The main topic of this dissertation is the spectroscopic and scanning probe studies of single-walled carbon nanotubes (SWNTs). Current synthetic methods for SWNT growth have limitations such as impurities, poor dispersibility in aqueous solvents, and the lack of ordered arrays. This dissertation includes a three part study to discuss the improvement of the limitations. The first part demonstrates multiple cycles of centrifugation as a method for nondestructive purification. Atomic force microscopy (AFM) and spectroscopies show this mild purification to be effective in order to obtain unbundled and purified high-aspect ratio SWNTs.

In second part of this dissertation, the effect of Nafion on the dispersion of SWNT suspensions in bisolvents is discussed. Nafion is an ambipolar dispersant consisting of hydrophilic and hydrophobic groups. Nafion was used as a polymeric dispersant of SWNT suspensions in water/ethanol or water/isopropanol. The defect of SWNT-Nafion suspensions decreased in an aqueous solution with the addition of alcohol due to improved dispersion. The debundling of SWNT-Nafion suspensions in water/alcohol also was demonstrated by blue-shifted peaks in near-infrared (NIR) spectroscopy.
In the final section, well-ordered arrays of SWNT networks were investigated by depositing carbon nanotubes on self-assembled molecule-coated substrates. Aminosilane and aminothiol were coated on Si/SiO$_2$ and Au substrates, respectively, to produce self-assembled monolayers (SAMs). An improved surface morphology with decreased defects occurred when a high concentration of self-assembled molecules was absorbed for a long period of time.

INDEX WORDS: Single-walled carbon nanotubes (SWNTs), Purification, Centrifugation, Atomic force microscopy (AFM), Nafion, Dispersion, Near-infrared (NIR) spectroscopy, Self-assembled monolayers (SAMs)
SPECTROSCOPIC AND SCANNING PROBE STUDIES OF SINGLE-WALLED CARBON NANOTUBES

by

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SPECTROSCOPIC AND SCANNING PROBE STUDIES OF SINGLE-WALLED CARBON NANOTUBES

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To My Parents and My Brother
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CHAPTER 1

INTRODUCTION

Carbon nanotubes (CNTs) belong to the fullerene family of carbon allotropes. They are tubular and hollow cylindrical molecules. Since CNTs were discovered by Iijima in 1991, they have received attention from many scientists.[1] A single-walled carbon nanotube (SWNT) is a sheet of graphite rolled into a tube with bonds at the end of the sheet. Due to their unique physical, chemical, and mechanical properties, SWNTs have applications in a wide variety of industrial areas.[2-4]

However, most synthesis methods for SWNT growth produce carbonaceous impurities and metal catalyst residues which interfere with the desired properties of SWNTs.[5, 6] Various purification methods including oxidation for SWNTs have been investigated.[6-8] The methods often involve oxidation during chemical treatments. Although these purification methods can remove impurities to some extent, the ends or sidewalls of SWNTs are modified and destructed.[5, 9] Therefore, it is very important to develop a method for a nondestructive purification of SWNTs. In Chapter 3, multiple cycles of centrifugation is introduced as a nondestructive purification of SWNTs. This method is effective to obtain bulk purification of SWNT soot, without removal of unbundled, high-aspect ratio SWNTs.

Another limitation of SWNT applications is poor solubility of carbon nanotubes as well as the presence of impurities.[10] The practical applications of SWNTs have been limited due to their poor solubility which stems from hydrophobicity and van der Waals interactions.[11] The use of covalent and noncovalent functionalization to obtain stable and homogeneous dispersion of SWNTs has been extensively suggested.[12-14] However, some covalent methods modify the
intrinsic properties of SWNTs by the formation of other covalent bonds on the wall. To overcome this problem, noncovalent functionalization using polymers and surfactants has been investigated. In Chapter 4, the dispersion of SWNTs using Nafion is introduced. Nafion is an ambipolar dispersant consisting of hydrophilic sulfonic acid terminated perfluorovinyl ether pendants that are spaced regularly along the hydrophobic perfluoroalkyl backbone.[15] The influence of Nafion on the dispersion of SWNTs is proposed in water, alcohol, and the mixture of water/alcohol.

Well-ordered arrays of SWNT networks are necessary for utilization in applications. However, current synthetic methods produce SWNTs in random arrays.[16] It still remains a great challenge to produce highly organized SWNTs on a wide variety of substrates. In Chapter 5, the application of self-assembled monolayers for SWNT deposits is introduced to obtain well-ordered SWNT networks on Si/SiO$_2$ and Au substrates. In this chapter, the optimization of concentration, adsorption time, and nature of SAMs on substrates were investigated.

Each chapter introduces Atomic force microscopy (AFM), Near Infrared (NIR) spectroscopy, and Raman spectroscopy as methods to characterize the SWNT networks. AFM was used to observe the surface of SWNT deposits. NIR and Raman spectroscopies were used to characterize the electronic properties and the defects of SWNT, respectively.

References


CHAPTER 2
LITERATURE REVIEW

Single-Walled Carbon Nanotubes (SWNTs)

Carbon nanotubes (CNTs) are allotropes of carbon in the fullerene family. CNTs are hollow cylindrical molecules.[1] There are two main types of CNTs: single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). A SWNT can be considered as an sp$^2$-bonded graphene sheet that is rolled up into seamless cylinders.[2] A MWNT is a collection of several concentric SWNTs with multiple layers of graphite rolled in on one another to form a tube shape.

Iijima reported experimental evidence of the existence of multiwalled carbon nanotubes (MWNTs) using a transmission electron microscope (TEM) in 1991.[3] In his work, he discovered MWNTs in the insoluble material of graphite needle-like tubes using arc-discharge evaporation method. Nanotube research developed greatly following the independent discoveries by Iijima and Bethune. Iijima et al.[4] and Bethune et al.[5] simultaneously discovered single-walled carbon nanotubes (SWNTs) in 1993. They developed methods to specifically produce SWNTs by adding transition metal catalysts to the carbon in an arc discharge. The arc discharge technique was already known to produce the famed Buckminster fullerene on a preparative scale.[6]

Most SWNTs have a diameter of close to 1 nm with various tube lengths. A SWNT is a rolled graphene sheet (Figure 2.1). The way the graphene sheet is rolled determines the fundamental properties of the tube. The hexagonal arrays of carbon atoms wind around in a
helical structure. Therefore, the electronic properties of SWNTs depend on how distorted the planar graphene sheet is. Each nanotube can be specified by a pair of indices \((n,m)\) that corresponds to a chiral angle \(\Phi\) and diameter \(d\).\(^2\) A pair of indices \((n,m)\) is called the chiral vector. These indices can in principle be obtained by measuring both \(\Phi\) and \(d\) from either transmission electron microscopy (TEM) and diffraction or by scanning tunneling microscopy (STM).\(^4, 7\) The integers \(n\) and \(m\) describe the number of unit vectors along two directions in the crystal lattice of graphene. As shown in Figure 2.1, a vector \(\mathbf{C}\) defines the circumference pointing from one carbon site to another equivalent site in the hexagonal lattice. A seamless cylinder can be obtained with the diameter, by cutting out the sheet along the dashed lines perpendicular to \(\mathbf{C}\) and wrapping up the sheet in the direction of the vector.\(^2\) The vector \(\mathbf{C}\) can be expressed as \(\mathbf{C} = na_1 + ma_2\), where \(a_1\) and \(a_2\) are the two basis vectors. The pair of indices \((n,m)\) defines the nanotubes. The corresponding chiral angle \(\Phi\) and diameter \(d\) are expressed as

\[
\Phi = \arccos\left[\sqrt{3(n + m)/2 (n^2 + mn + m^2)^{1/2}}\right]
\]

\[
d = a(m^2 + mn + n^2)^{1/2}/\pi = |\mathbf{C}|/\pi
\]

where \(a\) is the lattice constant, 0.246 nm.\(^2\) The chiral angle is used to categorize nanotubes into three classes by their electronic properties: armchair \((n = m, \Phi = 0^\circ)\), zig-zag \((m = 0, n > 0, \Phi = 30^\circ)\), and chiral \((0 < |m| < n, 0 < \Phi < 30^\circ)\) (Figure 2.1). Armchair carbon nanotubes are metallic. Zig-zag and chiral nanotubes can be semimetallic, if \((n-m)\) is a multiple of 3, or semiconductors in all other cases.\(^8\)

**Properties of SWNTs**

SWNTs are insoluble in water because they have high aspect ratios (length to diameter ratio) with nonpolar bonds. The solubility of SWNTs in water can be enhanced by adding a chemical modifier such as a surfactant.\(^9\) Hydrophobic SWNTs are expected to be dissolved by organic solvents in order to avoid debundles. However, only limited organic solvents, such as
dimethyl formamid, dimethyl acetamide, and dimethyl pyrrolidone, have been used to improve the solubility of SWNTs.[9]

SWNTs have a good surface area to volume ratio. They can be useful for gas filtration, sensing, and energy storage devices because of their good van der Waals physisorption properties.[10]

SWNTs have strong tensile force due to their covalent sp² bonds between individual carbon atoms. Also, they have very high elastic moduli, on the order of ~1000 GPa (1 TPa) which is 5 times higher than that for carbon steel.[11] The specific strength of SWNTs is up to 48,462 kN·m/kg compared to that of high-carbon steel, 154 kN·m/kg.[12] The permanent deformation of SWNTs keeps them under excessive tensile strain and begins at strains of approximately 5%.[13]

All SWNTs exhibit good thermal stability with ballistic conduction and remain stable at up to 1200 °C in inert atmosphere.[13] The temperature stability of SWNTs is estimated to be up to 2800° C in vacuum and about 750° C in air.[12] SWNTs are used as stationary phases in gas chromatography due to this thermal property.

**Synthesis of SWNTs**

The development of practical applications of carbon nanotubes (CNTs) requires designing new synthesis methods to obtain more homogeneous materials. Most CNTs reported to date have been prepared by using arc discharge,[14] laser ablation,[15] or thermal synthesis. In thermal methods, there are chemical vapor deposition (CVD),[16] high-pressure carbon monoxide synthesis (HiPco),[17] and flame synthesis.[8]
Arc discharge was the first recognized method to produce both SWNTs and MWNTs. In arc discharge synthesis (Figure 2.2), an arc is produced across a 1 nm gap between two graphite electrodes with 5~20 nm in diameter. This method is performed with a low voltage (~12 to 25 V) and high-current (50 to 120 amps) power supply.[17] There are several factors to control the arc discharge process. A current synthetic method using arc discharge is carried out in an Ar:He gas mixture. The diameter of the SWNTs can be varied by controlling the ratio of Ar:He.[17, 18] The pressure of gas affects the weight percent yield of SWNTs.[19] Several metals can be used as catalysts, however, a Y:Ni mixture is widely used to obtain 90 % SWNTs, with an average diameter of 1.2 to 1.4 nm.[14]

Another method for synthesis of SWNTs is laser ablation. (Figure 2.3) In the laser ablation process, a pulsed- or continuous-wave laser vaporizes a graphite source at a high temperature while an inert gas is bled into the chamber. Theoretically, the methods of arc discharge and laser ablation are similar because both use a metal-impregnated graphite target.

Commonly, this laser ablation technique uses a 1.2 % of Co/Ni with 98.8 % of graphite target that is placed in a 1200°C quartz tube furnace with an inert gas of ~500 torr of Ar or He.[8] The metal particles, Co/Ni, catalyze the growth of SWNTs in the plasma plume, but there are many simultaneous by-products, such as graphitic and amorphous carbon. The SWNTs and by-products are collected by condensation on a cold finger downstream from the target showing various yield, 20~80 %. The diameter of distribution of SWNTs is roughly between 1.0 and 1.6 nm in this method. Unlike the above plasma-based syntheses, SWNTs can be prepared by using thermal synthesis which depends on only thermal energy and metal catalysts such as Fe, Ni, and Co. In the thermal synthesis, there are chemical vapor deposition (CVD), High-pressure carbon monoxide synthesis (HiPco), and flame synthesis. CVD (Figure 2.4) uses hydrocarbon gases,
such as methane, acetylene, ethylene, and ethanol, as sources of carbon. Ni, Co, Fe or their combinations are commonly used as metal catalysts for the growth of SWNTs. Y, Mo, Ru, and Pt have led to massive increases in yield under certain conditions.[20] The metal catalysts can also be produced by the reduction of oxides. During the CVD process, the SWNT arrays can be obtained at controllable positions and with the desired orientation on substrates.[13] This CVD synthesis produces SWNT material of higher atomic quality and higher percent yield than the other methods.[8] The diameter of SWNTs can be 0.4 ~ 5 nm and the weight percent yield can exceed 99 % depending on the conditions in the CVD process.

One of the recent methods for SWNTs synthesis is the High-pressure carbon monoxide (HiPco) process.(Figure 2.5) This process could be related to CVD synthesis, but recently it has become a separate method in thermal synthesis due to the production of SWNTs with high-quality and narrow-diameter distribution. In this method, Fe(CO)$_5$ or Ni(CO)$_4$ is injected into the reactor along with a stream of carbon monoxide (CO) gas at 900 ~ 1100 °C and at a pressure of 30~50 atm.[17] The diameters of SWNTs are between 0.7 and 1.1 nm and the yields are claimed to be ~97 % purity.[21]

Flame synthesis has the potential to become an extremely simple method to produce SWNTs. Vander Wal et al. produced SWNTs using this flame synthesis for the first time. They ignited a hydrocarbon flame composed of ethylene or acetylene with Fe or Co particles in H$_2$/He or H$_2$/Ar.[8] Since then, many researchers have prepared SWNTs by using this method.[22, 23] Although the percent yield is low in this technique, it is extremely attractive and cheap for production of SWNTs.
**Purification of SWNTs**

Although the production of SWNTs using synthetic methods is effective, it still requires a substantial improvement in the purity of the as-prepared (AP) SWNT material. All current synthetic techniques of SWNTs generate significant amounts of carbonaceous impurities, such as amorphous carbon and carbon nanoparticles with metal catalyst residues.\[24\] There are three categories in the impurities of AP-SWNTs: carbonaceous impurities, transition metal catalysts, and the mixture of carbonaceous and metal impurities.\[14, 17, 24\] Carbonaceous impurities include amorphous carbon and nanocrystalline graphitic particles.\[25\] These impurities can interfere with desired properties of SWNTs for accurate analyses and applications. In order to reduce the impurities, there are many methods to purify AP-SWNTs. The common industrial techniques use strong oxidation and acid refluxing processes.

Several attempts have been made to purify the SWNT. The purification techniques can be divided into two classifications, structure selective and size selective separations.\[26\] In the structure selective separations, the SWNTs form is separated from the impurities. The size selective separations give a more homogeneous diameter or size distribution. There are many purification methods of AP-SWNTs such as oxidation, acid treatment, annealing, sonication, micro filtration, ferromagnetic separation, chromatographic techniques, and functionalization.

Oxidation is a purification method that has been proven to successfully remove carbonaceous impurities.\[25-27\] However, the critical disadvantage of this technique is the oxidation of the SWNTs as well as the impurities. Fortunately, the damage to the SWNTs by this oxidation is less than that of the impurities. These impurities have relatively more defects or more open structures. The efficiency and the percent yield of the oxidation process rely on many factors, such as the existence of metals, temperature, oxidation time, and oxidizing agents. Most commonly, soluble oxidizing agents, such as HClO₄, H₂O₂ and H₂SO₄, are used to oxidize the
defects.[27] During these oxidation processes, the metal catalysts remain intact. However, the metal in the outer layer is oxidized when oxygen is used in a wet atmosphere.[28] Finally, the metal catalyst residues as well as carbonaceous impurities can be partially oxidized and exposed.

Acid treatment is commonly used for the purification of the SWNT. Generally, carbonaceous impurities are removed by refluxing AP-SWNTs in boiling acid or burning them in air under a relatively high temperature.[25, 29] Several acids, HNO$_3$, HCl, and H$_2$SO$_4$, are used for acid purification.[25, 30, 31] Although acid treatments using those acids have an effect on the metal catalyst, the SWNTs are usually cut into small lengths and sometimes broken completely. The remaining walls are severely damaged with strong acid solution.

Using thermal annealing in high temperature, the metal is melted and can be removed. Due to high temperature, 873~1873 K, the SWNTs are rearranged.[26, 28] The high temperature also causes the graphitic carbon and the short fullerenes to pyrolyze.

Sonication is used as a purification method because particles are separated by sonic vibrations. During sonication, the aggregate nanoparticles are vibrated and dispersed. The nanoparticles can be separated depending on the surfactant, solvent, etc.[32]

The SWNT material can be purified by using the ferromagnetic method. This method does not require large and complex equipment. In this method, ferromagnetic (catalytic) particles are mechanically removed from their graphitic shells.[32, 33] After the SWNT suspension is mixed with inorganic nanoparticles, such as ZrO$_2$ or CaCO$_3$, in an ultrasonic bath, the particles are caught with permanent magnetic poles. Then, by using chemical treatment, a high purity SWNT material is obtained. When this ferromagnetic method is used, the SWNTs are produced without magnetic impurities.
Microfiltration is a purification based on size and particle separation. The SWNTs and a small amount of carbon nanoparticles are trapped and collected in a filter. The other nanoparticles including carbonaceous impurities and metal catalysts pass through the filter.[25] SWNTs are purified by functionalization of the nanotubes using chemical compounds. The SWNTs are more soluble and are separated easily from insoluble impurities by the attachment of another functional group to the end of the nanotubes.[34] In the case of covalent functionalization, the amidation or esterification of the carboxylic acid groups of oxidized SWNT material were reported.[35] However, this functionalization by chemical compounds can cause the modification of SWNT material. This modification by covalent functionalization can drastically affect the absorption spectroscopy, indicating a complete loss of spectral features.[36]

Chromatography is used to separate all quantities of SWNTs into fractions with small length and diameter distribution.[36] The SWNTs pass through a column with a porous material. Depending on pore sizes, the size distribution to be separated can be determined. In general, GPC (gel permeation chromatography) and HPLC (high performance liquid chromatography) columns are used.

**Dispersion of SWNTs**

The poor stability of SWNTs in most solvents has seriously restricted the uses and the developments for their characterization. Therefore, the dispersion of individual SWNTs in organic or aqueous solvents is very important for many applications. However, SWNTs are not soluble in organic or aqueous solvents, because of their strong hydrophobicity and van der Waals interactions.[37] The insolubility and the bundling in carbon nanotubes can prevent high-quality solutions of SWNTs. In order to overcome these problems, a variety of covalent[38, 39] and
noncovalent [40, 41] functionalizations have been investigated to ensure efficient dispersion and
debundling in carbon nanotubes.

For the dispersion of SWNTs in organic solvents, covalent functionalization using
functional groups has been proposed because it enhances the solubility of carbon nanotubes.
Covalent functionalizations have been achieved by sidewall halogenations of carbon nanotubes.
Margrave, et al. reported extensive sidewall functionalization, fluorination, as the first study of
covalent modification in SWNTs.[42] Bahr, et al. first reported the use of a bucky paper
electrode in an electrochemical reaction.[43] Since then, they have developed the reactivity of
SWNTs with aryl diazonium compounds.[43] Haddon, et al. have reported functionalization of
SWNTs with dichlorocarbene, first generated from chloroform in the conventional method with
have recently reported functionalization with the nucleophilic carbene, generated by
deprotonation of the stable imidizolinium cation.[46] Prato, et al. have very recently discovered a
method of functionalizing SWNTs utilizing 1,3-dipolar addition of azomethine ylides.[47] This
type of chemistry was originally developed for C_{60} modification. In this work, the SWNTs were
suspended in dimethylformamide with an aldehyde and an N-substituted glycine derivative
indicating the formation of substituted pyrrolidine moieties on the surface of carbon nanotubes.
Despite of successful results in covalent modifications, however, these methods are often
problematic because the intrinsic properties of SWNTs can be degraded by the disruption of the
π networks.[48]

Noncovalent functionalization approaches have been developed to overcome the problem
caused from the work of covalent modification. The noncovalent methods that utilize the
hydrophobic interactions of amphiphilic molecules such as surfactants, polymers, and
biomolecules are more frequently used than covalent methods.[40, 49] It has been noticed that
noncovalent procedures preserve the intrinsic properties and can efficiently debundle raw SWNTs.[50] Islam, et al. reported noncovalent modification using surfactants, octylphenol ethoxylate (Triton X-100) and sodium dodecylbenzenesulfonate in water.[51] Sodium dodecylsulfate (SDS) has been used more commonly as a surfactant in a noncovalent functionalization.[52, 53] These surfactants bind to carbon nanotubes due to a long and hydrophobic chain tail. Also they possess a hydrophilic head group that mediates the interaction with water. Kim, et al. discovered starch can solubilize SWNTs by hydrophobic interactions and improve their stabilization in aqueous media.[54] Rice, et al. and Star, et al. reported the noncovalent functionalization using poly (aryleneethynylene)[55] and poly(m-phenylenevinylene)[56], respectively. These surfactants have been considered as the most effective surfactants containing benzene rings, which are expected to have a high affinity for SWNT surfaces. In the case of SDS, it can coat and disperse carbon nanotubes efficiently even though there is no benzene ring. The SDS at low levels of critical micelle concentration can efficiently coat SWNTs. The mechanism of noncovalent methods using surfactants is not clear. However, the tentative roles can be explained.[13] A surfactant can coat and organize the surface of SWNTs because it facilitates random adsorption of the nanotubes with the head and tail. Also the surfactant can enhance the micelle adsorption on the surface of carbon nanotubes and can encapsulate the SWNTs in cylindrical surfactant micelles.

**Self-Assembled Monolayers (SAMs)**

Self-assembly has become a very effective and promising approach to synthesize a wide range of novel nanoscale materials.[57] Self-assembly is described as a term that refers to the spontaneous formation of nanoscale units forming an organized array from simple building blocks on metal surfaces.[57] In the self-assembly processes, atoms, molecules, particles, and
other building blocks combine themselves into functional structures.[58] The driving force for self-assembly is the interaction energies between the subunits, such as atoms, molecules, or particles.[57] The interactions can be classified into three categories: Coulomb interactions due to the electrostatic effects, van der Waals interactions due to polarizations induced by the neighboring molecules, and short range strong repulsions.[59] The simplest examples are the so-called self-assembled monolayers (SAMs). In the SAMs on solid surfaces, they can be easily formed by spontaneous adsorption from gas or liquid phases. Each molecule is divided into three parts: the head, the backbone (main chain), and the tail group (Figure 2.6). The hydrophilic ‘tail groups’ assemble together on the substrate, while the hydrophobic ‘backbone’ and ‘head groups’ assemble far from the substrate. The head group attached to main chain can be functionalized to vary interfacial properties.[60] The examples of SAMs on solid surfaces are thiols on Au, silanes on Si/SiO$_2$, and phosphonates on TiO$_2$.[61, 62]

Metal substrates for use in SAMs can be produced by physical vapor deposition, electrodeposition or electroless deposition.[63] For example, alkanethiol SAMs are the most popular self-assembly systems and are prepared by immersing a substrate into a solution of alkanethiol in ethanol for over 12 hours at room temperature.[62, 63]

Applications for SAMs in several fields of biology and chemistry have been developed for biosensor, bio-recognition devices, drug delivery, and electronic devices.[63] SAMs are also used for preparation of carbon nanotube deposits on substrates. Most SWNT deposits are formed on silane-coated Si/SiO$_2$ substrates. Recently, alkanethiol-assembled SAMs have been used on Au or Ag substrates as the surfaces where SWNT arrays form. Zhongfan, et al. reported a wet chemical approach for organizing randomly tangled SWNTs on aminoalkane thiol (cysteamine)-coated Au surface in 2000.[64] More recently, Wei, et al. reported a new method ‘chemical transfer’ for well-ordered SWNT deposits. Chemical transfer is a two-step assembly process.[65]
In first step, well-aligned carbon nanotubes are functionalized during a chemical vapor deposition method. Then, functionalized SWNTs are attached onto the Au-coated substrate by forming covalent bonds between the SWNTs and the Au surface. Another SAM was also used for formation of SWNT deposits. Xiaomiao, et al. reported surface-enhanced Raman scattering of SWNTs on a modified silver electrode. In their work, the gold/silver nanoparticles modified on the roughed silver electrode surface can not only make sure of the strong adsorption of SWNTs in this system but also play an important role in magnifying the local electric field near the electrode surface.[66]

References


Figure 2.1 A graphene sheet that can be rolled up into a single-walled carbon nanotube.
Figure 2.2 The schematic of an electric arc discharge chamber
Figure 2.3 The schematic of a laser ablation furnace
Figure 2.4 The schematic of chemical vapor deposition (CVD) furnace
Cold CO and Catalyst precursor (Fe(CO)$_5$ or Ni(CO)$_5$) 900~1100°C

Figure 2.5 The schematic of a high-pressure carbon monoxide (HiPco) furnace.
Figure 2.6 The schematic of Self-Assembled Monolayers (SAMs)
CHAPTER 3

SPECTROSCOPIC AND SCANNING PROBE STUDIES

OF A NON-DESTRUCTIVE PURIFICATION METHOD

FOR SINGLE-WALLED CARBON NANOTUBE (SWNT) SUSPENSIONS

Abstract

There is a great need for methods for enrichment of SWNT soot that do not damage the enhanced electrical properties of the single-walled carbon nanotubes (SWNTs). A mild method for the bulk enrichment of high-aspect ratio SWNTs, while avoiding the damaging effects of acid purification methods, has been developed. Raman spectroscopy is used to verify that this method produces suspension of purified SWNTs, with significantly less damage than acid-treated SWNTs. Near-Infrared (NIR) spectroscopy of these suspensions shows more prominent semiconducting and metallic interband transitions of the SWNT. And, atomic force microscopy (AFM) data of low-density SWNT networks formed from these suspensions indicates that the size and occurrence of globular impurities is lessened, while small bundles of high-aspect-ratio SWNTs remain.

Introduction

Due to their unique physical, chemical and mechanical properties,[1],[2] SWNTs have applications in a wide variety of scientific disciplines, including field-emission devices,[3] electronic devices,[4] chemical sensors,[5] batteries,[6] hydrogen storage,[7] and polymeric composites.[7, 8] However, most commercial synthesis methods for SWNT growth produce a large percentage (up to 60%) of carbonaceous impurities, such as amorphous carbons, fullerenes, nanocrystalline graphite, and transition metal nanoparticles that are used as a catalyst during the synthesis.[9] These impurities have a deleterious effect on the performance of various device structures such as resistors, transistors and sensors.[10] Therefore, efficient post-production procedures for the purification of SWNT soot are needed for further development of most of the electronic applications of SWNTs.
Reported methods for purification, such as gas- or liquid-phase oxidation, significantly damage pristine as-produced (AP) SWNTs. For example, gas-phase oxidation, used for the removal of carbonaceous impurities, usually occurs in an atmosphere containing a mixture of some of the following gasses at elevated temperatures: air, oxygen, ozone, hydrogen chloride, chlorine, CCl$_4$, or CO$_2$.\[^{11, 12}\] Any single one of these gasses was not effective at purifying SWNT soot. Of the dual-gas mixtures used, HCl$_{(g)}$ and H$_2$O$_{(g)}$ were most effective at etching carbonaceous impurities. However, because the SWNTs are also composed entirely of carbon, these gasses also etched the SWNTs, leaving either hydroxyl or chloride functional groups along the ends and sidewalls. Further, after purification, it is very difficult to remove these gasses from the sidewalls of the SWNTs. Therefore, in addition to creating defects in the SWNTs, the incomplete removal of these gasses presents another problem, as electron-donating gasses reduce the conductivity of SWNTs, which act as p-type semiconductors.\[^{13, 14}\] Additionally, gas phase methods have not proven effective for bulk purification of SWNT soot.

Liquid-phase oxidation processes, in strong acids such as HNO$_3$, HCl, HClO$_4$ and H$_2$SO$_4$, are an alternative commonly used for bulk oxidative purification of SWNT soot. While effective at reduction in carbonaceous impurities and metal nanocatalyst particles, acid treatments also attack the sp$^2$ hybridized structure of the SWNTs, thus changing their intrinsic electronic transport properties.\[^{15, 16}\]

Therefore, the development of non-damaging methods for the purification of SWNTs is of great interest. The most common mild purification methods involve first creating an aqueous suspension of SWNTs in a surfactant. The surfactant increases the solubility of the SWNTs without the need for chemical modification. The next step involves separation of SWNTs via filtration or centrifugation.\[^{17, 18}\] Filtration methods work well for the production of 3-dimensional networks of transparent SWNTs. This material exhibits near metallic conduction, so it has
applications similar to indium tin oxide (ITO). For example, when a dilute suspension of single-walled carbon nanotubes (SWNTs) in surfactant was vacuum filtered onto a filtration membrane, followed by dissolving the membrane in solvent, the result was an SWNT film of thickness 50 to 150 nm. [19] Although these films were composed of SWNTs that were bundled together, these films exhibited a high transmittance in the visible and near-IR. The advantage of the purification and deposition method presented herein is that low-density, 2-dimensional networks behave as transparent semiconductive materials.

Recently, a combination of high-speed centrifugation and membrane filtration has been used for purification of SWNTs pretreated by oxidation with HNO$_3$ or K$_2$S$_2$O$_8$.[20, 21] The oxidation process was used to chemically modify the SWNTs in order to increase their solubility in H$_2$O. Although bulk separation of carbonaceous impurities from SWNTs was accomplished, chemical modification of the SWNTs was crucial to the success of this work. The authors did not investigate the effect of these chemical modifications on the electronic properties of the SWNTs.

Ultracentrifugation, which uses centrifugal forces of at least 100,000 G, is an effective way of removing carbonaceous and metallic impurities from aqueous suspensions of SWNTs, as impurities usually have higher densities than short, unbundled SWNTs.[22] However, in this technique, long unbundled SWNTs, which are useful for numerous electronic applications, are also removed due to their higher mass; the average length of SWNTs observed was 200 nm. Therefore, it is important to develop an effective method for purification that removes the various impurities, but leaves unbundled, high-aspect ratio SWNTs in suspension.

In this manuscript, we report an efficient method for the purification of SWNTs by multiple cycles of centrifugation at low centrifugal force. This is an effective way to obtain bulk purification of SWNT soot, without removal of unbundled, high-aspect ratio SWNTs; the
average length observed by AFM is 1.2 µm. The effectiveness of this method for removal of impurities is confirmed with Raman microscopy and near-IR transmission studies of SWNT suspensions.

The effectiveness of this method to produce deposits composed largely of individual, high-aspect ratio SWNTs was determined by forming 2-dimensional networks of SWNTs using laminar flow deposition (LDF). As previously reported, liquid laminar flow deposition (LFD) prevents the formation of bundles of SWNT during the deposition process.[22, 23] This provides a distinct advantage over other liquid deposition methods, that result in formation of large bundles of SWNTs,[20] and allows determination of the effectiveness of the purification method presented herein.

Experimental Section

Preparation and Purification of SWNT solutions

As-produced (AP) grade CarboLex Inc. arc discharge soot, with a guaranteed purity of 50-70 wt% SWNTs, was used for all experiments. Solutions of 1 mg/ml SWNT soot were prepared in 1 % (w/v) sodium dodecyl sulfate (SDS) by dispersion of SWNTs via probe sonication (Model 500, Fisher) at 12 W for 30 min, followed by multiple centrifugation (Beckman Microfuge) cycles of 30 min. each at 18,000 g. Each centrifugation cycle was followed by carefully collecting the upper half of the supernatant. Spectroscopic and scanning probe data was obtained after each centrifugation cycle in order to quantitate the effectiveness of this method for removal of impurities and enrichment in high-aspect ratio SWNTs.
Formation of SWNT Deposits through Laminar Flow Deposition

Si/SiO$_2$ substrates were cut into fragments and then cleaned with compressed CO$_2$. The substrates were then functionalized to produce an amine-terminated surface by immersion in a fresh solution of 10 mM of 3-aminopropyl triethoxysilane in 99.5 % ethanol for 45 min. Then ten deposition cycles were used to form a low-density SWNT network. The deposition cycle has been described elsewhere.[24] Briefly, each cycle is defined as depositing the SWNT solution onto the silane coated Si/SiO$_2$ substrate by drying in a stream of N$_2$. The substrate was then rinsed with DI-H$_2$O and dried with under a stream of N$_2$.

Characterization of Purified SWNT Suspensions by AFM and Electromagnetic Spectroscopy

AFM images were obtained in air using intermittent contact mode (Molecular Imaging PicoPlus). In order to determine the extent of purification, image analysis software (WSxM) was used to create a histogram of the height measurements for each pixel. This is an effective analysis method because the various impurities were consistently observed to have higher height than the average SWNT (~1.2nm). Aqueous suspensions, as well as solid deposits on Si wafer fragments (Si/SiO$_X$), were characterized with Raman microscopy. Raman spectra were recorded on a Renishaw InVia Raman microscope, using a diode laser with an excitation wavelength of 785 nm and 7 mW laser power at the sample. For aqueous suspensions, a capillary tube (1.5-1.8 x 90 mm) was used. 2-diemensional networks of SWNTs on Si/SiO$_X$ were analyzed using without further modification. All Raman spectra were collected with a charge-coupled device (CCD) detector. Analysis of the heights of bands in the Raman spectra was performed with WiRe 2.0 software. Transmission near infrared (NIR) spectroscopy (Thermo 6700 Nicolet FT-IR spectroscope) was performed on aqueous suspensions of SWNTs after each purification cycle,
using a quartz cell with a path length of 1 cm. Ultraviolet-visible (UV-Vis) absorption spectroscopy was performed on a Varian Cary 300 spectrophotometer in a similar quartz cell.

**Results and Discussion**

**AFM Morphology**

A major advantage of liquid deposition processes is that they decouple the SWNT growth process (which occurs ~800°C) from the deposition process, which occurs at room temperature. This allows intermediate purification steps, as well as the use of heat sensitive substrates as electronic materials. However, a major concern with liquid deposition processes is bundle formation during the deposition process. Laminar flow deposition is an effective way to prevent SWNT bundle formation during deposition of SWNT networks.[23] Therefore, AFM analysis of deposits formed with LFD allows quantitation of the change in the coverage and size of impurities as a function of purification cycles, when the number of deposition cycles is held constant. The results indicate that an increase in centrifugation cycles decreases the size and density of impurities and bundled SWNTs.

Figure 3.1 shows the effect of centrifugation cycles at low G on the quality of SWNT networks deposited onto Si/SiO$_x$ substrates. Figure 3.1 (a) shows a deposit formed from an unpurified SWNT suspension. An average height of 15.7 nm was observed and large, globular impurities, which obstructed view of any SWNTs present, were the only visible structures. This type of deposit is typical of untreated suspensions. However, a dramatic improvement in the quality of deposit was observed after just one centrifugation cycle at low G (Figure 3.1 (b)). The average height decreased to 9.8 nm, due to removal of a significant portion of the larger impurities. Although long, tubular structures are present in large numbers, the very low occurrence of heights around 1.4 nm, the average height of a single SWNT, indicates that the
SWNTs observed in this deposit are composed of bundles of SWNTs adhering to one another by van der Waals interactions along their side walls.[21]

As the number of centrifugation cycles increases, the average height observed continues to decrease. After two centrifugation cycles (Figure 3.1 (c)), cross-section analysis showed that the bundles of SWNTs were smaller, with an average height of 5.3 nm. Further, there is a significant contribution from heights around 2 nm.

Analysis of Figures 3.1 (d)-(f) revealed that the average height of the SWNT bundles decreased to 4.0 nm, 3.4 nm and 2.6 nm, respectively, as the number of centrifugation cycles increased from three to five cycles. As the average height of a single SWNT is ~1.2 nm, this would indicate that after five centrifugation cycles were performed on the deposition solution, the deposit is composed largely of either individual or small bundles of two SWNTs. The size of impurities and bundled SWNT decreased as the number of centrifugation cycles increased. This indicates that multiple centrifugation cycles are an efficient, non-oxidizing way to remove impurities as well as large bundles of SWNTs.

**Raman Spectroscopy of SWNT Suspensions and Deposits.**

**Raman Spectroscopy of SWNT Suspensions**

Raman scattering has been used for many years as a probe of disorder in the carbon skeleton of sp² and sp³ carbon materials.[25] There are two Raman bands which are typically observed for sp² carbon;[26] the “G-band,” which is called a “tangential mode,” is seen in the range 1580–1600 cm⁻¹. It is indicative of the pristine, symmetrical graphene lattice.[27] The second band observed is the “D-band,” which is called a ‘dispersive’ band. It is a relatively broad, disorder-induced band in the range of 1300–1370 cm⁻¹.[26, 27] The D-band, which is
indicative of the presence of disordered sp² hybridized carbon atoms, is caused by C-atom vacancies, impurities in the C lattice, or any other imperfections in the graphene lattice.[28]

Figure 3.2 shows the Raman spectra of SWNT suspensions treated with zero (0C, i.e. without centrifugation) to five low-G centrifugation cycles (5C). The G- and D-bands are observed at 1591-1595 cm⁻¹ and 1290-1310 cm⁻¹, respectively. There is a consistent increase in the decrease I_G/I_D ratio, as the D-band was observed to decrease in magnitude with increasing low-G centrifugation cycles.

The magnitude of the I_G/I_D is an indicator of the purity of SWNTs.[29] As shown in Table 3.1, the I_G/I_D ratio increases with number of low-G centrifugation cycles. Indeed, the I_G/I_D ratio increased from 4.34 to 17.05 over the course of 5 centrifugation cycles. This increase indicates enrichment in well-ordered sp² bonds (such as those observed in defect-free SWNTs) and a corresponding reduction in defect containing carbonaceous impurities.[30]

Raman Spectroscopy of 2-D SWNT Networks on Si/SiO₂

A reduction in carbonaceous impurities was also observed in deposits formed from these purified suspensions. A similar trend was observed in SWNT deposits. Table 3.1 shows the effect of low-G centrifugation cycles on the quality of 2-D networks formed; the I_G/I_D ratio increased from 4.92 to 17.21 with centrifugation cycles. Like the SWNT suspensions, the deposits show the highest I_G/I_D ratio after five centrifugation cycles. Therefore, Raman spectroscopy concurs with AFM data with regard to the effectiveness of low-G centrifugation for purification of SWNT soot.

Near-Infrared Spectroscopy of SWNT Suspensions

The effectiveness of low-G centrifugation cycles for bulk purification of SWNT soot was also evaluated by near-infrared (NIR) spectroscopy in transmission mode. NIR spectroscopy has been reported as an important tool for characterizing the electronic band structure of
SWNTs.[31] When unbundled SWNTs are present in aqueous suspensions, a series of characteristic interband electronic transitions are observed; semiconducting SWNTs have first and second transitions starting with $S_{11}=2\alpha\beta/d$ and $S_{22}=4\alpha\beta/d$ whereas the first transitions of the metallic SWNTs appear at $M_{11}=6\alpha\beta/d$, where $\alpha$ is the C-C bond length (0.1424 nm), $\beta=\sim2.9$ eV, the transfer integral between $\pi$ orbitals (an interaction energy between neighboring C atoms) and $d$ is the SWNT’s diameter (nm).[31, 32] These interband transitions produce prominent features in the NIR spectral range, provided the electronic transitions are not quenched by inter-SWNT interactions that occur in bundles, so they can be a basis for the evaluation of the enrichment of the suspension in unbundled SWNTs.

Figure 3.4 shows NIR spectra of SWNT suspensions at varying degrees of processing. The $S_{11}$, $S_{22}$, and $M_{11}$ transitions were observed at 1150, 980, and 750 nm, respectively. All of these absorption bands are suppressed in the untreated SWNT suspension. However, the intensities of these bands increase with increasing low-G centrifugation cycles.

Studies by Haddon et al., have shown that the second semiconducting interband transition, $S_{22}$, can be used for purity evaluation because it is less affected by doping during chemical processing.[9, 32] In this study, the $S_{22}$ transition was used because it was observed distinctly at a constant wavelength in all SWNT suspensions. The extent of enrichment in unbundled SWNTs was quantified via the ratio $A(S)/A(T)$, where $A(S)$ is the area of the $S_{22}$ absorption feature after baseline subtraction, and $A(T)$ is the total area under the spectral curve. In the Haddon et al. study, a reference sample with a purity ratio of 0.141, was used in order to evaluate the purity of samples. The purity ratio, $A(S)/A(T)$, is taken as the simplest possible unit of SWNT purity. The purity ratio of the samples can be normalized by dividing by 0.141. In our samples, the relative purity was over 100% after normalization. This signifies that our samples purified by multiple centrifugation cycles have much higher purity than the reference sample.
In Table 3.2, it is shown that multiple centrifugation cycles increase the purity ratio. The one cycle centrifugation had a purity of 96.52 %. The purities of the SWNT suspensions after two and three cycles of centrifugation were increased to 97.22 % and 97.43 %, respectively. Four cycles showed a higher increase in purity compared with those that were subjected to fewer cycles. In five centrifugation cycles, the purity was remarkably high at 99.96 %.

**UV-Vis Absorption Spectroscopy of SWNT suspensions**

The absorbance of SWNT suspensions depending on centrifugation cycles was monitored by UV-Vis absorption spectroscopy. The spectra showed that more centrifugation cycles decreased the absorbance of SWNT. Current synthetic methods produce the mixtures of metallic and semiconducting SWNTs.[31] In the UV-vis range, metallic SWNT showed first transition, \( M_{11} \), in 700–800nm and the semiconducting transitions were shown in NIR range.[31, 32]

In Figure 3.5, the change of absorbance at 750 nm was plotted in the SWNT from zero (i.e. without centrifugation) to five centrifugation cycles. This Figure 3.5 showed exponential decay and leveling off with the decrease of the absorbances from 2.576 to 0.175, as centrifugation cycles increased. The un-centrifuged SWNT suspension had the highest absorbance due to bundles and other impurities. This indicates that most of the contaminants are removed in the first 2 centrifugation cycles. This corroborates the observations made with AFM, where much of the larger amorphous C contaminants are removed after the first 2 centrifugation cycles. Then, subsequent centrifugation cycles remove bundles of SWNTs, as well as smaller globular contaminants.
Conclusions

Multiple cycles of centrifugation at low-G are an efficient and non-oxidizing method for the purification of SWNT soot. Experimental results showed that most of the heavier/larger contaminants are removed in the first centrifugation cycle, while subsequent cycles remove bundles of SWNTs and smaller globular contaminants. This results in suspensions enriched in long unbundled/undamaged SWNTs. The largest bundles of SWNTs observed by AFM after five centrifugation cycles were likely composed of about two SWNTs, as the total height was 2.6 nm. NIR study showed more prominent metallic and semiconducting transition interbands with higher purity ratio, A(S)/A(T), according to the increasing number of centrifugation cycles. Also, both deposits and suspensions-phase Raman spectroscopy provided higher ratios of I_G/I_D as the number of centrifugation cycles increased, indicating a reduced presence of defect sites due to C vacancies. Therefore, this mild purification technique can be applied for efficient and nondestructive purification of SWNT soot.

References


Figure 3.1 (a). AFM image and histogram of a deposit formed from an unpuified SWNT suspension with a concentration of 1 mg/mL SWNT soot. The average height observed on this deposit is 15.7 nm
Figure 3.1 (b) AFM image and histogram of a SWNT deposit formed from a suspension that underwent one centrifugation cycle. The average height observed is 9.8 nm
Figure 3.1 (c) AFM image and histogram of a SWNT deposit formed from the suspensions after 2 purification cycles. The average height observed is 5.3 nm. The shoulder on the left side of the peak in the histogram is indicative of the presence of a bimodal distribution, with heights of significantly less than 5.3 nm strongly represented.
Figure 3.1 (d) AFM image and histogram of a SWNT deposit formed from the suspensions after 3 purification cycles. The average height is 3.7 nm.
Figure 3.1 (e) AFM image and histogram of a SWNT deposit formed from the suspensions after four centrifugation cycles, the average height is 3.2 nm.
Figure 3.1 (f). AFM image and histogram of a SWNT deposit. Five low G centrifugation cycles result in an average height of 2.6 nm, indicating the continued removal of various impurities and bundles, without the use of oxidizing treatments.
Table 3.1. $I_G/I_D$ ratios of the SWNTs in Raman spectroscopy

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<th>0C</th>
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<td>suspensions</td>
<td>4.34</td>
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<td>11.29</td>
<td>12.93</td>
<td>14.47</td>
<td>17.05</td>
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<tr>
<td>SWNT</td>
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<tr>
<td>Depositions</td>
<td>4.92</td>
<td>10.23</td>
<td>12.46</td>
<td>13.97</td>
<td>14.54</td>
<td>17.21</td>
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Figure 3.2. Raman spectra showing the D-band (1290-1310 cm$^{-1}$) and the G-band (1591-1595 cm$^{-1}$) of the SWNT suspensions before centrifugation (0C) and after centrifugation from one to five cycles. (1C ~ 5C). As the number of centrifugation cycles increased, $I_G/I_D$ ratios increased.
Figure 3.3. Raman spectra, showing the D-band (1290-1310 cm\(^{-1}\)) and G-band (1591-1595 cm\(^{-1}\)), for SWNT deposits formed from suspension treated with no centrifugation (0C), up to 5 (1C ~ 5C). As the number of centrifugation cycles increased, \(I_G/I_D\) ratios increased.
Figure 3.4. NIR spectra showing metallic ($M_{11}$), second semiconducting ($S_{22}$), and first semiconducting ($S_{11}$) transitions at 750–800 nm, 980 nm, and 1150 nm, respectively of the SWNT suspensions before and after centrifugation.
Table 3.2. The ratios, $A(S)/A(T)$, of the SWNT suspensions in NIR spectroscopy

<table>
<thead>
<tr>
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<td>x100%</td>
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<td>99.10</td>
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<td>$A(T)$</td>
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Figure 3.5. Plot of absorbance at 650 nm vs number of centrifugation cycles for an AP-grade SWNT soot suspension a starting concentration of 1 mg/mL SWNT soot. The absorbances decrease from 2.576 to 0.175 as the number of centrifugation cycles increase.
CHAPTER 4

SPECTROSCOPIC AND SCANNING PROBE STUDIES OF SINGLE-WALLED CARBON NANOTUBES USING NAFION

\[ \text{1 J. Shim and M.D. Lay, To be submitted to } J \text{ of physical chemistry C (2009)} \]
Abstract

The effect of Nafion on the dispersion of single-walled carbon nanotubes (SWNTs) was investigated. Nafion, which includes hydrophobic and hydrophilic groups was used as a polymeric dispersant. SWNTs were dispersed by Nafion in water/ethanol or water/isopropanol with different ratios. Atomic force microscopy (AFM) images show decreased bundle sizes with the addition of alcohol to water. The decreased defect and better dispersion of the SWNT-Nafion suspensions in water/alcohol were investigated by Raman spectroscopy and Near-infrared (NIR) spectroscopy.

Introduction

Single-walled carbon nanotubes (SWNTs) have received much attention due to their unique physical, chemical, and mechanical properties.[1, 2] SWNTs have high potentials for many applications including field emission devices, chemical sensors, electronic devices, batteries, hydrogen storage, and polymeric composites.[3, 4] However, their practical applications have been limited due to their poor solubility which stems from hydrophobicity and van der Waals interactions.[5-7] SWNTs have been known to be entangled easily by van der Waals interactions between carbon nanotubes and to form an agglomeration.[8, 9] Although this agglomeration is broken by sonication to some extent, it still prevents good solubility in various solvents.[6]

The use of covalent [10, 11] and noncovalent functionalization [12, 13] to obtain stable and homogeneous dispersions of carbon nanotubes has been extensively suggested. Covalent functionalizations, using functional groups, are achieved by sidewall halogenations of carbon nanotubes, cycloadditions with the surface, or electrochemical reactions with radicals.[14, 15]
However, the covalent functionalization modifies the intrinsic properties of SWNTs by the formation of other covalent bonds on the wall and the disruption of the π-networks of carbon nanotubes.[16, 17] To overcome this problem, noncovalent functionalization using polymers,[18] surfactants,[19] and biomolecules[20] has been investigated. In the noncovalent methods, the intrinsic properties of SWNTs are preserved because there is no disruption of the π-networks. It has been known that this noncovalent functionalization is useful to improve solubility and dispersibility.[6] Among various surfactants, sodium dodecylbenzene sulfonate (SDBS) or sodium dodecyl sulfate (SDS) are commonly used as effective dispersants.[20, 21] These surfactants are effective in water due to the presence of hydrophobic alkyl interaction and π-π interaction with SWNTs as well as the electrostatic interaction with hydrophilic parts by sulfonic acid.[19] Although these methods using SDBS or SDS can achieve improved dispersion to some extent,[22] most of the SWNTs are lost during centrifugation to remove impurities and bundles. In order to achieve more stable dispersion without loss, it is necessary to wrap SWNTs strongly by polymeric chains.[16] For better stabilization, the hydrophobic backbone of the polymer or surfactant should be strongly anchored to the hydrophobic carbon nanotubes with a thick polymer layer, while hydrophilic parts are ionized to share ionic charge to the SWNT surfaces.[6]

In this research, Nafion was used as a dispersant of SWNTs. Nafion is an ambipolar dispersant consisting hydrophilic sulfonic acid-terminated perfluorovinyl ether pendants that are spaced regularly along the hydrophobic perfluoroalkyl backbone.[23, 24] Therefore, the influence of Nafion on the dispersion of SWNTs was investigated in water, alcohol (ethanol or isopropanol), and the mixtures of water/ethanol or water/isopropanol. Atomic force microscopy (AFM) was used to observe the surface of SWNT deposits. The electronic properties and the
defects of SWNTs were characterized by Raman spectroscopy and Near Infrared (NIR) spectroscopy, respectively.

**Experimental Section**

**Preparation of SWNT solutions in Nafion**

As-produced (AP) grade Carbon Solution, Inc.(CSI) arc discharge soot was used for all experiments. Nafion (Figure 4.1) was purchased from Aldrich as a 5 wt % solution in a mixture of lower aliphatic alcohols and 45 wt % water. Nafion was diluted to 0.1 wt % with the mixtures of water/ethanol or isopropanol in different ratios (100:0, 50:50, and 0:100) to get different Nafion solutions. First, 2 mg of SWNTs was dispersed in 40 mg of different Nafion solutions by bath ultrasonication (FS110H ultrasonics, Fisher Scientific) for 2 h. Second, the sonicated solution was centrifuged at 17,700 g for 3 h (Avanti centrifuge, Bechman) The top half of the supernatant was carefully collected and subjected to another round of centrifugation (Microfuge, Bechman) at 18,000 g for 30 min. The top half of the supernatant was diluted with Nafion-water/ethanol or Nafion-water/isopropanol in different ratios.

**Formation of SWNT Deposits through Laminar Flow Deposition**

A glass coated with 30 A Glass coated with 3-aminopropyltriethoxy silane was used as a substrate after cleaning with compressed CO₂. Then, five deposition cycles were used to form a low-density SWNT network. Each cycle is defined as depositing the SWNT solution onto the silane-coated glass substrate by drying in a stream of N₂. The substrate was then rinsed with DI-H₂O and dried under a stream of N₂.
Characterization of SWNT Suspensions by AFM and Electromagnetic Spectroscopy

The morphology of SWNTs dispersed using Nafion was observed by atomic force microscopy (AFM). AFM images were taken with a Molecular Imaging PicoPlus. Image analysis software (WSxM) was used to create a histogram in order to observe the size of impurities and bundled SWNTs. The characterization of the Nafion-SWNT suspensions was determined with Raman spectroscopy and Near Infrared (NIR) spectroscopy. The Raman spectra were recorded on a Renishaw InVia Raman microscope with excitation wavelength of 785 nm and 7 mW laser power, using a NIR diode laser. The Raman spectra of Nafion-SWNT suspensions were collected by a charge-coupled device (CCD) detector. The heights of bands in the Raman spectra were obtained by WiRe 2.0 software. NIR spectroscopy was performed on a Thermo 6700 Nicolet FT-IR spectrocope. For NIR spectroscopy, Nafion-SWNT suspension was added to a quartz cell with a path length of 1 cm.

Results and Discussion

AFM Morphology

The SWNT-Nafion suspensions in the water/alcohol bisolvents were deposited onto a silane-coated glass substrate. The AFM images of the SWNT deposits are shown in Figure 4.2. Figure 4.2 (a) ~ (d) show a histogram indicating the bundle diameter of the SWNT deposits as well as their morphology. In Figure 4.2 (a), the average bundle size of the SWNT-Nafion in isopropanol was observed to be 16.387 nm. Figure 4.2 (b) indicates the average bundle size of the SWNT-Nafion in water/isopropanol (50:50) was 7.214 nm. It turned out the average bundle sizes decreased as alcohol was added to water. For SWNTs dispersed in Nafion-ethanol and in Nafion-water/ethanol (50:50) solutions, the bundle sizes also decreased from 9.936 nm 4.315 nm.
as shown in Figures 4.2 (c) and (d). In case of the SWNT-Nafion suspensions in water, no SWNTs were observed. For SWNTs dispersed in Nafion-water, the hydrophobic backbone in Nafion can interact with SWNTs, and the hydrophilic polar group can dissolve well in water. [6, 25] However, the Nafion was easy to aggregate in water and the SWNTs didn’t disperse well in water, showing large bundles of SWNTs. Figure 4.3 shows the visual comparison of the SWNT-Nafion in water/alcohol. It appeared the SWNT-Nafion suspension did not disperse well in water and instead formed aggregates at the bottom of vials even after ultrasonication process.

Therefore, it can be concluded that as the alcohol was added to the water, the solubility of Nafion in bisolvents was improved, showing the small bundles and good stability of SWNTs. Nafion has already been known as a good dispersant of SWNTs because the hydrophilic polar group in Nafion interacts strongly with water and the hydrophobic backbone in Nafion interacts with the carbon nanotubes.[16, 26] Especially, the solubility of SWNT suspensions with Nafion can be significantly improved by introducing a bisolvent such as water and alcohol.[6] The bisolvent has been introduced to improve solubility of Nafion resulting in the conformational change of Nafion adsorbed on the walls of SWNTs from an aggregated to a stretched-out structure.[6, 27] In the solubility of Nafion with a bisolvent, water interacts more strongly with the sulfonic acid residue, while the alcohols preferentially solvate the fluoroether side chain.[28]

**Raman Spectroscopy of SWNT Suspensions**

Raman spectroscopy has been used to analyze the structural properties of SWNTs. It also has been employed as a powerful probe of disorder in the carbon skeleton of sp² and sp³ carbon materials.[29] Raman scattering is so intense that individual carbon nanotubes can be investigated. There are two Raman bands which are typically observed for sp² carbons in the
1200–1850 cm\(^{-1}\).[30] The band in the the 1580–1600 cm\(^{-1}\) appears for well-ordered graphite, and it is therefore often called the ‘G-band’. [31] The G-band, which is called a ‘tangential mode’, is indicative of the pristine, symmetrical graphene lattice. [30] The second band observed is the ‘D-band’, which is called a ‘dispersive’ band. It is a relatively broad, disorder-induced band in the 1300–1370 cm\(^{-1}\). The D-band indicates the presence of disordered sp\(^2\) carbon material and the degree of conjugation disruption. [16, 32] The intensity ratio of the G and to the D-bands ((I\(_G\)/I\(_D\)) is widely used as a measure of defect. [33] The higher ratios mean well-ordered carbon nanotubes with perfect cylindrical symmetry are formed and the defects due to disordered sp\(^2\) carbon are decreased. [34]

Figure 4.4 shows the Raman spectra of the SWNT-Nafion suspensions in water/alcohol. The SWNT-Nafion in water didn’t show the G-band. However, the G-bands of SWNT-Nafion in water/isopropanol (50:50 and 0:100) and in water/ethanol (50:50 and 0:100) were observed in 1591.4–1591.7 cm\(^{-1}\). The D-bands of the different SWNT-Nafion suspensions were also found in 1295.7–1302.3 cm\(^{-1}\). The intensity ratios, I\(_G\)/I\(_D\), were shown in Table 4.1. The I\(_G\)/I\(_D\) values were 4.05, 11.74, 4.47, and 18.43 for SWNT-Nafion in isopropanol, SWNT-Nafion in water/isopropanol (50:50), SWNT-Nafion in ethanol, and SWNT-Nafion in water/ethanol (50:50), respectively. The I\(_G\)/I\(_D\) ratios became remarkably increased as the amounts of alcohol were added to water. This suggests that the defect of SWNTs decreases due to improved dispersion of Nafion in an aqueous solution with the addition of alcohol. Consistent with the results of AFM, the solubility of SWNT suspensions with Nafion can be significantly improved by introducing a bisolvent such as water and alcohol. [6]
Near-Infrared Spectroscopy of SWNT Suspensions

The electronic properties of SWNTs was investigated by near-infrared (NIR) spectroscopy. NIR spectroscopy has been reported as an important tool for characterizing the electronic band structure of SWNTs.[35] The SWNTs cause a series of interband electronic transitions. The semiconducting SWNTs cause first and second transitions starting with $S_{11} = 2\alpha\beta/d$ and $S_{22} = 4\alpha\beta/d$ whereas the first transitions of the metallic SWNTs appear at $M_{11} = 6\alpha\beta/d$, where $\alpha$ is the C-C bond length (0.1424 nm), $\beta$ is the transfer integral between $p\pi$ orbitals as an interaction energy between neighboring C atoms, ($\beta = \sim2.9$ eV) and d is SWNT diameter (nm).[35, 36] These interband transitions show prominent features in the NIR spectral range, which can be useful for characterizing electronic structure of SWNTs. Also the spectral features become more prominent when the SWNTs are individually dispersed.[37-39] Thus, the appearance of the spectral features has been used as a useful indicator of nanodispersion where carbon nanotubes are individually dissolved in the solvent.[6, 40] Following the previous studies by Haddon et al.,[35, 41, 42] the $A(S)/A(T)$ is taken as a useful ratio to evaluate electronic structure of SWNTs quantitatively. $A(S)$ is the area of $S_{22}$ interband transition after linear baseline subtraction and $A(T)$ is the total area under the spectral curve. In the study by Haddon et al., the $S_{22}$ transition has been used to calculate the ratio because it is observed distinctly and it is much less affected by chemical process.[42, 43]

In Figure 4.5, NIR spectra of the SWNT-Nafion suspensions in water/alcohol are shown. The spectral range of 6865~7750 cm$^{-1}$ was used to capture the $S_{22}$ transition in all SWNT-Nafion suspensions in water/alcohol. A strong upshift of $S_{22}$ was observed relative to the reference sample of the Haddon group with an $S_{22}$ transition from 7750 to 11750 cm$^{-1}$.[41] The $S_{22}$ absorption can be shifted depending on the diameters of SWNTs.[34, 44] As shown in Table 4.1, it was observed the value of ‘$A(S)/A(T) \times 100 \%$’ increased from 27.52 % to 68.27 % in
isopropanol and from 43.10 % to 85.16 % in ethanol as the alcohol was added to water. It means that the $S_{22}$ transition becomes more prominent and SWNTs dissolve individually in the bisolvent.

In Figure 4.5, the blue-shifted spectral peaks of SWNT-Nafion suspensions are shown as the alcohol was added to water. The peaks of SWNT-Nafion in bisolvents were blue-shifted by 877 cm$^{-1}$ from 6873 cm$^{-1}$ in isopropanol to 7750 cm$^{-1}$ in water/isopropanol. Another blue shift was also found by 852 cm$^{-1}$ in the peaks of SWNT-Nafion in water/ethanol at 7717 cm$^{-1}$ from the peak of SWNT-Nafion in only ethanol at 6865 cm$^{-1}$. According to Smalley et al., the spectral peaks can be blue-shifted due to the debundling of carbon nanotubes.[22] Therefore, the NIR data suggest that the SWNTs are mostly debundled and dispersed into individual ones in the bisolvent with corroborating results in the AFM images.

Conclusions

Nafion in water/alcohol bisolvents was used as a dispersant of SWNT suspensions to investigate the effect of the dispersibility. The Nafion, which includes hydrophobic and hydrophilic groups, was used as a polymeric dispersant in water/ethanol or water/isopropanol. Atomic force microscopy (AFM) images showed bundle sizes decreased with the addition of alcohol to water. The decreased defects of the SWNT-Nafion suspensions in water/alcohol were observed by Raman spectroscopy. The ratios, $I_G/I_D$ values were 4.05, 11.74, 4.47, and 18.43 for SWNT-Nafion in isopropanol, SWNT-Nafion in water/isopropanol (50:50), SWNT-Nafion in ethanol, and SWNT-Nafion in water/ethanol (50:50), respectively. The defect of SWNTs decreased due to improved dispersion of Nafion in an aqueous solution with the addition of alcohol. In Near-infrared (NIR) spectroscopy, the peaks of SWNT-Nafion in bisolvents were blue-shifted due to the debundling of carbon nanotubes.
References


Figure 4.1 Chemical structure of Nafion
Figure 4.2 (a) AFM image and height histogram of SWNTs-Nafion suspension in isopropanol.

The average height observed is 16.387 nm.
**Figure 4.2 (b)** AFM image and height histogram of SWNTs-Nafion suspension in water/isopropanol. The average height observed is 7.214 nm.
Figure 4.2 (c) AFM image and height histogram of SWNTs-Nafion suspension in ethanol.

The average height observed is 9.936 nm.
Figure 4.2 (d) AFM image and height histogram of SWNTs-Nafion suspension in water/ethanol.

The average height observed is 4.315 nm.
Figure 4.3 Visual comparison of the dispersibility of SWNTs-Nafion

in (a) isopropanol, (b) water/isopropanol, (c) ethanol, (d) water/ethanol, and (e) water.

The SWNTs-Nafion was not dissolved well in the water as shown in (e).
Figure 4.4 Raman spectra showing the D-band (1295.7~1302.3 cm$^{-1}$) and the G-band (1591.4~1591.7 cm$^{-1}$) of SWNTs-Nafion suspensions in water/alcohols. The D-band indicating the defect of SWNTs decreased as the amounts of alcohol were added to water.
Table 4.1 The ratios of $I_G/I_D$ in SWNTs-Nafion suspensions

<table>
<thead>
<tr>
<th>Sample</th>
<th>SWNTs-Nafion in isopropanol</th>
<th>SWNTs-Nafion in water/isopropanol</th>
<th>SWNTs-Nafion in ethanol</th>
<th>SWNTs-Nafion In Water/ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_G/I_D$</td>
<td>4.05</td>
<td>11.74</td>
<td>4.47</td>
<td>18.43</td>
</tr>
<tr>
<td>$A(S)/A(T) \times 100%$</td>
<td>27.52</td>
<td>68.27</td>
<td>43.10</td>
<td>85.16</td>
</tr>
</tbody>
</table>
Figure 4.5 NIR spectra of SWNTs-Nafion suspensions in water/alcohol. More prominent S_{22} transition bands and blue-shifted spectral peaks are observed as the alcohol was added to water.
CHAPTER 5

EFFECTS OF SELF-ASSEMBLED MONOLAYERS ON SINGLE-WALLED CARBON NANOTUBES

\[1\]

\[1\] J. Shim and M. D. Lay, To be submitted to J of Physical Chemistry C (2009)
Abstract

The optimization of self-assembled monolayers (SAMs) on Si/SiO$_2$ and Au substrates was investigated in order to obtain well-ordered arrays of single-walled carbon nanotube (SWNT) networks. The SWNT networks were deposited onto the SAMs formed with aminosilane and aminothiol on Si/SiO$_2$ and Au, respectively. Depending on concentration, adsorption time and nature of SAMs, surface morphology and the degree of defect in the SWNTs were characterized by atomic force microscopy (AFM) and Raman spectroscopy, respectively. The results indicated improved surface morphology and decreased defect of SWNTs as the concentration of self-assembled molecules and the adsorption time increased.

Introduction

Carbon nanotubes (CNTs) have been studied for many applications, such as sensors, [1-3] electrodes,[4, 5] field emission materials,[6, 7] batteries,[8] and hydrogen storage[9] due to their unique electrical, mechanical, and structural features. For these promising applications, well-ordered arrays of CNT networks are necessary to maintain their unique properties.[10, 11] However, current synthetic methods, such as arc discharge,[12, 13] laser ablation,[14] and chemical vapor deposition[15] only produce CNTs in random arrays. It still remains a great challenge to produce controlled deposition of highly organized single-walled carbon nanotubes (SWNTs) on a wide variety of substrates.[10] The fabrication of highly ordered SWNT networks requires the optimization of self-assembled monolayers (SAMs) on which CNT networks form. SAMs are chemisorbed organic layers formed on a metal substrate by spontaneous adsorption of the molecules with polar head groups which create stable, highly organized arrays of thin films.[5, 16, 17] SAMs provide a model platform for engineering surfaces at the molecular
level.[18, 19] There are many applications of SAMs because the monolayers provide surfaces of well-organized organic materials. SAMs of n-alkylsilanes[20] and n-alkanethiols[16] have been widely used for surface modification, protein adsorption, and molecular device fabrication due to the ease of fabrication.[21] Alkylsilanes were coated on a Si/SiO$_2$ substrate by a self-assembled technique followed by deposition of SWNT networks. Aminosilanes were specifically used because they are self-assembled molecules that have many applications in nylon, phenolic, epoxy, and melamine resin based composites.[22] The formation of SAMs of organomolecules on a gold surface has attracted attention due to their importance in biology, chemistry and supramolecular nanotechnology.[5] Well-organized alkanethiol SAMs on gold have been applied for fabrication of biosensors,[23, 24] bio-recognition devices[16], drug delivery [16], electrochemical sensors,[25, 26] and electronic devices.[27, 28] Surface structures and SAM defects depend strongly on the conditions, such as adsorption times, type of substrate, temperature, solution concentration, etc.[29]

In this study, the optimization of concentration, adsorption time, and nature of SAMs on metal substrates, such as Si/SiO$_2$ and Au, was investigated to prepare well-ordered SWNT networks. Atomic force microscopy (AFM) was used to characterize the morphology and the height of SWNTs. The degree of disorder and defect were characterized by Raman spectroscopy.

**Experimental Section**

**Preparation of SWNT solutions**

As-produced (AP) grade CarboLex Inc. arc discharge soot, with a guaranteed purity of 50-70 wt% SWNTs, was used for all experiments. Solutions with 1 mg/ml SWNT soot were prepared in 1 % (w/v) sodium dodecyl sulfate (SDS). This solution was dispersed by probe
sonication (Model 500, Fisher Scientific) at 12 W for 30 min, followed by centrifugation (Bechman Avanti centrifuge) at 17,700 g for 3 h and microcentrifugation (Beckman Microfuge) at 18,000 g for 1h. After each centrifugation, the upper half of the supernatant was collected and used for deposition on metal substrates.

**Preparation of SAMs on Si/SiO$_2$ substrates.**

Si/SiO$_2$ substrates were cut into fragments and then cleaned with compressed CO$_2$. The substrates were then functionalized to produce an amine-terminated surface by exposure for 30 min to a solution containing fresh 1 mM, 10 mM, and 50 mM solutions of 3-aminopropyltriethoxysilane (APS, Figure 5.1 (a)) in 99.5 % ethanol. The various assembling time was applied to 10 min, 30 min, and 90 min at fixed concentration of 50 mM APS. N-propyltriethoxysilane (Figure 5.1 (b)) was also used to prepare SAMs without an amino group on a Si/SiO$_2$.

**Preparation of SAMs on Au substrates.**

Au foils were cleaned with Piranha solution (1:3, v/v; 30% H$_2$O$_2$ and concentrated H$_2$SO$_4$) for 2.0 min and rinsed thoroughly with distilled water. (Caution : Piranha solution is known to react violently with organic materials and can explode when stored in closed containers, so it must be handled with care.) The Au substrates were immersed in 1.0 mM solution of 6-amino-1-hexanethiol (AHT, Figure5.1 (c)) in 99.5 % ethanol for 3 h, 6 h, 12 h, and 17 h at room temperature.

**Formation of SWNT Deposits through Laminar Flow Deposition**

The SWNT solutions were deposited onto the SAMs on Si/SiO$_2$ and Au substrates. Ten deposition cycles were used to form a SWNT network. Each cycle is defined as depositing the
SWNT solution onto the SAMs on the substrates by drying in a stream of N₂. The substrate was then rinsed with distilled water and dried under a stream of N₂.

**Characterization of SWNT deposits by AFM and Raman Spectroscopy**

Atomic force microscopy (AFM) images were taken with a Molecular Imaging PicoPlus. Image analysis software (WSxM) was used to create a histogram in order to observe the size of impurities and bundled SWNT. The degree of disorder and defect was characterized by Raman spectroscopy. The Raman spectra were recorded on a Renishaw InVia Raman microscope with excitation wavelength of 785 nm and 7 mW laser power, using a diode laser. The Raman spectra of deposited SWNTs were collected by a charge-couple device (CCD) detector. The heights of bands in the Raman spectra were obtained by WiRe 2.0 software.

**Results and Discussion**

**AFM Morphology**

The morphology of the SAMs-coated SWNT deposits was observed by AFM. AFM analysis of SWNT deposits allows quantitation of the change in the coverage and size of impurities because the various impurities were observed to be larger in height than the average SWNT. Figure 5.2 (a) – (c) show the AFM images of APS-coated SWNTs deposits on Si/SiO₂ substrate at different concentrations of 1 mM, 10 mM, and 50 mM APS. The AFM image of 1 mM APS-coated SWNT deposit is shown with the average height of 8.305 nm in Figure 5.2 (a). In Figure 5.2 (b), the average height decreased to 7.237 nm in the 10 mM APS-coated SWNT deposit. A dramatic improvement in the quality of SWNT deposit was observed for the 50 mM APS-coated carbon nanotube deposit as displayed in Figure 5.2 (c). The average height of the 50
mM APS-coated SWNT deposit measured 4.168 nm. The results indicate that the average height of impurities and bundled SWNTs decreases at higher concentration of APS on Si/SiO₂. As the concentration of APS increases, the densely-packed SAMs can form on a substrate. The concentration is the major factor for highly-densed SAMs. The growth of monolayers at the liquid/solid interface was found to depend on the concentration of the deposition solution.[30] As the concentration of SAMs increased, it was observed that the density of the adsorbate molecules increased.[30] The densely-packed APS can attribute to unbundled SWNTs with less impurities because the head group of APS, NH₂, has a strong and stable covalent interaction with the SWNTs. This strong and stable interaction between SAMs and SWNTs can decrease the invasion of impurities and the formation of bundled carbon nanotubes.

In Figures 5.3 (a)~(c), it was observed that the average height of the SWNTs decreased to 4.437 nm, 4.168 nm, and 3.540 nm, respectively, as the assembling time of APS increased to 5 min, 30 min, and 90 min. As the SAM assembling time increased, the size of impurities and bundled SWNTs decreased. This result was also consistent with the formation of SWNTs on thiol-coated Au. Figure 5.4 (a)~(d) show the AFM image and the histograms of the SWNTs on thiol-coated Au deposits which were assembled for various adsorption times, 3 h, 6 h, 12 h, and 17 h. It was noticed that the surface of SWNTs on Au is not enough to form complete nanotube networks. As shown in Figure 5.4 c), the AFM image of the SWNTs on 17 h-assembled Au was able to be obtained. The other images of the SWNTs in 3 h, 6 h, and 12 h-assembled Au deposits showed a lot of impurities and large bundles. The sizes of impurities and bundled SWNTs in Au deposits were larger than those in Si/SiO₂. However, these Au deposits also showed the size of impurities and bundled SWNTs decreased with the increased assembling time of thiol at 3 h, 6 h, 12 h, and 17 h. In Figure 5.4 b) and c), the sizes of impurities and bundles at 3 h and 6 h, respectively. In this result, the size of impurities and bundles at 3 h was smaller than
the size at 6 h. However, as the assembling time increases to over 10 h, the sizes of impurities and bundles remarkably decreased to ~33 nm. As shown in Figure 5.4 d) and e), the sizes were observed to 38.720 nm and 33.255 nm at 12 h and 17 h assembled Au deposits, respectively.

In the formation of SAMs, the density of monolayers on metal substrate increase with increasing the adsorption time.[10] This highly-densed SAMs form a densely-packed surface. The assembling time, as well as concentration, is also major factor for formation of densely-packed SAMs. The densely-packed SAMs with longer adsorption times can have strong and stable interactions with SWNTs. As mentioned above in Figure 5.2, the formation of impurities and bundles can decrease due to this strong interaction between SAMs and SWNTs.

**Raman Spectroscopy of SWNT Deposits**

Raman spectroscopy is a powerful tool for characterizing SWNTs owing to the characteristic peaks that occur due to disordered carbon and grapheme sheetlike vibration.[31] Raman scattering has been used for many years as a probe of disorder in the carbon skeleton of sp² and sp³ carbon materials.[32] There are two Raman bands which are typically observed for sp² carbon in the 1200~1850 cm⁻¹ region.[33] The ‘G-band’, which is called a ‘tangential modes’, is seen in the 1580~1600 cm⁻¹ region. It is observed for pristine, well-ordered graphite.[33, 34] The G-band in well-ordered nanotubes has several components that stem from the perfect cylindrical symmetry of the nanotube.[35] The band with maximum near ~1300 cm⁻¹ is common in disordered sp² carbon material and has been called the D-band.[34] This broad D-band is caused by C-atom vacancies, impurities, or any other imperfections in the grapheme lattice.[34]

Figure 5.5 shows the Raman spectra of the SWNT deposits depending on the concentration of 3-aminopropyltryethoxysilane (APS)-coated Si/SiO₂ at 1 mM, 10 mM, and 50
mM APS. In Figure 5.5, the G-band and D-band were observed at 1585~1590 cm\(^{-1}\) and 1290-1310 cm\(^{-1}\) respectively. Figure 5.5 shows the highest G-band at 50 mM APS in the Raman spectrum of the SWNT deposits. The intensity ratio of the G and D-bands (I\(_G\)/I\(_D\)) is an indicator to estimate the purity of SWNTs.[36] As shown in Table 5.1, the I\(_G\)/I\(_D\) ratios increased from 4.96 to 15.45 as the concentration of APS increased. The higher ratios mean well-ordered carbon nanotubes with perfect cylindrical symmetry are formed and the defects due to disordered sp\(^2\) carbon are decreased.[35] Therefore, it is demonstrated that higher concentration of APS decreases the defects and disorder of sp\(^2\) carbon materials. As the concentration of APS increases, densely-packed APS is formed on the Si/SiO\(_2\) substrate because the density of the adsorbate molecules increases.[30] The close-packed APS can attribute to the strong and stable interaction with SWNTs. This provides well-ordered SWNT networks with decreased defects as proved by the I\(_G\)/I\(_D\) ratios in Table 5.1.

In Figure 5.6, it is shown that the Raman spectra of the SWNT deposits depend on the assembling time for formation of APS-coated Si/SiO\(_2\). The SAMs using 50 mM APS were assembled on Si/SiO\(_2\) for 5 min, 30 min, and 90 min. Each G and D-band was observed at 1585~1590 cm\(^{-1}\) and 1290-1310 cm\(^{-1}\) respectively. Figure 5.6 shows a remarkably increased G-band in the Raman spectrum of APS-assembled SWNT deposits at 90min adsorption. In Table 5.1, it is shown that the I\(_G\)/I\(_D\) ratios increased from 9.85 to 24.23 with assembling time. It turns out that longer assembling time for formation of APS on Si/SiO\(_2\) decreases the defects of SWNTs. As the assembling time increases, APS can be assembled in a densely-packed structure with strong covalent siloxane bonds. The covalent nature of siloxane bonds within silane SAMs provides stability and durability for nanostructures.[37] These stable SAMs can be substructures for well-ordered SWNTs.
There is a similar trend in the Raman spectra of the SWNT deposit on 6-amino-1-hexanethiol (AHT)-assembled Au. In Figure 5.7 (a), as the assembling time for formation of thiol-coated Au increases from 3 h to 17 h, the increased G-band and decreased D-band are shown. Table 5.2 shows the $I_G/I_D$ ratios increase from 1.59 to 2.20 with the increase of assembling time. As noted above, it is likely that SAMs pack more densely at longer assembling times. The densely-packed SAMs on a substrate form strong substructure. This strong substructure of SAMs makes it more likely to interact strongly with carbon nanotubes and form well-ordered SWNTs.

In Figure 5.7 (b), the Raman spectrum of the 6-amino-1-hexanethiol (AHT)-coated Au without deposition of SWNTs is shown. The main bands of AHT appear at 683 and 1295 cm$^{-1}$ and can be assigned to the -CH$_2$-S-[38, 39] and –CH$_2$[40]. Also, there are small bands assigned to -NH$_2$ [41] in the 735–815 cm$^{-1}$ region[41, 42]. Figure 5.7 (c) shows the Raman spectra of the SWNT deposits on AHT-coated Au at 3 h and 17 h assembling time in the 600–1300 cm$^{-1}$. Most significantly, the bands of CH$_2$-S- and –NH$_2$ in the 683–815 cm$^{-1}$ region were disappeared when AHT was assembled for 17 h. This is reasonable evidence of strong covalent interaction between NH$_2$ in AHT and C in SWNTs at longer assembling times. Therefore, the bands of CH$_2$-S- and –NH$_2$ in the 683–815 cm$^{-1}$ were not observed at 17 h adsorption time because well-ordered SWNT networks covered the AHT assembled layer thoroughly.

In Figure 5.8, it is appeared that the Raman spectrum of the SWNTs deposits on n'-propyltriethoxysilane-coated Si/SiO$_2$. In Figures 5.5–5.7, the SAMs with –NH$_2$ group, such as APS and AHT, were used to get the Raman spectra for SWNT deposits. Figure 5.8 shows the G-band at 1590 cm$^{-1}$ and D-band at 1300 cm$^{-1}$. In Table 5.1, the $I_G/I_D$ ratio, 9.93, is appeared. This ratio is compared with the ratio,13.62, of the 10 mM aminosilane, APS, coated-SWNTs deposits.
in Figure 5.5 and Table 5.1. It was demonstrated that the SWNTs with aminosilane had decreased defects and highly-ordered networks.

Conclusions

In this work, the SWNT networks were deposited on the SAMs formed with aminosilane and aminothiol on Si/SiO$_2$ and Au substrates, respectively. Depending on concentration, adsorption time and nature of SAMs, surface morphology and the degree of defect in the SWNTs were characterized by atomic force microscopy (AFM) and Raman spectroscopy. The high concentration of self-assembled molecules and long adsorption time for the formation of SAMs provided the possibilities to improve surface morphology and to decrease the defect of SWNTs.

References


Figure 5.1 Chemical structures of (a) 3-aminopropyltriethoxysilane (APS),
(b) n-propyltriethoxysilane, and (c) 6-amino-1-hexanethiol (AHT)
Figure 5.2 (a) AFM image and height histogram of the 1mM 3-aminopropyltriethoxysilane (APS)-coated SWNTs deposit on Si/SiO₂ substrate. The average size of impurities and bundles is 8.305 nm.
Figure 5.2 (b) AFM image and height histogram of the 10 mM 3-aminopropyltriethoxysilane (APS)-coated SWNTs deposit on Si/SiO₂ substrate. The average size of impurities and bundles is 7.237 nm.
Figure 5.2 (c) AFM image and height histogram of the 50 mM 3-aminopropyltriethoxysilane (APS)-coated SWNTs deposit on Si/SiO$_2$ substrate. The average size of impurities and bundles is 4.168 nm.
Figure 5.3 (a) AFM image and height histogram of the 50 mM 3-aminopropyltriethoxysilane (APS)-coated SWNTs deposit on Si/SiO$_2$ substrate at 5 min assembling time.

The average size of impurities and bundles is 4.437 nm.
Figure 5.3 (b) AFM image and height histogram of the 50 mM 3-aminopropyltriethoxysilane (APS)-coated SWNTs deposit on Si/SiO₂ substrate at 10 min assembling time.

The average size of impurities and bundles is 4.168 nm.
Figure 5.3 (c) AFM image and height histogram of the 50 mM 3-aminopropyltriethoxysilane (APS)-coated SWNTs deposit on Si/SiO$_2$ substrate at 10 min assembling time.

The average size of impurities and bundles is 3.540 nm.
Figure 5.4 (a) AFM image of the SWNT networks on the 6-amino-1-hexanethiol coated Au substrate.
**Figure 5.4 (b)** Height histogram of the SWNT networks on the 6-amino-1-hexanethiol coated Au substrate at 3 hour assembling time.

The average size of impurities and bundles is 52.325 nm.
Figure 5.4 (c) Height histogram of the SWNT networks on the 6-amino-1-hexanethiol coated Au substrate at 6 hour assembling time.

The average size of impurities and bundles is 61.251 nm.
Figure 5.4 (d) Height histogram of the SWNT networks on the 6-amino-1-hexanethiol coated Au substrate at 12 hour assembling time.

The average size of impurities and bundles is 38.720 nm.
Figure 5.4 (e) Height histogram of the SWNT networks on the 6-amino-1-hexanethiol coated Au substrate at 17 hour assembling time.

The average size of impurities and bundles is 33.455 nm.
Table 5.1 Raman ratios of the silane-coated SWNT deposits on Si/SiO$_2$ substrates

<table>
<thead>
<tr>
<th>samples</th>
<th>$I_G/I_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1mM of APS at 30min assembling time</td>
<td>4.96</td>
</tr>
<tr>
<td>10mM of APS at 30min assembling time</td>
<td>13.62</td>
</tr>
<tr>
<td>50mM of APS at 30min assembling time</td>
<td>15.45</td>
</tr>
<tr>
<td>50mM of APS at 5min assembling time</td>
<td>9.85</td>
</tr>
<tr>
<td>50mM of APS at 90min assembling time</td>
<td>15.45</td>
</tr>
<tr>
<td>10mM of $n$-propyltriethoxysilane at 30min assembling time</td>
<td>9.93</td>
</tr>
</tbody>
</table>
Table 5.2 Raman ratios of the 6-amino-1-hexanethiol (AHT)-coated SWNT deposits on Au substrates

<table>
<thead>
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<th>Assembling time for 6-amino-1-hexanethiol-coated Au deposits</th>
<th>$I_G/I_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 hour</td>
<td>1.59</td>
</tr>
<tr>
<td>6 hour</td>
<td>1.83</td>
</tr>
<tr>
<td>12 hour</td>
<td>1.97</td>
</tr>
<tr>
<td>17 hour</td>
<td>2.20</td>
</tr>
</tbody>
</table>
Figure 5.5 Raman spectra showing the D-band (1290~1310 cm$^{-1}$) and the G-band (1589~1590 cm$^{-1}$) of the SWNT deposits on the various concentrations of 3-aminopropyltriethoxysilane (APS)-coated Si/SiO$_2$ substrates. As the concentration of APS increased, the defect of SWNTs decreased.
Figure 5.6 Raman spectra showing the D-band (1290~1310 cm\(^{-1}\)) and the G-band (1589~1590 cm\(^{-1}\)) of the SWNT deposits on the 3-aminopropyltriethoxysilane (APS)-coated Si/SiO\(_2\) substrates at various assembling times. A longer assembling time for formation of APS on Si/SiO\(_2\) decreased the defect of SWNTs.
Figure 5.7 (a) Raman spectra of the 6-amino-1-hexanethiol (AHT)-coated SWNT deposits on Au substrates at various assembling times. As the assembling time for formation of AHT-coated Au deposits increases from 3 h to 17 h, the decreased D-band and the increased G-band are shown.
Figure 5.7 (b) Raman spectrum of the 6-amino-1-hexanethiol-coated Au substrate without deposition of carbon nanotubes. The main bands at 683 cm$^{-1}$ and 1295 cm$^{-1}$ are assigned to $-$CH$_2$-S- and $-$CH$_2$. The small bands are assigned to $-$NH$_2$ in the 735–815 cm$^{-1}$. 
Figure 5.7 (c) Raman spectra of the SWNT networks on the 6-amino-1-hexanethiol-coated Au substrates at 3 h and 17 h assembling times in 500 ~ 1500 cm$^{-1}$ region. The bands of CH$_2$-S- and –NH$_2$ in the 683~815 cm$^{-1}$ region were disappeared when AHT was assembled for 17 h.
Figure 5.8 Raman spectra of the SWNT deposits on different silanes with and without an amino group: 3-aminopropyltriethoxysilane and n-propyltriethoxysilane.

The 3-aminopropyltriethoxysilane-coated SWNT deposit showed a larger ratio, $I_G/I_D$, than the n-propyltriethoxysilane-coated deposit.
CHAPTER 6

CONCLUSIONS

Although single-walled carbon nanotubes (SWNTs) have been applied to many industrial fields, their impurities, poor dispersibility, and the random arrays of SWNT networks have become obstacles in many applications. In this dissertation, the purification, dispersion, and well-ordered arrays of SWNTs were investigated by spectroscopy and scanning probe microscopy.

In Chapter 3, a simple and nondestructive purification of SWNTs by multiple cycles of centrifugation was demonstrated. Experimental results show that more cycles of centrifugation improve the purity of SWNTs. Atomic force microscopy (AFM) images showed that increasing centrifugation cycles decreases the size of impurities and bundled-SWNTs. More prominent metallic and semiconducting transition interbands with high purity ratios, $A(S)/A(T)$, were observed in near-infrared (NIR) spectroscopy as the number of centrifugation cycles increased. It was demonstrated that more cycles increased high-aspect-ratios SWNTs and decreased the defects by Raman spectroscopy.

The effect on dispersion of SWNT suspensions in Nafion was discussed in Chapter 4. Nafion is an ambipolar dispersant consisting of hydrophilic and hydrophobic groups. In Chapter 4, Nafion was used as a polymeric dispersant in water/ethanol and water/isopropanol. AFM images showed bundled-SWNT sizes decreased with the addition of alcohol to water. Raman spectroscopy confirmed the defects of the SWNT-Nafion suspensions decreased in water/alcohol bisolvents. As alcohol was added to water, the defect of SWNTs dramatically decreased in an aqueous solution with Nafion due to improved dispersion. Further evidence of the debundling of SWNTs-Nafion in water/alcohol was given by blue-shifted peaks in NIR spectroscopy.
In Chapter 5, well-ordered arrays of SWNT networks were investigated by depositing carbon nanotubes on self-assembled molecule-coated substrates. Aminosilane and aminothiol were used to form self-assembled monolayers (SAMs) on Si/SiO$_2$ and Au substrates. On these self-assembly systems, SWNT networks were formed by laminar flow deposition and characterized by AFM and Raman spectroscopy. Results indicated that the high concentration of self-assembled molecules and long adsorption time for the formation of SAMs provided an improved surface morphology and decreased the defect of SWNT.

Purified, homogeneous and well-ordered SWNTs can be applied for many industrial fields because they can maintain their intrinsic properties. Therefore, Chemical sensors can become one of the applicable areas in SWNTs in the future. SWNT sensors can offer high sensitivity and selectivity for some gases with lower detection limits. In addition, the functionalization of SWNTs using polymers can improve the selectivity of the sensors.