:4). The molar concentration of SC is kept the same as that of SDS/SC co-surfactant solution. Instead of the weight ratio, the molar ratio of SDBS/SC co-

surfactant was further adjusted to that of the SDS/SC combinations. The PL 2D maps of these samples are shown in Figure 5-6; and no selectivity could be observed.

Figure 5-6 PLE maps of SWCNTs suspended in SDBS-SC co-surfactant solutions. (a) 1 wt% SDBS, (b)-(d) are corresponding to the descriptions in Table 5-2.

McDonald *et al.* demonstrated that SDS has a stronger binding to smaller-diameter nanotubes, whereas SDBS displays weaker diameter dependence [14]. SC binds strongly to certain (n,m) nanotubes. They proposed that the van der Waals stabilization energy of surfactants on a nanotube surface relies on the nanotube lattice, which, in turn, depends on

the nanotube chirality and diameter. It is proposed that a competing co-surfactant could optimize the binding to a specific (n,m) structure, which may cause the selectivity reported here. Further work is on the way to understand the details of the selection mechanism.

The absorption-desorption of different surfactants on graphite or large multi-walled carbon nanotubes have been extensively studied by the means of AFM, SEM, surface tension and other techniques [18-21]. But things change drastically when surfactants molecules interact with SWCNTs, whose diameters are less than 2 nm. Until now, only small angle neutron scattering (SANS) would provide a quasi-experimental *in situ* examination of the interaction between surfactant molecules and nanotubes in a suspension [22-24].

5.3 Multi-iteration extraction by SDS-SC co-surfactant

Compared with SWCNT enrichment by DNA [1-2] and polymer wrapping [3-4], an advantage of co-surfactant extraction is that most surfactants can be easily washed away, resulting in “clean” nanotubes. This is important for applications in which intrinsic electronic and optical properties of SWCNTs are desired. Furthermore, “clean” nanotubes enable the multistep extraction process. SWCNTs obtained after the first extraction using the co-surfactant solution (SDS/SC = 1:4) were filtrated, washed, and redispersed in the co-surfactant solution. This procedure was repeated twice. Fluorescence intensity maps of SWCNTs obtained after the second and third extraction are shown in Figure 5-6. Abundance of (6,5) and (8,3) are also illustrated in Figure 5-7 and listed in Table A I-13 and Table A I-14 in Appendix I. The (6,5) abundance increases to 69% among semiconducting nanotubes after the third extraction iteration. The total abundance of

smaller diameter nanotubes, (6,5) and (8,3), could be enriched from less than 20% in the starting material to more than 90%

Figure 5-7 (a) PLE maps for SWCNT samples after each extraction, Sample 0 stands for the starting material suspended in 2 wt% SC aqueous solution and (b) abundance of (6,5) and (8,3) nanotubes after each extraction.

5.4 Conclusion

In this chapter, the selective enrichment of (6,5) and (8,3) SWCNTs to 90% after three extraction iterations using SDS and SC co-surfactant was studied. The enriched nanotubes can be easily recovered from the solution by vacuum filtration; and the remaining surfactant molecules would be simply cleaned by heating the sample to 350 °C in air flow as described in chapter 3. The co-surfactant extraction process provides an easily scalable

approach for obtaining SWCNTs with a desired (n,m) structure, though the detail of the surfactant-nanotube interaction is still under investigation.

5.5 Reference

1. Zheng, M. and E.D. Semke, *Enrichment of Single Chirality Carbon Nanotubes*. Journal of the American Chemical Society, 2007. **129**(19): p. 6084-6085.
2. Zheng, M., A. Jagota, M.S. Strano, A.P. Santos, P. Barone, S.G. Chou, B.A. Diner, M.S. Dresselhaus, R.S. McLean, G.B. Onoa, G.G. Samsonidze, E.D. Semke, M. Usrey, and D.J. Walls, *Structure-based carbon nanotube sorting by sequence-dependent DNA assembly*. Science, 2003. **302**(5650): p. 1545-1548.
3. Chen, F., B. Wang, Y. Chen, and L.-J. Li, *Toward the Extraction of Single Species of Single-Walled Carbon Nanotubes Using Fluorene-Based Polymers*. Nano Letters, 2007. **7**(10): p. 3013-3017.
4. Nish, A., J.-Y. Hwang, J. Doig, and R.J. Nicholas, *Highly selective dispersion of single-walled carbon nanotubes using aromatic polymers*. Nat Nano, 2007. **2**(10): p. 640-646.
5. Arnold, M.S., A.A. Green, J.F. Hulvat, S.I. Stupp, and M.C. Hersam, *Sorting carbon nanotubes by electronic structure using density differentiation*. Nature Nanotechnology, 2006. **1**(1): p. 60-65.
6. Niyogi, S., S. Boukhalfa, S.B. Chikkannanavar, T.J. McDonald, M.J. Heben, and S.K. Doorn, *Selective aggregation of single-walled carbon nanotubes via salt addition*. Journal of the American Chemical Society, 2007. **129**(7): p. 1898-+.
7. Niyogi, S., C.G. Densmore, and S.K. Doorn, *Electrolyte Tuning of Surfactant Interfacial Behavior for Enhanced Density-Based Separations of Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2009. **131**(3): p. 1144-1153.
8. Yanagi, K., Y. Miyata, and H. Kataura, *Optical and Conductive Characteristics of Metallic Single-Wall Carbon Nanotubes with Three Basic Colors; Cyan, Magenta, and Yellow*. Applied Physics Express. **1**(Copyright (c) 2008 The Japan Society of Applied Physics): p. 034003.

9. Zhao, P., E. Einarsson, R. Xiang, Y. Murakami, and S. Maruyama, *Controllable Expansion of Single-Walled Carbon Nanotube Dispersions Using Density Gradient Ultracentrifugation*. The Journal of Physical Chemistry C, 2010. **114**(11): p. 4831-4834.
10. Chen, Y., D. Ciuparu, S. Lim, Y. Yang, G.L. Haller, and L. Pfefferle, *Synthesis of uniform diameter single-wall carbon nanotubes in Co-MCM-41: effects of the catalyst prereduction and nanotube growth temperatures*. Journal of Catalysis, 2004. **225**(2): p. 453-465.
11. Chen, Y., D. Ciuparu, S. Lim, Y. Yang, G.L. Haller, and L. Pfefferle, *Synthesis of uniform diameter single wall carbon nanotubes in Co-MCM-41: effects of CO pressure and reaction time*. Journal of Catalysis, 2004. **226**(2): p. 351-362.
12. Ciuparu, D., Y. Chen, S. Lim, G.L. Haller, and L. Pfefferle, *Uniform-Diameter Single-Walled Carbon Nanotubes Catalytically Grown in Cobalt-Incorporated MCM-41*. The Journal of Physical Chemistry B, 2003. **108**(2): p. 503-507.
13. Wei, L., B. Wang, Q. Wang, L.-J. Li, Y. Yang, and Y. Chen, *Effect of Centrifugation on the Purity of Single-Walled Carbon Nanotubes from MCM-41 Containing Cobalt*. The Journal of Physical Chemistry C, 2008. **112**(45): p. 17567-17575.
14. McDonald, T.J., C. Entrakul, M. Jones, G. Rumbles, and M.J. Heben, *Kinetics of PL Quenching during Single-Walled Carbon Nanotube Rebundling and Diameter-Dependent Surfactant Interactions*. The Journal of Physical Chemistry B, 2006. **110**(50): p. 25339-25346.
15. Fagan, J.A., J.R. Simpson, B.J. Bauer, S.H. De Paoli Lacerda, M.L. Becker, J. Chun, K.B. Migler, A.R. Hight Walker, and E.K. Hobbie, *Length-Dependent Optical Effects in Single-Wall Carbon Nanotubes*. Journal of the American Chemical Society, 2007. **129**(34): p. 10607-10612.
16. Fagan, J.A., M.L. Becker, J. Chun, P. Nie, B.J. Bauer, J.R. Simpson, A. Hight-Walker, and E.K. Hobbie, *Centrifugal Length Separation of Carbon Nanotubes*. Langmuir, 2008. **24**(24): p. 13880-13889.

17. Simien, D., J.A. Fagan, W. Luo, J.F. Douglas, K. Migler, and J. Obrzut, *Influence of Nanotube Length on the Optical and Conductivity Properties of Thin Single-Wall Carbon Nanotube Networks*. ACS Nano, 2008. **2**(9): p. 1879-1884.
18. Ducker, W.A. and L.M. Grant, *Effect of substrate hydrophobicity on surfactant surface-aggregate geometry*. Journal of Physical Chemistry, 1996. **100**(28): p. 11507-11511.
19. Manne, S., T.E. Schaffer, Q. Huo, P.K. Hansma, D.E. Morse, G.D. Stucky, and I.A. Aksay, *Gemini surfactants at solid-liquid interfaces: Control of interfacial aggregate geometry*. Langmuir, 1997. **13**(24): p. 6382-6387.
20. Richard, C., F. Balavoine, P. Schultz, T.W. Ebbesen, and C. Mioskowski, *Supramolecular Self-Assembly of Lipid Derivatives on Carbon Nanotubes*. Science, 2003. **300**(5620): p. 775-778.
21. Paruchuri, V.K., A.V. Nguyen, and J.D. Miller, *Zeta-potentials of self-assembled surface micelles of ionic surfactants adsorbed at hydrophobic graphite surfaces*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2004. **250**(1-3): p. 519-526.
22. Yurekli, K., C.A. Mitchell, and R. Krishnamoorti, *Small-Angle Neutron Scattering from Surfactant-Assisted Aqueous Dispersions of Carbon Nanotubes*. Journal of the American Chemical Society, 2004. **126**(32): p. 9902-9903.
23. Zhou, W., M.F. Islam, H. Wang, D.L. Ho, A.G. Yodh, K.I. Winey, and J.E. Fischer, *Small angle neutron scattering from single-wall carbon nanotube suspensions: evidence for isolated rigid rods and rod networks*. Chemical Physics Letters, 2004. **384**(1-3): p. 185-189.
24. Bauer, B.J., E.K. Hobbie, and M.L. Becker, *Small-Angle Neutron Scattering from Labeled Single-Wall Carbon Nanotubes*. Macromolecules, 2006. **39**(7): p. 2637-2642.

Chapter 6

Assessment of (n, m) Selectively Enriched SWCNTs

Future macroelectronic applications require mono-dispersed SWCNT samples which can exhibit isotropic properties. However, such samples are yet unavailable. Small diameter SWCNTs can be enriched from highly purified SWCNT samples by co-surfactant extraction. With the aim to achieve ulterior chiral sorting, density gradient ultracentrifugation is applied on the co-surfactant extracted sample and SC suspended samples.

The separated solutions are characterized by PL, Raman, UV-vis-NIR absorption spectroscopies which show similar spectroscopic results. These samples are used to fabricate TF-FETs and the electronic transport characterization results of the devices indicate different semiconducting nanotube content among the samples. Though the results obtained here are different from previous reported data obtained from large diameter nanotubes ($d_t = 1.1\sim 1.4$ nm) prepared by laser-ablation method [1], it suggests more comprehensive study is needed to understand the chiral selectivity of surfactants.

6. 1 Sample preparation

Narrowly (n,m) -distributed SWNTs were obtained from Co-MCM-41 catalysts as described in Chapter 2. The precise control of cobalt reduction and nucleation through the MCM-41 template enable size uniform cobalt clusters for the SWNT structure control in CVD synthesis. As-synthesized nanotubes were purified by using an ultracentrifugation based method as discussed in Chapter 3. Purified SWNTs were enriched following the

schematic diagram shown in Figure 6-1. Sample A enriched in (7,5) SWNTs was obtained by dispersing purified SWNTs in 2 wt % SC (SigmaUltra) water solution, whereas sample B enriched in (6,5) SWNTs was obtained through a co-surfactant extraction process studied in Chapter 5. A 10.0 mg amount of purified SWNTs was dispersed in 10 mL of surfactant solution by sonication using an ultrasonicator (SONICS, VCX-130) at 20 W for 30 min in an ice bath. Co-surfactant solutions were subsequently prepared by dissolving a total of 2 wt % surfactants in a 10% (w/v) iodixanol (60% (w/v) (Sigma) water solution with the weight ratio of SDS (MP Biomedicals) to SC surfactant at 1:4. After sonication, suspensions of samples A and B were centrifuged for 1 h at 50, 000 g (Hitachi-Koki, CS150GXL) to remove nanotube bundles and unwrapped nanotubes.

Sample A and Sample B were further sorted by density differentiation following the previously reported procedure [1]. SWNT dispersions of sample A and B were concentrated before insert into a linear density gradient. The SWNT dispersion layer of ~ 3 cm thickness was compressed to a dense black layer of 3 mm. The density of the dense SWNT dispersion was adjusted to that of 25% (w/v) iodixanol solution (1.132 g/cm^3). Density gradient solutions were prepared by laying 60% (w/v) iodixanol solution with the same surfactant type and concentration as that of SWNT dispersions at the bottom of the centrifugation tube. Then 10% (w/v) ($\rho = 1.086 \text{ g/cm}^3$) and 30% (w/v) ($\rho = 1.171 \text{ g/cm}^3$) iodixanol stock solutions were put into two reservoir chambers of a linear gradient maker (SG 15, Hoefer, Inc.) to create a linear gradient layer on top of the stop layer. After the formation of the gradient, the concentrated and density adjusted SWNT dispersion was inserted. DGU was then carried at 276,000 g for 14 h. After the DGU, three layers of dispersions with distinctive colours were observed. The upper two layers contain (n,m)

enriched SWNTs, and are close to each other with ~ 0.5 mm (layer 1) and ~ 1 mm (layer 2) thickness. The first layer has a faint pink colour, whereas the second layer is of a dark green colour. The third broad layer has a black colour, containing nonenriched SWNTs, SWNT bundles and other aggregates. The upper two layers with well-defined colours were characterized by spectroscopies, as well as utilized for SWNT thin film FET fabrication.

Figure 6-1 Schematic diagram of the (n,m) selective enrichment process.

(n,m) distribution of SWNT samples were characterized using PLE, UV-vis-NIR, and Raman spectroscopy. PLE measurement was performed on a Jobin-Yvon Nanolog-3 spectrofluorometer with an InGaAs detector. UV-vis-NIR absorption was conducted in the transmission mode on a Varian Cary 5000 UV-vis-NIR spectrophotometer using a 10 mm light path quartz cuvette. SWNT dispersions were filtered onto 25 nm mixed cellulose ester membrane (Millipore) to form homogeneous films. Raman spectra were collected directly from SWNT films on a Renishaw inVia Raman microscope with 633 nm (1.96 eV) laser in a backscattering configuration, and on an Alpha 300 (WITec) Raman microscope with 488 nm (2.54 eV) laser in a scanning mode.

SWNT thin film FETs were fabricated by the drop-casting method. The concentration of all SWNT dispersions (sample A-F) was adjusted by adding surfactant solutions according to their absorption spectra. First, we adjusted the absorbance at 800 nm of SWNT dispersions to approximately 0.002, which corresponds to a SWNT concentration of ~ 0.006 mg/mL [2]. Next, we used an integrated area of the absorbance between 904 to 1232 nm (belonging to the E_{11} band of small semiconducting SWNTs) as the second criterion to control the SWNT concentration. Finally, SWNT dispersions were dropped on bottom-contact FET devices, where Pt electrodes with Ti as adhesion layer were patterned on the top of SiO₂/Si substrates using standard lithography techniques. The gate dielectrics SiO₂ is 300 nm thick. The geometry of the FET devices is around 8 μ m in the source-drain distance and 20 μ m in the channel width. 10 μ L of SWNT suspensions was added, followed by drying and rinsing of deionized water. To improve the SWNT film uniformity, the devices were heated up when the same amount of SWNT dispersions were dropped in the middle of device channel for each device. The high evaporation rate at heated device

surfaces helps to limit the coffeeering effect [3]. It has been observed that the dispersion stain is significant larger than the $8 \times 20 \mu\text{m}$ device channel. This helps to obtain relatively uniform SWNT films in the device channel, because the device channel stays in the center of the stain. All electrical measurements were carried out in ambient using a Kiethley semiconductor parameter analyzer model 4200-SCS. Atomic force microscopy (AFM) was conducted using a MFP 3D microscope (Asylum Research, Santa Barbara, CA) with a cantilever (Arrow NC, Nanoworld) in ac mode. The scan rate was set to 1 Hz at various scan sizes.

6.2 Optical spectroscopy analysis

SWNTs grown from Co-MCM-41 have narrow (n,m) distribution, which can be observed from the PLE maps of SC dispersed SWNTs (sample A) as shown in panel (a) of Figure 6-2. The dominating species is (7,5) nanotubes with diameter of 0.829 nm. As discussed in Chapter 5, selective enrichment of (6,5) and (8,3) SWNTs can be achieved through extraction by co-surfactant mixtures of SDS:SC at 1:4. Part B of Figure 6-2 depicts that the dominate species in sample B are (6,5) SWNTs with diameter of 0.757 nm. After DGU, SWNTs dispersed in SC or SC/SDS illustrates similar PLE maps. Peaks of (6,5) and (8,3) SWNTs can be noted in parts C and D of Figure 6-2, indicating that smaller diameter SWNTs are enriched in the first pink layers of SWNT dispersions. Peaks of (7,5), (8,4), (7,6), and (9,4) SWNTs can be identified in parts E and F of Figure 6-2, showing that slightly larger diameter nanotubes are enriched in the second dark green layers. These diameter selective enrichment results are similar to the study using CoMoCAT SWNTs [1].

It is reasonable as SWNTs produced from both CoMo catalysts and Co-MCM-41 catalysts are at the similar diameter range (main species <0.9 nm).

Figure 6-2 (a) 2D PLE maps and (b) UV-vis-NIR absorption spectra of (n, m) selectively enriched SWNTs samples. Sample A to F were assigned following the described procedures illustrated in Figure 6-1.

The relative PLE intensities can be used to determine the abundance of different semiconducting SWNTs. In this study, the intensity extracted from PLE map is directly used to quantify the nanotube abundance. The results of two most dominant (n, m) species ((6,5) and (7,5)) were listed in Table 6-1. The complete sets of abundance analysis data were available in Table A II-1 to A II-6 of the Appendix II. In sample A, the (6,5) to (7,5) abundance ratio is only 0.41. After co-surfactant extraction, the (6,5) to (7,5) ratio increases

to 1.83, indicating significant enrichment of (6,5) SWNTs. Results also reveal that the DGU is very effective in enriching smaller nanotubes. From sample A to sample C, the (6,5) to (7,5) ratio increases 30 times to 12.49; whereas from sample B to sample D, the ratio increases 13 times to 23.90. Samples E and F present the similar abundance distribution as that of sample A.

Effective separation of semiconducting and metallic nanotubes is a critical step in deciding whether SWNT-based macroelectronic devices will perform to the required specifications. PLE is very sensitive to characterize semiconducting SWNTs, but metallic SWNTs do not present in PLE. UV-vis-NIR spectra have been employed to provide information about metallic nanotubes in many studies [1, 4]. However, it is difficult to obtain such information on metallicity separation for small diameter nanotubes (<0.9 nm). As illustrated in panel (b) of Figure 6-2, the lowest absorption E_{11} peaks for all small metallic SWNTs are overlapped below 500 nm with high-energy absorption background that is associated with either the SWNT π -plasmon oscillation or carbonaceous impurities. No changes can be observed for all six samples; therefore, tracking any absorption peak of a specific metallic nanotube as an indicator of enrichment is not feasible. On the other hand, the selective enrichment of various semiconducting nanotubes is present in UV-vis-NIR spectra. As shown in panel (b) of Figure 6-2, both E_{11} (the lowest semiconducting band) and E_{22} (the second lowest semiconducting band) indicate the consistent enrichment trend as that observed in the PLE analysis.

Figure 6-3 Raman spectra of samples A and D. Spectra of sample A is offset 30% in Y-axis for comparison: (a) obtained under 633 nm laser excitation, (b) obtained under 514 nm laser excitation, and (c) obtained under 488 nm laser excitation.

Table 6-1 Abundance of the 2 major (n, m) nanotubes and their ratios in different samples

Samples	(n, m) abundance, %		Ratio
	$(6, 5)$	$(7, 5)$	$(6,5)/(7, 5)$
A	14.27	34.90	0.41
B	34.67	18.95	1.83
C	57.13	4.57	12.49
D	62.46	2.61	23.90
E	13.91	41.44	0.34
F	15.22	36.15	0.42

Raman spectroscopy is also commonly used to distinguish metallic and semiconducting SWNTs through the following two features: (1) the lower frequency G -band for metallic nanotubes has a Breit-Wigner-Fano line shape, which is broader and downshifted in frequency from semiconducting nanotubes of similar diameter; (2) whenever the energy of the incident photons matches optical transition energy (subject to selection rules for optical transitions) of particular (n,m) SWNTs, Raman intensity enhancement in radical breathing mode (RBM) of those particular (n,m) SWNTs can be expected [5]. All six samples were measured by Raman spectroscopy. Typical spectra were presented in Figure 6-3. As shown in part (a) of Figure 6-3, no changes were observed in the G -band feature using 633 nm laser. The line shape in part (a) of Figure 6-3 also suggests both samples are enriched with semiconducting SWNTs. D -band features, which contributed by defects on SWNTs or amorphous carbon, are neglectable, indicating the

high purity of SWNTs. A sharp single RBM peak indicates the narrow (n,m) distribution. 488 nm and 514 nm lasers were also used as shown in panel (b) and panel (c) of Figure 6-3, because this laser wavelength is known to have strong resonance with smaller diameter metallic nanotubes. Slight changes in the G-band features can be observed under 488 nm excitation, suggesting that sample D may have higher concentration of metallic nanotubes compared to sample A. The relative intensity of the Raman peak at 301 nm (may come from $(6,6)$ nanotubes, $d_t = 0.825$ nm,) increases, which could be linked to the enrichment of the metallic species. However, because the enhancement of the relative intensity is quite small and various specific Raman wavelengths are necessary to probe different species in resonance [5], the Raman spectroscopy may not serve as a simple characterization methodology.

6.3 Field effect transistor device characterization

Three spectroscopic techniques have difficulties in characterizing metallic SWNTs presented in our enriched samples. It is reasonable that these samples are already highly enriched with semiconducting SWNTs. Metallic SWNTs do exist at low concentration, which make them difficult to be observed in spectroscopic studies. Nevertheless, quantification of small diameter metallic SWNTs based on our spectroscopy data was not feasible, for which we carried out electrical transport measurements as described below. Because of their nearly one-dimensional and defect-free electronic structure, the electron transport in individual semiconducting SWNTs manifests superior field-effect behavior.¹ However, SWNT thin film FETs have significant lower mobility and on/off ratio. High on/off ratio could be obtained if low density applied [6]. With the increase of metallic

nanotube concentration, metallic nanotubes in SWNT networks can easily form continuous paths to lower the on-off ratio [7]. Ideally, SWNT networks with pure semiconducting nanotubes can achieve both high on-off ratio and mobility. The purpose of this study is to evaluate the (n,m) selective enrichment of SWNTs synthesized from Co-MCM-41, rather than to achieve the best performance macroelectronic devices. SWNT thin film FET tests were designed to discern the difference among various (n,m) enriched samples. Under the same device fabrication and characterization condition, it is expected that devices obtained from SWNT samples with higher semiconducting purity can yield better on-off ratios compared to samples containing more metallic nanotubes. Panel (a) of Figure 6-4 shows the schematic drawing of SWCNT thin film FETs. SWNT networks lie on the top of Pt electrodes which permit the efficient testing of various SWNT samples. Generally, metallic nanotubes are easier to form continuous pathways that bridge the source and drain over shorter channels. To achieve higher sensitivity in the detection of metallic nanotubes, 8 μm in source-drain distance was used instead of 20 μm adopted by Arnold *et al.* [1]. To monitor the SWNT film uniformity in the device channel, detailed AFM characterization of SWNT films was performed. In panel (b) and (c) of Figure 6-4, AFM images show both the Pt electrode and SWNT networks. A $5 \times 5 \mu\text{m}$ scan of SWNT networks in the device channel is presented in panel (d) of Figure 6-4. The AFM sampling for the network structures on various devices show that the network density in the channel area is around 30~50 tubes/ μm^2 . On the basis of previous results [8], the variation in on-off ratio caused by the network density difference is relatively not significant (a factor smaller than 5) compared with the difference reported later in this study.

Figure 6-4 (a) Schematic illustration of SWNT thin-film FET structure as described in this chapter. (b) A typical AFM image of a device. The left part of the image is the Pt electrode. (c) 3D reconstruction of the AFM image in (b) and (d) uniform SWNT network deposited in the device channel.

Large contact resistance between electrodes and SWNT networks may dominate FET device performance [9]. A series of devices with different source-drain distances ranging from 2 to 26 μm were fabricated. The network resistance versus the source-drain distance for SWNT networks of the same density was measured. Resistances of the devices used in this study (8 μm in source-drain distance) have about 10-20% contributions from the electrode/nanotube interface at the contacts, similar to previous results [8]. At negative gate biases, SWNT networks exhibited similar sheet resistances of about $10^6 \Omega/\square$.

Figure 6-5 (a) and (b) Typical electrical transport characteristics (I_{ds} - V_{gs}) of a typical semiconducting and metallic device; (c) and (d) Typical electronic responses (I_{ds} - V_{ds}) of a semiconducting and a metallic device A to F correspond to sample A to sample F as described in Figure 6-1.

Typical transfer characteristics (I_{ds} - V_{gs} curves) and current-voltage characteristics (I_{ds} - V_{ds}) of semiconducting and metallic SWCNT networks are presented in Figure 6-5. When metallic nanotubes form fewer paths between source and drain, devices exhibit higher I_{on}/I_{off} ratio (panel (a) and panel (c) Figure 6-5). On the contrary, when the number of conducting path in SWNT films increases, devices exhibit lower I_{on}/I_{off} ratio (panel (b) and panel (d) Figure 6-5). Several other transistor properties for the (n,m) enriched samples (samples C-F) were listed in Table 6-2. Property values in Table 6-2 are the average for the

specified number of devices from different SWNT samples (shown in Figure 6-6). In addition to the on/off ratio differences presented in Figure 6-6, the effective mobility of devices from samples C and E (with higher on-off ratio) is lower than the effective mobility of devices from samples D and F (with lower on-off ratio). This result is expected and consistent with previous result [8].

Figure 6-6 Histograms of device percentages with various on/off current ratios for devices made of (n,m) enriched SWNTs. A-F correspond to samples A-F as described in Figure 6-1. The numbers of devices measured for each sample are marked in the figure.

Another observation is that the hysteretic behaviours of devices from samples C and D are more pronounced than those of devices from samples E and F. The details require further investigations. Nevertheless, in this study, efforts have been focused on assessing the purity of semiconducting SWNTs by device on-off ratios. Subsequently, analysis of different SWNT samples have been done in terms of their device on-off ratio on three aspects: (1) the effect of co-surfactant extraction without gradient differentiation, (2) the effect of DGU, and (3) the difference between SC and SC/SDS co-surfactant assisted DGU. Comparison between sample A and sample B in Figure 6-6 suggests that more residue metallic nanotubes exist in the co-surfactant extracted sample B. No device fabricated from sample B has $I_{\text{on}}/I_{\text{off}}$ ratio larger than 10^4 , while 16% of devices obtained from sample A have $I_{\text{on}}/I_{\text{off}}$ ratio larger than 1×10^4 . Comparison among sample A, C, and E in Figure 6-6 implies that DGU helps to improve the device performance. Devices from both samples C and E have higher $I_{\text{on}}/I_{\text{off}}$ ratios, compared to those from sample A. When an individual surfactant (SC) is applied, sample C shows good enrichment of semiconducting nanotubes with >75% of its devices having $I_{\text{on}}/I_{\text{off}}$ ratio larger than 10^3 . However, such a trend is not found among parts B, D, and F in Figure 6-6. After SC/SDS co-surfactant assisted DGU, sample D contains more metallic devices, more than 70% of its devices having $I_{\text{on}}/I_{\text{off}}$ ratios less than 100. Difference between samples C and D can also be noted between samples E and F. About 60% of devices from sample E have $I_{\text{on}}/I_{\text{off}}$ ratio larger than 10^4 compared to 20% of devices from sample F. It should be noted that in Figure 6-6, the summation of sample C and sample E or sample D and sample F do not match with sample A or B, because after DGU only the upper two layers of dispersions with distinctive colors were

extracted for device fabrication, and nanotubes/bundles in the lower portion of dispersions were discarded.

Table 6-2 Average properties of devices fabricated from sample C to sample F

Sample	I_{off} , A	I_{on} , A	On/off ratio order	Mobility, $\text{cm}^2/\text{V}\cdot\text{s}$
C	9.03×10^{-9}	3.57×10^{-6}	3	1.73
D	1.75×10^{-8}	6.98×10^{-6}	2	2.83
E	1.72×10^{-8}	1.02×10^{-6}	2	0.81
F	6.30×10^{-9}	2.88×10^{-6}	3	2.61

6.4 Comparison of the various characterization methods

Spectroscopic studies show that all six samples are enriched with semiconducting SWNTs, yet characterization of SWNT thin film FETs fabricated from those enriched SWNTs reveal that small changes in their semiconducting SWNT purity lead to significant differences in device performance. First, the effects of co-surfactant extraction without gradient differentiation, which include both diameter and metallicity selections, should be addressed. Without gradient differentiation, the enrichment of (n,m) nanotubes mainly is caused by the selective absorption of surfactants on SWNTs. In Chapter 5, direct experimental results have demonstrated that the selection of (6,5) and (8,3) nanotubes (smaller diameter) is optimized when SDS/SC co-surfactant is at 1:4. Although McDonald *et al.* [10] demonstrated that SDS has a stronger binding to smaller diameter nanotubes, it is showed that SDS or SC alone has no selection toward smaller nanotubes. It is speculated that the selection to smaller diameter nanotubes is caused by a particular surfactant shell arrangement of SDS and SC on SWNT surfaces at 1:4, but it remains unclear in precisely

which way the surfactant molecules adsorb on the surfaces of SWNTs [11]. In this chapter, FET device on-off ratios shown in Figure 6-6 further demonstrates the increase of metallic nanotube concentration in sample B. The metallicity selection of SDS/SC (1:4) co-surfactant may be caused by the stronger interaction between SC and metallic nanotubes, because the proximity of the hydroxyl groups in the cholate molecule to the nanotube surface results in electronic polarization toward SWNTs [10]. Metallic nanotubes have delocalized electrons at the Fermi level, and are more receptive to induced charges [12]. However, it should be noted that metallicity selection is observed only when a mixture of SDS/SC surfactants is used. SC alone (sample A) does not have metallicity selection. Another issue that contributes to the observed metallic tube enrichment is as-synthesized SWNTs at diameter around 0.75 nm may contain higher metallic fractions compared to tubes at larger diameter around 0.81 nm. As shown in Figure 6-7, the (7,4) nanotube is metallic sitting right between the (6,5) and (8,3) tubes. Previously results have demonstrated that as-synthesized SWNTs are predominately in this same higher chiral-angle region [13]. When smaller diameter (6,5) and (8,3) SWNTs are enriched from sample A to sample B, it is likely that (7,4) nanotubes or other metallic residues at the similar diameter are also enriched, leading to more metallic nanotubes in sample B. This is consistent with results obtained from chirality separated DNA functionalized HiPco SWNTs, where more residue metallic nanotubes exist in the fraction enriched with the (6,5) SWNTs [4].

Next, what is the effect of DGU? Hersam [14] has summarized that the extent of adsorption of the surfactant on nanotubes of varying chiralities is non-uniform, and creates assemblies with different buoyant densities. This facilitates their separation by isopycnic

centrifugation, where particles migrate to regions of like density. DGU sorts SWNTs by their buoyant density leading to layers in the centrifuge tube based on their buoyant density. Nair *et al.* have proposed a hydrodynamic model to further describe the motion of surfactant-suspended SWNTs in DGU [12]. They suggested that 2.09 and 2.14 SC molecules adsorbed per nanometer along the length of the (6,5) and (7,5) nanotubes respectively. It is easy to comprehend the difference between samples A and E, as well as samples B and F, because large-diameter SWNTs with higher density can be removed by DGU. Removal of large diameter nanotubes helps to enhance the on-off ratios of devices, as demonstrated in Figure 6-6.

Nonetheless, it is harder to explain the difference observed between samples C and D, as well as sample E and sample F based on this hydrodynamic model. Although they show almost identical spectra in PLE, absorption, and Raman spectroscopy, devices fabricated from them are significantly different. Samples C and E using SC alone have less metallic residues compared to samples D and F using SDS/SC (1:4) co-surfactant. For smaller diameter nanotubes (<0.9 nm) in this study, the results are different from those observed for larger nanotubes reported previously. In the case of laser-ablation-grown SWNTs (1.1-1.4 nm), enrichment of semiconducting nanotubes were observed at surfactant ratio 1:4, whereas enrichment of metallic nanotubes were found at surfactant ratio 3:2 [1]. More SC molecules should be adsorbed on metallic nanotubes such as (7,4) and (6,6) if the adsorption follows the hydrodynamic model [12]. When SC is used alone, the first layer after DGU should be metallic enriched. However, the results in Figure 6-6 suggest that both samples C and E contain less metallic nanotubes than sample A. SDS/SC (1:4) assisted DGU also shows better selection to metallic nanotubes other than semiconducting

nanotubes for smaller diameter nanotubes. These two results suggest that metallicity selection in DGU is diameter-dependent. To elucidate the observed results, an understanding of molecular level concerning the adsorption of surfactant on SWNTs and dynamics of SWNT-surfactant assemblies in DGU is required. Currently, it is still not available. This study encourages further research on interactions between surfactants and various SWNT species.

Figure 6-7 Chirality maps of major (n,m) SWNT species concerned in this study. Purple hexagons are smaller semiconducting nanotubes identified in PL spectroscopy of sample C or D; green hexagons are larger semiconducting nanotubes identified in PL maps of sample E or F. Blue hexagons are possible metallic species that cannot be observed in PLE map.

6.5 Conclusion

(n,m) selective enrichment by both co-surfactant extraction and DGU method were performed to sort small diameter SWCNT samples ($d_t < 0.9\text{nm}$) obtained from Co-MCM-41 catalyst. Even though results from PLE, UV-vis-NIR, and Raman spectroscopy illustrate

very similar results among samples, characterization of SWNT thin-film FETs fabricated from those (n,m) enriched SWNTs reveals that small changes in their semiconducting SWNT purity lead to significant differences in device performance. Co-surfactant extraction (SDS/SC) can enrich smaller diameter nanotubes, such as (6,5) and (8,3), as well as metallic nanotubes. Using SC surfactant alone in DGU, higher semiconducting fractions can be obtained from the first two layers; however, more metallic nanotubes exist in the first two layers when SDS/SC (1:4) co-surfactant is applied in DGU. Electronic transfer measurement of SWNT thin film FETs (by on-off ratio) is more sensitive than spectroscopical studies to assess semiconducting SWNT purity for macroelectronics. The success of SWNT networks in macroelectronics relies heavily on the purity of semiconducting SWNTs similar to the success of Si materials.

6.6 Reference

1. Arnold, M.S., A.A. Green, J.F. Hulvat, S.I. Stupp, and M.C. Hersam, *Sorting carbon nanotubes by electronic structure using density differentiation*. Nature Nanotechnology, 2006. **1**(1): p. 60-65.
2. Itkis, M.E., D.E. Perea, R. Jung, S. Niyogi, and R.C. Haddon, *Comparison of Analytical Techniques for Purity Evaluation of Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2005. **127**(10): p. 3439-3448.
3. Deegan, R.D., O. Bakajin, T.F. Dupont, G. Huber, S.R. Nagel, and T.A. Witten, *Capillary flow as the cause of ring stains from dried liquid drops*. Nature, 1997. **389**(6653): p. 827-829.
4. Zhang, L., S. Zaric, X. Tu, X. Wang, W. Zhao, and H. Dai, *Assessment of Chemically Separated Carbon Nanotubes for Nanoelectronics*. Journal of the American Chemical Society, 2008. **130**(8): p. 2686-2691.

5. Dresselhaus, M.S., G. Dresselhaus, and A. Jorio, *Raman Spectroscopy of Carbon Nanotubes in 1997 and 2007†*. The Journal of Physical Chemistry C, 2007. **111**(48): p. 17887-17893.
6. Unalan, H.E., G. Fanchini, A. Kanwal, A. Du Pasquier, and M. Chhowalla, *Design Criteria for Transparent Single-Wall Carbon Nanotube Thin-Film Transistors*. Nano Letters, 2006. **6**(4): p. 677-682.
7. Snow, E.S., J.P. Novak, P.M. Campbell, and D. Park, *Random networks of carbon nanotubes as an electronic material*. Applied Physics Letters, 2003. **82**(13): p. 2145-2147.
8. Lee, C.W., C.-H. Weng, L. Wei, Y. Chen, M.B. Chan-Park, C.-H. Tsai, K.-C. Leou, C.H.P. Poa, J. Wang, and L.-J. Li, *Toward High-Performance Solution-Processed Carbon Nanotube Network Transistors by Removing Nanotube Bundles*. The Journal of Physical Chemistry C, 2008. **112**(32): p. 12089-12091.
9. Zhou, Y., A. Gaur, S.-H. Hur, C. Kocabas, M.A. Meitl, M. Shim, and J.A. Rogers, *p-Channel, n-Channel Thin Film Transistors and p-n Diodes Based on Single Wall Carbon Nanotube Networks*. Nano Letters, 2004. **4**(10): p. 2031-2035.
10. McDonald, T.J., C. Engtrakul, M. Jones, G. Rumbles, and M.J. Heben, *Kinetics of PL Quenching during Single-Walled Carbon Nanotube Rebundling and Diameter-Dependent Surfactant Interactions*. The Journal of Physical Chemistry B, 2006. **110**(50): p. 25339-25346.
11. Grossiord, N., P. van der Schoot, J. Meuldijk, and C.E. Koning, *Determination of the Surface Coverage of Exfoliated Carbon Nanotubes by Surfactant Molecules in Aqueous Solution*. Langmuir, 2007. **23**(7): p. 3646-3653.
12. Nair, N., W.-J. Kim, R.D. Braatz, and M.S. Strano, *Dynamics of Surfactant-Suspended Single-Walled Carbon Nanotubes in a Centrifugal Field*. Langmuir, 2008. **24**(5): p. 1790-1795.
13. Wang, B., C.H.P. Poa, L. Wei, L.-J. Li, Y. Yang, and Y. Chen, *(n,m) Selectivity of Single-Walled Carbon Nanotubes by Different Carbon Precursors on CoMo Catalysts*. Journal of the American Chemical Society, 2007. **129**(29): p. 9014-9019.
14. Hersam, M.C., *Progress towards monodisperse single-walled carbon nanotubes*. Nat Nano, 2008. **3**(7): p. 387-394.

Chapter 7

Formation of a Thin Film of Semiconducting SWCNTs for an Improved Photocurrent Generation

Other than the applications in field effect transistors discussed in Chapter 6, SWCNTs have been intensively studied for photoelectrochemical and photovoltaic devices because of their unique optical, electrical and electronic properties, wide electrochemical stability window, and high surface area [1-2]. Individual nanotubes and nanotube thin films can generate electron-hole pairs through direct bandgap visible light excitation [3]. SWCNTs can also act as charge-transport pathway to improve the transport of charge carriers generated by other light-harvesting molecules, and as nanoscale structural scaffolds to assemble light-harvesting molecules [1-2]. Current experimental results reveal that the incident photon-to-current conversion efficiency (IPCE) of solar cells based on SWCNT direct bandgap excitation is very low (0.15 %) [4]. Various photoelectrochemical devices, containing SWCNTs in their photoactive layers, also show limited cell performance [5-6]. The relatively low performances have been contributed to metallic nanotubes because they may cause short circuits, which would simultaneously annihilate separated charge carriers generated by photons [2, 7]. Thus, the utilization of pure semiconducting SWCNTs is desired to boost the performance of SWCNT-based solar devices. However, all currently available SWCNT synthesis methods inevitably result in a mixture of both semiconducting and metallic nanotubes. Various methods have been proposed to separate metallic and semiconducting nanotubes [8]. SWCNT samples obtained from most separation methods

suffer from several important shortcomings for potential solar energy conversion applications: (1) the intrinsic optical and electronic properties of SWCNTs may be altered during the separation process, which may deteriorate their photoresponses; (2) the scalability of most separation methods is poor, which results in too few samples to be fabricated into solar devices for meaningful tests; and (3) the selectivity toward semiconducting nanotubes is too low to demonstrate significant device performance differences. Until now, the improvement of photocurrent generation by samples containing a high density of semiconducting SWCNTs has not been experimentally demonstrated.

In this Chapter, a film was prepared, which contained a high density of semiconducting SWCNTs obtained by a gel-centrifugation method. The thickness and transmittance of the films can be controlled for photoelectrochemical devices. Photocurrents generated by the films are 15–35 % higher than those from unsorted SWCNT films due to the reduction of exciton recombination channels as a result of the removal of metallic nanotubes. Thinner films generate higher photocurrents because of shorter travel distances for carriers to reach electrodes. Developing more scalable and selective methods for high purity semiconducting SWCNTs is crucial to improve the photocurrent generation efficiency by using SWCNT-based solar devices.

7.1 Gel-Centrifugation Enrichment of Semiconducting SWCNTs

Several non-covalent semiconducting-metallic SWCNT separation methods have been reported, which include DGU [9-10], dielectrophoresis [11-14], octadecylamine selective wrapping [15-16], single strand DNA assisted separation [17-19] and oligo-acene adduct assisted separation [20]. Although these methods have achieved relatively high separation

efficiency, a common drawback is their relative low throughput. For example, the dielectrophoresis method would extract 100 pg of metallic nanotubes from 100 ng of starting materials, which account for only 0.1 wt % of the starting materials [12].

Recently, a simple agarose-gel based electrophoresis or centrifugation method was reported [21-24]. SWCNT samples containing 95% of semiconducting nanotubes were obtained [21]. This gel based separation method includes three main steps: (1) as-prepared SWCNT suspensions and the agarose solution are mixed to form a SWCNT-gel matrix. (2) The SWCNT-gel matrix can be either centrifuged or placed into a direct-current vertical gel electrophoresis apparatus. And then, centrifugation force or voltage can be applied to promote the separation of metallic and semiconducting nanotubes. (3) Finally, the separated gels are dissolved in certain solvents to recover the separated nanotubes. It has been proposed that SDS would be more effectively disperse metallic nanotubes, thus enabling them to more easily through the agarose gel under voltage or centrifugation forces. Both the electrophoresis and the centrifugation routes are scalable. However, if the scalability of these two methods is compared, electrophoresis would require more sophisticated instruments, while centrifugation can be easily scaled up by widely available preparative centrifuges. Thus, the agarose-gel based centrifugation method was chosen to obtain semiconducting nanotube enriched SWCNT samples in mg scale. Two key experimental parameters, gel concentration and centrifugation force, were carefully investigated to achieve an optimized separation result.

7.2 Optimization of the Gel-Centrifugation Separation Method

Agarose powder (Merck) was used as received without any other treatments. SWCNTs produced by an arc-discharge method were purchased from Carbon Solution Inc. The samples were further purified by the centrifugation based method discussed in the Chapter 3 [25]. The resulting samples were suspended in 2 wt% SDS solution by sonication at 20 W in ice-water bath for 4 hours, and then they were centrifuged at 120,000 g for 1 hour. After centrifugation, the upper 80 % of the supernatant was collected with an approximate SWCNT concentration of about 0.2 mg/mL. Certain amount of agarose in 2X TB buffer (tris- boric buffer, 100 mM tris(hydroxymethyl) aminomethane and 97 mM boric acid) was dissolved by microwave oven heating, and then the agarose was mixed with equal volume of SWCNT suspension to make the SWCNT-gel matrix. The mixed matrix was cooled to room temperature and kept in a 4 °C fridge for 30 min to enable a full solidification. Finally, the SWCNT-gel matrix was centrifuged for 3 hours to achieve the separation of metallic and semiconducting nanotubes.

After centrifugation, metallic SWCNTs which have relatively lower affinity to the gel matrix were squeezed out the gel, while most semiconducting nanotubes were still entrapped in the gel matrix [22]. Squeezed solutions containing more metallic nanotubes were first removed from centrifugation tubes. Then, remaining gels were recovered and dissolved by refluxing in 1 wt% citric acid for 3 hours. The nanotubes were filtered on a 0.2 μm pore size nylon membrane, and washed with DI water and methanol to further remove the remaining gel and/or surfactant molecules. The washing was repeated twice before the recovered SWCNTs were dried in oven and resuspended in 1% SDS solution by sonication for 1 hour at 20W and centrifugation for 1 hour at 120,000g before spectroscopic

characterization. In the gel-centrifugation separation process, two key parameters may significantly influence its separation efficiency: gel concentration and centrifugation force.

Figure 7-1 (a) Absorption peak ratio ($S_{22}/(S_{22}+M_{11})$) of nanotube samples recovered from SWCNT-gel matrixes with different gel concentrations. The ratio at 0 % gel concentration refers to the concentration of semiconducting nanotubes in un-separated samples. (b) Absorption spectra of semiconducting nanotube enriched samples recovered from the squeezed gel. M_{11} refers to the first band transition of metallic nanotubes, and S_{22} refers to the second band transition of semiconducting nanotubes.

Seven different gel concentrations were compared, varying from 0.05 to 0.6 wt% in the final SWCNT-gel matrix. The solidified gels were centrifuged at 18,000 g for 3 hours before the gels and solutions were separated and characterized. Figure 7-1 shows the absorption spectra of SWCNT samples enriched with semiconducting nanotubes recovered from the gels. The fraction of semiconducting nanotubes was determined by deconvolving absorption spectra. Based on previous publications, the peak areas in the range 610 – 800

nm and 800 - 1220 nm belong to metallic nanotube M_{11} and semiconducting nanotube S_{22} bands, respectively. The ratio of $S_{22}/(S_{22}+M_{11})$ was used to evaluate the abundance of semiconducting nanotubes.

Figure 7-2 (a) Absorption peak ratios ($S_{22}/(S_{22}+M_{11})$) of nanotube samples recovered from SWCNT-gel matrixes after centrifugation at different centrifugation forces. The ratio at 0 % gel concentration refers to the concentration of semiconducting nanotubes in un-separated samples. (b) Absorption spectra of semiconducting nanotube enriched samples recovered from the squeezed gel.

From Figure 7-1, the absorption peak ratio reaches a maximum of 0.9 at 0.1 % gel concentration. A previous study has proposed that the separation of semiconducting-metallic nanotubes in the gel is correlated with the relative affinity of SWCNTs toward agarose [22]. Agarose gel has a water richened porous structure. The gel is harder when the gel concentration is higher, because more agarose molecules would form denser matrixes. When the gel concentration was too high, the gel can hardly be squeezed. Thus, few

nanotubes (both semiconducting and metallic ones) can be squeezed out of the gel, resulting in low separation efficiency. On the other hand, when the gel concentration was too low, not only metallic nanotubes but also semiconducting ones would be squeezed out. The gel concentration of 0.1 wt% was found to be the optimized condition.

Table 7-1 Absorption peak ratios $S_{22}/(S_{22}+M_{11})$ after separation under various conditions

Gel concentrations, wt%								
Peak	Unseparated	0.05	0.1	0.2	0.3	0.4	0.5	0.6
ratios	0.835	0.858	0.902	0.849	0.846	0.843	0.844	0.850
Centrifugation forces, $\times 10^3$ g								
Peak	Unseparated	1.8	5	10	18	40	80	
ratios	0.835	0.840	0.869	0.876	0.904	0.892	0.896	

The second parameter investigated is the centrifugation force, which controls the deformation imposed on the gel. When larger centrifugation forces were applied, the deformation of the gel would be larger, and more liquid entrapped in the gel matrix would be squeezed out. Total six different centrifugation forces, 1,800, 5,000, 10,000, 18,000, 40,000 and 80,000 g were applied on the 0.1 wt % SWCNT-gel matrixes for 3 hours. Absorption spectra of the recovered semiconducting nanotubes were plotted in Figure 7-2. The absorption peak ratios obtained under different conditions were also listed in Table 7-1. The results showed that the absorption peak ratios were similar after centrifugation under 18000, 40000 and 80000 g. It suggested that the concentrations of semiconducting

nanotubes in the resulting gel were very similar when the centrifugation force is higher than 18,000 g.

In order to improve the recovery rate of semiconducting nanotubes, large gel volume after centrifugation with high semiconducting nanotube concentration is desired. Among the seven agarose gel concentration tested here, 0.1 wt% would retain most semiconducting nanotubes after centrifugation (peak ratio = 0.902). After determination of the gel concentration, different centrifugation forces were applied which would result in different volumes of compressed gel and liquid. In order to recover more semiconducting nanotubes, larger gel volume is desired. If the smallest compress gel volume (obtained after 80,000 g) was set to 1, the relative gel volume of the 40,000 g and 18,000 g centrifuged gel was 1.5 and 6, respectively. The semiconducting nanotube concentration, represented by the peak area ratios, is 0.896, 0.892 and 0.904, respectively. Their concentration is very similar. Overall, the highest semiconducting nanotube enrichment efficiency can be achieved by using 0.1 wt% agarose gel and 18,000 g centrifugation force. Semiconducting nanotube enriched samples were obtained in mini gram scale via the parameters determined above, and they are used for further applications.

7.3 SWCNT electrode fabrication and characterization

Figure 7-3 shows a schematic illustration of a SWCNT based photocurrent generation system. Nanotubes inside such a system function as both electron-hole separator and carrier transport channels.

Figure 7-3 Schematic illustration of the SWCNT based photocurrent generation system

For SWCNT thin film fabrication, unsorted and enriched nanotube samples were both suspended in 1 wt % SDBS solution. The concentration of nanotube suspensions was further adjusted to the similar level using 1 wt% SDBS solution. The areas under absorption spectra between 610 and 1220 nm from the concentration adjusted nanotube suspensions were comparable. Different amount of SWCNT suspensions (1, 2 and 4 mL) from each nanotube sample were filtered on mixed cellulose ester (MCE) membranes (Millipore, 50 nm pore) by vacuum filtration. The films were further washed by water and 0.1 M nitric acid to remove SDBS adsorbed on nanotube surfaces. The films deposited on filtration membranes were then transferred on ITO substrates following a reported method [26]. Briefly, ITO glass substrates ($R_s = 7\sim 10 \Omega/\square$, Geomatec), serving as transparent electrodes, were first bath sonicated in *iso*-propanol (IPA), followed by ozone treatment to remove surface contaminations. Membranes together with SWCNTs were pressed directly on ITO substrates. MCE membranes were then dissolved by acetone, and left only SWCNT films on ITO substrates.

Figure 7-4 (a) AFM image showing the edge of a SWCNT thin film. (b) AFM height profile crossing the edge of the SWCNT film along the white line indicated in (a). (c) Transmittance spectra of SWCNT films deposited on ITO substrates.

Table 7-2 Fabrication parameters, thickness, and transparency of SWCNT films.

Sample Label	SWCNT suspension used (mL)	Integrated area under transmittance spectra between 610-1220 nm	Film thickness by AFM (nm)	Transmittance at 550 nm (%)
U*1	4	20439 $\pm$ 171	258.6 $\pm$ 2.67	25.6 $\pm$ 0.4
E*1	4	20532 $\pm$ 164	258.7 $\pm$ 2.91	27.3 $\pm$ 0.3
U2	2	32606 $\pm$ 292	132.3 $\pm$ 2.11	52.1 $\pm$ 0.3
E2	2	32685 $\pm$ 310	131.4 $\pm$ 1.77	52.9 $\pm$ 0.2
U3	1	45624 $\pm$ 376	65.9 $\pm$ 1.03	74.5 $\pm$ 0.4
E3	1	45833 $\pm$ 339	64.8 $\pm$ 1.33	75.1 $\pm$ 0.4
U4	1.5	37594 $\pm$ 275	97.9 $\pm$ 2.32	59.6 $\pm$ 0.3
E4	1.5	37841 $\pm$ 201	95.2 $\pm$ 1.80	61.6 $\pm$ 0.2

AFM measurements were utilized to determine the thickness of the SWCNT films. As shown in Figure 7-4, the film has uniform thickness. The height profile from AFM crossing the edge of the thin film illustrates its thickness. Transmittance of SWCNT films deposited on ITO substrates was measured on the Varian Cary 5000 spectrophotometer. Transmittance spectra of films deposited on ITO substrates were shown in Figure 7-4. Table 7-2 summarizes fabrication parameters, thickness, and transparency of films. When the amount of SWCNT suspensions used for filtration was increased from 1 to 4 mL, the film thickness increased from 65 to 259 nm, while the transmittances at 550 nm decreased from 75 to 26 %. Two additional films (labelled as U4 and E4) were fabricated using 1.5

mL of unsorted and separated SWCNT suspensions, and their properties agreed with our expected values. This verified the consistency of our SWCNT film fabrication procedure. Overall, these results demonstrate that the thickness and transmittance of SWCNT films from both unsorted and separated samples can be controlled for photoelectrochemical devices.

7.4 Evaluation of Photocurrent Responses

All photoelectrochemical measurements were carried out in a standard three-electrode system using an ALS 630a electrochemical analyzer. The SWCNT film deposited on an ITO substrate as a working electrode was immersed into an acetonitrile electrolyte solution containing 0.5 M LiI and 0.01 M I₂. A Pt wire covered with a glass capillary, whose tip was located near the working electrode, and a Pt coil were used as quasi-reference and counter electrodes, respectively. A 500 W xenon lamp (XB-50101AA-A; Ushio, Japan) was used as a light source.

Panel (a) and panel (b) of Figure 7-4 display photoelectrochemical responses of SWCNT films fabricated from unsorted and separated nanotube samples. The films were illuminated with white light ($\lambda > 380$ nm) at an input power of 37.4 mW cm^{-2} . No bias potential was applied against the saturated calomel electrode (SCE). The photoelectrochemical responses were prompt, steady, and reproducible during repeated on/off cycles. Blank ITO substrates without SWCNT films did not exhibit comparable photocurrent responses under the same condition. Two important trends can be observed from photocurrents illustrated in panel (c) of Figure 7-4.

First, the photocurrent intensities increase with the decrease of SWCNT film thickness. The photocurrents generated by the SWCNT films with thickness of 65 nm are 0.84 and 0.74 μA for unsorted and separated nanotube samples, respectively. In comparison, those generated from the 258 nm thick SWCNT films are 0.62 and 0.46 μA . The decrease in photocurrent intensity can be attributed to the recombination of free carriers induced by metallic nanotubes. Electron-hole pairs are generated in SWCNT films upon light illumination. The holes may diffuse to the ITO substrate; while electrons are scavenged by the I_3^-/I^- redox couple in the electrolyte. However, metallic nanotubes existing in SWCNT films facilitate the recombination of holes and electrons. Luer *et al.* [27] suggested that the length scale for surface quenching of excitons in SWCNTs is below 10 nm. The thicker the SWCNT films are, the longer the distance that holes or electrons have to travel to reach ITO substrates or electrolytes, leading to higher chances of recombination. Second, the photocurrent intensities generated from SWCNT films containing a high density of semiconducting nanotubes are about 15–35% higher than those from unsorted nanotube samples. This is the direct experimental evidence that thin films of semiconducting SWCNTs can enhance the photocurrent generation. Less metallic nanotubes in the films can reduce the quenching channels of recombination, and more holes and electrons are able to reach ITO substrates or electrolytes.

Figure 7-5 Photoelectrochemical response of SWCNT thin films fabricated with (a) unsorted nanotube samples; (b) nanotubes enriched with semiconducting nanotubes. (c) The intensities of photocurrents plotted against the SWCNT film thickness.

When external bias is applied to the working electrode, it creates an additional field to drive the electrons and holes to the electrolyte and the ITO electrode, respectively. This facilitates the suppression of the charge recombination process. Panel (a) of Figure 7-5 shows the current-applied potential curve of the device (E4) fabricated from the sample containing high density semiconducting nanotubes. Bias voltage was applied to the reference electrode and scanned from -0.2 to 0.2 V. With the increasing of the negative bias, the photocurrent increases compared to the dark current, and reach a maximum at 1.09 μA under -0.151 V vs SCE. The easy transport of charge carriers under the negative bias is responsible for the enhanced photocurrent generation. The SWCNT electrode was saturated under the bias voltage of 0.13 V. A clear capacitance charging trend can also be observed. To further evaluate the photoelectrochemical response of films containing high density semiconducting SWCNTs, the wavelength dependence of the IPCE of the SWCNT films was also examined. The monochromatic light through a monochromator (MC-10N; Ritsu, Japan) illuminated the area of the working electrode (0.20 cm^2) from the backside. The

light intensity was monitored and corrected by an optical power meter (ML9002A; Anritsu, Japan). Panel (b) of Figure 7-5 shows the result obtained on the E4 and U4 devices. The IPCE values are calculated by normalizing the photocurrent densities for incident light intensity and by the use of expression:

$$\text{IPCE (\%)} = 100 \times 1240 \times i / (W_{in} \times \lambda) \quad (1)$$

where i is the photocurrent density (A cm^{-2}), W_{in} is the incident light intensity (W cm^{-2}), and λ is the excitation wavelength (nm). The exhibited photocurrent generation has IPCE values of 0.68 % with no bias and 3.41 % under negative bias (-0.1 V vs SCE) at 400 nm, which are significantly higher than the values for unsorted SWCNT electrodes (0.60 and 2.81 %, respectively).

Figure 7-6 (a) Current vs applied-potential curve for the SWCNT thin film device (E4) (b) Photocurrent action spectra for the SWCNT thin film devices (U4 and E4).

7.5 Conclusion

Large diameter ($\sim 1.4\text{nm}$) SWCNT samples prepared by arc-discharge method was purified by a centrifugation based method and further enriched with semiconducting species by a agarose gel-centrifugation based method. By carefully tuning the gel concentration and centrifugation force applied, $> 90\%$ pure semiconducting SWCNT samples can be easily obtained at mg level. SWCNTs thin films prepared from the semiconducting enriched nanotubes as well as the unsorted samples with different but controllable thickness were transferred from filtration membrane to ITO glass to fabricated series of photochemical devices to test their photocurrent responses. Generally, the experimental results demonstrate that the films obtained from semiconducting enriched SWCNTs produce 15~35% higher photocurrent than that of the films prepared from unsorted samples with the same thickness under same experiment conditions. The results also advise that thinner films would generate higher photocurrent. The experimental observations can be explained by the removal of the metallic channels inside the SWCNT thin films formed by metallic SWCNTs which would locally recombine the photon excited electron-hole pairs, or the shortened travelling distance for the separated carries to reach the ITO electrode or the electrolytes in the SWCNT films. The results suggests that the key to improve the performance and understanding of SWCNT based photochemical devices relies on the carrier separation efficiency happened inside the SWCNT thin films, which can be improved by carefully designed electrode materials and more scalable and selective semiconducting enrichment methods, which are still under pursuit by the wide scientific research communities.

7.6 Reference

1. Kamat, P.V., *Harvesting Photons with Carbon Nanotubes*. Nano Today, 2006. **1**(4): p. 20-27.
2. Umeyama, T. and H. Imahori, *Carbon Nanotube-Modified Electrodes for Solar Energy Conversion*. Energy Environ. Sci., 2008. **1**(1): p. 120-133.
3. Freitag, M., Y. Martin, J.A. Misewich, R. Martel, and P. Avouris, *Photoconductivity of Single Carbon Nanotubes*. Nano Lett., 2003. **3**(8): p. 1067-1071.
4. Barazzouk, S., S. Hotchandani, K. Vinodgopal, and P.V. Kamat, *Single-Wall Carbon Nanotube Films for Photocurrent Generation. A Prompt Response to Visible-Light Irradiation*. J. Phys. Chem. B, 2004. **108**(44): p. 17015-17018.
5. Arranz-Andres, J. and W.J. Blau, *Enhanced Device Performance using Different Carbon Nanotube Types in Polymer Photovoltaic Devices*. Carbon, 2008. **46**(15): p. 2067-2075.
6. Merchant, C.A. and N. Markovic, *Effects of Diffusion on Photocurrent Generation in Single-Walled Carbon Nanotube Films*. Appl. Phys. Lett., 2008. **92**(24): p. 243510.
7. Liu, L., W.E. Stanchina, and G. Li, *Effects of Semiconducting and Metallic Single-Walled Carbon Nanotubes on Performance of Bulk Heterojunction Organic Solar Cells*. Appl. Phys. Lett., 2009. **94**(23): p. 233309-1.
8. Hersam, M.C., *Progress Towards Monodisperse Single-Walled Carbon Nanotubes*. Nat. Nanotechnol. , 2008. **3**(7): p. 387-394.
9. Arnold, M.S., A.A. Green, J.F. Hulvat, S.I. Stupp, and M.C. Hersam, *Sorting carbon nanotubes by electronic structure using density differentiation*. Nat Nano, 2006. **1**(1): p. 60-65.
10. Niyogi, S., C.G. Densmore, and S.K. Doorn, *Electrolyte Tuning of Surfactant Interfacial Behavior for Enhanced Density-Based Separations of Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2008. **131**(3): p. 1144-1153.
11. Krupke, R., F. Hennrich, M.M. Kappes, and H. v. Lohneysen, *Surface Conductance Induced Dielectrophoresis of Semiconducting Single-Walled Carbon Nanotubes*. Nano Letters, 2004. **4**(8): p. 1395-1399.

12. Krupke, R., F. Hennrich, H.v. Lohneysen, and M.M. Kappes, *Separation of Metallic from Semiconducting Single-Walled Carbon Nanotubes*. Science, 2003. **301**(5631): p. 344-347.
13. Krupke, R., S. Linden, M. Rapp, and F. Hennrich, *Thin Films of Metallic Carbon Nanotubes Prepared by Dielectrophoresis*. Advanced Materials, 2006. **18**(11): p. 1468-1470.
14. Peng, H., N.T. Alvarez, C. Kittrell, R.H. Hauge, and H.K. Schmidt, *Dielectrophoresis Field Flow Fractionation of Single-Walled Carbon Nanotubes*. Journal of the American Chemical Society, 2006. **128**(26): p. 8396-8397.
15. Chattopadhyay, D., I. Galeska, and F. Papadimitrakopoulos, *A Route for Bulk Separation of Semiconducting from¹² Metallic Single-Wall Carbon Nanotubes*. Journal of the American Chemical Society, 2003. **125**(11): p. 3370-3375.
16. Kim, S.N., Z. Luo, and F. Papadimitrakopoulos, *Diameter and Metallicity Dependent Redox Influences on the Separation of Single-Wall Carbon Nanotubes*. Nano Letters, 2005. **5**(12): p. 2500-2504.
17. Zheng, M., A. Jagota, E.D. Semke, B.A. Diner, R.S. McLean, S.R. Lustig, R.E. Richardson, and N.G. Tassi, *DNA-assisted dispersion and separation of carbon nanotubes*. Nat Mater, 2003. **2**(5): p. 338-342.
18. Zheng, M., A. Jagota, M.S. Strano, A.P. Santos, P. Barone, S.G. Chou, B.A. Diner, M.S. Dresselhaus, R.S. Mclean, G.B. Onoa, G.G. Samsonidze, E.D. Semke, M. Usrey, and D.J. Walls, *Structure-Based Carbon Nanotube Sorting by Sequence-Dependent DNA Assembly*. Science, 2003. **302**(5650): p. 1545-1548.
19. Zheng, M. and E.D. Semke, *Enrichment of Single Chirality Carbon Nanotubes*. Journal of the American Chemical Society, 2007. **129**(19): p. 6084-6085.
20. Tromp, R.M., A. Afzali, M. Freitag, D.B. Mitzi, and Z. Chen, *Novel Strategy for Diameter-Selective Separation and Functionalization of Single-Wall Carbon Nanotubes*. Nano Letters, 2008. **8**(2): p. 469-472.
21. Fujii, S., T. Tanaka, Y. Miyata, H. Suga, Y. Naitoh, T. Minari, T. Miyadera, K. Tsukagoshi, and H. Kataura, *Performance Enhancement of Thin-Film Transistors by Using High-Purity Semiconducting Single-Wall Carbon Nanotubes*. Applied

- Physics Express, 2009. **2**(Copyright (c) 2009 The Japan Society of Applied Physics): p. 071601.
22. Tanaka, T., H. Jin, Y. Miyata, S. Fujii, H. Suga, Y. Naitoh, T. Minari, T. Miyadera, K. Tsukagoshi, and H. Kataura, *Simple and Scalable Gel-Based Separation of Metallic and Semiconducting Carbon Nanotubes*. Nano Letters, 2009. **9**(4): p. 1497-1500.
 23. Tanaka, T., H. Jin, Y. Miyata, and H. Kataura, *High-Yield Separation of Metallic and Semiconducting Single-Wall Carbon Nanotubes by Agarose Gel Electrophoresis*. Applied Physics Express, 2008. **1**(Copyright (c) 2008 The Japan Society of Applied Physics): p. 114001.
 24. Tanaka, T., Y. Urabe, D. Nishide, and H. Kataura, *Continuous Separation of Metallic and Semiconducting Carbon Nanotubes Using Agarose Gel*. Applied Physics Express, 2009. **2**(Copyright (c) 2009 The Japan Society of Applied Physics): p. 125002.
 25. Wei, L., B. Wang, Q. Wang, L.-J. Li, Y. Yang, and Y. Chen, *Effect of Centrifugation on the Purity of Single-Walled Carbon Nanotubes from MCM-41 Containing Cobalt*. The Journal of Physical Chemistry C, 2008. **112**(47): p. 17567-17575.
 26. Wu, Z., Z. Chen, X. Du, J.M. Logan, J. Sippel, M. Nikolou, K. Kamaras, J.R. Reynolds, D.B. Tanner, A.F. Hebard, and A.G. Rinzler, *Transparent, Conductive Carbon Nanotube Films*. Science, 2004. **305**(5688): p. 1273-1276.
 27. Luer, L., S. Hoseinkhani, D. Polli, J. Crochet, T. Hertel, and G. Lanzani, *Size and Mobility of Excitons in (6, 5) Carbon Nanotubes*. Nat. Phys., 2009. **5**(1): p. 54-58.

Chapter 8

Summary

The year 2011 will be the 20th anniversary since the important discovery of CNTs in 1991. Although carbon nanotubes have already been put into some real applications, such as battery electrode enhancing layers and novel CNT-polymer composites, the pursuit of monodisperse SWCNTs has never stopped. In order to realize the full potential of SWCNTs in future electronic, energy, mechanical and medical applications, many obstacles still need to be conquered, *e.g.*, the precise control of nanotube structures (diameter, length and chirality), patterning and alignment of SWCNTs, scalable production of SWCNTs, as well as sensitive and accurate evaluation techniques for their purity and structural assessment. SWCNT production of kg scale has been achieved in the past 10 years. Various catalysts, such as Co-Mo, Fe-Ru bimetallic catalysts and Co-MCM-41 catalysts, have been developed to directly synthesize SWCNTs with narrow chirality distributions. Diverse purification protocols have been investigated to obtain high purity SWCNTs for both fundamental study and applications. However, the lack of monodisperse and impurity free SWCNT samples still hinders many applications. This thesis has made efforts to improve SWCNT purification and chiral selective enrichment methods.

Centrifugation has been applied to purify SWCNTs grown from Co-MCM-41 catalyst by CVD. After centrifugation at 120 000 g, SWCNT purity index based on absorption spectra of SC dispersed SWCNTs is 0.268. This value is the highest purity index value reported so far, approaching the previously estimated value of ~ 0.325 for analytically pure

SWCNTs. In PL study, (1) line width for E_{11} emission peaks at E_{22} excitation energy, (2) intensities of three sidebands, and (3) intensities of E_{11} emission peaks at E_{33} excitation energy are related to SWCNT purity. They may be used to evaluate the purity of SWCNT samples. Both TGA results and theoretical models demonstrated that SC molecules adsorbed on the SWCNT surface cannot be easily washed away. After removal of metallic residues, absorbed SC molecules can be eliminated by heating in air at 350 °C for 30 min. Combining UV-vis-NIR absorption, PL spectroscopic techniques, SEM, TEM, and TGA, it is feasible to have a reliable quality control of SWCNT products. Purification protocol toward analytically pure SWCNTs in this study may prove useful in evaluating health and environmental effects of SWCNT material and improving separation efficiencies of nanotube species according to electronic type, diameter, length, and chiral handedness.

Centrifugation purified SWCNT samples enriched with (6,5) and (7,5) chiral structures were used to establish the correlation between PL sidebands (the transverse sideband $E_{12,21}$, the phonon coupled sidebands $E_{22}+G$, G' and $E_{33}-E_{11}$ emission band) and nanotube aggregation state. SWCNT suspensions containing different bundle fractions were prepared via centrifugation of surfactant dispersed nanotube dispersions at different centrifugal forces ranging from 20,000 to 180,000 g. The aggregation of nanotubes can be further tuned by the controlled rebundling through dialysis. The intensity ratios between $E_{12,21}$ or $E_{22}+G$, G' , and the primary $E_{22}-E_{11}$ PL peak decreased with the removal of nanotube bundles. On the contrary, the intensity ratio between $E_{33}-E_{11}$ and $E_{22}-E_{11}$ PL peaks increased when fewer nanotube bundles existed in suspensions. These aggregation-dependent PL sidebands can also be observed under different dispersion conditions, such as

SDS, SDBS aqueous solutions, and PFO in toluene. They are more sensitive toward characterizing the aggregation of SWCNTs than absorption spectroscopy and AFM.

Selective enrichment of (6,5) and (8,3) SWCNTs to more than 85% after three extraction iterations using SDS and SC co-surfactant was achieved from SWCNTs obtained on Co-MCM-41 catalyst. The co-surfactant extraction process provides an easily scalable approach for obtaining SWCNTs with a desired (n,m) structure. DGU is applied to further sort the smaller diameter nanotube enriched sample and the starting SWCNT sample. Even though results from PL, UV-vis-NIR, and Raman spectroscopy illustrate very similar results among samples, characterization of SWNT thin-film FETs fabricated from those (n,m) enriched SWNTs reveals that small changes in their semiconducting SWNT purity lead to significant differences in device performance. Co-surfactant extraction (SDS/SC) can enrich smaller diameter tubes, such as (6,5) and (8,3), as well as metallic nanotubes. Higher semiconducting fractions can be obtained from the first two layers by using SC alone in DGU; however, more metallic tubes exist in the first two layers when SDS/SC (1:4) co-surfactant is applied in DGU. Electronic transfer measurement of SWNT thin film FETs (by on-off ratio) is more sensitive than spectroscopic studies to assess semiconducting SWNT purity for macroelectronics.

Furthermore, sufficient amount of semiconducting SWCNTs were obtained through a gel-centrifugation based method from centrifugation purified nanotubes prepared by arc-discharge method. The agarose gel-centrifugation based procedure yields > 90% pure semiconducting nanotube that can be utilized to construct photoelectrochemical devices, a typical example of macroelectronic applications. SWCNT thin films with controllable thickness and transmittance from both unsorted and enriched samples can be easily

fabricated on ITO substrates for photocurrent measurement. Photoelectrochemical responses generated from SWCNT thin films deposited on ITO substrates were measured. The results provide direct experimental evidences that semiconducting nanotube enriched thin films produce 15–35 % higher photocurrents compared to SWCNT films from unsorted samples. Furthermore, decreasing SWCNT film thickness helps to produce higher photocurrents. The observed trends can be explained by the reduction in the exciton recombination channels when metallic tubes are removed, and the shorter travelling distance for carriers to reach ITO substrates or electrolytes in thinner SWCNT films.

Future work is still needed towards scalable production of high purity monodisperse SWCNT samples for macroelectronic applications. Such efforts may focus on the following directions:

(1) Results in Chapter 5 and 6 indicate that the co-surfactant extraction of smaller diameter nanotubes is contributed by the different interaction strengths between surfactant molecules and nanotubes. Recently, several reports have emerged, focusing on experimental observation and theoretical modeling of such interactions. A better understanding of the surfactant-nanotube interactions may guild the new development in various separation methods.

(2) Chirality selective synthesis protocols should be developed to preferentially grow SWCNTs with desired chiral structures in large scale. Co-MCM-41 catalyst can produce high quality SWCNT samples with narrow chirality distribution. The as-synthesized SWCNTs are also easy to be purified. However, the carbon loading on Co-MCM-41 catalyst is approximately 5 wt%. It takes approximately one week to synthesize the catalyst. The limited scalability of the current SWCNT synthesis method hinders its large scale

industrial applications. Furthermore, Co-MCM-41 can preferentially grow small diameter nanotubes (less than 1 nm in diameter). However, in many electronic device applications, large diameter (*i.e.*, $d_t > 1.4$ nm) nanotubes are desired because large diameter SWCNTs may have higher carrier mobilities and less contact resistances between nanotubes and electrodes. Thus, it is important to better understand the nanotube growth mechanism so that novel growth methods can be developed to produce SWCNTs with large diameter and narrow chirality distribution.

(3) Assessment of semiconducting nanotubes by various characterization methods is a focused topic in this thesis. However, a feasible method to determine the (n,m) abundance of metallic nanotubes is still not available. The lack of such a method is an obstacle for developing efficient nanotube separation methods. Although the structures of metallic nanotubes can be determined by Raman spectroscopy equipped with continuously tunable laser sources or scanning probe microscope, more convenient and easy accessible techniques should be developed.

(4) Currently, the best (n,m) selective separation efficiency can be achieved by DGU and chromatographic separation of single strain DNA wrapped nanotubes. A major drawback of these two methods is their high cost and relatively low throughput. The commercial products obtained by DGU method are now available on market. The high price (USD 800 /mg) limits its application in research labs. Such a high cost makes SWCNT less competitive in various applications. Large scale and low cost methods need to be invented in the near future.

In the last five years, significant progress has been achieved towards large scale synthesis and enrichment of SWCNTs with precisely controlled structures. Such efforts

have made various proposed SWCNT applications closer to their reality. However, the long march hasn't reached its destination. Competition has also arisen from newly discovered nanomaterials, such as graphene. The future of SWCNT is in the hand of researchers to realize their full potentials.

Appendix I (n,m) abundance of SWCNT suspensions in Chapter 5**Table A I-1** Abundance evaluation of chiral species in SDS (1 wt %)

(n,m)	d_t , nm	θ , °	E_{11} , nm	E_{22} , nm	I^{exp}	$I^{cal a}$	Abundance, % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.757	27	984	566	46.2	0.67	12.17	12.14
(7,5)	0.829	24.5	1029	646	182.7	0.71	45.44	48.03
(7,6)	0.895	27.5	1125	646	19.3	0.47	7.25	5.08
(8,3)	0.782	15.3	956	644	56.0	2.13	4.64	14.73
(8,4)	0.84	19.1	1118	588	43.7	0.46	16.77	11.48
(8,6)	0.966	25.3	1173	718	9.1	0.49	3.29	2.40
(8,7)	1.032	27.8	1266	730	3.1	0.3	1.84	0.82
(9,2)	0.806	9.5	1138	551	2.1	0.4	1.06	0.55
(9,4)	0.916	17.5	1114	720	7.1	0.7	1.80	1.87
(9,5)	0.976	20.6	1241	672	3.8	0.28	2.38	0.99
(9,7)	1.103	25.9	1323	792	5.1	0.27	3.34	1.34
(10,2)	0.884	9.0	1063	738	2.1	2.38	0.16	0.56

a. I^{cal} adopted from Oyama, Y., R. Saito, K. Sato, J. Jiang, G.G. Samsonidze, A. Gruneis, Y. Miyauchi, S. Maruyama, A. Jorio, G. Dresselhaus, and M. S. Dresselhaus, *Photoluminescence intensity of single-wall carbon nanotubes*. Carbon, 2006. **44**(5): p. 873-879.

Table A I-2 Abundance of chiral species in total 2 wt % surfactants with SDS : SC=90 : 10

(n,m)	d_t , nm	θ , °	E_{11} , nm	E_{22} , nm	I^{exp}	I^{cal}	Abundance, % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.757	27	984	566	139.2	0.67	15.22	14.99
(7,5)	0.829	24.5	1029	646	388.9	0.71	40.12	41.87
(7,6)	0.895	27.5	1125	646	48	0.47	7.48	5.17
(8,3)	0.782	15.3	956	644	99.4	2.13	3.42	10.7
(8,4)	0.84	19.1	1118	588	137.5	0.46	21.9	14.81
(8,6)	0.966	25.3	1173	718	23.8	0.49	3.56	2.56
(8,7)	1.032	27.8	1266	730	0	0.3	0	0
(9,2)	0.806	9.5	1138	551	19.1	0.4	4.13	2.06
(9,4)	0.916	17.5	1114	720	34.8	0.7	3.64	3.74
(9,5)	0.976	20.6	1241	672	0	0.28	0	0
(9,7)	1.103	25.9	1323	792	0	0.27	0	0
(10,2)	0.884	9.0	1063	738	38.1	2.38	1.17	4.1

Table AI-3 Abundance of chiral species in total 2 wt % surfactants with SDS : SC=80 : 20

(n,m)	d_t , nm	θ , °	E_{11} , nm	E_{22} , nm	I^{exp}	I^{cal}	Abundance, % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.757	27	984	566	145.5	0.67	16.63	16.94
(7,5)	0.829	24.5	1029	646	364	0.71	39.26	42.36
(7,6)	0.895	27.5	1125	646	47.9	0.47	7.8	5.57
(8,3)	0.782	15.3	956	644	59	2.13	2.12	6.86
(8,4)	0.84	19.1	1118	588	139.4	0.46	23.21	16.22
(8,6)	0.966	25.3	1173	718	22	0.49	3.44	2.56
(8,7)	1.032	27.8	1266	730	0	0.3	0	0
(9,2)	0.806	9.5	1138	551	19.1	0.4	4.39	2.23
(9,4)	0.916	17.5	1114	720	24.2	0.7	2.65	2.82
(9,5)	0.976	20.6	1241	672	0	0.28	0	0
(9,7)	1.103	25.9	1323	792	0	0.27	0	0
(10,2)	0.884	9	1063	738	38.2	2.38	1.23	4.44

Table A I-4 Abundance of chiral species in total 2 wt % surfactants with SDS : SC=70 : 30

(n,m)	d_t , nm	θ , °	E_{11} , nm	E_{22} , nm	I^{exp}	I^{cal}	Abundance, % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.757	27	984	566	172.9	0.67	18.65%	18.84
(7,5)	0.829	24.5	1029	646	369.2	0.71	37.59%	40.24
(7,6)	0.895	27.5	1125	646	43.5	0.47	6.69%	4.74
(8,3)	0.782	15.3	956	644	70.3	2.13	2.39%	7.66
(8,4)	0.84	19.1	1118	588	165.0	0.46	25.94%	17.99
(8,6)	0.966	25.3	1173	718	13.4	0.49	1.98%	1.46
(8,7)	1.032	27.8	1266	730	0.0	0.3	0.00%	0.00
(9,2)	0.806	9.5	1138	551	19.1	0.4	4.25%	2.08
(9,4)	0.916	17.5	1114	720	18.8	0.7	1.94%	2.04
(9,5)	0.976	20.6	1241	672	0.0	0.28	0.00%	0.00
(9,7)	1.103	25.9	1323	792	0.0	0.27	0.00%	0.00
(10,2)	0.884	9.0	1063	738	45.3	2.38	1.38%	4.94

Table A I-5 Abundance of chiral species in total 2 wt % surfactants with SDS : SC=60 : 40

(n,m)	$d,$ nm	$\theta, ^\circ$	$E_{11},$ nm	$E_{22},$ nm	I^{exp}	I^{cal}	Abundance , % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.757	27	984	566	196.7	0.67	20.48	20.99
(7,5)	0.829	24.5	1029	646	371.9	0.71	36.52	40.32
(7,6)	0.895	27.5	1125	646	42.3	0.47	6.28	4.59
(8,3)	0.782	15.3	956	644	69.5	2.13	2.28	7.54
(8,4)	0.84	19.1	1118	588	182.1	0.46	27.61	19.75
(8,6)	0.966	25.3	1173	718	11.4	0.49	1.62	1.24
(8,7)	1.032	27.8	1266	730	0.0	0.3	0.00	0.00
(9,2)	0.806	9.5	1138	551	14.9	0.4	3.27	1.62
(9,4)	0.916	17.5	1114	720	17.0	0.7	1.69	1.84
(9,5)	0.976	20.6	1241	672	0.0	0.28	0.00	0.00
(9,7)	1.103	25.9	1323	792	0.0	0.27	0.00	0.00
(10,2)	0.884	9.0	1063	738	31.3	2.38	0.92	3.39

Table A I-6 Abundance of chiral species in total 2 wt % surfactants with SDS : SC=50 : 50

(n,m)	$d_{\perp}$ nm	$\theta, ^\circ$	$E_{11},$ nm	$E_{22},$ nm	I^{exp}	I^{cal}	Abundance, % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.757	27	984	566	395.5	0.67	23.99	22.90
(7,5)	0.829	24.5	1029	646	612.9	0.71	35.08	35.49
(7,6)	0.895	27.5	1125	646	49.1	0.47	4.25	2.85
(8,3)	0.782	15.3	956	644	280.0	2.13	5.34	16.21
(8,4)	0.84	19.1	1118	588	284.1	0.46	25.09	16.45
(8,6)	0.966	25.3	1173	718	26.3	0.49	2.18	1.52
(8,7)	1.032	27.8	1266	730	0.0	0.3	0.00	0.00
(9,2)	0.806	9.5	1138	551	23.1	0.4	3.09	1.34
(9,4)	0.916	17.5	1114	720	18.7	0.7	1.09	1.08
(9,5)	0.976	20.6	1241	672	0.0	0.28	0.00	0.00
(9,7)	1.103	25.9	1323	792	0.0	0.27	0.00	0.00
(10,2)	0.884	9.0	1063	738	37.4	2.38	0.64	2.17

Table A I-7 Abundance of chiral species in total 2 wt % surfactants with SDS : SC=40 : 60

(n,m)	d_l , nm	θ , °	E_{11} , nm	E_{22} , nm	I^{exp}	I^{cal}	Abundance , % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.757	27	984	566	201.5	0.67	26.76	26.35
(7,5)	0.829	24.5	1029	646	252.6	0.71	31.66	33.02
(7,6)	0.895	27.5	1125	646	37.3	0.47	7.06	4.88
(8,3)	0.782	15.3	956	644	103.2	2.13	4.31	13.49
(8,4)	0.84	19.1	1118	588	108.5	0.46	21.00	14.19
(8,6)	0.966	25.3	1173	718	10.5	0.49	1.91	1.38
(8,7)	1.032	27.8	1266	730	3.1	0.3	0.92	0.41
(9,2)	0.806	9.5	1138	551	15.1	0.4	4.59	1.98
(9,4)	0.916	17.5	1114	720	19.8	0.7	2.52	2.59
(9,5)	0.976	20.6	1241	672	0.0	0.28	0.00	0.00
(9,7)	1.103	25.9	1323	792	0.0	0.27	0.00	0.00
(10,2)	0.884	9.0	1063	738	13.2	2.38	0.49	1.72

Table A I-8 Abundance of chiral species in total 2 wt % surfactants with SDS : SC=30 : 70

(n,m)	d_s nm	$\theta, ^\circ$	$E_{11},$ nm	$E_{22},$ nm	I^{exp}	I^{cal}	Abundance, % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.757	27	984	566	361.7	0.67	33.52	32.44
(7,5)	0.829	24.5	1029	646	325.5	0.71	28.47	29.19
(7,6)	0.895	27.5	1125	646	49.2	0.47	6.50	4.42
(8,3)	0.782	15.3	956	644	152.0	2.13	4.43	13.63
(8,4)	0.84	19.1	1118	588	139.4	0.46	18.81	12.50
(8,6)	0.966	25.3	1173	718	13.8	0.49	1.74	1.23
(8,7)	1.032	27.8	1266	730	0.0	0.3	0.00	0.00
(9,2)	0.806	9.5	1138	551	23.1	0.4	5.40	2.07
(9,4)	0.916	17.5	1114	720	25.8	0.7	2.29	2.31
(9,5)	0.976	20.6	1241	672	0.0	0.28	0.00	0.00
(9,7)	1.103	25.9	1323	792	0.0	0.27	0.00	0.00
(10,2)	0.884	9.0	1063	738	24.6	2.38	0.64	2.20

Table A I-9 Abundance of chiral species in total 2 wt % surfactants with SDS : SC=20 : 80

(n,m)	$d_i,$ nm	$\theta, ^\circ$	$E_{11},$ nm	$E_{22},$ nm	I^{exp}	I^{cal}	Abundance, % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.757	27	984	566	515.8	0.67	47.28	39.55
(7,5)	0.829	24.5	1029	646	260.5	0.71	17.56	15.57
(7,6)	0.895	27.5	1125	646	27.7	0.47	3.72	2.18
(8,3)	0.782	15.3	956	644	372.0	2.13	10.43	27.75
(8,4)	0.84	19.1	1118	588	106.9	0.46	13.43	7.72
(8,6)	0.966	25.3	1173	718	23.1	0.49	2.97	1.82
(8,7)	1.032	27.8	1266	730	0.0	0.3	0.00	0.00
(9,2)	0.806	9.5	1138	551	15.3	0.4	3.68	0.97
(9,4)	0.916	17.5	1114	720	18.3	0.7	1.65	1.44
(9,5)	0.976	20.6	1241	672	0.0	0.28	0.00	0.00
(9,7)	1.103	25.9	1323	792	0.0	0.27	0.00	0.00
(10,2)	0.884	9.0	1063	738	38.2	2.38	1.01	3.01

Table A I-10 Abundance of chiral species in total 2 wt % surfactants with SDS:SC=15 : 85

(n,m)	$d,$ nm	$\theta, ^\circ$	$E_{11},$ nm	$E_{22},$ nm	I^{exp}	I^{cal}	Abundance , % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.757	27	984	566	460.4	0.67	27.31	25.74
(7,5)	0.829	24.5	1029	646	640.7	0.71	35.86	35.83
(7,6)	0.895	27.5	1125	646	58.9	0.47	4.98	3.29
(8,3)	0.782	15.3	956	644	265.0	2.13	4.94	14.82
(8,4)	0.84	19.1	1118	588	212.0	0.46	18.32	11.85
(8,6)	0.966	25.3	1173	718	27.2	0.49	2.21	1.52
(8,7)	1.032	27.8	1266	730	0.0	0.3	0.00	0.00
(9,2)	0.806	9.5	1138	551	31.0	0.4	3.08	1.73
(9,4)	0.916	17.5	1114	720	43.4	0.7	2.46	2.43
(9,5)	0.976	20.6	1241	672	0.0	0.28	0.00	0.00
(9,7)	1.103	25.9	1323	792	0.0	0.27	0.00	0.00
(10,2)	0.884	9.0	1063	738	49.8	2.38	0.83	2.78

Table A I-11 Abundance of chiral species in total 2 wt % surfactants with SDS:SC=10 : 90

(n,m)	d_t , nm	θ , °	E_{11} , nm	E_{22} , nm	I^{exp}	I^{cal}	Abundance, % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.757	27	984	566	359.1	0.67	20.16	20.32
(7,5)	0.829	24.5	1029	646	779.7	0.71	41.30	44.12
(7,6)	0.895	27.5	1125	646	50.0	0.47	4.00	2.83
(8,3)	0.782	15.3	956	644	94.7	2.13	1.67	5.36
(8,4)	0.84	19.1	1118	588	259.5	0.46	21.22	14.68
(8,6)	0.966	25.3	1173	718	48.0	0.49	3.68	2.71
(8,7)	1.032	27.8	1266	730	0.0	0.3	0.00	0.00
(9,2)	0.806	9.5	1138	551	41.0	0.4	4.83	2.32
(9,4)	0.916	17.5	1114	720	52.1	0.7	2.80	2.95
(9,5)	0.976	20.6	1241	672	0.0	0.28	0.00	0.00
(9,7)	1.103	25.9	1323	792	0.0	0.27	0.00	0.00
(10,2)	0.884	9.0	1063	738	83.3	2.38	1.32	4.71

Table A I-12 Abundance of chiral species in SC (2 wt %)

(n,m)	$d,$ nm	$\theta, ^\circ$	$E_{11},$ nm	$E_{22},$ nm	I^{exp}	I^{cal}	Abundance, % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.757	27	984	566	119.7	0.67	12.26	11.56
(7,5)	0.829	24.5	1029	646	461.7	0.71	44.62	44.59
(7,6)	0.895	27.5	1125	646	48.8	0.47	7.12	4.71
(8,3)	0.782	15.3	956	644	191.9	2.13	6.18	18.53
(8,4)	0.84	19.1	1118	588	95.9	0.46	14.30	9.26
(8,6)	0.966	25.3	1173	718	16.5	0.49	2.31	1.59
(8,7)	1.032	27.8	1266	730	10.9	0.3	2.49	1.05
(9,2)	0.806	9.5	1138	551	20.1	0.4	3.93	1.94
(9,4)	0.916	17.5	1114	720	36.9	0.7	3.62	3.56
(9,5)	0.976	20.6	1241	672	6.8	0.28	1.68	0.66
(9,7)	1.103	25.9	1323	792	5.4	0.27	1.36	0.52
(10,2)	0.884	9.0	1063	738	119.7	2.38	0.60	2.02

Table A I-13 Abundance of chiral species in total 2 wt % surfactants with SDS : SC= 20 :
80 after the 2nd iteration

(n,m)	d_t , nm	θ , °	E_{11} , nm	E_{22} , nm	I^{exp}	$I^{cal}[1]$	Abundance , % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.757	27	984	566	435.1	0.67	62.44	48.10
(7,5)	0.829	24.5	1029	646	48.6	0.71	6.58	5.37
(7,6)	0.895	27.5	1125	646	12.0	0.47	2.45	1.32
(8,3)	0.782	15.3	956	644	331.4	2.13	14.96	36.63
(8,4)	0.84	19.1	1118	588	35.8	0.46	7.48	3.95
(8,6)	0.966	25.3	1173	718	5.1	0.49	1.00	0.57
(8,7)	1.032	27.8	1266	730	0.0	0.3	0.00	0.00
(9,2)	0.806	9.5	1138	551	13.8	0.4	8.81	1.52
(9,4)	0.916	17.5	1114	720	8.9	0.7	1.22	0.98
(9,5)	0.976	20.6	1241	672	0.0	0.28	0.00	0.00
(9,7)	1.103	25.9	1323	792	0.0	0.27	0.00	0.00
(10,2)	0.884	9.0	1063	738	14.0	2.38	0.56	1.54

Table A I-14 Abundance of chiral species in total 2 wt % surfactants with SDS : SC=20 : 80 after the 3rd iteration

(n,m)	d_l , nm	θ , °	E_{11} , nm	E_{22} , nm	I^{exp}	$I^{cal}[1]$	Abundance, % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.757	27	984	566	302.1	0.67	68.79	51.49
(7,5)	0.829	24.5	1029	646	16.1	0.71	3.47	2.749
(7,6)	0.895	27.5	1125	646	7.7	0.47	2.49	1.307
(8,3)	0.782	15.3	956	644	234.9	2.13	16.82	40.03
(8,4)	0.84	19.1	1118	588	18.8	0.46	6.22	3.2
(8,6)	0.966	25.3	1173	718	0	0.49	0	0
(8,7)	1.032	27.8	1266	730	0	0.3	0	0
(9,2)	0.806	9.5	1138	551	4	0.4	4.9	0.68
(9,4)	0.916	17.5	1114	720	3.2	0.7	0.69	0.54
(9,5)	0.976	20.6	1241	672	0	0.28	0	0
(9,7)	1.103	25.9	1323	792	0	0.27	0	0
(10,2)	0.884	9	1063	738	0	2.38	0	0

Appendix II (n,m) abundance of sample A-F in Chapter 6**Table A II-1 (n,m) abundance evaluation of sample A**

(n,m)	d_t , nm	θ , °	E_{11} , nm	E_{22} , nm	I^{exp}	I^{cal}	Abundance, % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.76	27	976	566	280.6	0.67	14.57	14.27
(7,5)	0.83	24.5	1024	645	685.9	0.71	33.61	34.9
(7,6)	0.9	27.5	1120	648	108.6	0.47	8.04	5.52
(8,3)	0.78	15.3	952	665	293.3	2.13	4.79	14.92
(8,4)	0.84	19.1	1118	589	376.3	0.46	28.46	19.15
(8,6)	0.97	25.3	1173	718	21.6	0.49	1.53	1.1
(8,7)	1.03	27.8	1265	728	0	0.3	0.00	0
(9,2)	0.81	9.8	1138	551	45.1	0.4	3.92	2.29
(9,4)	0.92	17.5	1101	722	80.7	0.7	4.01	4.11
(10,2)	0.88	9	1053	737	73.2	2.38	1.07	3.73

Table A II-2 (n,m) abundance evaluation of sample B

(n,m)	d_h , nm	θ , °	E_{11} , nm	E_{22} , nm	I^{exp}	I^{cal}	Abundance, % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.76	27	976	566	411.6	0.67	37.99	34.67
(7,5)	0.83	24.5	1024	645	225.0	0.71	19.60	18.95
(7,6)	0.9	27.5	1120	648	20.8	0.47	2.74	1.75
(8,3)	0.78	15.3	952	665	307.0	2.13	8.91	25.86
(8,4)	0.84	19.1	1118	589	183.1	0.46	24.61	15.42
(8,6)	0.97	25.3	1173	718	0.0	0.49	0.00	0.00
(8,7)	1.03	27.8	1265	728	0.0	0.3	0.00	0.00
(9,2)	0.81	9.8	1138	551	39.8	0.4	6.15	3.35
(9,4)	0.92	17.5	1101	722	0.0	0.7	0.00	0.00
(10,2)	0.88	9	1053	737	0.0	2.38	0.00	0.00

Table A II-3 (n,m) abundance evaluation of sample C

(n,m)	d_h , nm	θ , °	E_{11} , nm	E_{22} , nm	I^{exp}	I^{cal}	Abundance, % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.76	27	976	566	324.2	0.67	65.34	57.1
(7,5)	0.83	24.5	1024	645	26.0	0.71	4.94	4.6
(7,6)	0.9	27.5	1120	648	0.0	0.47	0.00	0.0
(8,3)	0.78	15.3	952	665	156.1	2.13	9.90	27.5
(8,4)	0.84	19.1	1118	589	19.1	0.46	5.61	3.4
(8,6)	0.97	25.3	1173	718	0.0	0.49	0.00	0.0
(8,7)	1.03	27.8	1265	728	0.0	0.3	0.00	0.0
(9,2)	0.81	9.8	1138	551	42.1	0.4	14.21	7.4
(9,4)	0.92	17.5	1101	722	0.0	0.7	0.00	0.0
(10,2)	0.88	9	1053	737	0.0	2.38	0.00	0.0

Table A II-4 (n, m) abundance evaluation of sample D

(n, m)	d_t , nm	θ , °	E_{11} , nm	E_{22} , nm	I^{exp}	I^{cal}	Abundance, % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.76	27	976	566	267.0	0.67	74.08	62.5
(7,5)	0.83	24.5	1024	645	11.2	0.71	2.93	2.6
(7,6)	0.9	27.5	1120	648	0.0	0.47	0.00	0.0
(8,3)	0.78	15.3	952	665	121.3	2.13	10.59	28.4
(8,4)	0.84	19.1	1118	589	9.3	0.46	3.76	2.2
(8,6)	0.97	25.3	1173	718	0.0	0.49	0.00	0.0
(8,7)	1.03	27.8	1265	728	0.0	0.3	0.00	0.0
(9,2)	0.81	9.8	1138	551	18.6	0.4	8.64	4.4
(9,4)	0.92	17.5	1101	722	0.0	0.7	0.00	0.0
(10,2)	0.88	9	1053	737	0.0	2.38	0.00	0.0

Table A II-5 (n,m) abundance evaluation of sample E

(n,m)	d_h , nm	θ , °	E_{11} , nm	E_{22} , nm	I^{exp}	I^{cal}	Abundance, % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.76	27	976	566	87.6	0.67	13.03	13.9
(7,5)	0.83	24.5	1024	645	261.1	0.71	36.65	41.4
(7,6)	0.9	27.5	1120	648	68.7	0.47	14.57	10.9
(8,3)	0.78	15.3	952	665	25.3	2.13	1.18	4.0
(8,4)	0.84	19.1	1118	589	116.4	0.46	25.22	18.5
(8,6)	0.97	25.3	1173	718	17.9	0.49	3.64	2.8
(8,7)	1.03	27.8	1265	728	0.0	0.3	0.00	0.0
(9,2)	0.81	9.8	1138	551	0.0	0.4	0.00	0.0
(9,4)	0.92	17.5	1101	722	34.7	0.7	4.94	5.5
(10,2)	0.88	9	1053	737	18.4	2.38	0.77	2.9

Table A II-6 (n,m) abundance evaluation of sample F

(n,m)	d_h , nm	θ , °	E_{11} , nm	E_{22} , nm	I_{γ}^{exp}	I^{cal}	Abundance, % with I^{cal}	Abundance, % w/o I^{cal}
(6,5)	0.76	27	976	566	164.5	0.67	15.53	15.2
(7,5)	0.83	24.5	1024	645	390.6	0.71	34.81	36.2
(7,6)	0.9	27.5	1120	648	87.0	0.47	11.71	8.0
(8,3)	0.78	15.3	952	665	90.7	2.13	2.69	8.4
(8,4)	0.84	19.1	1118	589	143.6	0.46	19.75	13.3
(8,6)	0.97	25.3	1173	718	60.9	0.49	7.86	5.6
(8,7)	1.03	27.8	1265	728	0.0	0.3	0.00	0.0
(9,2)	0.81	9.8	1138	551	0.0	0.4	0.00	0.0
(9,4)	0.92	17.5	1101	722	60.0	0.7	5.42	5.6
(10,2)	0.88	9	1053	737	83.2	2.38	2.21	7.7

Appendix III Related publications

Chapter 3

Wei, L., Wang, B., Wang, Q., Li, L.J., Yang, Y. H., Chen, Y., *Effect of centrifugation on the purity of single-walled carbon nanotubes from MCM-41 containing cobalt*. Journal of Physical Chemistry C, **2008**, 112, 17567–17575

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

Chapter 4

Wei, L., Li, L.J., M.B., Chan-Park, Yang, Y.H., Chen, Y., *Aggregation-dependent Photoluminescence Sidebands in Single-Walled Carbon Nanotube*, Journal of Physical Chemistry C, **2010**, 114, 6704–6711.

Chen, F.M., Zhang, W.J., Jia, M.L., **Wei, L.**, Fan, X.F., Kuo, J.L., Chen, Y., M.B. Chan-Park, Xia, A.D., and Li, L.J., *Energy Transfer from Photo-Excited Fluorene Polymers to Single-Walled Carbon Nanotubes*. Journal of Physical Chemistry C, **2009**. 113, 14946-14952.

Chapter 5

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

Chapter 6

Wei, L., Lee, C.W., Li, L.J., Sudibya, H., Wang, B., Chen, L., Chen, P., Yang, Y.H., M.B., Chan-Park, Chen, Y., *Assessment of (n,m) selectively enriched small diameter single-walled carbon nanotubes by density differentiation from cobalt-incorporated MCM-41 for macroelectronics*. Chemistry of Materials, **2008**, 20, 7417–7424.

Lee, C.W., Weng, C.-H., **Wei, L.**, Chen, Y., M.B. Chan-Park, Tsai, C.-H., Leou, K.-C., Poa, C.H.P., Wang, J., and Li, L.-J., *Toward High-Performance Solution-Processed Carbon Nanotube Network Transistors by Removing Nanotube Bundles*. Journal of Physical Chemistry C, **2008**, 112, 12089-12091.

Chapter 7

Wei, L., Noriyasu Tezuka, Tomokazu Umeyama, Hiroshi Imahori, Chen, Y., *Enhanced Photocurrent Generation by Semiconducting Single Walled Carbon Nanotube Enriched Thin Film*, Submitted

Appendix IV Other publications

1. **Wei, L.**, Wang, B., Liu, D.P., Li, L.J., Yang, Y.H., Chen, Y., *In-situ formation of cobalt nanoclusters in sol-gel silica films for single-walled carbon nanotube growth*. Nano, **2009**, 4(2), 99-106
2. Yan, L.Y., Li W. F., Fan X.F., **Wei L.**, Chen Y., Kuo J.L., Li L.J., Kwak S.K., Mu Y.G., M. B. Chan-Park, *Enrichment of (8, 4) single-walled carbon nanotubes through co-extraction with heparin*, Small, **2010**, 6(1), 110–118
3. Liu, S.B, **Wei, L.**, Hao, L., Fang, N., Chang, M.W., Xu, R., Yang, Y.H., Chen, Y., *Sharper and faster “nano darts” kill more bacteria: a study of antibacterial activity of individually dispersed pristine single-walled carbon nanotube*, ACS Nano, **2009**, 3(12), 3891–3902
4. Chan, M. Y., **Wei, L.**, Chen, Y., Ho, V., Lee, P. S., *Charge-induced conductance modulation of carbon nanotube field effect transistor memory devices*, Carbon, **2009**, 47, 3063-3070
5. Chen, F.M., Zhang, W.J., Jia, M.L., **Wei, L.**, Fan, X.F., Kuo, J.L., Chen, Y.; M.B. Chan-Park, Xia, A.D., Li, L.J., *Energy Transfer from Photo-Excited Fluorene-Polymers to Single-Walled Carbon Nanotubes*, Journal of Physical Chemistry C, **2009**, 113, 14946–14952
6. Lee, C.W., Weng, C.H. **Wei, L.**, Chen, Y., M.B. Chan-Park, Tsai, C.H., Leou, K.C., Poa, C., Wang, J.L., Li, L.J., *Towards High Performance Solution-Processed Carbon Nanotube Network Transistors by Removing Nanotube Bundles*. Journal of Physical Chemistry C, **2008**, 112, 12089–12091

7. Wang, B.; **Wei, L.**; Yao, L.; Li, L.; Yang, Y.; Chen Y.; *Pressure-induced single-walled carbon nanotube (n,m) selectivity on Co-Mo catalysts*, Journal of Physical Chemistry C, **2007**, 111, 14612-14616.
8. Wang, B.; Poa, C.; **Wei, L.**; Li, L.; Yang, Y.; Chen, Y., *(n,m) Selectivity of Single-Walled Carbon Nanotubes by Different Carbon Precursors on Co-Mo Catalysts*. Journal of the American Chemical Society, **2007**, 129(29), 9014-9019