POST-PRODUCTION SEPARATION AND FUNCTIONALIZATION OF SINGLE-WALLED CARBON NANOTUBES

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POST-PRODUCTION SEPARATION AND FUNCTIONALIZATION OF SINGLE-WALLED CARBON NANOTUBES

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemistry

by
Kurukulasuriya Alexius Shiral Fernando
August 2007

Accepted by:
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ABSTRACT

Single-walled carbon nanotubes (SWNTs) are considered to have many potential applications due to their unique structural, physical, chemical and electronic properties. Because the rigid structure of carbon nanotube determines its toughness in dissolution, the processing capability of carbon nanotube is strongly limited. My carbon nanotube functionalization research was mainly focused on developing innovative methods to functionalize nanotubes with various polymers and large aromatic molecules to make them soluble to study their interesting properties and applications. In this dissertation, different methods for the functionalization and solubilization of carbon nanotubes are described.

The co-existence of metallic and semiconducting carbon nanotubes has often been a bottleneck in many applications including future nanoelectronic devices. Therefore, the separation of SWNTs based on electronic structure and diameter is very important. The separation of SWNTs based on electronic structure and diameter using non-covalent functionalization methods was performed. The separated nanotube samples were characterized using optical spectroscopy, Raman spectroscopy, thermal gravimetric analysis and electron microscopy and the results revealed that the separation of nanotubes based on electronic structure and diameter was achieved successfully. In addition, the electronic band gap transitions related to SWNTs (especially semiconducting band gap transitions) were found to be very sensitive to surrounding chemical species. The doping of these electronic transitions by larger aromatic species is also discussed.
DEDICATION

This dissertation is dedicated to my beloved father, late Mr. K.G.E Fernando, my mother Mrs. A. L. C. Fernando and especially my wife Mrs. Renuka Fernando for their sacrifice, love and unconditional support.
ACKNOWLEDGMENTS

I would like to thank my advisor, Professor Ya-Ping Sun, for his guidance, his time spent with me and patience during the last 5.5 years of my graduate study. His knowledge, guide, seriousness, diligence and philosophy in the science greatly affected me as a graduate student, which I have benefited from and shall certainly very much appreciate as a Ph.D. scientist for the rest of my life.

I am grateful to all those who loved and supported me. In particular, I would like to thank my wife Renuka for her sacrifice for last five years and my loving parents who were always there over the years supported me and helped me.

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CHAPTER

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CHAPTER 1

INTRODUCTION- A REVIEW ON POST-PRODUCTION SEPARATION OF METALLIC AND SEMICONDUCTING SINGLE-WALLED CARBON NANOTUBES

1.1 Post-Production Separation

As produced, single wall carbon nanotubes (SWNTs), irrespective to the synthesis method, are a mixture of metallic and semiconducting tubes (Figure 1.1).\(^1\) Because the co-existence of metallic and semiconducting carbon nanotubes has often been a bottleneck for creating the many applications, including the next generation of future electronics, determining how to separate semiconducting SWNTs from metallic SWNTs is of great importance. Initial separation efforts have exploited the potential to produce either semiconducting or metallic SWNTs selectively during the production. For example, semiconducting SWNT enriched samples were obtained using the CVD method.\(^2-6\) However, some of these methods are not scalable (sub-milligram quantity or less) and are perhaps only applicable at device level. Consequently, these inevitable limitations make the direct production of semiconducting and metallic SWNTs an inefficient and unreliable method for obtaining these SWNTs (for more details see the book chapter attached in the appendices). To overcome these limitations and to obtain the metallic and semiconducting enriched SWNT sample, the post-production separation techniques are essentially important. This chapter of the thesis summarizes and highlights the main post-production techniques available to separate SWNTs, based on electronic structure, while also providing detailed information on the recent developments and progress of these post-production methods since August 2005.
Figure 1.1  Schematic diagrams showing the possible wrapping of the two-dimensional grapheme sheet into tubular form. The two basis vectors $a_1$, $a_2$ are shown. Folding of the (8,8), (8,0) and (10,-2) vectors lead to arm chair (a), zig-zag (b) and chiral (c) tubes respectively. (From Ref. [1].)
1.2 Techniques for Characterizing the Separated Nanotubes

The purpose of this section is to provide a brief overview of the key analytical techniques that differentiate between metallic and semiconducting SWNTs. Three main methodologies, optical absorption spectroscopy, Raman spectroscopy and bulk conductivity measurements using four point probes, are widely used to characterize the separated SWNT fractions. Both semiconducting and metallic SWNTs have characteristic optical absorption features in both the visible and near IR wavelength region (Figure 1.2). The peak feature at 1240-3100 nm (1-0.4 eV) and 620-1550 nm (2-0.8 eV) are commonly assigned to groups of transitions corresponding to the first and second pairs of van Hove singularities in the density of states (DOS) for various semiconducting SWNTs (denoted as $S_{11}$ and $S_{22}$), respectively, while those at 400-650 nm correspond to the first transitions of various metallic SWNTs (denoted as $M_{11}$). Observing changes of intensity changes of these absorption features in separation fractions under the controlled conditions of sample preparation is very useful way to obtain enrichment information of different samples (both qualitatively and quantitatively). Raman spectroscopy is also very useful for obtaining information on metallic and semiconducting SWNTs (Figure 1.3). In Raman measurements of SWNTs, the nanotube signals are resonantly enhanced when the excitation wavelength is close to the optical transitions (usually $S_{22}$, $S_{33}$, $M_{11}$).
Figure 1.2  Absorption spectra of films of purified HiPco tubes, purified laser tubes and purified arc tubes after baseline treatment. (From Ref. [10].)
Figure 1.3  Typical Raman spectra of HiPco, Laser and arc SWNTs excited at 1064 nm (1.17 eV). (From Ref. [10].)
Three main features in Raman for SWNTs provide most of the information: G band at ~1550-1600 cm\(^{-1}\) from vibrations of graphitic sp\(^2\) carbons, D band at ~1350 cm\(^{-1}\) from disordered sp\(^3\) carbons, and radial breathing mode at 100-300 cm\(^{-1}\) due to tubular carbon vibration in radial direction. The G band and RBM peaks under controlled experimental conditions are more useful for obtaining both qualitative and quantitative evaluations of metallic and semiconducting tubes. The electrical conductivity of separated SWNTs is commonly measured using the classical four-point probe technique. For these conductivity measurements, the samples are usually prepared either as pellets or bulky papers in similar experimental conditions to get an accurate comparison.\(^{17-20}\) In addition to these three methods other micro and macroscopic techniques such as NMR spectroscopy,\(^{21-23}\) fluorescence spectroscopy,\(^{11,12,24}\) transmission electron microscopy (TEM) and atomic force microscopy (AFM),\(^{25-33}\) have been used to characterize semiconducting vs. metallic SWNTs in given samples. Details of these characterization techniques are available in the separation book chapter attached in the appendices.

All the SWNT production methods provide various chiralities in structure. In most cases, the two-thirds of SWNT are semiconducting chiralities with the remaining one-third being metallic.\(^{34}\) The post synthesis techniques available to separate SWNT mixture into metallic and semiconducting enriched fractions fall into two main groups; methods developed based upon the physical properties of SWNTs and the methods developed based upon the chemical reactivity differences between metallic and semiconducting tubes.\(^{35-37}\)
1.3 A Summary of Advances to 2005

The post-production separation methodologies developed since August 2005 are based on either the different physical properties of semiconducting and metallic SWNTs, such as different conductive behavior and static polarizability, or the chemical reactivity of metallic and semiconducting SWNTs, such as preferential covalent and non-covalent functionalization. Of these post-production separation methods, some permit the collection of one type of SWNTs by physically destroying the other type, while other methods separate both semiconducting and metallic SWNTs into two fractions without destroying the electronic properties of both fractions. These advances in post-production separation methods available since August 2005 were outlined in our chapter published in 2006 on separation. This information is briefly summarized below.

The selective destruction of metallic SWNTs via current induced breakdown was one of the first methods used to produce a single metallicity type of nanotubes.\textsuperscript{38-39} In this method, metallic SWNTs are selectively destroyed to obtain pure semiconducting SWNTs for FET devices. Although the results of the selective breakdown method were promising for obtaining electronically pure semiconducting SWNTs, they were only applicable for very small samples of no more than a few picograms. The alternating current dielectrophoresis method is also another known technique for obtaining electronically pure semiconducting and metallic SWNTs.\textsuperscript{40-45} Here, SWNTs were suspended to their individual level using SDS in water. Within an AC electric field, metallic SWNTs have a positive dielectrophoresis (DEP) and semiconducting SWNTs also have a negative DEP, thusly permitting the placement of metallic tubes on electrodes.
while semiconducting tubes remain in the solution. Buik et al., repeating the same technique under similar experimental conditions, determined that both metallic and semiconducting tubes could be deposited on electrodes without requiring full selectivity. However, because these results were somewhat controversial, further exploration is obviously essential before this technique can be established as a method to separate SWNTs based on metallicity. Details of the post-production separations using the different physical properties of semiconducting and metallic SWNTs are available in the book chapter attached in the appendices.

DNA assisted separation, preferential covalent functionalization, preferential doping, amine based separation, and planar aromatic based separation are the main post-production separation techniques that depend upon the different chemical reactivity of semiconducting and metallic SWNTs. In the DNA assisted separation technique, SWNTs were individually suspended in water using SDS as a surfactant; separation was then performed using the anionic exchange chromatograph. The principle behind this separation technique is based upon the higher polarizibility of metallic SWNTs, instead of their semiconducting counterparts. However, the requirement that the starting materials be individually dispersed SWNTs renders this technique most challenging in the scale-up.

The second method, more specifically known as the preferential covalent functionalization method, uses the different chemical reactivity of two species of SWNTs (semiconducting and metallic SWNTs) which may also be useful for structural sorting. Metallic SWNTs were found to be more vulnerable than their semiconducting counter
parts to various covalent functionalization reactions, some of which led to an increase the concentration of semiconducting SWNTs resulting from the destruction of metallic ones. As Strano et al. discovered, when SWNTs suspended in SDS in D$_2$O were reacted with aryl diazonium reagents and observed in the optical absorption spectrum, the absorption features corresponding to the metallic-SWNTs selectively decayed, whereas the same optical absorption related to the semiconducting-SWNTs remained well preserved.$^7,48,50$ Therefore this method can be used to selectively destroy metallic SWNTs due to their high reactivity with diazonium reagents, while leaving the semiconducting SWNTs fully intact and well-preserved. Because this method permits the metallic SWNTs to retain a higher electron density in their Fermi levels than in the semiconducting SWNTs, more electrons are available in metallic tubes to stabilize the charge transfer complex. 

Selective bromination of metallic SWNTs were achieved by Rinzler and co-workers.$^{51,52}$ Initially, SWNTs were individually dispersed in water using SDS as a surfactant and then the bromination was performed. Their theoretical calculations suggest that the binding energies of bromine with metallic SWNTs were larger than those with semiconducting SWNTs.$^{51,52}$ The preferential doping of bromines on metallic SWNTs also provided a higher density for metallic SWNTs than their semiconducting counterparts. Using simple centrifugation, Rinzler et al. precipitated away the metallic SWNTs so that the semiconducting enriched fraction remained in the solution. The characterization performed using optical absorption spectroscopy, determined that the precipitate was indeed enriched with metallic SWNTs.
Several metallicity separation techniques for bulk samples (on the order of milligram to gram quantities) have also been explored.\textsuperscript{19,35,53-55} The common characteristic all of these methods share is that they are based on the selective noncovalent interactions between certain organic molecules and SWNTs.\textsuperscript{19} For example, Papadimitrakopoulos and coworkers discovered that the reaction of octadecylamine (ODA) with purified SWNTs under typical thermal reaction (zwitterions formation) conditions prefers semiconducting SWNTs over metallic SWNTs; this preference can be used to obtain samples enriched with either metallicity type.\textsuperscript{19} Later studies using the same functionalization reaction revealed that the ODA is highly selective toward smaller diameter SWNTs (~0.9 nm).\textsuperscript{54} Both the residue and supernatant fractions were characterized using the multiple wavelength Raman wavelength of 514 nm and 632 nm respectively. Quantitative calculations performed using the peaks in RBM region showed that semiconducting tubes with smaller diameters were functionalized out, leaving only the metallic SWNTs with similar diameters in the residue. Papadimitrakopoulos \textit{et al.} contend that both metallacity separation and diameter separation occur simultaneously. They also contend that while the reasons for this diameter dependence of metallicity separation are not currently understood, this diameter dependence may originate from either electronic amine-SWNT interactions or from curvature induced stabilization.

In similar work, Sun and co-workers reported that larger aromatic molecules such as tetra-substituted free-base porphyrin (5,10,15,20-tetrakis (hexadecyloxyphenyl)-21\textit{H},23\textit{H}-porphine, or THPP) were selective toward semiconducting SWNTs via noncovalent interactions, when the compound was sonicated with SWNTs in organic
solvents, resulting in enriched semiconducting nanotubes in the soluble fraction and enrich metallic nanotubes in the insoluble residue. In addition to THPP, other planar aromatic molecules such as derivatives of pyrene (for example 1-docosyloxymethyl-pyrene (DomP)) were also found to be effective in selectively solubilizing semiconducting SWNTs. Details of these chemical methods for separating SWNTs based on electronic structure are presented in the book chapter attached in the appendices.

1.4 Advances Since 2005

Selective destruction of either metallic or semiconducting SWNTs using external sources such as electric current is an established method for isolating one type of nanotube from another. However, there have only been two new selective destruction methods (hydro carbonation reaction and laser irradiation) developed since mid-2005, the results of which are discussed below. Zhang et al. reported selective etching of metallic SWNTs by hydro-carbonation reaction. Their studies revealed during the reaction all the smaller (both metallic and semiconducting SWNTs) and larger diameter metallic tubes were selectively destroyed, leaving only the larger diameter semiconducting tubes. Their process involved first heating the samples, contained in a medium of methane plasma, to 400 °C. Next, the sample was annealed in a vacuum and placed in a 4-inch quartz tube furnace equipped with a remote plasma system. Subsequent AFM characterization revealed that the smaller diameter SWNTs (d<1.4 nm) were completely destroyed. Regarding SWNTs with diameter ranges falling between 1.4 nm and 2 nm only metallic SWNTs were seen to be etched selectively, with only the semiconducting
tubes remaining. One particular observation concerning the limitations of this method was rather striking; this method was unable to destroy either the metallic or the semiconducting SWNTs if they possessed diameters greater than 2 nm. Consequently Zhang et al. concluded that the selective etching of metallic tubes is highly dependent upon the selection of the diameter of the nanotubes to be destroyed, and that nearly all tubes with smaller diameters, (d<1.4 nm), are completely destroyed.

Huang and co-workers reported that they were able to selectively destroy metallic SWNTs in carbon nanotube thin films using laser irradiation, thusly leaving behind their semiconducting counterparts (Figure 1.4). They irradiated samples using the micro-Raman system equipped with 514.5 nm (Ar+) and 632 nm (He-Ne) lasers (Jobin Yvon, Horiba, HR800). For this experiment, the power of the 514.5 nm laser was adjusted in the range of 0-100 mW while the 632.8 nm laser intensity was fixed at 20 mW. They performed their SWNT characterizations using multiple Raman excitation wavelengths of 514 nm and 632 nm. Subsequent results, showing the sample to be highly enriched with semiconducting SWNTs after laser irradiation indicates the process developed by Huang et al., is a direct and simple method with particular importance for use in constructing future FET devices.

In addition to these selective destruction methods, Smalley et. al. recently reported that they were able to generate SWNTs with diameter and surface orientation similar to the original short SWNT seed. Using a short SWNT seed several nanometers long for their template, they were able to produce individual SWNTs with average
Figure 1.4  Schematic drawing of carbon nanotubes exposed to laser irradiation. (From Ref. [58].)
Figure 1.5  The sequential steps of selective amplification of SWNTs starting from very short SWNT segment. (From Ref. [59].)
lengths of 6.7µm. This method is expected to result in the development of methods to generate electronically pure SWNTs with desired chirality (n, m). This procedure comprised three steps (Figure 1.5). In step one, the SWNTs were baked in hot moist air and extensively washed in hydrochloric acid to break the carbon shells around the metal catalyst (Fe) in HiPco tubes, and expose the Fe to dissolution in acid. The SWNTs were then excised into segments by using fluorine gas, followed by the H₂SO₄-H₂O₂ treatment to generate carboxylic acid groups. This procedure further removed the remaining Fe catalyst from shorten SWNTs. In step two, the shortened SWNTs were wrapped in pluronic F87 (MW=7700, BASF) polymer. In step three, the polymer SWNTs were mixed with polyethylene (PEI)-Fe(NO₃)₃ solutions and then grown using the Vapor Liquid Solid (VLS) method. In this process, Fe salts were used as the growth catalyst. The characterization performed using the AFM technique revealed that the templated VLS long growth SWNTs had diameter and surface orientations similar to their original short SWNT seed. Despite these strikingly gratifying results, the question remains if this method can indeed be used to amplify the original SWNT with same chirality (n, m). Despite these, this method has a potential to use it in near future to duplicate any desired chirality with high purity.

As with the relative few new methods for using the physical properties of SWNTs to isolate the electronically pure fractions, few new methods have been created, since August 2005, to separate SWNTs using the different chemical reactivity of metallic and
Figure 1.6  (a) UV-vis-NIR absorption spectra of the H$_2$O$_2$-treated SWNT thin films taken at different treatment times. (b) Raman spectra of the SWNTs before and after H$_2$O$_2$ treatment at 514 nm excitation and (c) is the same Raman comparison at 632 nm. (From Ref. [60].)
semiconducting tubes. Of these, one, as reported by Miyata et al, involves the selective oxidation of semiconducting SWNTs by hole doping using hydrogen peroxide ($\text{H}_2\text{O}_2$) as an oxidizing agent.\textsuperscript{60} The optical UV/vis/NIR absorption spectra (Figure 1.6)\textsuperscript{60} of SWNTs measured at different heating times in $\text{H}_2\text{O}_2$ and resonance Raman characterization at 514 nm and 632 nm excitations revealed that $\text{H}_2\text{O}_2$ oxidizes semiconducting SWNTs more favorably than metallic SWNTs (especially semiconducting SWNTs with smaller diameters). It is generally assumed that metallic SWNTs have a higher chemical reactivity than semiconducting SWNTs because of their higher electron density at the Fermi level. Mechanistically, Miyata et. al. suggests that $\text{H}_2\text{O}_2$ acts as a weak hole-dopant that selectively shifts the Fermi level to the first Van Hove Singularity band of semiconducting SWNTs. If the Fermi level shifts to the first Van Hove singularity band of semiconducting SWNTs through hole doping, then the electron density of semiconducting tubes is expected to be higher than the density observed for metallic tubes. Therefore, it is also expected that semiconducting SWNTs have a higher chemical reactivity in $\text{H}_2\text{O}_2$ than metallic SWNTs. After the $\text{H}_2\text{O}_2$ treatment, metallic SWNT concentration was found to be greater than 80 % based on their quantitative UV/vis/NIR absorption characterization.

In a another study using the physical properties of SWNTs to isolate the electronically pure fractions, Tour, Smalley and coworkers reported that some highly reactive species such as diazonium salts were preferentially added to the side walls of metallic SWNTs.\textsuperscript{7} Toyoda et al. also recently reported that diazonium salt, containing a long alkyl chain of 4-dodecyloxybenzenediazonium tetra fluoroborate, can be used to
functionalize metallic SWNTs selectively. Because these functionalized SWNTs are soluble in THF, metallic SWNTs can be extracted to THF leaving the insoluble semiconducting SWNTs in the residue. The Raman at 514 nm excitation wavelength and optical absorption studies showed the solution to be enriched with metallic tubes while the corresponding residue to be enriched with semiconducting tubes. Similar to the diazonium salts, An et al. also found that nitronium ions were selectively adsorbed on side wall of the metallic SWNTs with higher binding energies, forming a charge transfer complex between SWNT surface and nitronium ions. This selective adsorption was due to the higher availability of electron density at the Fermi level of the metallic SWNTs than within the semiconducting SWNTs. After this reaction, the semiconducting SWNTs remained intact while the metallic SWNTs were completely destroyed and removed, especially for those SWNTs with diameters of less than 1.1 nm. By using the simple filtration, the soluble carboneous species can be easily removed to recover the semiconducting SWNT enriched sample. The main limitation of this method was that the notronium ions destroyed only the smaller diameter metallic SWNTs, leaving behind both semiconducting SWNTs in all diameters and in the larger diameter metallic tubes (> 1.1 nm). An et al. also reported the selective removal of metallic SWNTs in a gas phase reaction using fluorine gas. The characterization results obtained at multiple wavelengths of 514 nm, 633 nm and 785 nm and UV/vis/NIR absorption spectroscopy (Figure 1.7) showed that the fluorine gas selectively destroyed the metallic SWNTs having smaller diameters (less than 1.1 nm) while the semiconducting SWNTs with the
Figure 1.7  Raman spectra at 514 nm excitation wavelength. RBM region before and after the fluorination (left) and the changes in G band (right). (From Ref. [61].)
Figure 1.8 Characterization of separated fractions using absorption (a) and Raman excitation wavelength at 514 nm (b). (From Ref. [64].)
same diameters are remained intact. Like the nitronium ion reaction this fluorine gas reaction method possessed the same inadequacy; only the smaller diameter metallic tubes were destroyed, leaving intact all semiconducting SWNTs with all diameters and all metallic SWNTs with larger diameters (d>1.1 nm).

Maeda et al. reported that bulk separation might be achieved through the use of smaller amine molecules such as octylamine, propylamine and iso-propylamine, which were found to be selective toward metallic SWNTs in organic solvents. After the reaction, the mixture was centrifuged at ~45000 g for 12 h to obtain the solution and final residue, the separated fractions were characterized using resonance Raman spectroscopy at multiple excitation wavelengths of 514 nm and 632 nm and UV/vis/NIR absorption spectroscopy (Figure 1.8). For the 514 nm excitation, smaller diameter metallic tubes and larger diameter semiconducting HiPco-SWNTs were in resonance. The Raman characterization results at this wavelength revealed that the smaller diameter metallic tubes were preferentially solubilized out to the supernatant fraction and that the final precipitate was enriched with larger diameter semiconducting tubes. For the 632 nm Raman excitation, the smaller diameter semiconducting tubes and larger diameter metallic tubes were both in resonance. The Raman results at this wavelength suggested that the supernatant was enriched with larger diameter metallic tubes. These multiple wavelength Raman results, at 514 nm and 632 nm, clearly showed the supernatant was enriched with metallic tubes (both the smaller and larger diameter metallic SWNT) and that the residue was enriched with semiconducting tubes with no observable diameter effect in their metallacity separation. The UV/vis /NIR absorption studies also showed
the high intensity $M_{11}$ peaks for supernatant fraction and weak intensity of same $M_{11}$ peak for residue fraction. These absorption comparison results also provided direct evidence that the supernatant was enriched with metallic tubes and the residue was enriched with semiconducting tubes. Maeda et al. also performed four point probe conductivity studies for the two separated fractions by developing them into bulky papers. The conductivity results showed the metallic SWNT enriched supernatant fraction possessed conductivity almost six times higher than that of the prepared SWNT samples.

The above results obtained by Maeda et al. for HiPco SWNTs is somewhat contradictory over the results obtained from ODA results by Papadimitrakopoulos and co-workers. Because ODA was found to be selective toward semiconducting SWNTs (especially those SWNTs with smaller diameters$^{54}$) the supernatant was enriched with semiconducting SWNTs and the residue was enriched with metallic SWNTs. However, Maeda et al. determined that shorter chain alkyl amines preferentially interact with metallic SWNTs with essentially effect on diameter. As previously stated, it is widely accepted that smaller diameter SWNTs were more reactive because of their smaller pyramadization angle and their $\pi$ orbital misalignment. Therefore, the reactivity of SWNTs with different polymers or organic molecules is mainly dependent upon the population balance between the smaller semiconducting SWNTs and the smaller metallic SWNTs in the starting nanotube sample. Thus, if the starting sample is populated with more smaller diameter semiconducting SWNTs than the sample for their metallic counterparts, the solution fraction eventually will be enriched with semiconducting
SWNTs upon functionalization, leaving behind the metallic tubes in residue, and *vice versa*.

In recent work, Mioskowski and co-workers recently reported that they were able to derive azomethine yelides from trialkylamine-N-oxide react with side walls of SWNTs in the presence of lithium diisopropylamide (LDA).\(^6^8\) This trialkylamine-N-oxide group also contained a polycyclic aromatic side chain, such as pyrene or antracene. Since the aromatic derivatives were \(\pi\) stacking to the nanotube surface, they observed this reaction was selectively functionalized out the semiconducting SWNTs, leaving behind their metallic SWNT counterparts in the precipitate.\(^6^8\) The Raman characterizations were performed at multiple excitation wavelengths of 514 nm and 632 nm. The G band and RBM comparisons of both excitation wavelengths showed the supernatant was enriched with semiconducting tubes and the residue was enriched with metallic tubes.

Arnold *et al.* reported their ability to sort carbon nanotubes according to their diameter, bandgap and electronic type, using density-gradient ultra speed centrifugation.\(^6^9\) For this separation reaction, SWNTs were dispersed using SDS via sonication followed by the ultracentrifugation at 64,000 rpm and 41,000 rpm for different time intervals. Upon centrifugation, the nanotubes formed discrete colored bands in the centrifuge tubes. Optical absorption studies showed that these discrete bands were due to SWNTs of different average diameters and different metallacity.\(^6^9\)
1.5 Limitations and Challenges

When the book chapter (attached in appendices) was written in August 2005, two main limitations were identified in the separation of SWNTs. Most of the separation methods available during that time could either only generate very small quantities of SWNT sample or their ability to engage in metallicity separation was hindered by diameter selectivity in the chemical reaction. In addition to these limitations, most of the reported post-production separation experiments were centered on HiPco SWNTs with only a few exceptions. It is widely accepted that the pyramidization and π-orbital misalignment contribute to the nanotube reactivity resulted from the curvature and thus with an inverse relationship with the nanotube diameter. Therefore, smaller diameter SWNTs are more reactive than larger diameter SWNTs. In other words, if the starting sample is populated with semiconducting SWNTs possessing smaller diameters than their metallic counterparts, their preferential solubilization obviously leaves more metallic nanotubes in the insoluble residue and vice versa. For example, octadecylamine (ODA) was found to be highly selective toward smaller diameter SWNTs (average diameter ~0.9 nm). The quantitative characterization results obtained, using the multiple excitation wavelength of 632 nm and 514 nm, clearly showed that the diameter selectivity controlled the metallacity separation.

However, despite these new innovations created since August 2005, there is as yet no ready solution to the vexing problems and limitations involved with the separation of SWNTs. These issues have yet to be addressed. For example, the hydrocarboration reaction completely destroyed the SWNTs with diameters of less than 1.4 nm and the
selective destruction of metallic tubes with laser irradiation is limited to nano gram quantities or less of the sample.\textsuperscript{58} Nitronium ion and fluorine gas were found to be selectively destroy smaller diameter metallic SWNTs (d<1.1 nm) leaving the larger diameter metallic and semiconducting SWNTs with all the diameters.\textsuperscript{62-64} Therefore, these methods are only applicable for the smaller diameter SWNT mixtures (d \sim 1.1 nm) which are difficult to find and are unsuitable to separate as opposed to SWNT samples from more commonly available arc discharge, HiPco or laser methods. In addition, other methods including the separation of SWNTs using smaller amine molecules,\textsuperscript{65-67} the separation of SWNTs using azomethine yelides\textsuperscript{68} and the separation of SWNTs using ultra high speed centrifugation,\textsuperscript{69} are far from being suitable applications for use in obtaining larger quantities of either metallic or semiconducting SWNTs.

Therefore, to achieve effective separation for samples in bulk quantities, highly selective (on metalacity and not on diameter) but less invasive techniques are obviously more desirable. In addition, final products should also be easily distinguishable using the simple characterization techniques. A careful consideration of these facts leads us to suggest that the separation technique developed based upon planar aromatic molecules is the most promising and simple method for obtaining large quantities of both metallic and semiconducting SWNTs.\textsuperscript{20} Since the interactions between SWNTs and aromatic molecules are non-covalent, by using a simple method (dialysis or solvent washing) the surface functionality of SWNTs can be easily removed to recover the separated fractions. Because of the simplicity of this separation method is efficient and the recovery of separated fractions (metallic and semiconducting tubes), this method can easily be scaled
up to achieve gram quantities of separated samples. Unlike most of the separation techniques described here which center on HiPco tubes, our separation technique performs non-covalent functionalization using arc SWNTs. Because arc produced SWNTs have narrow diameter distributions (~1.4 nm) over HiPco produced SWNTs (~0.7 nm to 1.3 nm), the interference of diameter selectivity during the metalacity separation is minimized by using arc tubes to achieve better separation based on semiconducting and metallic characteristics.
References


CHAPTER 2

SEPARATION OF SEMICONDUCTING AND METALLIC SWNTs

2.1 Separation of Semiconducting and Metallic SWNTs

Using Derivatized Porphyrin

Single-walled carbon nanotubes (SWNTs) produced via various techniques are generally mixtures of metallic (1/3) and semiconducting SWNTs (2/3). In the separation of semiconducting SWNTs from metallic SWNTs, our group previously used 5, 10, 15, 20-tetrakis (hexadecyloxyphenyl)-21H, 23H-porphyrin (THPP) as a functionalization agent. In typical experiment procedure, a purified SWNT sample (100 mg) was added to a solution of THPP in chloroform (10mg/ml, 20 ml) and the mixture was sonicated (Fisher scientific FS20, 70W, 42 KHz) for 48 h. Upon the sonication, the mixture was centrifuged at 1380 g for 15 minutes to obtain the residue and solution fraction. The residue from the first cycle was used as the starting material for the second cycle of separation reaction and the same procedure was repeated total of three times to complete the reaction. After the third cycle the reaction did not work. The three soluble fractions were combined. Since the interactions between SWNTs and aromatic molecules are non-covalent, using a simple method (dialysis followed by solvent washing the sample with acetic acid coupled with vigorous centrifugation) easily removes the surface functionality of SWNTs to recover the separated fractions. The characterization was performed for both soluble and residue fractions using optical absorption, Raman and bulk conductivity measurements, and the results showed that the soluble fraction was enriched with semiconducting SWNTs and the insoluble residue was enriched with metallic SWNTs. In
addition to THPP, other planar aromatic molecules such as derivatives of pyrene (for example 1-docosyloxyethyl-pyrene (DomP)) were also effective in selectively solubilizing semiconducting SWNTs and their affects on diminishing the optical absorption spectra, especially $S_{11}$ and $S_{22}$ absorption bands. Since the complexation is reversible, the characteristic bands can be turned on and off with the complexation in a reversible fashion. This reversible diminishing of semiconducting band gap transition is discussed in section 2.2.

Similar to THPP, the derivative of pyrene (DomP) selectively interact with and solubilize semiconducting SWNTs from the starting purified nanotube, leaving metallic SWNTs in residue. Since the DomP is readily prepared and largely recoverable from the extraction experiment, the separation of SWNTs using DomP may be an effective and convenient method for the separation of semiconducting SWNTs from metallic SWNTs. The details of the experimental procedure of the separation of SWNTs by using DomP and the mechanistic implications of this reaction were extensively studied and are discussed in section 2.3.
References


2.2 Diminished Band-Gap Transitions of Single-Walled Carbon Nanotubes in Complexation with Aromatic Molecules

2.2.1 Introduction

The electronic and optical properties of single-walled carbon nanotubes (SWNTs) have been investigated by many research groups.\textsuperscript{1-5} It is now well-established that the electronic structures of semiconducting SWNTs are characterized by several pairs of van Hove singularities in the electronic density of states.\textsuperscript{3,4} Transitions associated with the first (S\textsubscript{11}) and second (S\textsubscript{22}) singularity pairs are widely observed in absorption spectra of SWNT samples produced by various methods and thus of different diameters and diameter distributions.\textsuperscript{4,5} It has also been reported that the doping of SWNT surface could have a significant effect on the S\textsubscript{11} absorption,\textsuperscript{4,6-8} and more dramatically that the surface modification via chemical functionalization could effectively eliminate the S\textsubscript{11} and S\textsubscript{22} absorption bands.\textsuperscript{9} The latter was attributed to significant perturbations in the electronic structure by the surface modification and a disruption to the extended π-network of the nanotube.\textsuperscript{9} We report here that similarly significant effect on the van Hove singularity pairs can be caused by non-covalent complexation of the nanotube with planar aromatic molecules such as pyrenes in solution, resulting in the absence of S\textsubscript{11} and S\textsubscript{22} bands in the near-IR absorption spectrum. Since the complexation is reversible, the characteristic absorption bands can be turned on and off with the complexation in a reversible fashion.

The attachment of pyrene and other aromatic species to the carbon nanotube surface via non-covalent interactions ("π-π stacking") has already been reported in the
Similar in previous chapter, we used pyrene derivative with a long alkyl tail, 1-docosyloxymethyl-pyrene (DomP), for the solubilization of SWNTs via non-covalent interactions.

2.2.2 Experimental Section

2.2.2.1 Materials

1-Bromodocosane, 1-pyrenemethanol, 9-Antracenemethanol and sodium hydride (NaH) were purchased from Aldrich. THF, CHCl₃ and hexane were purchased from Burdick and Jackson. THF was dried over molecular sieves and then distilled over sodium before use. Other solvents either were of spectrophotometry /HPLC grade or were purified via simple distillation. The SWNT sample was produced in Professor A. M. Rao’s laboratory (Physics Department, Clemson University) by using the arc discharge method. It was purified by oxidative acid treatment according to an established procedure.

2.2.2.2 1-Docosyloxymethyl pyrene (DomP)

1-Pyrenemethanol (1.2 g, 5.2 mmol) was refluxed with 1-bromodocosane (2.3 g, 5.9 mmol) in the presence of NaH (1.5 g) in dry THF (150 mL) for 48 h. The crude product was purified on a silica gel column using hexane as eluent. Final product was obtained as a light yellow solid (70% yield). ¹H-NMR (CDCl₃, 500 MHz) δ 8.38 (d, 1H, J = 9.1 Hz), 8.21-8.11 (m, 4H), 8.07-7.98 (m, 4H), 5.21 (s, 2H), 3.61-3.59 (t, 2H, J = 6.4 Hz), 1.69-1.63 (m, 2H), 1.38-1.35 (m, 2H), 1.29-1.20 (broad, 36H), 0.89-0.86 (t, 3H, J =
6.4 Hz). $^{13}$C-NMR (CDCl$_3$, 125 MHz) δ 131.9, 131.4, 131.3, 130.9, 129.4, 127.7, 127.5, 127.4, 127.0, 126.0, 125.2, 125.0, 124.8, 124.6, 123.6, 71.6, 70.7, 32.0, 29.8, 29.8, 29.7, 29.5, 29.5, 26.3, 22.8, 14.2. MALDI-TOF: (m/z) = 540 (M$^+$.)

2.2.2.3 9-Docosyloxymethyl-antracene (DomA)

9-Antracenemethanol (1g, 4.8 mmol) was refluxed with bromodocosane (1.8g, 4.8 mmol) in the presence of NaH (1 g) in dry THF (150 ml) for 48 h. The crude product was purified on a silica gel column using hexane: chloroform (9:1). Then hexane: chloroform (7:3) was used as eluent to recover the final product with light yellow color. $^1$H-NMR (CDCl$_3$, 500 MHz) * 8.43 (s, 1H), 8.37 (d, 2H, J= 8.25 Hz), 7.99 (d, 2H, J= 8.75 Hz), 7.53-7.50 (m, 2H), 7.46-7.42 (m, 2H), 5.43 (s, 2H), 3.66- 3.64 (t, 2H, J= 6.4), 1.65-1.59 (m, 2H), 1.33-1.14 (broad, 38H), 0.87-0.84 (t, 3H, J=6.85). $^{13}$C-NMR (CDCl$_3$, 125MHz) * 131.55, 131.10, 129.06, 128.30, 126.14, 124.99, 124.52, 70.90, 65.07, 32.00, 29.95, 29.81, 29.50, 26.30, 22.80,14.20. MALDI-TOF: (m/z) = 516 (M$^+$.).

2.2.2.4 Measurements

UV/vis/near-IR absorption spectra were recorded on Shimadzu UV3100 and Thermo-Nicolet Nexus 670 FT-NIR spectrometers. Raman spectra were obtained on a Renishaw Raman spectrometer equipped with a 50 mW diode laser source for 785 nm excitation and a CCD detector. Thermo gravimetric analysis (TGA) was carried out on a Mettler-Toledo TGA/SDTA851e system. Transmission electron microscopy was conducted on Hitachi HD-2000 STEM and Hitachi HF-2000 TEM systems with digital
imaging capabilities. Sonication was done using fisher scientific FS 20, 70 W, 42 KHz. The centrifugation was carried out with using Fisher scientific centricfic model 228 and Eppendorf centrifuge 5417R.

2.2.2.5 Carbon Nanotube Functionalization

In the functionalization of SWNTs with DomP, a purified SWNT sample (150 mg)\(^{23}\) was added to a THF solution of DomP (10 mg/mL, 30 mL). The mixture was sonicated for 24 h, followed by centrifuging at 1380 g for 20 min. The solid residue was used as the starting material to undergo another round of sonication-centrifuging under the same experimental conditions. The solution in THF thus obtained was centrifuged at a higher speed (25,000 g) for 3 h. The apparently homogeneous supernatant contained an equivalent of about 22 mg SWNTs, namely that the non-covalent SWNT-DomP interactions kept about 15% of the starting SWNT sample in solution without precipitation even in such a strong centrifuging field (25,000 g).

2.2.3 Results and Discussion

The supernatant containing the solubilized SWNTs and the entire DomP sample was used to prepare specimen for Raman spectroscopy (785 nm excitation), scanning transmission electron microscopy (STEM, Hitachi HD-2000) and transmission electron microscopy (TEM, Hitachi HF-2000) characterizations. The Raman results are typical of SWNTs (Figure 2.2.1), and the STEM and TEM images exhibit composite-like
Figure 2.2.1. Raman spectrum (785 nm excitation) of the DomP-SWNT sample after dialysis
morphology with clear evidence for the substantial presence of exfoliated SWNTs (Figure 2.2.2 and 2.2.3).

The THF solution of the DomP-solubilized SWNTs in the presence of DomP was used in absorption measurements. The nanotube equivalent concentration in the solution was 0.7 mg/mL, with the DomP concentration of 8.8 mg/mL. While the nanotube equivalent concentration was relatively high, there were no $S_{11}$ and $S_{22}$ bands in the observed vis/near-IR absorption spectrum (Figure 2.2.4). The same solution was dropped onto a glass slide to evaporate off the solvent THF. The absorption spectrum of the sample (SWNTs with DomP) in the solid state also exhibited no $S_{11}$ and $S_{22}$ bands (Figure 2.2.5). On the other hand, the deposition of an equivalent amount of purified SWNT sample without DomP on the same substrate allows ready observation of the characteristic $S_{11}$ and $S_{22}$ transitions at 1,850 nm and 1,030 nm, respectively.

The absence of the $S_{11}$ and $S_{22}$ absorption bands for SWNTs in the solution with DomP may be attributed to effects associated with the complexation of the nanotube with DomP species, which is responsible for the nanotube solubilization. Such complexation is likely based on the non-covalent attachment of the planar pyrene moiety in DomP to the nanotube surface$^{10,11}$ and thus reversible under different experimental conditions. In order to remove the attached DomP species from the nanotube surface, the solution of SWNTs with DomP was treated in two different ways. One was to transfer the solution into a polyvinylidene fluoride (PVDF) membrane tubing (cutoff molecular weight ~ 250,000, Spectrum Laboratories) for dialysis against THF until the disappearance of the characteristic pyrene absorption peaks at 330-350 nm. As a result of the DomP removal
Figure 2.2.2. STEM image (acquired in the SE mode) of the DomP-solubilized SWNT sample.
Figure 2.2.3. HR-TEM images of the DomP-SWNT sample showing individual nanotubes and thin-bundles.
Figure 2.2.4. Absorption spectra of the DomP-solubilized SWNTs sample in THF (----) and in D$_2$O/SDS suspension after the removal of DomP via dialysis.
Figure 2.2.5. The NIR absorption spectra of the sample in the solid state before (----) and after (——) the removal of DomP.
in the dialysis, most of the nanotubes precipitated out of the solution. The other way was to reflux the SWNT-DomP sample with cyclohexane for 12 h, followed by repeated cycles of cyclohexane washing - vigorous centrifuging. The solid residue contained primarily the recovered nanotubes according to thermogravimetric analysis. Both treatments were purposely designed to be under relatively mild experimental conditions so as not to invoke any processes for defunctionalizing covalently attached species. The successful removal of DomP from the nanotube in both treatments lends strong support to the conclusion that the complexation is non-covalent in nature. As expected, the recovered SWNTs exhibit the characteristic $S_{11}$ and $S_{22}$ absorption bands (Figure 2.2.4 and 2.2.5). These results suggest that the diminished band-gap transitions of semiconducting SWNTs are due to the non-covalent complexation and that the effect on the transitions is reversible in accordance with the reversibility of the complexation.

It is known in the literature that the doping of SWNT surface could have significant effect on the $S_{11}$ absorption band, resulting in a reduction or even elimination in absorptivity, but much less effect on the $S_{22}$ absorption band because of the higher energy.\(^8\) So far, an elimination of both $S_{11}$ and $S_{22}$ absorption bands can only be achieved via covalent chemical modification of the SWNT sidewalls.\(^9\) Thus, it is often suggested that the solubilization of SWNTs by non-covalent techniques, such as those based on interactions with aromatic species, better preserves the nanotube electronic structures. What reported here represents the first experimental demonstration that the non-covalent complexation of a semiconducting SWNT with aromatic molecules can also affect the nanotube electronic structures and the associated optical transitions in a dramatic fashion.
In addition to DomP, the planar aromatic molecules such as a tetra-substituted free-base porphyrin$^{15}$ (THPP) which we previously reported for similar selective interactions with semiconducting SWNTs, could also reversibly diminish SWNT band-gap transitions under similar conditions (not shown). However, our further experiments using different planar aromatic systems showed, such interactions might not be universal for all aromatic molecules. For example, an antracene analog of DomP, 1-docosyloxymethyl-antracene (DomA), failed to solubilize any SWNTs in THF and no absorption diminishment was found. This may be the interactions between DomA and SWNTs were too weak or in some unfavorable structural conjugation configurations to solubilize any nanotubes even if there were some selectivity at the given conditions.

“π-π stacking” has been a common description for the interactions between the two π-electron systems of aromatic molecules and the graphitic surface of carbon nanotubes.$^{10-22}$ While the mechanism for diminishing effect is not clear, we suspect that the SWNT-DomP complexation via non-covalent interactions probably changes the nanotube electronic density of states. Conceptually, a complex in which a SWNT is non-covalently covered by a layer of planar aromatic moieties (Scheme 2.2.1)$^{25}$ may be viewed as a highly defective double-walled carbon nanotube (DWNT), so that the electronic density of states may be significantly different from that in the naked SWNT. In fact, theoretical calculations have shown that in a DWNT the electronic structure of the inner (semiconducting) tube is strongly perturbed by the external layer, with energy gaps vanishing as a result from the overlap of the conductance and valence bands.$^{24}$
Scheme 2.2.1. A schematic representation of a semiconducting SWNT covered with a DomP monolayer, which is conceptually similar to highly defective double wall carbon nanotubes. (From Ref. [25].)
Recent reports based on calculations and transistor device measurements suggested the presence of charge transfer effects in a SWNT adsorbed with small aromatic molecules.\textsuperscript{26,27} The results presented here demonstrate that the electronic properties of SWNTs are indeed vulnerable to effects of planar aromatic moieties in a relatively strong and non-invasive fashion. Thus, there might be opportunities to manipulate or even control such properties for specific applications.
References


23. SWNT samples were produced via conventional arc-discharge method and purified by refluxing in nitric acid (2.6 M) for 48 h.


2.3 Separation of Semiconducting and Metallic Single-Walled Carbon Nanotubes Using 1-docosyloxyethyl pyrene (DomP)

2.3.1 Introduction.

Single-walled carbon nanotubes (SWNTs) are of various chiralities in structure; statistically two-thirds are semiconducting while the rest remain metallic often due to mere structural differences.\(^1,2\) The excellent mechanical properties and the one-dimensional structure of SWNTs make them attractive candidates for use in various applications. However, while many of these applications require only metallic or semiconducting SWNTs, currently available as-produced SWNT samples are always a mixture, making the availability of one nanotube metallicity type (i.e. metallic vs. semiconducting) of paramount importance.

Despite some recent progress in the preferential production of certain metallicity or chirality types\(^3,4\) sorting nanotubes in the post-production is perhaps a more tangible topic, partially because metallic and semiconducting SWNTs were found to have many different chemical and physical properties which may be utilized in the structural sorting. For example, metallic SWNTs were found to be more vulnerable than their semiconducting counterparts to various covalent functionalization reactions,\(^5,6\) some of which had led to the concentration of semiconducting SWNTs by destroying metallic ones.\(^7-9\) Separations to obtain both metallicity types have been explored using dielectrophoresis of surfactant-dispersed SWNTs and anionic exchange chromatography of DNA-wrapped SWNTs in aqueous environments.\(^10-12\) The principle for these
separation techniques is based on the higher polarizibility of metallic SWNTs. However, individually dispersed SWNTs are required as starting materials, making the relevant scale-up rather challenging. Several metallicity separation techniques for bulk samples (on the order of milligram to gram quantities) have also been explored. One common characteristics for most of these methods is that they are based on the selective noncovalent interactions between certain organic molecules and SWNTs. For example, Papadimitrakopoulos and coworkers found that the reaction of octadecylamine with purified SWNTs under typical thermal reaction (zwitterion formation) conditions is preferential toward semiconducting SWNTs over metallic ones (and also toward smaller diameter nanotubes), which could be used to obtain samples that are enriched with either metallicity type. Maeda et al. reported that the bulk separation might be achieved by using some smaller amine molecules (e.g. octylamine and propylamine), which were found to be selective toward metallic SWNTs in organic solvents.

We previously reported that a tetra-substituted free-base porphyrin (5,10,15,20-tetrakis (hexadecyloxyphenyl)-21H,23H-porphine, or THPP) is selective toward semiconducting SWNTs via noncovalent interactions when the compound was sonicated with SWNTs in organic solvents, leading to enriched semiconducting nanotubes in the soluble fraction and enrich metallic ones in the insoluble residue. More recently, we found peculiar interactions occurring between SWNTs and other large aromatic molecules, such as a pyrene-containing molecule with a long alkyl chain (1-docosyloxyethyl pyrene, or DomP), that diminished the SWNT band-gap transitions upon noncovalent conjugation while the mechanistic details are yet to be understood (see
Here we report that DomP, similar to THPP, is also selective toward semiconducting SWNTs. The preferential solubilization of semiconducting SWNTs makes it possible to separate/enrich the two metallicity types in bulk quantity. The outcome of metallicity separation is supported by comprehensive studies including optical absorption spectroscopy, Raman, and conductivity studies of bulk samples. The SWNT metallicity selectivities of DomP and THPP also likely share a similar mechanistic origin.

2.3.2 Experimental Section

2.3.2.1 Materials

Tetrahydrofuran (THF) and dimethyl formamide (DMF) were obtained from Mallinckrodt and distilled before use over sodium and calcium hydride, respectively. Dialysis tubing (PVDF membrane) with molecular weight cutoff-250,000 was purchased from Spectrum Laboratories, Inc. and Sigma Aldrich, respectively. The SWNT sample (from arc-discharge) was purchased from Carbon Solutions, Inc. and purified by a combination of thermal oxidation and oxidative acid treatments as reported previously. Briefly, the as-received sample (1 g) was heated in a furnace to 300 °C in air for 30 min and then refluxed in diluted nitric acid (2.6 M, 500 mL) for 48 h. The solid was collected via simple centrifugation at 1380 g and it was repeatedly washed with deionized water till the supernatant was neutral pH. The residue was dried using rotary evaporation and then the collected SWNT sample was kept overnight in a vacuum oven.
prior to use in the separation reaction (330 mg). DomP was synthesized using the same procedure as described earlier.\textsuperscript{17}

2.3.2.3 DomP-Assisted SWNT Separation

In a typical experiment (Scheme 2.3.1 and 2.3.2), a purified SWNT sample (150 mg) was added to a solution of DomP in dry THF (10 mg/mL, 60 mL). The mixture was homogenized (Fisher Scientific Power Gen 125) for 1 h and sonicated (VWR Model 250D) for 24 h. The reaction mixture was then centrifuged at 1,380 g for 1-2 min to separate dark-colored supernatant from insoluble solid. The solid was then subject to another two rounds of reaction with DomP. The supernatant solutions were combined as the soluble fraction while the remaining residue was collected as the insoluble fraction (59 mg).

2.3.2.4 Measurements

UV/vis/NIR absorption spectrum was recorded on a Shimadzu UV3600 spectrophotometer. Raman spectra were obtained on a Renishaw Raman spectrometer equipped with a 50 mW diode laser source for 785 nm excitation and Jobin Yvon T64000 Raman spectrometer equipped with a triple monochromator, a research grade Olympus BX-41 microscope, a liquid nitrogen-cooled symphony detector, and excitation source of a melles-Griot 35 mW He:Ne laser at 632 nm. Thermogravimetric analysis (TGA) experiments were performed on a Mettler-Toledo TGA/SDTA851e system or a TA Instrument TGA Q500 analyzer. Two centrifuge machines were used: for low-speed
Scheme 2.3.1. A schematic illustration for the selective interactions of pyrene with semiconducting SWNTs.

1-Docosyloxymethyl pyrene (DomP)
Arc produced SWNTs

Refluxing in 2.6M HNO₃ for 48 h

Dispersion of 150 mg SWNTs in dry THF solution

Addition of 300 mg of DomP and homogenization for 30 minutes

Sonication for 24 h

Centrifugation at 1380 g for 1-2 minutes

Residue

Supernatant

For 2nd and 3rd Cycles

Scheme 2.3.2. Separation reaction of SWNTs with DomP.
centrifugation (the Fisher Scientific, centric model 228) and for high-speed centrifugation (the Beckman-Coulter Optima L90K ultracentrifuge with a type 90 Ti fixed-angle rotor). Scanning electron microscopy (SEM) images were obtained on a Hitachi S4700 field emission system. Current-voltage ($I-V$) relationships of the nanotube “bucky paper” samples were measured using traditional four point probe technique with Keithley 2400 multimeter controlled by Lab Tracer 2.0 software (Keithley Instruments, Inc.). Electrical conductivity values were calculated according to $\sigma = [(\pi/\ln2)\cdot(I/V)]/t$, where $t$ is the specimen thickness.

2.3.3 Results

2.3.3.1 Separation Reaction

The separation of the purified arc SWNT samples was achieved via three sequentially repeated functionalization reactions using DomP under the same sonication conditions (Scheme 2.3.1 and 2.3.2). From each round of the reaction, a soluble fraction was obtained from extraction of the reaction mixture with THF, while the insoluble fraction was used as the starting material for the next round until the completion of three cycles. Upon the completion of three cycles, the fourth cycle was also attempted and no SWNTs were solubilized out. The solutions of all three solution fractions were colored, serving as visual indication for the presence of carbon nanotubes; they remained stable only for short period of time (0.5-1h) before they were precipitated down. The three solution fractions were combined and denoted as “solution” and the final residue after three cycles of separated reaction was denoted as “residue”. The next step involved the
removal of DomP from SWNT surface to recover SWNTs from solution and residue fractions as well as recovering DomP.

For this purpose we used the two step “soft” removal technique. In the first step both the solution and residue from the DomP-SWNT reaction were subjected to dialysis against chloroform for 3 days by using a PVDF membrane (molecular weight cutoff 250,000). Before dialysis more than 90 % of DomP and less than 10 % of SWNT was present in the solution sample according to the TGA analysis (25 °C to 800 °C at 10 °C/minute in N₂) (Figure 2.3.1). Compared to the solution, the residue contained less DomP (34 % DomP and 66% SWNTs) according to same TGA analysis. Although the residue contained less DomP than solution, the dialysis was first performed to remove most of the DomP from the nanotube surface. The TGA analysis, performed under the same conditions, showed that most of the DomP was removed from SWNT surface. Only 10-15% and 5-6 % was left after the dialysis in solution and residue, respectively. In order to remove all the DomP from the SWNT surface, the precipitants were collected and refluxed thoroughly with CHCl₃ overnight. The recovered final samples of solution and residue after the solvent washing showed no meaningful weight loss (<3 %) up to 400 °C under inert atmosphere in TGA (figure 2.3.1). In addition to this two step soft removal method, as confirmed by TGA studies, thermal annealing at 600-800 °C in inert atmosphere completely removed DomP from the SWNT samples. As shown in the SEM images in figure 2.3.2, SWNTs from both soluble and insoluble fractions after such thermal treatment appear similar with little observable organic coatings.
Figure 2.3.1  TGA traces (N$_2$, 10 °C/min) of the solution (—), residue (—) before DomP is removed and the solution (---) and residue (---) after the DomP is removed by dialysis followed by refluxing with CHCl$_3$. 
Figure 2.3.2 SEM images of purified SWNTs (a), solution fraction (b) and final residue (c) after the dialysis and solvent washing to remove DomP.
The separation reaction was started with 150 mg of purified arc-SWNTs mixing with 300 mg of DomP. The same reaction was continued for two more cycles (300 mg of DomP was used in each cycle) using the residue as the starting material from the previous cycle. The weight of the solution fractions, before the DomP was removed by dialysis and refluxing in CHCl₃, were 333 mg, 301 mg and 306 mg for fraction 1, fraction 2 and fraction 3, respectively, and the weight of the final residue was 79 mg. Thermal defunctionalization via TGA at 10 °C/ min in nitrogen atmosphere was used to obtain the nanotube content in each sample to assess the total solubilization yield. According to TGA analysis, the SWNT equivalent content in three solution fractions were approximately 55 mg, 24 mg and 12 mg, respectively, (total of 91 mg). The nanotube content in residue should be ~ 59 mg according to the weight balance (the separation reaction was started with 150 mg). Similar to the solution fractions, the same TGA analysis was performed for the residue fraction and the results showed ~ 52 mg of SWNTs within. Therefore, the total of 98 mg should be functionalized into the solution fractions according to the weight balance. These data clearly suggested the three cycles of repeated functionalization reaction separated approximately 91-98 mg (~ 2/3) of the starting SWNT sample into the solution leaving behind 59-52 mg (~) 1/3 of SWNTs in the final residue.
2.3.3.2 Re-use of DomP

The DomP recovered after the two-step soft removal method (dialysis followed by solvent washing) showed little difference in the DomP structure before and after the separation reaction. The recovered DomP sample was analyzed using UV/vis spectroscopy (Figure 2.3.3a) and NMR (Figure 2.3.3b), and the optical absorption studies showed more than 90% DomP could be recovered after the separation reaction. The NMR analysis also showed little meaningful differences among all the characteristic peaks related to DomP for recovered samples. In the investigation of reactivity, a separation reaction was performed using recovered DomP subsequent to washing with hexane: chloroform (1:1).

Similar to the previous separation reaction, 150 mg of purified SWNTs was mixed with 300 mg of recovered DomP and the mixture was sonicated for 24 h followed by centrifugation for 1 minute at 1380 g to separate the solution and the residue fractions. Similar to the previous separation reaction, this reaction was continued for two more cycles using the residue from the previous cycle as starting material to obtain the second and third solution fractions and the final residue. The dialysis was performed for solution fractions and final residue to remove the DomP. Subsequent to the dialysis, the solution and residue fractions were washed by refluxing overnight in CHCl₃. The results showed that the three cycles of repeated functionalization reaction using recovered DomP separated approximately 95 mg of the starting SWNT sample into the solution leaving a residue of 55 mg of SWNTs. This weight ratio is comparable with the same weight ratio obtained for the separation reaction performed using the “as synthesized” DomP.
Figure 2.3.3  (a) The absorption of as synthesized DomP (blue) according to standard procedure and the recovered DomP (red) after the separation. (b) NMR spectra of as synthesized (bottom/blue) and recovered (top/red) DomP.
2.3.3.3 Bulk Conductivity.

The specimens in the form of “bucky paper” of comparable thicknesses (~45 µm) were used for bulk conductivity measurements, and these papers were prepared using a procedure already reported in literature.\textsuperscript{20,21} In the specimen fabrication, a homogenized DMF suspension of a given nanotube sample (0.6 mg/mL, 20 mL) was filtered through a PVDF membrane (Whatman, 0.45 µm, 47 mm diameter). The thin layer of bucky paper formed on the membrane was then subsequently peeled away. The bucky paper was vacuum-dried at 40 °C for 12 h and then annealed at 600 °C for 2 h before the measurements. The voltage-current relationships for the specimens were measured using the traditional four-point probe method (Figure 2.3.4). The conductivity values for residue, purified tubes and solution fraction were 53.9, 17.9, and 10.4 S/cm, respectively.

2.3.3.4 Raman Characterization

The Raman measurements were performed at multiple excitation wavelengths of 785 nm (1.58 eV), and 632 nm (1.96 eV). In order to avoid the known luminescence interferences, the soluble fraction, residue fraction and purified SWNTs were annealed at 800 °C for 30 minutes before Raman characterization was performed. The Raman spectrum of the starting purified SWNT sample at 785 nm and 632 nm excitation exhibits typical Raman features: G-band at ~1592 cm\textsuperscript{-1}, D-band at ~1330 cm\textsuperscript{-1}, and RBM feature groups in the range of 20-200 cm\textsuperscript{-1}.

As shown in figure 2.3.5, the G-bands from residue SWNTs at both excitation wavelengths exhibited significant BWF components, which is lacking in the spectra of
Figure 2.3.4 I-V curves for residue fraction (red), purified SWNTs (black) and solution fraction (blue) in bulky papers made with thickness of ~ 45 µm.
Figure 2.3.5  Raman G bands with 785 nm (a) and 632 nm (b) excitation wavelengths are compared for the starting purified sample (black), residue fraction (red) and solution fraction (blue). All the fractions were annealed at 800 °C for 30 minutes before measurements.
solution SWNT. The G-band shape from starting purified SWNTs appeared largely in between. Since large and small diameter metallic SWNTs were excited at 785 nm and 632 nm, respectively, these observations strongly support that the metallic SWNTs of all diameters become enriched over semiconducting ones in residue SWNTs while being depleted from solution SWNTs.

As shown in figure 2.3.6, for both excitation wavelengths of 785 nm and 632 nm, the radial breathing modes (RBM) of residue fraction showed higher intensity than those in the solution fraction while the RBM of starting purified SWNTs appeared largely in-between. As noted above, large and small diameter metallic SWNTs were excited at 785 nm and 632 nm, respectively. Therefore, these RBM comparison results also show that metallic SWNTs of all diameters are enriched in residue while the solution is enriched with semiconducting SWNTs of all diameters.

### 2.3.3.5 Optical Absorption

In the specimen preparations for optical absorption studies, the non-covalently attached DomP was removed from the SWNT surface by using the same soft removal method described in the previous section. The specimen preparation procedure was essentially the same for both the solution and residue SWNTs. In a typical experiment, a nanotube sample was dispersed into DMF (to ~0.5 mg/mL) and spray-coated onto a glass slide to form a thin, transparent, and homogeneous layer. To ensure the complete removal of the residual attached DomP molecules and other possible dopants, the specimen was further annealed at 600 °C for 2 h in inert atmosphere before the measurements.
Figure 2.3.6  Raman RBM regions with 785 nm (a) and 632 nm (b) excitation wavelengths are compared for the starting purified sample (black), residue fraction (red) and solution fraction (blue). All the fractions were annealed at 800 °C for 30 minutes before measurements.
The two prominent peak features centered at ~1,800 nm (or ~0.7 eV) and ~1,000 nm (or ~1.2 eV) have been commonly attributed to the electronic transitions between the first and second pairs of van Hove singularities (vHs) in the density of states (DOS) of semiconducting SWNTs (known as S\textsubscript{11} and S\textsubscript{22}), respectively\textsuperscript{5,10,11,22-24}. Another peak feature centered at ~700 nm (or ~1.8 eV) has been considered to consist of the transitions between the first vHs pairs of metallic SWNTs (known as M\textsubscript{11})\textsuperscript{5,10,11,22-24}. As shown in figure 2.3.7, the optical absorption spectra for both solution fraction and residue fraction exhibited all the characteristic SWNT features, including S\textsubscript{11}, S\textsubscript{22} and M\textsubscript{11}. However, the signal intensities from these two specimens significantly differ. In particular, while the M\textsubscript{11} intensity for solution fraction is somewhat lower than that for residue fraction, the S\textsubscript{11} and S\textsubscript{22} peaks of the solution fraction are much more intensive than those in the residue fraction. Even though the intensity of S\textsubscript{11} and S\textsubscript{22} between solution fraction and residue fraction showed a clear difference (solution fraction has much higher intensity) the peak intensities of M\textsubscript{11} does not show a significant difference between two fractions, as one might expect. This might be because of the overlap of M\textsubscript{11} peak with S\textsubscript{33} peak and this issue is further explained in the last paragraph of the results section.

2.3.3.6 Evaluation of the Enrichment

For our separated SWNT samples, the enrichment calculation was performed using the comparison of S\textsubscript{11} peak areas of the purified, solution and residue fractions. Because the S\textsubscript{11} intensity may be more vulnerable to various environmental factors (such as the presence of dopants) the films were annealed at 600 °C for two hours to remove
Figure 2.3.7 UV/vis/near-IR absorption spectra of the starting material (black), final residue (red) and the solution fraction (blue) on glass slides. All three glass slides were annealed at 600 °C for 2 h in inert atmosphere before measurements.
any doping effect prior to performing the absorption studies. It is widely accepted that the ratio of metallic to semiconducting in arc produced SWNTs is 1:2\(^1\). Therefore, we assumed in the calculation that the purified SWNTs encompass 66.6 \% of semiconducting SWNTs and 33.3 \% of metallic SWNTs.

The exact location of baseline is unclear when the area of S\(_{11}\) peak is calculated with different fractions. Therefore two arbitrary baselines were selected as shown in figure 2.3.7 to determine the areas of the S\(_{11}\) peak. The calculations were performed for five different batches with two different baselines. The results showed that the solution fraction was enriched with 92-98\% of semiconducting tubes and 2-8\% of metallic tubes. The same enrichment calculations also showed that the residue fraction was enriched with 82-87 \% of metallic tubes and 13-18 \% of semiconducting tubes.

2.3.3.7 Interference of M\(_{11}\) Peak by S\(_{33}\) Peak

In the investigation of the absorption feature at 600-800 nm (interference of M\(_{11}\) peak with S\(_{33}\)) we analyzed empirical Kataura plots in the literature, especially in the work published by Weisman and coworkers using Contour plots of band gap fluorescence and absorption spectroscopy to measure the energy of each peak (S\(_{11}\), S\(_{22}\) and S\(_{33}\)) vs. diameter.\(^{23,24}\) In addition to above-mentioned work, we analyzed the similar work of empirical Kataura plots and energy of band gap transitions (S\(_{11}\), S\(_{22}\), M\(_{11}\) and S\(_{33}\)) vs. the diameter of SWNTs with using optical absorption studies published by other groups.\(^{22-26}\) All these empirical energy values of S\(_{33}\) and M\(_{11}\) obtained for different nanotube diameters are summarized as shown in table 2.3.1 and plotted (band gap transition energy
Table 2.2.1 Energy of S$_{33}$ and M$_{11}$ vs. diameter of SWNTs$^{a,b,c,d}$

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$^a$Weisman et.al. Nano Lett. 2003, 3, 1235.$^{23b}$

$^b$Strano, et. al. J. Am. Chem. Soc. 2003, 125, 16148.$^{24}$


$^d$Determined from the absorption spectra of figure 3.8
Figure 2.3.8Energy of $S_{33}$ (red) and $M_{11}$ (blue) vs. diameter of SWNTs

Weisman et. al. M. Nano Lett. 2003, 3, 1235 (ES$_{33}$ (▲))$^{23b}$

Strano, M. S. J. Am. Chem. Soc. 2003, 125, 16148 (EM$_{11}$ (●))$^{24}$

Hamon et. al. J Am. Chem. Soc. 2001, 123, 11292 (EM$_{11}$ (■))$^{22}$

Determined from the absorption spectra of figure 3.8 (EM$_{11}$ (♦)) and ES$_{33}$ (♦)
vs. diameter) as shown in figure 2.3.8. The energy values of $S_{33}$ and $M_{11}$ are high for smaller diameter SWNTs, which gradually decrease when the tube diameter is increased (in both $S_{33}$ and $M_{11}$). As compared to $M_{11}$ peak, the energy of $S_{33}$ decreases at a slightly faster rate with an increase in the tube diameter. As shown in figure 2.3.8, the simple regression plot was drawn for these data (band gap energy vs. diameter) and the results showed that the energy of $S_{33}$ peak overlaps with the energy of $M_{11}$ when the diameter is larger than 1.4 nm. Because the arc produced SWNTs have a diameter approximately 1.4 nm$^{22}$, the band gap transition energy of $S_{33}$ peak should also overlap with band gap transition energy of $M_{11}$ peak. This may be one possible reason why the peak intensity in 600-800 nm region of solution and residue fractions showed little significant difference when the separation reaction was performed.

2.3.4 Discussion

The separation reaction of arc SWNTs with DomP was carried out under sonication conditions. At such conditions, it has been proposed that non-covalent formation (directly on SWNT graphitic surface) is the major mechanism for the functionalization and resulting solubilization. In the separation, three functionalization reactions solubilized approximately 2/3 of starting material to the solution, leaving 1/3 in final residue. This suggests that either remaining nanotube in the residue was mostly not solubilized or that their morphology became inefficient for further functionalization reaction at similar conditions. As reported previously, the presence of DomP on SWNT surface may alter the electronic structure of the nanotubes, resulting in apparent
diminishment of the band gap transitions.\textsuperscript{17} Therefore, the attached DomP molecules must be removed in order to accurately assess the intrinsic metalacitry composition of both soluble and insoluble fractions, although the latter was of somewhat less concern due to low DomP content (<30 %).

We used two methods to remove the free and attached DomP to recover the separated SWNTs: i) annealing the sample at 600-800 °C for 2 h in nitrogen protection or ii) “soft” removal method using dialysis followed by a solvent wash using CHCl\textsubscript{3}. Thermal annealing under these conditions is an effective way to remove (>99\%) of DomP from the separated nanotube samples. However, the SWNT after such treatments were heavily bundled and difficult to be dispersed in any solvent, preventing further processing (such as specimen preparation for optical absorption). To overcome these limitations, the “soft” removal technique (dialysis followed by CHCl\textsubscript{3} wash) was used. The success of this technique is a direct consequence of and strong evidence for the non-covalent nature of DomP-SWNT interactions. The clean samples thus obtained (>97 \%) were readily dispersible in various solvents, making the samples amenable for further processing and evaluation. Some of these material properties are similar among different fractions. For example, SEM technique used to characterize the solution fraction, residue and as purified SWNTs (after thermal annealing) did not show an apparent difference among them. Our conductivity studies showed the residue has higher conductivity (lower slope in the voltage-current plot) than purified SWNTs and the solution. This conductivity study is direct evidence that the residue obtained after the separation reaction is enriched with metallic SWNTs while the solution was enriched with semiconducting SWNTs.
Resonant Raman spectroscopy has been most useful in the characterization of the nature (e.g. metallicity and diameter) of SWNTs in resonance with the laser excitation.\textsuperscript{27-30} For example, it is known that the broad and unsymmetrical Breit-Wigner-Fano (BWF) lineshape of the lower frequency components of G-band ($\sim 1550$ cm\textsuperscript{-1}) is only typical for metallic SWNTs, while both semiconducting and metallic SWNTs share rather sharp Lorenzian components at higher frequencies ($\sim 1590$ cm\textsuperscript{-1}).\textsuperscript{31,32} These two excitation wavelengths are located at the upper and lower wavelength boundaries of the M\textsubscript{11} feature in the optical absorption spectrum of SWNTs in this study, respectively. Therefore, theoretically (refer to the Kataura Plot\textsuperscript{24-33}) for the 785 nm excitation, larger diameter metallic and smaller diameter semiconducting arc-SWNTs are in resonance while the 632-nm excitation exhibits mostly smaller-diameter metallic SWNTs and larger-diameter semiconducting arc-SWNTs that are in resonance.

The frequencies of radial breathing mode (RBM) peaks in Raman are inversely proportional to the corresponding nanotube diameters. When correlated with the diameter-band gap energy relationship (such as a Kataura Plot), it has been possible to assign individual RBM signals from different nanotube diameters to either semiconducting or metallic SWNTs (especially for HiPco-SWNTs with $\sim 0.7$-1.3 nm in diameter).\textsuperscript{29-32} The diameter distribution for SWNTs from arc-discharge is rather narrow (usually $\sim 1.3$-1.4 nm),\textsuperscript{22} making it a challenge to identify the metallicity solely from the peak position (if only one peak feature is present). Nevertheless, the RBM intensities from solution SWNT are lower than those from residue SWNT at both excitation wavelengths at which metallic SWNTs are predominantly in resonance, again consistent
with the enrichment of metallic SWNTs in residue SWNTs (Figure 2.3.7). However, in the Raman spectrum of solution SWNT at 632-nm excitation, the RBM peak (~164 cm\(^{-1}\)) that has been presumably attributed to resonant smaller-diameter metallic SWNTs show a significant presence in intensity, while the BWF lineshape is almost absent. This interesting observation suggests that there are perhaps more semiconducting SWNTs in resonance at 632 nm than have been commonly acknowledged. Consequently, the absorption peak most commonly assigned to M\(_{11}\) (~600-800 nm) might actually contain more contributions from the absorption of semiconducting SWNTs in this region, especially for the spectrum of solution SWNTs. Hence, the enrichment values using the ratio between area of M\(_{11}\) and S\(_{11}\) or S\(_{22}\) were underestimated from actual enrichment values. Therefore, our direct comparison of both the S\(_{11}\) regions of solution SWNTs and the residue SWNTs were more accurate in the sense of estimation of enrichment.

As shown in figure 2.3.5, the optical absorption spectrum of the starting purified sample is typical of arc-SWNTs after similar purification treatment.\(^{22}\) Similar to starting purified SWNTs, the solution fraction and the residue fraction also showed all the characteristic band gap transition features (S\(_{11}\), S\(_{22}\) and M\(_{11}\)). Since the two specimens (solution and residue) were prepared and measured under near identical conditions, the intensity difference of the above-mentioned band gap transition peaks may be readily attributed to the enrichment of semiconducting and metallic SWNTs in both the solution and the residue fractions. The argument of preferential doping of SWNTs in the residue fraction (thus with weaker S\(_{11}/S_{22}\) peaks) is hardly valid, not only because the thermal treatments should have eliminated all molecular dopants, but also because the SWNTs in
solution fraction would have been doped more than the SWNTs in residue fraction (even if any doping occurred) because the SWNTs of solution fraction have stronger interactions with the DomP molecules.

A common practice in the attempts to evaluate the enrichment extent of semiconducting and metallic SWNTs via optical absorption data has been to simply subtract the background, leaving only the peak features, the areas of which ($A_{S1}$ for $S_{11}$, $A_{S2}$ for $S_{22}$, and $A_{M}$ for $M_{11}$) were then used in the related calculations.\textsuperscript{31-35} When the three absorption bands are compared, the total area of $M_{11}$ band is strongly contributed from the area of $\pi$-plasmon of SWNTs and area of carbonaceous impurities. Therefore, the aerial absorption of SWNTs after base line treatment is small. In addition, we found that because the $M_{11}$ peak overlaps with the $S_{33}$ peak, the intensity of the peak in the $M_{11}$ region is caused by both semiconducting and metallic SWNTs. The same $\pi$-plasmon of SWNTs and carbonaceous impurity contribution for the total area of the $S_{11}$ peak is weak and as a result the total absorption is mainly caused by the absorption of semiconducting SWNTs. Therefore, the enrichment calculations performed by using the $S_{11}$ peak areas of solution and residue fractions, is a reasonable method for evaluating the enrichment of separated fractions.

In addition, the similar optical absorption studies were performed for the SWNT samples obtained from the separation reaction using the recovered DomP. The results, which are comparable with the same absorption measurements obtained for the separated samples using “as synthesized” DomP, suggest that the chemical reactivity and structure
of DomP is well preserved under the sonication conditions provided in the separation reaction.

The peak features at 600-800 nm are commonly assigned to the electronic transitions corresponding to the first transitions of various metallic SWNTs of arc SWNTs (denoted as M11).5,10,11,22-24 Although the S11 and S22 peaks showed a significant intensity difference between the solution and the residue fractions, the peak in the M11 region exhibited no expected intensity difference between the two fractions. A Kataura plot basically explains the relationship between the band gap energies of S11, S22, M11 and S33 with nanotube diameters. The Kataura plot indicates that when the tube diameter enlarges the electronic transition energies of all the peaks corresponding to the semiconducting and metallic tubes decrease. Our literature survey (empirical Kataura plots and absorption studies) to obtain information about the energy of band gap transitions vs. diameter showed the band gap energy of M11 overlaps with the band gap energy of S33 when the diameter is greater than 1.4 nm. If the peak at 600-800 nm is from only metallic SWNTs, then the intensity of this peak is expected to be weak for the solution fraction, as compared to the residue fraction, because the enrichment calculations showed the solution fraction is highly enriched with semiconducting SWNTs (>90%). In addition, the intensity of the S11 and S22 peaks of the solution fraction are significantly higher than the same intensity values of the residue fraction. Similar to the S11 and S22 peaks, the S33 peak partially embedded in the M11 peak should also have a significant intensity increase for the solution fraction. This intensity increase may be the reason as to why the 600-800
nm has a similar intensity for both residue and solution fractions. This peak of the solution fraction is caused by the S$_{33}$ band gap transition energy, while the same peak for the residue fraction is caused by the M$_{11}$ band gap transition. This divergence between the solution and residue fractions is another reason why the commonly acknowledged M$_{11}$ region is unsuitable for enrichment calculations.

2.3.4.1 Mechanistic Implications

Lu et al. considered SWNTs as an extended π-electron system that can combine with other π electron systems, such as aromatic molecules via same π-π stacking interactions. The increase in the size of the aromatic system also results in a corresponding increase in the binding energy between the carbon nanotube surface and the aromatic molecules. Larger aromatic molecules, with their larger polarizability, may be able to detect the difference in adsorption energy between metallic and semiconducting SWNTs, according to the London formula. According to their first principle calculations using the DFT model, the smaller aromatic molecules such as benzene showed no selective interaction with either metallic or semiconducting tubes. The same calculations also showed that bi-benzene had higher binding energy with semiconducting SWNTs than with metallic SWNTs. Therefore, bi-benzene was found to be selective toward semiconducting SWNTs. Even though the calculations based on bi-benzene closely agrees with our experimental results, their calculations showed opposite results for naphthalene and anthracene. According to their calculations, both anthracene and naphthalene have higher binding energies with metallic SWNTs than with
semiconducting tubes. Many factors, especially those related to the reaction conditions and sample history, could have contributed to such differences. For example, the effects from the defects of SWNT surface and the solvent in their calculations were not considered. Although, the interactions between DomP and SWNTs are non-covalent, our experiments showed without first treating the SWNTs with oxidative acid, this non-covalent functionalization reaction could not be performed efficiently. We also discovered that the reaction between DomP and SWNT was solvent dependent. “As prepared” DomP is very soluble in both THF and CHCl₃. However, the reaction performed between SWNTs and DomP in THF always provided better functionalization efficiency and better separation based on metallacity than it did in CHCl₃ (the reaction did not work in CHCl₃). These results clearly suggested both surface defects and solvents play a major role in our separation; thusly this is an interesting mechanistic issue for further experimental and theoretical investigations.

It also appears that the selective and strong interactions of the large planar aromatic molecules (such as DomP) with semiconducting SWNTs may have more complicated origins. In particular, the surface properties of semiconducting and metallic SWNTs significantly differ in that the former is similar to a conjugated macromolecule or radical ion pairs (charge-separated states). This difference makes SWNTs more amenable for interactions with large planar aromatic molecules via charge-transfer interactions, which then induce the alteration of underlying nanotube electronic structures. However, such interactions are likely inhomogeneous even on one single nanotube due to different interaction configurations and the unavoidable presence of defects, thus becoming
significantly broadened (and appearing to be “diminished”) when enough molecules become conjugated on the band-gap absorptions.
References


   Fang, S.; Subbaswamy, K. R.; Menon, M.; Thess, A.; Smalley, R. E.; Dresselhaus,

29. Dresselhaus, M. S.; Dresselhaus, G.; Jorio, A.; Souza Filho, A. G.; Pimenta, M.


31. Pimenta, M. A.; Marucchi, A.; Empedocles, S. A.; Bawendi, M. G.; Hanlon, E.
    B.; Rao, A. M.; Eklund, P. C.; Smalley, R. E.; Dresselhaus, G.; Dresselhaus, M. S.

32. Brown, S. D. M.; Jorio, A.; Corio, P.; Dresselhaus, M. S.; Dresselhaus, G.; Saito,


35. An, K. H.; Park, J. S.; Yang, C. M.; Jeong, S. Y.; Lim, S. C.; Kang, C.; Son, J.

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CHAPTER 3

DIAMETER-SELECTIVE FRACTIONATION OF HiPco SINGLE WALLED CARBON NAOTUBES IN REPEATED FUNCTIONALIZATION REACTIONS

3.1 Introduction

A single-walled carbon nanotubes (SWNT) is characterized by a pair of chiral indices \((n, m)\), which determine the tube diameter \(d\) in terms of the relationship as follows.\(^1\)

\[
d = \left[3(n^2 + nm + m^2)\right]^{1/2} a_{c-c}/\pi
\]

where \(a_{c-c}\) is the nearest neighbor carbon-carbon distance. The indices also define the metallicity of the nanotube: a semiconducting SWNT with \(\text{mod } [(n-m), 3] \neq 0\) and a metallic SWNT with \(\text{mod } [(n-m), 3] = 0.\)\(^1\) Various production methods for SWNTs generally yield mixtures of different chiralities. In fact, it is well known that the SWNTs from the high pressure CO disproportionation (HiPco) process are of a particularly broad distribution in tube diameters (~0.7 - 1.3 nm).\(^2,3\)

There have been significant efforts on post-production separation of SWNTs aimed toward their ultimate “purification” in terms of chiralities, with especially heavy emphasis on harvesting semiconducting- or metallic-enriched SWNTs.\(^4,6\) Interestingly, with only few exceptions,\(^7,9\) the reported post-production separation experiments have been centered on HiPco-SWNTs.\(^10-16\) The separation effort exploits the potentially
selective interactions of functional molecules with semiconducting or metallic SWNTs. For example, Tour, Smalley, and coworkers-reported that some highly reactive species such as diazonium salts were preferentially added to the sidewalls of metallic HiPco-SWNTs, so were nitronium ions and fluorine gas as recently reported by others. Papadimitrakopoulos and coworkers initiated the approach of using long-chain molecules bearing amino moieties to remove some semiconducting HiPco-SWNTs from the purified mixture, where the basis of separation is apparently the selectivity of the functionalization agent octadecylamine (ODA) toward semiconducting nanotubes for their solubilization. Maeda, et al. reported recently that an opposite selectivity could be achieved with the use of smaller amine molecules such as octylamine and propylamine, namely metallic instead of semiconducting nanotubes were enriched in the supernatant. On the other hand, the reactivity of a nanotube and its interactions with other species are known to be dependent on the tube diameter (or the graphene curvature corresponding to pyramidalization and π-orbital misalignment). In fact, there is an inverse relationship between the nanotube reactivity and diameter, with the smaller SWNTs being more reactive. Therefore, a significant issue in the post-production separation of SWNTs is the likely interplay between the selectivity toward the tube diameter and the selectivity toward the semiconducting or metallic characteristics. According to reports on the reactivity-based post-production separation, the nitronium ion attack prefers smaller-diameter metallic SWNTs, while the ozonation reaction is selective toward smaller-diameter SWNTs regardless of metallicity. Also, the selective interactions of ODA
molecules with semiconducting SWNTs were found to be more pronounced with the nanotubes of smaller diameters.\textsuperscript{16}

We reported previously an investigation on repeated functionalization reactions to sequentially extract soluble fractions from arc-discharge-produced SWNTs.\textsuperscript{20} Despite the intrinsically narrow diameter distribution in the starting nanotube sample, the fractionation results with the diamine-terminated oligomeric poly(ethylene glycol) (PEG\textsubscript{1500N}) as functionalization agent suggest a clear preference of the functionalization reaction toward smaller-diameter SWNTs. In the work presented here, the same approach and similar experimental conditions were applied to the repeated functionalization reactions with HiPco-SWNTs, in which the diameter-selective fractionation in the solubilization became more evident. The results from the characterization of the fractionated samples are described, and their implication to the effort on using similar functionalization reactions for post-production separation of semiconducting and metallic SWNTs is discussed.

3.2 Experimental Section
3.2.1 Materials

Diamine-terminated oligomeric poly(ethylene glycol) (PEG\textsubscript{1500N}) and sodium dodecyl sulfate (SDS) were purchased from Aldrich, and deuterated chloroform and D\textsubscript{2}O from Cambridge Isotope Laboratories. Dialysis tubing (cellulose membrane) with molecular weight cutoff \(\sim 12,000\) was obtained from Sigma Aldrich. The HiPco-SWNT sample was supplied by Carbon Nanotechnologies, Inc. and was purified by using a
procedure adapted from what is reported in the literature. In the purification, the as-supplied nanotube sample (500 mg) was treated with intermittent microwave (800 W) for 20 cycles of 60-second on and 300-second off, followed by refluxing in diluted nitric acid solution (2.6 M, 250 mL) for 12 h. Upon centrifugation to discard the supernatant, the solid was repeatedly washed with deionized water until neutral pH and then dried under vacuum to yield the purified HiPco-SWNT sample (257 mg).

3.2.2 Measurements

Several centrifuge machines were used for low- (Fisher Scientific, Centrifuge Model 228) and high-speed centrifugation (Beckman-Coulter Optima L90K ultracentrifuge with a type 90 Ti fixed-angle rotor). UV/vis/near-IR absorption spectra were recorded on Shimadzu UV3600 spectrophotometer. Raman spectra were obtained on a Renishaw Raman spectrometer equipped with a 50 mW diode laser source for 785 nm excitation and a Jobin-Yvon T64000 spectrometer equipped with a triple monochromator, a research-grade Olympus BX-41 microscope, a liquid nitrogen-cooled symphony detector, and two excitation sources of a Melles-Griot 35 mW He:Ne laser (632 nm) and a Spectra-Physics 40 mW argon-ion laser (514 nm). Thermogravimetric analysis (TGA) experiments were performed on a Mettler-Toledo TGA/SDTA851e system. Transmission electron microscopy (TEM) digital images were taken on Hitachi HF-2000 TEM and Hitachi HD-2000 S-TEM/TEM systems.
3.2.3 Functionalization Reactions

In a typical experiment, a mixture of purified HiPco-SWNTs (225 mg) and PEG_{1500N} (3.8 g) was heated to 120 °C and stirred under nitrogen protection for 4 days. After the reaction, the mixture was cooled to room temperature and then extracted repeatedly with water for the soluble fraction. Each extraction involved the addition of deionized water (15 mL) and then centrifuging at 1,380 g to collect the colored supernatant. Typically five repeats were necessary until the supernatant became colorless. The combined soluble fraction was cleaned via dialysis (membrane molecular weight cutoff ~12,000) against fresh deionized water for 3 days, and then evaporated to remove water. The insoluble residue after the repeated extractions was dried under vacuum for the next round of functionalization reaction. In each subsequent functionalization reaction, the same PEG_{1500N}/nanotube weight ratio of 17/1 was used, so were the reaction conditions. The reaction mixture was extracted in the same procedure to separate the soluble and insoluble fractions. All soluble fractions from the repeated functionalization reactions and the final insoluble residue were dried for their various characterization experiments.

3.3 Results and Discussion

The functionalization of HiPco-SWNTs with PEG_{1500N} was under thermal reaction conditions. Mechanistically, there is presumably the formation of a zwitterionic bond between the amino group in PEG_{1500N} and the nanotube-bound carboxylic acid (due to the oxidation of carbon defect), though non-covalently direct
adsorption of PEG_{1500N} species on the nanotube graphitic surface may also play a significant role in the solubilization of the nanotube. Nevertheless, the functionalization of HiPco-SWNTs with PEG_{1500N} for the nanotube solubilization was relatively robust. The solid samples of the soluble fractions from the repeated functionalization reactions could readily be dissolved in water or various polar organic solvents. These aqueous or organic solutions were stable over an extended period of time (at least several months), again demonstrating the robustness of the functionalization and solubilization.

3.3.1 Fractionation

A total of five soluble fractions were collected from the five repeats of functionalization reactions. The amount of nanotubes solubilized in each functionalization reaction varied, with the first and second reactions solubilizing 32% and 28% of the starting HiPco-SWNTs, respectively (Table 3.1). By the fifth reaction, the amount of nanotubes solubilized decreased to 2% of the starting HiPco-SWNTs (Table 3.1), suggesting no need for further repeats.

The nanotube contents in the soluble fractions and the final residue (listed in Table 3.1) were determined by using TGA. Shown in Figure 3.1 are typical TGA traces for the samples. At a heating rate of 10 °C/min in nitrogen atmosphere, the PEG_{1500N} functional groups can be removed completely at about 450 °C, while the defunctionalized HiPco-SWNTs remain stable. Quantitatively, the amount of recovered nanotubes from the five soluble fractions and the final residue totals 235 mg, in reasonable agreement with the amount of starting HiPco-SWNTs (225 mg), and about
Table 3.1 Nanotube Contents in the Soluble Fractions and the Final Residue

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Nanotube Content $^a$ (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>71 (30%) $^b$</td>
</tr>
<tr>
<td>2</td>
<td>65 (28%)</td>
</tr>
<tr>
<td>3</td>
<td>17 (7.2%)</td>
</tr>
<tr>
<td>4</td>
<td>11 (4.7%)</td>
</tr>
<tr>
<td>5</td>
<td>5 (2.1%)</td>
</tr>
<tr>
<td>Final Residue</td>
<td>66 (28%)</td>
</tr>
</tbody>
</table>

$^a$ Determined by TGA in inert (nitrogen) atmosphere.

$^b$ Shown in parentheses are weight percents against the total amount including all
Figure 3.1  TGA traces (N$_2$, 10 °C/min) of the first soluble fraction (—), second soluble fraction (- - -) and the final residue (....).
71% is in the soluble fractions and 29% in the final residue. As detailed in Table 3.1, the nanotube contents in the soluble fractions decrease significantly in subsequent functionalization reactions after the first two repeats, indicating the inhomogeneous nature of the starting purified HiPco-SWNT sample with respect to functionalization and solubilization.

Some of the material properties are similar among different fractions. For example, TEM techniques were used to characterize the soluble fractions and the final residue. In the specimen preparation, a drop of diluted aqueous solution of the soluble fraction (or aqueous suspension for the final residue) was placed onto a carbon or holey carbon-coated copper grid, followed by solvent evaporation. The TEM images of the soluble fractions show no meaningful differences, as compared in Figure 3.2. For the final residue, the TEM image suggests that the nanotubes are in larger bundles than those in the soluble fractions, as one might expect.

The soluble fractions were also evaluated by using $^1$H NMR. At a relatively dilute concentration of 10 mg/mL in CDCl$_3$, the observed spectra of the fractions appear similar, each with a broad signal centered at $\sim$3.6 ppm. This is readily assigned to the ethylene protons in the PEG$_{1500N}$ functional groups. The broadness of the peak is consistent with the functional groups being attached to SWNTs, which are species with large molecular weights and low mobilities.$^{24}$
Figure 3.2  TEM images of the five soluble fractions and the final residue (all scale bars 200 nm).
3.3.2 Diameter Selectivity

The optical spectroscopy results of the soluble fractions and the final residue suggest significant diameter preference in the repeated functionalization reactions, resulting in different diameter distributions of HiPco-SWNTs in the various fractions. The solution-phase optical absorption spectra of the soluble fractions (except for the fifth fraction due to limited sample quantity) were measured in D_2O to avoid spectral interference in the near-IR region. The solutions were prepared by directly dissolving the solid samples into D_2O. Similarly, the starting purified HiPco-SWNT sample and the final residue were suspended in D_2O with the assistance of SDS (0.5 mg/mL), which is a surfactant widely used in the literature for optical spectroscopy of SWNTs. These solutions and suspensions in D_2O (all with 2 mg/mL nanotube-equivalent concentrations) were centrifuged at 137,000 g for 2 h before the optical spectral measurements. As shown in Figure 3.3, the spectrum of the starting purified sample is resolved with spectral features typical of HiPco-SWNTs after similar purification treatment. The peak features at 900-1,600 nm and 550-900 nm are commonly assigned to groups of electronic transitions corresponding to the first and second pairs of van Hove singularities in the density of states (DOS) for various semiconducting SWNTs (denoted as S_{11} and S_{22}), respectively, and those at 400-650 nm corresponding to first transitions of various metallic SWNTs (denoted as M_{11}). The absorption spectra of the solubilized samples remain similarly resolved with S_{11}, S_{22} and M_{11} peak features in their spectral range (Figure 3.3), suggesting that the nanotube electronic structures are retained in the
Figure 3.3  UV/vis/NIR absorption spectra of different SWNT samples in D$_2$O after ultrahigh speed centrifugation. From bottom to top: SDS-assisted suspension of the starting purified HiPco SWNTs, solutions of the first to the fourth soluble fractions, the SDS-assisted suspension of the final residue. The spectra were offset for clearance.
functionalization with PEG1500N. This is consistent with previously reported results on the PEG1500N functionalization of SWNTs from other production methods.\textsuperscript{20,22}

A closer examination of the absorption spectra reveals significant and systematic changes in the detailed spectral peak features from fraction to fraction, reflecting the underlying variations in diameter distributions of the HiPco-SWNTs. For the $S_{11}$ bands, the features of the first soluble fraction are more at shorter wavelengths (roughly below 1,200 nm) in comparison with those of the starting purified sample. In the later soluble fractions, however, more significant spectral features are in the longer wavelength region (especially above 1,200 nm). The changes in $S_{22}$ bands are in a similar trend, with the first soluble fraction featured more in the 650-750 nm region, while later fractions more in the 750-900 nm region (Figure 3.3). It is known that electronic transition energies of SWNTs are inversely related to the nanotube diameters. Thus, the absorption results suggest that the smaller diameter semiconducting SWNTs are preferentially solubilized in the earlier fractions.

The diameter-selective fractionation in the repeated functionalization reactions is more evident in the results of resonance Raman spectroscopy. The Raman measurements were performed at multiple excitation wavelengths of 785 nm (1.58 eV), 632 nm (1.96 eV), and 514 nm (2.41 eV). In order to avoid the known luminescence interference with functionalized nanotube samples,\textsuperscript{24} the soluble fractions and the final residue were thermally defunctionalized (heated to 600 °C and kept for 2 h in inert atmosphere) before the Raman characterization.
For the starting purified sample, the Raman spectrum at 785 nm excitation exhibits typical features of the G-band at 1,592 cm\(^{-1}\), D-band at 1,330 cm\(^{-1}\), and radial breathing modes (RBMs) at 100-300 cm\(^{-1}\) (Figure 3.4), agreeing with those reported previously.\(^{10-16}\) Here the 785 nm excitation is in resonance with mostly semiconducting HiPco-SWNTs of various diameters, but few of their metallic counterparts.\(^{12}\) Also shown in Figure 3.4 are Raman spectra of the soluble fractions and the final residue with the same 785 nm excitation. The G-band features are similar among all these samples, with the bands being relatively narrow and symmetrical. However, there are systematic changes in the RBM region, with the spectra of the earlier fractions enriched with higher frequency features (or smaller diameter semiconducting SWNTs) and the later fractions and the final residue with lower frequency features (or larger diameter semiconducting SWNTs). For example, the spectrum of the first soluble fraction shows the 264 cm\(^{-1}\) peak higher in intensity than peaks in 188-216 cm\(^{-1}\) and 217-242 cm\(^{-1}\) regions, but the spectrum of the fifth soluble fraction exhibits a nearly opposite peak intensity pattern (those of the other fractions apparently intermediate between the two) (Figure 3.4). In the spectrum of the final residue, only peaks at 189 cm\(^{-1}\) and 206 cm\(^{-1}\) could be observed. It is known that the RBM peak frequency (\(\omega_{\text{RBM}}, \text{cm}^{-1}\)) is inversely related to the corresponding SWNT diameter (\(d, \text{nm}\)) in terms of the equation \(\omega_{\text{RBM}} = 223.5/d + 12.5.\(^{27}\) Thus, the initial functionalization reaction in multiple repeats is obviously selective toward the smaller diameter nanotubes among the population of semiconducting HiPco-SWNTs.
Figure 3.4  Full Raman spectra and the RBM region at 785 nm excitation for, from bottom to top: the starting purified HiPco SWNT sample, the first to the fifth soluble fractions, and the final residue.
The Raman spectra were also measured with 632 nm and 514 nm excitations (coupled with the use of a triple monochromator) for a closer examination of the low frequency region, despite the fact that different HiPco-SWNTs (from those with 785 nm excitation) are in resonance with these excitation wavelengths. The RBM features in the spectra exhibit systematic changes in a trend similar to that found with the 785 nm excitation. Generally the earlier fractions are with more intense higher-frequency RBM features, and the later fractions and the final residue with more intense lower-frequency RBM features (Figure 3.5). For the 632 nm excitation, smaller diameter semiconducting and larger diameter metallic HiPco-SWNTs are in resonance. The Raman RBMs again suggest that the smaller diameter semiconducting nanotubes are preferentially solubilized in the initial functionalization reactions. The Raman results obtained with 514 nm excitation also suggest similarly preferential solubilization of smaller diameter nanotubes, except that the resonance of 514 nm is with smaller diameter metallic (short M11 wavelengths) and larger diameter semiconducting (long S33 wavelengths) HiPco-SWNTs.7,12-16

For both 632 nm and 514 nm excitations, the corresponding G-band features in the Raman spectra of the different fractions also exhibit systemic changes in opposite patterns. As compared in Figure 3.6, the G-bands from 632 nm excitation became broader and increasingly unsymmetrical in subsequent soluble fractions and then the final residue. An opposite trend is associated with the 514 nm excitation, where the G-bands of the earlier soluble fractions are unsymmetrical and those of the later soluble fractions and the
Figure 3.6  G-band regions at 632 nm and 514 nm excitations for, from bottom to top: the starting purified HiPco SWNT sample, the first to the fourth soluble fractions, and the final residue.
final residue are narrower and more symmetrical (Figure 3.6). It is known that the broadened and unsymmetrical appearance of the G-band (or the BWF line-shape)\textsuperscript{28} serves as a signature for the significant presence of metallic SWNTs in the sample.\textsuperscript{4-16} Thus, the Raman G-band results with 632 nm and 514 nm excitations are consistent with the enrichment of larger diameter semiconducting and metallic HiPco-SWNTs in the later soluble fractions and the final residue.

Overall the optical absorption spectra and resonance Raman results with three different excitation wavelengths apparently suggest that the functionalization reaction of PEG\textsubscript{1500N} with the purified HiPco-SWNT sample is selective toward those nanotubes of smaller diameters, regardless of their being semiconducting or metallic. This may have significant implications to the effort on the post-production separation of semiconducting and metallic SWNTs.\textsuperscript{4-16}

3.3.3 Mechanistic and Other Implications

A characteristic feature of as-supplied or purified HiPco-SWNTs is the broad distribution of nanotubes of different diameters. Therefore, it is hardly surprising that the diameter selectivity becomes an issue in various functionalization reactions. For the thermal reaction conditions used in this study, the preference of PEG\textsubscript{1500N} molecules toward smaller diameter HiPco-SWNTs is probably associated with their direct adsorption onto the nanotube surface. The role of such non-covalent but specific interactions in the solubilization of carbon nanotubes has been suggested for other long-chain functionalization agents with primary amine moieties.\textsuperscript{7,16} As for the selectivity
toward smaller diameter HiPco-SWNTs, the specific interactions responsible for the
direct adsorption may be similar mechanistically to those found in the addition of highly
reactive species to the nanotube sidewalls.\textsuperscript{10,13,15}

The diameter selectivity in functionalization reactions (including the adsorption)
could potentially alter the population balance between semiconducting and metallic
nanotubes, if the two nanotube types were of different diameter distributions, which
could thus result in the observation of enrichment in one over the other in various
reaction mixtures or fractions. Hypothetically, should the starting sample be populated
with more smaller diameter semiconducting nanotubes than their metallic counterparts,
the preferential solubilization of the former would obviously leave more metallic
nanotubes in the insoluble residue, and \textit{vice versa}. Therefore, it might in principle be a
possibility that the interplay between diameter and metallicity fractionations in the
functionalization and solubilization of HiPco-SWNTs with long-chain amino compounds
like PEG\textsubscript{1500N} and ODA is driven primarily by the diameter selectivity. This may be an
interesting topic for further investigations.

In summary, the repeated functionalization reactions of PEG\textsubscript{1500N} molecules with
purified HiPco-SWNTs resulted in multiple soluble factions and the final insoluble
residue. These fractions have different nanotube diameter distributions from that found in
the starting purified HiPco-SWNT sample. A general conclusion is that the first
solubilized are smaller diameter nanotubes, regardless of their being semiconducting or
metallic. The results reported here and those already in the literature suggest that because
of the intrinsically broad diameter distribution in HiPco-SWNTs, diameter selectivity
plays an important role in the reactions or specific interactions designed or exploited for the post-production separation of the nanotubes into semiconducting and metallic enriched fractions. Further experimental investigations on the existing and other amine-bearing functionalization or dispersion agents are required for a better understanding of the various selectivities.
References


Lian, Y.; Wakahara, T.; Akasaka, T.; Kazaoui, S.; Minami, N.; Okazaki, 
128, 12239.


16. (a) Samsonidze, G. G.; Chou, S. G.; Santos, A. P.; Brar, V. W.; Dresselhaus, G.; 
Dresselhaus, M. S.; Selbst, A.; Swan, A. K.; Unlu, M. S.; Goldberg, B. B.; 
2004, 85, 100; (b) Brar, V. W.; Samsonidze, G. G.; Santos, A. P.; Chou, S. G.; 
Onoa, G. B.; Swan, A. K.; Ünlü, M. S.; Goldberg, B. B.; Dresselhaus, G.; 


20. Huang, W.; Fernando, S.; Lin, Y.; Zhou, B.; Allard, L. F.; Sun, Y.-P. *Langmuir* 
2003, 19, 7084.

Andres, J. M.; Schreiber, J.; Chauvet, O.; Fierro, J. L. G. *Chem Comm.* 
2002, 1000.


4.1 High Aqueous Solubility of Functionalized Single-walled Carbon Nanotubes

4.1.1 Introduction

Single-walled carbon nanotubes (SWNTs) are severely bundled and essentially insoluble in any solvents. The insolubility is generally considered as a significant barrier in both fundamental research and technological development toward the practical uses of SWNTs. Thus, several chemical modification methods have been developed to functionalize and solubilize SWNTs. In particular, the functionalization of SWNTs to introduce aqueous solubility has received much recent attention for investigations targeting potential biological applications of carbon nanotubes. A widely employed functionalization strategy is to attach oligomeric or polymeric molecules to the nanotube-bound carboxylic acid moieties, which are generated in the oxidative acid treatment of the intrinsic or induced (due to the shortening of the nanotubes, for example) nanotube surface defects. The functionalized carbon nanotubes are soluble in water when hydrophilic oligomeric or polymeric molecules are attached.

4.1.2 Experimental section

4.1.2.1 Materials

PVA (Mw ~ 70,000-100,000, 99% hydrolyzed) and PVA (Mw ~ 22,000, 99% hydrolyzed) was purchased from Alfar Aesar. Thionyl chloride, N,N- Dicyclohexyl
carbodiimide (DCC, 99%) and 4-(dimethylamino) pyridine (DMAP, 99%) were obtained from Acros. 1-hydroxybenzotriazole (HOBT, containing less than 5% H_2O) was from Aldrich. Dimethyl sulfoxide (DMSO, 99.5%) and N, N–dimethylformamide (DMF, 99%) were purchased from Burdick and Jackson. Deuterated chloroform was purchased from Cambridge Isotope Laboratories. Dialysis membranes were supplied by spectrum Laboratories. Diamine terminated oligomeric poly (ethylene glycol), H_2NCH_2CH_2CH_2(OCH_2CH_2)_nCH_2NH_2, with n ~ 35 (PEG_{1500N}) and poly(propionylethlenimine) (PPEI, Mw of 50,000 and 200,000) were purchased from Aldrich. The residual water of PEG_{1500N} was removed via azeotropic distillation.

4.1.2.2 Measurements

NMR measurements were performed on Bruker AC-300 and JEOL Eclipse + 500 NMR spectrometers. Dichloromethane was used as the internal standard. Thermal gravimetric analysis (TGA) was carried out on a Mettler-Toledo TGA/SDTA851e system.

4.1.2.3 Carbon Nanotubes

The SWNT sample was produced in Professor A. M. Rao’s laboratory (Department of Physics and Astronomy, Clemson University) by using the arc discharge method with Ni/Y as catalyst. In the purification, the sample was refluxed in an aqueous HNO_3 solution (2.6 M) for 48 h. Upon Centrifugation to remove the liquid phase, the
remaining solid were washed repeatedly with deionized water until neutral pH and then
dried under vacuum (Figure 4.1.1).

4.1.2.4 PPEI-EI Copolymer

Poly(propionylethylenimine-co-ethylenimine) (PPEI-EI) random copolymer was
prepared via partially hydrolyzing PPEI polymers. In a typical reaction, a PPEI sample
(Mw ~ 200,000, 1 g) was dissolved in methanol (5 mL). After water (50 mL) was added,
methanol was evaporated via heating and the solution became opaque. 2 ml of
concentrated HCl was added to the solution and refluxed the mixture for 24 h. The
reaction mixture was cooled to ambient and then was neutralized with aqueous NaOH to
a pH of ~10. Upon the removal of water, the product was extracted with chloroform and
then precipitated into hexane, followed by drying under vacuum to yield the PPEI-EI co-
polymer as white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$=3.6- 3.2 (broad (broad, 2×NCH$_2$),
2.9-2.6 (broad, 2×NHCH$_2$), 2.5-2.2(broad, COCH$_2$CH$_3$), 2.1-1.8 (broad, NHCH$_2$), 1.2-
1.0 (broad, COCH$_2$CH$_3$) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ = 174 (C=O), 48.5
(2×NHCH$_2$), 44 (2×NHCH$_2$), 26 (COCH$_2$CH$_3$), 9.3 (COCH$_2$CH$_3$) ppm. The EI mole
fraction of random co-polymer $x_{\text{NH}}$ was estimated in terms of the $^1$H NMR signal
intergration.

$$x_{\text{NH}} = \frac{I_{2.8}}{I_{2.8} + I_{3.4}}$$

The mole fraction $x_{\text{NH}}$ could be controlled via varying the hydrolysis reaction time. For
the PPEI-EI copolymers used in this study, $x_{\text{NH}}$ values were generally ~20%.
Figure 4.1.1. SEM image of purified SWNTs produced by arc discharged method.
4.1.2.5 Functionalization

The nanotube surface-bound carboxylic acid groups were generated during the oxidative acid treatment. The functionalization of SWNTs, targeting the defect site carboxylic groups were done using PEG$_{1500N}$, PPEI-EI and PVA using different reaction conditions. Three main functionalization methods: Thermal method, acylation-mediated amidation, carbodiimide-activated amidation were used to functionalize SWNTs with PEG$_{1500N}$ and PPEI-EI (Scheme 4.2.1). For PVA, carbodiimide-activated esterification reaction method was used to functionalize SWNTs (Scheme 4.1.1).

4.1.2.5.1 PEG1500N-SWNT Functionalization

4.1.2.5.1.1 Thermal Method

In a typical reaction, purified SWNT sample (50 mg) was mixed with PEG$_{1500N}$ (1000 mg), and the mixture was stirred at ~120 °C under nitrogen protection for 4 days. Upon the addition deionized water to the mixture, the resulting dispersion was centrifuged at 1380 g for 15 minutes. Then the solution retained in the upper part of centrifuged tube was dialyzed (cutoff molecular weight ~12,000) against fresh deionized water for 3 days. $^1$H NMR (500 MHz, CDCl$_3$) δ =3.6 ppm (broad).

4.1.2.5.1.2 Carbodiimide-Activated Coupling

In a typical reaction, a purified SWNT sample (50 mg) was mixed with 150 mg of EDAC in 25 ml of pH= 7.2 buffer solution and sonicated for 1 hour. Then 1000 mg of PEG$_{1500N}$ was added and the mixture was further sonicated for 24 h. After the completion
Scheme 4.1.1. Water soluble functionalities used for SWNT functionalization.
of sonication time period, the extraction and purification procedures were the same as those described above. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 3.6\) ppm (broad).

4.1.2.5.1.3 Acylation-Mediated Amidation

In a typical reaction, a purified SWNT sample (50 mg) was refluxed with SOCl\(_2\) (20 ml) for 24 h to convert the carboxylic acids into acyl chlorides.\(^{22-27}\) Upon evaporating the unreacted SOCl\(_2\) under vacuum, 1000 mg of PEG\(_{1500N}\) was added to the acylated nanotube sample. The mixture was heated to the 120 ¹C and kept in that temperature range under nitrogen protection for 24 h. After the completion of reaction time, the extraction and purification procedures were the same as those described above. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 3.6\) ppm (broad)

4.1.5.2 PPEI-EI-SWNT Functionalization

4.1.2.5.2.1 Thermal Method

50 mg of purified SWNT sample was heated with PPEI-EI (Mw ~ 200,000, 500 mg) at 180-190 ¹C under nitrogen protection for 12 h. The extraction and purification procedures were the same as those described above. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 4.5-2.9\) (broad), 2.9-2.7 (broad), 2.7-1.9 (broad) ppm.

4.1.2.5.2.2 Acylation-Mediated Amidation

50 mg of purified SWNT sample was refluxed with 20 ml of SOCl\(_2\) for 24 h. Upon evaporating the unreacted SOCl\(_2\) under vacuum, PPEI-EI (Mw~200,000, 500 mg)
was added to the acylated nanotube sample. The mixture was heated to 180-190 °C and kept in that temperature range under nitrogen protection for 24 h. The extraction and purification procedures were the same as those described above. \(^1\)H NMR (500 MHz, CDCl₃) \(\delta = 4.5-2.9\) (broad), 2.9-2.7 (broad), 2.7-1.9 (broad) ppm.

4.1.2.5.2.3 Carbodiimide-Activated Coupling

50 mg purified SWNT sample was mixed with 150 mg of EDAC in 25 ml of pH=7.2 buffer solution and sonicated for 1 hour. Then PPEI-EI (Mw~200,000, 500 mg) was added and the mixture was further sonicated for 24 h. After the completion of sonication time period, the extraction and purification procedures were the same as those described above. \(^1\)H NMR (500 MHz, CDCl₃) \(\delta = 4.5-2.9\) (broad), 2.9-2.7 (broad), 2.7-1.9 (broad) ppm.

4.1.2.5.3 PVA-SWNT Functionalization

In a typical reaction, purified SWNT (80 mg), DCC (200 mg, 0.6 mmol), DMAP (33 mg, 0.15 mmol) and HOBT (65 mg, 0.3 mmol) were dissolved in DMSO (10 ml) and sonicated it for 1 h. Then a solution of PVA (Mw~70000) in DMSO (80mg/ml, 10 ml) was added, and the mixture was sonicated for another 24 h. After the completion of reaction time, the extraction and purification procedures were the same as those described above. Functionalization of SWNTs with PVA (Mw~22000) was done very similar method described above. DMF was used as the solvent instead of DMSO. \(^1\)H NMR (500 MHz, CDCl₃) \(\delta = 3.95-3.75\) (broad), 1.6-1.2 (broad), 5-4 (broad) ppm.
4.1.3 Results and Discussion

For the nanotube-equivalent aqueous solubilities of the functionalized SWNTs, an accurate determination of the nanotube contents in the soluble samples is required. The thermal gravimetric analysis (TGA) and $^1$H NMR methods were employed for such a purpose. Quantitative TGA measurements were performed on the functionalized SWNT samples in the solid state. Under the condition of a relatively slow heating rate of 10 °C/min to 800 °C in a nitrogen atmosphere, the organic/polymeric functional groups (PEG$_{1500N}$, PPEI-EI, and PVA) were selectively removed, leaving behind the defunctionalized SWNTs. The nanotube contents thus obtained are shown in Table 4.1.1. Separately, quantitative $^1$H NMR analyses of the samples were carried out in solution by using several internal $^1$H standards, including acetonitrile and dichloromethane. The internal standards were calibrated against one another for consistency. The results thus obtained are compared with those from the TGA measurements in Table 4.1.1. The SWNT content results obtained by using the two different methods are in reasonable agreement.

In a typical experiment for solubility determination, a functionalized SWNT sample was added in fractions of 25 mg each to 1 mL deionized water. After each 25 mg addition, the solution was vigorously stirred and then centrifuged at ~3,000 g (IEC Centra CL-2) for 15 min. The procedure was repeated until the solution was saturated. The clear supernatant was carefully evaporated for the removal of water to recover the
<table>
<thead>
<tr>
<th>Sample</th>
<th>TGA (wt%)</th>
<th>NMR (wt%)</th>
<th>mean (wt%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG&lt;sub&gt;1500N&lt;/sub&gt;-SWNT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>thermal reaction</td>
<td>26</td>
<td>32</td>
<td>29</td>
</tr>
<tr>
<td>diimide-coupling</td>
<td>43</td>
<td>36</td>
<td>39.5</td>
</tr>
<tr>
<td>acylation-amidation</td>
<td>57</td>
<td>54</td>
<td>55.5</td>
</tr>
<tr>
<td>PPEI-EI-SWNT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>thermal reaction</td>
<td>17</td>
<td>16</td>
<td>16.5</td>
</tr>
<tr>
<td>diimide-coupling</td>
<td>23</td>
<td>13</td>
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<tr>
<td>acylation-amidation</td>
<td>17</td>
<td>---</td>
<td>17</td>
</tr>
<tr>
<td>PVA(20k)-SWNT</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>diimide-coupling</td>
<td>12</td>
<td>17</td>
<td>14.5</td>
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<td>PVA(70k)-SWNT</td>
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<td></td>
</tr>
<tr>
<td>diimide-coupling</td>
<td>18</td>
<td>18</td>
<td>18</td>
</tr>
</tbody>
</table>

<sup>a</sup> The value used in the calculation of nanotube-equivalent aqueous solubility.
functionalized SWNTs. The weight of the recovered solid sample was determined for the solubility calculation. The aqueous solubility values thus obtained for the functionalized SWNT samples are shown in Table 4.1.2. Since the nanotube contents in the soluble samples are known, as summarized in Table 4.1.1, the nanotube-equivalent aqueous solubilities of the functionalized SWNTs can be calculated, which are also shown in Table 4.1.2.

The PEG\textsubscript{1500N}-SWNT sample from the direct thermal reaction has the highest nanotube-equivalent aqueous solubility of >87 mg/mL (Table 4.1.2). The sign “>” used with this and other solubility results indicates that the reported value represents the lower limit. A technical difficulty that hindered the determination of actual solubilities was the high viscosity associated with most of the solutions. For the PEG\textsubscript{1500N}-SWNT sample from the direct thermal reaction, as an example, the solution at 300 mg/mL concentration (or 87mg/mL nanotube-equivalent concentration) became rather viscous, making it marginal to use vigorous centrifuging to remove any undissolved solid residue. In fact, more of the PEG\textsubscript{1500N}-SWNT sample could be dissolved into the solution, but the even higher viscosity made it impossible centrifuge the solution. The same situation was found for other PEG\textsubscript{1500N}-SWNT and PPEI-EI-SWNT solutions (Table 4.1.2). However, the PVA-SWNT samples have obviously lower aqueous solubilities. The solutions became saturated before reaching the point of too viscous to centrifuge.

The functionalization of SWNTs via covalently attaching water-soluble oligomeric or polymeric species or biomolecules have been reported\textsuperscript{2-13} but systematic aqueous solubility data of the functionalized nanotube samples are hardly available for
Table 4.1.2. Aqueous solubilities of functionalized SWNTs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aqueous solubility (mg/mL)</th>
<th>Nanotube-equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>solubility (mg/ml)</td>
<td></td>
</tr>
<tr>
<td>PEG$_{1500}$-SWNT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>thermal reaction</td>
<td>&gt;300</td>
<td>&gt;87</td>
</tr>
<tr>
<td>diimide-coupling</td>
<td>97</td>
<td>38</td>
</tr>
<tr>
<td>acylation-amidation</td>
<td>&gt;103</td>
<td>&gt;57</td>
</tr>
<tr>
<td>PPEI-EI-SWNT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>thermal reaction</td>
<td>&gt;121</td>
<td>&gt;20</td>
</tr>
<tr>
<td>diimide-coupling</td>
<td>&gt;84</td>
<td>&gt;15</td>
</tr>
<tr>
<td>acylation-amidation</td>
<td>&gt;135</td>
<td>&gt;23</td>
</tr>
<tr>
<td>PVA(20k)-SWNT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>diimide-coupling</td>
<td>48</td>
<td>7</td>
</tr>
<tr>
<td>PVA(70k)-SWNT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>diimide-coupling$^a$</td>
<td>45</td>
<td>8</td>
</tr>
</tbody>
</table>

$^a$ The saturated aqueous solution was first prepared at 80 °C and then cooled to room temperature.
comparison. However, there have been some efforts on the use of other methods to disperse SWNTs into aqueous medium. Examples of the available methods include the oxidative acid treatment,\textsuperscript{29} the surfactant-assisted dispersion,\textsuperscript{14} and the nanotube surface adsorption of polymeric and biological species.$^{15-18}$ Most of these methods yield nanotube-equivalent concentrations typically on the order of only a few mg/mL. Thus, the functionalization of SWNTs with hydrophilic oligomeric or polymeric molecules used in this work represents a generally more effective strategy to introduce a significant amount of SWNTs into water to form a homogeneous aqueous solution. In a related comparison, the nanotube-equivalent aqueous solubilities of these functionalized SWNT samples are similar to those (fullerene-equivalent) of the most hydrophilic fullerene C\textsubscript{60} derivatives.\textsuperscript{30} The highly water-soluble SWNTs may find valuable materials and biologically significant applications. For example, the PEG\textsubscript{1500N}-functionalized carbon nanotubes are likely strongly protein-resistant in an aqueous solution, a property important to the use of carbon nanotubes in biosensors.
References


4.2 Poly (ethylene-co-vinyl alcohol)-Functionalized Single-Walled Carbon Nanotubes and Related Nanocomposites

4.2.1 Introduction

Carbon nanotubes have attracted considerable research interest for their promising optical, electronic, and mechanical properties.\(^1,2\) In particular, the dispersion of single-walled carbon nanotubes (SWNTs) into polymeric matrices has been widely investigated for the development of novel or improved polymer/carbon nanocomposites.\(^3-5\) For example, Dalton, \textit{et al.} were able to spin continuous fibers from SWNTs dispersed in a polymer matrix, and reported that these composite fibers possess extraordinary mechanical properties.\(^3\)

In the development of polymer/SWNT nanocomposites, the poor dispersibility associated largely with the bundling of the nanotubes represents a significant technical barrier. The chemical modification of SWNTs to impart solubility in common organic solvents and water has emerged as an effective approach for the homogeneous dispersion of SWNTs in polymeric matrices.\(^6\) Both non-covalent and covalent modifications of carbon nanotubes have been investigated and reported extensively.\(^6-9\) Among the most popular covalent modification methods is the functionalization that takes advantage of the nanotube surface defects, in particular nanotube-bound carboxylic acid groups.\(^6,9\) The functionalization of carbon nanotubes with various polymers via amide and ester linkages has been accomplished.\(^6,10-15\) For the fabrication of high-quality polymer/carbon
nanocomposites, however, the polymeric species used in the functionalization must be structurally similar or even identical to the matrix polymer. For example, derivatized polystyrene and polyimide are desirable in the functionalization and solubilization of carbon nanotubes to be homogeneously dispersed into polystyrene and polyimide matrices, respectively.\textsuperscript{11,13} In a more special case, poly(vinyl alcohol) was used to functionalize carbon nanotubes for the fabrication of “impurity-free” poly(vinyl alcohol)/carbon nanotube composite materials.\textsuperscript{12}

Poly(ethylene-\textit{co}-vinyl alcohol) (also known as ethylene vinyl alcohol copolymer, or EVOH) shares some structural elements with poly(vinyl alcohol), but property-wise quite different. EVOH is a polymeric material well-known for its outstanding gas barrier properties.\textsuperscript{16} In this paper we report results from the functionalization of SWNTs with EVOH and the characterization of the soluble sample. The functionalization and solubilization allowed the homogeneous dispersion of SWNTs into the EVOH polymer matrix, which serves as another example for the preparation of impurity-free polymer/carbon nanocomposites.

4.2.2 Experimental Section

4.2.2.1 Materials

EVOH with ethylene mole fraction of ~44% was purchased from Aldrich. \textit{N},\textit{N’}-dicyclohexyl carbodiimide (DCC, 99\%) and 4-dimethylaminopyridine (DMAP, 99\%) were obtained from Acros, and 1-hydroxybenzotriazole (HOBT, containing less than 5\% water) from Aldrich. DMSO (99.5\%) from Burdick & Jackson was dried over molecular
sieves before use. Deuterated solvents for NMR experiments were supplied by Cambridge Isotope Laboratories.

The SWNT sample produced in arc discharge was provided by Prof. A. M. Rao (Department of Physics and Astronomy, Clemson University). The sample was purified via oxidative acid treatment (2.6 M HNO₃, 48 h), followed by the cross-flow filtration (Minikros Lab System) according to established procedures.¹²

### 4.2.2.2 Measurements

Optical absorption spectra were recorded on a Thermo-Nicolet Nexus 670 FT-Near-IR spectrometer. Raman spectra were obtained on a Renishaw Raman spectrometer equipped with a 50 mW diode laser source for 785 nm excitation and a CCD detector. NMR measurements were performed on a JEOL Eclipse +500 NMR spectrometer. Thermo gravimetric analysis (TGA) was carried out on a Mettler-Toledo TGA/SDTA 851e system. Scanning electron microscopy (SEM) images were obtained on a Hitachi S4700 field-emission SEM system. Transmission electron microscopy (TEM) analyses were conducted on Hitachi HF-2000 (200 kV) TEM system equipped with a Gatan Multi-Scan CCD camera for digital imaging.

### 4.2.2.3 Carbon Nanotubes Functionalization

The functionalization of SWNTs with EVOH was carried out under esterification reaction conditions. In a typical experiment, DCC (240 mg, 1.2 mmol), DMAP (40 mg, 0.3 mmol), and HOBT (80 mg, 0.6 mmol) were dissolved in DMSO (10 mL). The
purified SWNT sample (100 mg) was added to the solution, and the resulting suspension was sonicated for 1 h. A DMSO solution of EVOH (10 mL, 0.1 g/mL) was added to the suspension, followed by sonication for 24 h. The reaction mixture was centrifuged at 7,200 rpm (Centra CL-2, 3,000 g) to separate the dark-colored solution from the insoluble residue. Upon the solvent removal from the dark-colored solution, the EVOH-functionalized SWNT sample (EVOH-SWNT) was obtained as blackish flaky solids.

4.2.2.4 Nanocomposites

In a typical procedure, EVOH was dissolved in hot ethanol-water mixture (4/1, v/v, 80 °C) to form a viscous solution (150 mg/mL). Separately, a measured amount of the EVOH-SWNT sample was also dissolved in the same hot solvent to form a homogeneous solution. The two hot solutions were mixed, and the mixture was vigorously stirred at the same temperature (80 °C) for 4 h until it appeared homogeneous and visually free from any air bubbles. The solution-casting was performed a glass substrate with an adjustable film applicator (Gardco). Upon drying at room temperature in a dust-free environment for 24 h, a grayish, opaque, but visually homogeneous composite film was obtained.

4.2.3 Results and Discussion

The functionalization of SWNTs by EVOH was carried out under typical carbodiimide-activated esterification reaction conditions, facilitating the formation of ester linkages between the SWNT-bound carboxylic acids and the pendant hydroxyl
groups of the vinyl alcohol units in EVOH copolymer. The EVOH-SWNT sample is soluble in DMSO with moderate heating (~60 °C), similar to the parent EVOH copolymer, forming a dark-colored solution. The solution is stable over time and remains homogeneous at room temperature. The sample is also soluble in ethanol-water mixture (4/1, v/v) with heating. However, the solution in ethanol-water becomes unstable below 60 °C with the observation of significant precipitation, though the precipitate can be re-dissolved again upon heating.

The optical absorption spectrum of the EVOH-SWNT sample was measured in the solid-state to avoid solvent interference in the near-IR region. As shown in Figure 4.2.1, the spectrum exhibits the characteristic absorption bands at 1,870 nm (0.66 eV) and 1,050 nm (1.19 eV) for transitions corresponding to the first and second pairs of van Hove singularities, respectively, in the electronic density of states of semiconducting SWNTs. The absorption results are consistent with those already reported in the literature, namely that the polymer functionalization via ester largely preserves the electronic properties of SWNTs. The solubility of EVOH-SWNT made it possible to carry out solution-phase NMR characterization of the sample. Shown in Figure 4.2.2 is a comparison of the 1H NMR spectrum of the EVOH-SWNT in room-temperature DMSO-$d_6$ with that of the parent EVOH. The spectra appear rather similar, except that the broad proton signals in EVOH are further broadened in EVOH-SWNT. This is consistent with the reduction in the mobility of EVOH upon the nanotube attachment in functionalization. Quantitatively, the NMR signal integrations were used to
Figure 4.2.1. The near-IR spectrum of the EVOH-SWNT sample (measured in the solid state).
Figure 4.2.2. The $^1$H NMR spectrum of the EVOH-SWNT sample in DMSO d6 (top) is compared with that of the neat EVOH (bottom).
estimate the nanotube content in the EVOH-SWNT sample. The results thus obtained by using dichloromethane as a proton concentration standard suggest that the nanotube content in the EVOH-SWNT sample is about 14% (wt/wt). Separately, the polymer in the EVOH-SWNT sample could be selectively removed in a thermal defunctionalization process. The defunctionalization was achieved in a TGA scan to 600 °C (heating rate ~ 10 °C/min) under the condition of steady nitrogen flow (Figure 4.2.3). The residual weight for the thermally defunctionalized SWNTs was equivalent to nanotube content in the EVOH-SWNT sample of about 10% (wt/wt), which is comparable with the result from the quantitative $^1$H NMR signal integration experiment.

The specimen for TEM characterization was prepared by placing a drop of diluted solution of EVOH-SWNT in DMSO onto a holey carbon-coated copper grid on top of a piece of filter paper, followed by the solvent evaporation. At low magnification, TEM images show well-dispersed SWNTs of various lengths, though the contrast in the images was not high. However, some nanotubes did lie across the holes on the holey carbon grid, which is an excellent condition for imaging at high-resolution. Shown in Figure 4.2.4 is a clear image of an individual functionalized SWNT of ~1.5 nm in diameter. The amorphous coating on some part of the nanotube surface is likely due to the EVOH polymeric functionalities. Overall, the TEM results suggest that the EVOH-SWNT sample contains primarily functionalized individual or thin bundles of nanotubes. This is consistent with the expected exfoliation of the bundled SWNTs in the polymer functionalization reaction. The carbon nanotubes are well-dispersed in the EVOH-SWNT sample, which causes significant luminescence interference in Raman measurements.
Figure 4.2.3. The TGA Trace (N$_2$, 10 °C/min) of the EVOH-SWNT sample.
Figure 4.2.4. A high-resolution TEM image of an EVOH-functionalized SWNT.
Figure 4.2.5. Raman spectra of the EVOH-SWNT sample before (top) and after (bottom) thermal defunctionalization.
As shown in Figure 4.2.5, the Raman signals of the EVOH-SWNT are on top of a strong luminescence background, though the peak features from SWNTs are still identifiable. Upon the removal of EVOH in the thermal defunctionalization, the luminescence interference became much less significant. Also compared in Figure 4.2.5 is the Raman spectrum of the thermally defunctionalized sample. The spectral features, including the radial breathing mode (RBM, ~153 and 170 cm\(^{-1}\)), D-band (~1,298 cm\(^{-1}\)), G-band (~1,592 cm\(^{-1}\)), and D*-band (~2,576 cm\(^{-1}\)), are characteristic of SWNTs.

The thermally defunctionalized sample was also analyzed by SEM. The image thus obtained shows abundant SWNTs (Figure 4.2.6), confirming the substantial nanotube content in the original EVOH-SWNT sample. The solubility of EVOH-SWNT in DMSO was measured by following a procedure reported previously.\(^\text{19}\) In the experiment, the EVOH-SWNT sample was added in fractions to DMSO (1 mL) at 60 °C. Each fraction was 25 mg, and the resulting solution after each addition was vigorously stirred and then centrifuged (1380 g). The process was repeated until the solution was saturated. The amount of EVOH-SWNT in the solution was determined gravimetrically upon a complete removal of the solvent DMSO. The solubility thus obtained for the EVOH-SWNT sample in DMSO with a dissolution temperature of 60 °C is 40 mg/mL. As discussed above, the nanotube content in the EVOH-SWNT sample was estimated as 14% and 10% (wt/wt) in terms of the NMR and TGA methods, respectively. Thus, the nanotube-equivalent solubility of the EVOH-SWNT sample in DMSO is on the order of 5 mg/mL.
Figure 4.2.6. SEM image of the EVOH-SWNT sample after thermal defunctionalization.
The soluble EVOH-SWNT sample may itself be cast into a nanocomposite thin film of a high SWNT content (more than 10% wt/wt). Since the EVOH-SWNT sample is soluble in the same solvents as neat EVOH, the same solution casting method may be used to prepare EVOH/SWNT nanocomposites of lower nanotube contents. The dilution was achieved by mixing the solution of EVOH-SWNT with a concentrated solution of neat EVOH. As described above, the SWNT content in the EVOH-SWNT sample is known (10-14% wt/wt). Thus, the nanotube content in the EVOH/SWNT nanocomposite films can be conveniently calculated from the amounts of EVOH-SWNT and neat EVOH used in the solution mixing. A series of EVOH/SWNT nanocomposite films of the nanotube content less than 10% (such as 3% wt/wt) were fabricated. The EVOH/SWNT nanocomposite films appeared homogeneous with a greyish color, but not optically transparent. As a result, absorption measurements of the films were unsuccessful. However, Raman spectra of the films exhibit the characteristic SWNT features (RBM ~153 and 169 cm⁻¹, D-band ~1,310 cm⁻¹, G-band ~1,587 cm⁻¹, and D*-band ~2,575 cm⁻¹), similar to those of the EVOH-SWNT sample. The overall Raman intensities of the films also increase with the known nanotube contents.

In summary, SWNTs were functionalized with EVOH copolymer in carbodiimide-activated esterification reactions. Similar to EVOH, the EVOH-functionalized SWNT sample is soluble in DMSO and other polar solvent systems such as hot ethanol/water mixture, forming dark-colored solutions. The common solubility of EVOH-SWNT and neat EVOH makes it possible to conveniently fabricate EVOH/SWNT nanocomposite films via wet-casting. These nanocomposite films are
conceptually similar to those based on poly (vinyl alcohol)-functionalized carbon nanotubes. Thus, this work presents another example of homogeneously dispersing SWNTs into polymeric matrices without introducing any other materials for impurity-free nanocomposites.
References


CHAPTER 5
SUMMARY

My carbon nanotube research mainly focused on topics involving the separation of SWNTs based on their electronic structure (semiconducting SWNTs from metallic SWNTs) and their size (diameter). However, because the purity of as-produced SWNTs is only between 30-40%, the purification of SWNTs is important before any functionalization or separation reactions can be performed. Impurities in pristine SWNT sample often include metal catalysts, amorphous carbon, and carbon nanoparticles with multiple graphitic layers. In addition, some metal catalysts are usually encapsulated in the carbon nanoparticles. Therefore, effective purification of SWNTs using a simple method is very important to remove these impurities. The purification of SWNT samples was performed using a combination of air oxidation and nitric acid, and the subsequent TGA, analysis in air showed the purity of SWNTs after the above purification procedure to be over 80%.

In the process of separating SWNTs based on electronic structure, the purified SWNTs (from arc discharged method) were reacted with larger aromatic molecules such as THPP and DomP by the using non-covalent functionalization method. The separation of the purified SWNT samples was achieved via three sequentially repeated functionalization reactions under the same sonication condition. Upon the completion of three cycles, the fourth cycle was also attempted and the reaction did not work. The three solution fractions were combined leaving the final residue. In order to remove free and attached DomP to recover the separated SWNTs, we used the “soft” removal method.
using dialysis followed by a solvent wash with CHCl₃. The characterization results obtained using optical absorption, Raman spectroscopic studies of multiple wavelengths and the conductivity studies using four point probe method showed the solution fraction to be enriched with semiconducting SWNTs and the insoluble residue was enriched with metallic SWNTs. Our further investigations using a literature survey showed that the band gap energy of M₁₁ peak overlaps with the band gap energy of S₃₃ peak when the nanotube diameter is greater than 1.4 nm. In addition both the M₁₁ peak and the S₃₃ peak are strongly enhanced by the area of \( \pi \)-plasmon of SWNTs and the area of carbonaceous impurities. Therefore, the enrichment calculations were performed by using the area comparison of S₁₁ peaks of purified, solution and residue fractions. The quantitative evaluations performed for 5 different batches of separated samples showed that the solution fraction was enriched with 92-98% of semiconducting SWNTs and 2-8% of metallic SWNTs. Similar optical absorption studies were performed for the SWNT samples obtained from the separation reaction using the recovered DomP (after the washing with hexane and chloroform). The results, which are comparable with the same absorption measurements obtained for the separated sample using “as synthesized” DomP, suggest that the chemical reactivity and structure of DomP is well preserved under the sonication conditions provided in the separation reaction.

We also determined that the non-covalent complexation of a semiconducting SWNT with aromatic molecules could also dramatically affect the nanotube electronic structures and the associated optical transitions. Indeed, these non covalent interactions between DomP and SWNTs are strong enough to diminish the band gap transitions
related to semiconducting tubes ($S_{11}$ and $S_{22}$). Since the complexation is reversible the characteristic bands can be turned on and off with the complexation in a reversible fashion. However, our further experiments using different planar aromatic systems showed that such interactions might not be universal for all aromatic molecules. For example the antracene analog of DomP, 1-docosyloxyethyl-antracene (DomA), failed to solubilize any SWNTs in THF; consequently no absorption diminishment was found. The lack of absorption diminishment may be due to week interactions between DomA and SWNTs or because some unfavorable structural conjugation configurations were unable to solubilize nanotubes even if there were some selectivity under the given conditions.

As compared to arc SWNTs, the HiPco SWNTs have broad diameter distribution. Therefore, in our study of diameter separation, the HiPco SWNTs were functionalized by using PEG$_{1500N}$ molecules to obtain multiple soluble fractions and final insoluble residue. The characterization results obtained using multiple wavelengths of 632 nm, 514 nm and 785 nm showed that the first soluble fractions are enriched with smaller diameter nanotube, irrespective as to whether or not these nanotubes were either semiconducting or metallic, leaving the larger diameter SWNTs in both the later soluble fractions and the final residue. In addition to Raman characterization, the absorption spectra revealed significant and systematic changes in the detailed spectral peak features from fraction to fraction, reflecting the underlying variations in diameter distribution of the HiPco SWNTs. For the $S_{11}$ bands, the features of the first soluble fractions were greater at shorter wavelengths while the same features of later soluble fractions and final residue
were found to exist in longer wavelength region in comparison with those of the starting purified sample. The changes in $S_{22}$ bands showed similar trends, with the first soluble fraction featured more in the shorter wavelength region, while the later fractions were featured more in the longer wavelength region. It is known that electronic transition energies of SWNTs are inversely related to the nanotube diameters. Thus, the absorption results suggest that the smaller diameter semiconducting SWNTs are preferentially solubilized in the earlier fractions.

In addition to these separation studies, carbon nanotubes (both SWNTs and MWNTs) were functionalized using amidation and esterification with various polymers. The insolubility of carbon nanotubes due to the bundles is generally considered a significant barrier in both fundamental research and technological developments toward the practical uses of carbon nanotubes. Therefore, my carbon nanotube functionalization research was extended to study the solubility of these functionalized SWNTs in both aqueous and organic mediums. The solubility results in aqueous medium showed that the PEG$_{1500N}$-SWNT sample from direct thermal reaction has the highest nanotube-equivalent aqueous solubility of $>87$ mg/mL. In addition to these solubility studies, the PVA and EVOH functionalized SWNTs were used to fabricate nanocomposite films via the wet casting method.
APPENDIX


Selective Interactions of Porphyrins with Semiconducting Single-Walled Carbon Nanotubes

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Single-walled carbon nanotube (SWNT) samples produced via various techniques are generally mixtures of metallic and semiconducting SWNTs, which correspond to different electrical conductivities and other related properties. These properties are important to a variety of technological applications of SWNTs including, for example, the electrical conductivity and charge dissipation in polymer/carbon nanocomposites and thin films.1,2 The enrichment of metallic or semiconducting SWNTs or vice versa in a nanotube sample, toward a complete separation of the two different kinds of SWNTs, has attracted much recent attention.3,4 In this communication, we report on the selectivity of a derivatized porphyrin toward semiconducting SWNTs in presumably inefficient interactions,6 resulting in significantly enriched semiconducting SWNTs in the solubilized sample and predominantly metallic SWNTs in the residual solid sample according to Raman, near-IR absorption, and bulk conductivity characterization.

The SWNT sample was produced in Professor A. M. Rao’s laboratory (Physics Department, Clemson University) by using the arc-discharge method. It was purified via oxidative acid treatment according to an established procedure.7,8 10,15,30-triethylphenalenylporphyrin (THPP) was synthesized by coupling p-benzoquinone to wt. wt. in glacial acetic acid, followed by column chromatography separation and structural characterization.

In a typical noncovalent solubilization experiment, a purified SWNT sample (100 mg) was added to a solution of THPP in chloroform (10 mg/mL, 20 mL), and the mixture was sonicated (Fisher Scientific FS500, 70 W, 42 kHz) for 48 h. After the removal of chloroform on a rotary evaporator, the solid residue was extracted repeatedly with hexane, coupled with vigorous centrifuging (~3100g) for 20 min, to remove free THPP. Then, THPP (10 mL) was added to the solid sample to dissolve the THPP-attached SWNTs. Upon vigorous centrifuging for 20 min, the solid residue was collected and then used to go through the same noncovalent solubilization procedure again (note: the third repeat was tried, but no further solubilization was observed. The unfractionated SWNT sample largely free from the porphyrin was obtained as the final solid residue (59 mg, denoted as “free-SWNT” sample). The soluble THPP--SWNT samples from the two repeated experiments were combined, followed by a complete evaporation of the solvent THF. The removal of THF from the THPP-complexed soluble sample was accomplished via washing the sample with acetic acid, coupled with vigorous centrifuging, resulting in the recovery of insoluble SWNTs (denoted as “recovered-SWNT” sample). The results from scanning electron microscopy analyses show that the two samples are largely similar. To ensure a rigorous comparison between the free-SWNT and recovered-SWNT samples in subsequent spectro-

copy and conductivity characterizations, both solid-state samples were thermally treated under the same experimental conditions of 800 °C for 14 h in a nitrogen atmosphere.

The recovered-SWNT sample is enriched in semiconducting SWNTs, while the free-SWNT sample contains predominantly metallic SWNTs. Their Raman spectra obtained with 785 nm (1.58 eV) excitation exhibit different features (Figure 1a). According to the widely cited work of Eremets and co-workers,9 while noncovalently and metallic SWNTs may have different tangential mode G-bands, the difference is not expected to be obvious for the arc-produced SWNTs used in this work with the 785 nm excitation. The recent results and analyses by Papeleutakopoulos and co-workers on laser ablation-produced SWNTs confirmed such a conclusion (Figure 4 in ref 5). As shown in Figure 1a, however, the G-band of the free-SWNT sample is broader and more asymmetric than that of the recovered-SWNT sample, indicative of substantial enrichment in metallic SWNTs (Bredt–Wagner–Fine line shape).9,10 The Raman features in the radial breathing mode region are also consistent with an enrichment of metallic SWNTs in the free-SWNT sample.11

The significant enrichment of semiconducting nanotubes (in recovered-SWNT samples) from metallic nanotubes (in free-SWNT sample) is made more evident by a quantitative comparison of the near-IR absorption spectra. The spectra shown in Figure 1b were obtained by measuring (Thermo-Nicolet Nexus 670) the thermally treated solid-state samples of the same quantity under the same experimental conditions. No surfactant or other dispersing agents were used in the preparation of the specimens for measurements to avoid even the remote possibility of any doping effects. For the semiconducting recovered-SWNT sample, the near-IR absorption spectrum contains significant bands at ~1030 cm⁻¹ (1.86 μm, 0.67 eV) and ~971 cm⁻¹ (1.06 μm, 1.19 eV), corresponding to transitions associated with the first (5π) and second (3π) gaps, respectively, of van Hove singularities in the electronic density of states for semiconducting SWNTs.8 On the other hand, the absorption of the metallic free-SWNT sample is negligible over the near-IR region.4 The results suggest that most of the semiconducting SWNTs in the starting sample ended up in the

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recovered SWNT sample, namely that the porphyrin interactions were selective toward semiconducting SWNTs.

The bulk electrical conductivities of the free-SWNT and recovered-SWNT samples (thermally treated under the same conditions, as described above) are very different. In a comparative conductivity evaluation, the two samples were pressed separately into pellets of approximately 9 mm × 3 mm × 1 mm in dimension. Results from the classical four-probe conductivity measurements under ambient conditions show that the bulk conductivities of the two samples differ by more than two orders of magnitude, 1.1 S/cm for the metallic free-SWNT vs 0.007 S/cm for the semiconducting recovered-SWNT.

To examine the effect of the nanotube on the THPP species on the surface, the soluble THPP-SWNT sample in solution was characterized by H NMR (data not shown). The NMR signals of THPP are significantly broadened upon the attachment to SWNTs, which is likely due largely to the significantly reduced mobility of the THPP species. Consistent with the NMR results it seems that the porphyrin ring is probably bound to the SWNT surface, leading long alkyl chains to waggle around in solution. Such a picture is supported by the high-resolution TEM results, which show soft materials on the surface of individual nanotubes (Figure 2).\(^\text{11}\)

Figure 2. High-resolution TEM image (scale bar = 5 nm) of the soluble THPP-SWNT sample.

The interactions of THPP with SWNT are apparently specific to the porphyrin free base, hindered upon the coalescence of a metal cation. For example, the Zn–THPP was used in the place of THPP under the same experimental conditions, but no interactions leading to the solubilization of SWNTs was observed. The negative results with the use of metalloporphyrins also suggest that the selectivity toward semiconducting SWNTs reported above is associated with THPP, not fragments of decomposed THPP, because porphyrin with and without the center-CaIolated metal share similar decomposition patterns.\(^\text{12}\)

In summary, the derivatized porphyrin THPP selectively interacts with and stabilizes semiconducting SWNTs, resulting in the 'extraction' of most of the semiconducting SWNTs from the starting purified nanotube sample. Mechanistically, we suspect that the semiconducting and metallic SWNTs have significantly different surface properties. A speculation is that a semiconducting SWNT is more likely to conjugate micromolecules with the nanotube surface properties conceptually similar to those found in radical ion pairs, thus unavailable to interactions with the free-base porphyrin molecules.\(^\text{12}\) Since the porphyrin is readily prepared and largely recoverable from the extraction experiment, the reported procedure may become an effective and convenient method for the separation of semiconducting SWNTs from metallic SWNTs.

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Supporting Information Available. Additional figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

Solubilization of Single-Walled Carbon Nanotubes with Diamine-Terminated Oligomeric Poly(ethylene Glycol) in Different Functionalization Reactions

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ABSTRACT

A comparative study is reported on the solubilization of as-prepared and purified single-walled carbon nanotubes with diamine-terminated oligomeric poly(ethylene glycol) in different functionalization reactions under various conditions. The soluble nanotube samples were characterized by using spectrosopic, microscopic, and gravimetric techniques. The results were used in the evaluation of the functionalization reactions.

Single-walled carbon nanotubes (SWNTs) are essentially insoluble in any solvents because of their rigid structure and presence in bundles. As a result, solubilization of SWNTs via chemical functionalization has attracted much recent attention.1-11 Two different approaches have been developed: addition to the sidewall2-4 and functionalization at defect sites.5-12 The latter typically takes advantage of the carboxylic acid moieties at the defect sites to link polymeric and oligomeric functional groups. There has already been strong experimental evidence for the existence of nanotube-bound carboxylic acids and also evidence showing that reactions targeted the carboxylic acids result in the solubilization of the nanotubes. However, many issues, including a comparative evaluation of various functionalization reactions and unambiguous characterization of the linkages from these reactions, remain to be addressed.

There are generally three different reactions with the nanotube-bound carboxylic acids: acid-base interaction, acylation-mediated amidation or esterification, and carbodiimide-activated coupling (amidation or esterification). These reactions correspond to somewhat different experimental conditions and may serve different purposes. For example, the carbodiimide-activated coupling is particularly useful in the functionalization of carbon nanotubes with biomolecules and biological species.13-15 In this letter, we report a comparative study of these reactions in the functionalization of as-prepared and purified SWNT samples with diamine-terminated oligomeric poly(ethylene glycol), O(CH₂-OH)-₃·nh₂-₃·O(CH₂-OH)₃ (PEG₃₉₀₀) (Aldrich).

The SWNT sample was produced by using the arc-discharge method.10 In the purification, the sample was refluxed in aqueous nitric acid solution (2.6 M) for 48 h to eliminate catalyst particles, followed by cross-flow filtration (MiniKros Lab System) to remove carbon particles and impurities according to an established procedure.21 The Raman and scanning electron microscopy (SEM) characterization results show that the purification was effective.

The as-prepared and purified SWNT samples were compared in the functionalization with PEG₃₉₀₀. In a reaction, an as-prepared SWNT sample (28 mg) was mixed with PEG₃₉₀₀ (474 mg), and the mixture was stirred at ~100 °C under nitrogen protection for 6 days. Upon the addition of deionized water to the mixture, the resulting suspension was placed in a membrane tubing (cut-off molecular weight ~12 000) for dialysis against fresh deionized water for 3 days. The solid residue was separated from the dispersion via vigorous centrifuging, yielding a dark-colored solution of PEG₃₉₀₀-functionalized SWNTs. The same reaction condition was applied to the functionalization of a purified SWNT sample with PEG₃₉₀₀, also yielding a dark-colored homogeneous solution. A comparison of the residual weights of the unfunctionalized SWNTs from the reactions23 suggests that the functionalization of the purified SWNT sample is
Table 1: Results from Thermal Reactions of SWNT Samples with PEG$_{1000}$

<table>
<thead>
<tr>
<th>sample</th>
<th>−COOH reaction</th>
<th>reaction time (days)</th>
<th>reaction temp (°C)</th>
<th>($W_0 - W_0^<em>/W_0^</em>$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-prepared</td>
<td>0.4%</td>
<td>6</td>
<td>100</td>
<td>12%</td>
</tr>
<tr>
<td>purified</td>
<td>2.8%</td>
<td>6</td>
<td>~120</td>
<td>~70%</td>
</tr>
</tbody>
</table>

* Determined from the acid–base titration. $^\dagger$ $W_0$ is the weight of the starting SWNT sample, and $W_0^*$ is the weight of the solid residue from the functionalization reaction after the TGA correction for partial functionalization.

Figure 1. Raman spectra of the soluble samples from as-prepared SWNTs (top) and purified SWNTs before (bottom, dashed line) and after (bottom, solid line) thermal defunctionalization.

Figure 2. TEM images of the soluble samples from as-prepared SWNTs (A, scale bar = 30 nm) and purified SWNTs (B, scale bar = 10 nm, on a holey LaCrO$_3$ grid after thermal treatment at an air at 400 °C for 30 min).

SWNTs is close to that of the sample before functionalization, whereas the soluble sample from the purified SWNTs exhibits more homogeneity background, indicating effective functionalization and dispersion of the SWNTs.$^2$

Typical transmission electron microscopy (TEM) images of the functionalized SWNTs are shown in Figure 2. Since TEM imaging is hardly an appropriate technique for a quantitative comparison of the functionalized SWNT samples, the results simply serve the purpose to show that there are SWNTs in the solubilized samples and that the nanotubes are dispersed either individually or in small bundles. It does appear, however, that the soluble sample from the functionalization of as-prepared SWNTs contains relatively more impurities.

Strong evidence for the presence of SWNTs in the soluble samples is also provided by the thermal defunctionalization results. The defunctionalization is based on the fact that the temperature required for the evaporation of the nanotube-bound functional groups (PEG$_{1000}$) is considerably lower than that for the nanotube itself, enabling the selective removal of the functional groups in a thermal gravimetric analysis (TGA) scan.$^{1,14-17}$ In a typical experiment, a functionalized SWNT sample (~10 mg) was loaded into an

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was loaded into a membrane tubing (cutoff molecular weight ~12,000) for dialysis against fresh deionized water for 3 days. The solid residue was separated via vigorous centrifuging to yield a dark-colored homogeneous solution of functionalized SWNTs.

In a typical experiment for acylation–amination, a purified SWNT sample (24.7 mg) was refluxed in neat SOCl₂ for 24 h to convert the nanotube-bound carboxylic acids into acyl chlorides. After a complete removal of residual SOCl₂ on a rotary evaporator with a vacuum pump, the sample was mixed well with the carefully dried PEG₁₂₅₀ (420 mg) in a flask, heated to ~140 °C, and vigorously stirred under nitrogen protection for either 24 h or 6 days. The reaction mixture was dispersed into deionized water and transferred into a dialysis tubing (cutoff molecular weight ~12,000). After the dialysis for 3 days, a dark-colored solution was obtained from the vigorous centrifuging to remove the solid residue.

These functionalization reactions were evaluated in terms of the amount of SWNTs being functionalized and solubilized. The determination was based on the mass balance for the nanotubes, namely the difference between the starting weight and residual weight of the nanotube sample. The results are compared in Table 2. The three different functionalization methods (direct thermal reaction, acylation–amination, and carbodiimide-activated coupling) resulted in different amounts of solubilized SWNTs in a comparable period of reaction time. While the solubilized samples from all these reactions form homogeneous solutions, qualitatively the sample from the carbodiimide activation likely contains relatively more bundled nanotubes, as reflected by the stronger scattering of the solution. This might be a result of the relatively mild reaction condition associated with the carbodiimide activation.

The reaction time obviously plays a significant role in the functionalization and solubilization of SWNTs. In the thermal reaction, for example, a longer reaction time of 6 days vs 24 h resulted in the solubilization of a significantly larger amount of SWNTs (Table 2). The reaction temperature appears to play a role as well, with a higher reaction temperature resulting in more solubilized SWNTs. For example, the thermal reaction at ~140 °C for 24 h yielded more solubilized SWNTs than the same reaction at a lower
reaction temperature of 100 °C for 4 days (Table 2). Interestingly, there has been a recent report on the solubilization of HiPco SWNTs via stirring with 2-ammoniomethyl-18-crown-6 ether at room temperature, suggesting that a high-temperature reaction condition is not required for the functionalization via zwitterionic interactions. It should be recognized, however, that the SWNTs produced via the arc-discharge method and the HiPco method are of significantly different average diameters. A more detailed study is necessary to understand the difference between the SWNTs produced from different methods with respect to their chemical functionalization and solubility. The 1H NMR spectra of all soluble samples are characterized by a broad signal at ~3.6 ppm, broader than that in the spectrum of neat PEG<sub>1000</sub>. No structural details on the SWNT-PEG<sub>1000</sub> linkages are revealed by the NMR results, nor are indicated any other reactions between the nanotubes and the functional groups. The significant broadening in the proton signal of PEG<sub>1000</sub> upon the functionalization reaction is likely due to the immobilization of PEG<sub>1000</sub> chains on the SWNT surface, with perhaps one or both ends of each PEG<sub>1000</sub> attached to the nanotube. This is probably quite different from the situation in which carbon nanotubes are simply mixed with oligomeric PEG species. Under the latter condition, there was hardly any wrapping of carbon nanotubes by the PEG species.

In summary, the interactions between SWNTs and amine-terminated organic species are probably complex and dependent on the functionalization reaction conditions. The purified SWNT sample, for which the purification process involves refluxing in aqueous nitric acid solution, is apparently preferred in the functionalization and solubilization. Both direct thermal reaction and acylation–aminec–amide are efficient in the solubilization of SWNTs, yielding better-dispersed nanotubes, though the carbodiimide– activated coupling is also useful, especially for some special purposes. Longer reaction time and relatively higher reaction temperature are favorable to the functionalization and solubilization of SWNTs by the diamine-terminated PEG compound.

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References

(22) Since the insoluble fraction from the functionalization reaction also contained partially functionalized SWNTs yet to become soluble, the weight of the residual solid sample was corrected by using the result from their thermal defunctionalization in TGA.
(23) The titration was based on a procedure reported by Huddon and co-workers. In a typical titration experiment, a SWNT sample (0.1 mg) was dispersed in aqueous Na2CO3 solution (0.05 M, 50 mL) and stirred for 3 days. Upon the removal of solids via vacuum centrifuging, the remaining solution was diluted to 250 mL in a volumetric flask. A portion (50 mL) of this stock solution was mixed with aqueous HCl solution (0.05 M, 10 mL). The resulting solution was boiled for 30 min to remove CO2 completely. Followed by the titration of the excess HCl with aqueous NaOH (0.05 M). The titration was repeated three times for each sample to obtain an average value.

Preferential Solubilization of Smaller Single-Walled Carbon Nanotubes in Sequential Functionalization Reactions

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A purified single-walled carbon nanotube (SWNT) sample was fractionated in sequential functionalization reactions with a diamine-terminated polymeric polyethylene glycol to produce five soluble fractions and a final solid residue. These fractions and the residue were characterized by using optical spectroscopy, electron microscopy, thermal gravimetric analysis, and other techniques. The results show that the soluble fractions all contain primarily functionalized SWNTs and that there are no obvious systematic changes from one fraction to the next. However, one exception made evident by the Raman spectroscopy results is that the functionalization reactions preferentially solubilize the SWNTs of smaller diameters, resulting in an enrichment of larger diameter nanotubes in the final solid residue. In addition, the nanotube contents in different soluble fractions obtained from the sequential functionalization reactions are apparently different, with higher nanotube contents in the later fractions. The difference between the fractions of SWNTs and the fractionation of multi-walled carbon nanotubes (MWNTs) reported previously is discussed.

Introduction

There has been significant recent progress in the development of methods for solubilizing both single-walled (SWNT) and multi-walled (MWNT) carbon nanotubes. The chemical functionalization of carbon nanotubes can be either direct addition to the graphitic walls, attachment of functional groups at the defect sites, or the latter typically involves the nanotube-bound carboxylic acids, which allow the formation of ionic, ester, or amide linkages with various functionalities. An interesting issue is the potential selectivity in the solubilization of carbon nanotubes via functionalization reactions. For example, Prato and co-workers recently suggested that a HiPco SWNT sample could be purified in terms of the difference in solubility between the functionalized nanotubes and impurities. During the course of this study, Papadimitrakopoulos and co-workers reported that the solubilization of SWNTs in the functionalization reaction with octadecylamine is selective against metallic nanotubes, yielding a solubilized sample rich in semiconducting SWNTs.

In an effort to examine the selectivity issue we have attempted to fractionate a MWNT sample in repeated functionalization reactions. The functionalization was based on the esterification of the nanotube-bound carboxylic acids. However, results from detailed characterizations of the different soluble fractions suggested that there was no obvious preferential solubilization of MWNTs in terms of their sizes and also no significant selectivity in the removal of carbon impurities. Here we report a similar attempt to fractionate a SWNT sample in se-

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Sequential functionalization reactions. There are several noticeable differences between the SWNT and MWNT samples. The MWNT sample used in the functionalization atacticity was produced via the thermal vapor deposition method, thus containing considerably less carbon impurities. MWNTs are also much more complicated than SWNTs with respect to the nanotube diameters. In fact, the results reported here suggest that the functionalization reaction is somewhat selective, resulting in an enrichment in SWNTs of larger diameters in the residue sample from the repeated reactions.

Experimental Section

Materials. Diamine-terminated aliphatic polyethylene glycol, H,NCH₂CH₂CH₂OCH₂CH₂CH₂NH₂ with n = 35 (PEG₃₅) was purchased from Aldrich and used after removal of the residual water via azeotropic distillation. All solvents were either spectroscopy−HPLC grade or purified via simple distillation. Deuterated solvents for NMR measurements were supplied by Cambridge Isotope Laboratories.

The SWNT sample was produced in Professor A. M. Rao’s laboratory (Department of Physics and Astronomy, Clemson University) by using the arc-discharge method with Ni/Al as catalyst. In the purification, the sample was refluxed in an aqueous HNO₃ solution (2.6 M) for 48 h. Upon centrifugation to remove the liquid phase, the remaining solids were washed repeatedly with deionized water until neutral pH and then dried under vacuum.

Measurements. UV/vis/NIR absorption spectra were recorded on a Shimadzu UV2100-PC and UV1600 spectrophotometers and a Thermo-Nicolet Nexus 670 FT-NIR spectrometer. Raman spectra were obtained on a Renishaw Ramana spectrometer equipped with a 632 nm diode laser source for 785 nm excitation and a CCD detector. NMR spectra were measured on a Joel Eclipse +500 NMR spectrometer. Thermal gravimetric analysis (TGA) was performed on a Mettler-Toledo TGA/SDTA 851e system. Dynamic light scattering characterization was carried out on a Beckman Coulter N4 plus particle size analyzer. Scanning electron microscopy (SEM) images were obtained on a Hitachi S2500 field emission SEM system. Transmission electron microscopy (TEM) analyses were conducted on a Hitachi H-7650 TEM system equipped with a Gatan Multiscan on CCD camera for digital imaging.

Functionalization Reactions. The functionalization of SWNTs was accomplished via direct heating with PEG₃₅ to form ionic linkages (Scheme 1). In a typical experiment, a mixture of purified SWNT sample (255 mg) and PEG₃₅ (4.5 g) was heated to 100 °C and vigorously stirred under nitrogen protection for 4 days. The reaction was quenched by the addition of deionized water. The reaction mixture was repeatedly extracted with deionized water, coupled with centrifuging at 7500 rpm (~3000 g). The colored supernatant was collected and placed in a dialysis membrane tubing (cutoff molecular weight ~12 000) for the removal of unreacted PEG₃₅ via dialysis against fresh demineralized water for 5 days. The sample of PEG₃₅-functionalized SWNTs thus obtained was designated as the first soluble fraction. On the other hand, the insoluble residue from the functionalization reaction was dried to be used as starting material in the next functionalization reaction.

The procedure was repeated several times to obtain the second, third, fourth, and fifth soluble fractions. The final solid residue was also collected for characterization. The soluble fractions were also obtained in the solid state by removing the water from aqueous solutions on a rotary evaporator.

Results and Discussion

The soluble fractions from the sequential functionalization reactions of the SWNT sample with PEG₃₅ are all dark-colored, forming stable homogeneous solutions in polar organic solvents and water. The solubility allowed solution-phase NMR characterizations. As compared in Figure 1, the proton NMR spectra of all soluble fractions are similar, exhibiting a broad signal at ~3.6 ppm corresponding to the protons in nanotube-attached PEG₃₅ species. The significant broadening in the NMR signals is consistent with the considerably reduced mobility in the PEG₃₅ species upon their attachment to SWNTs in the functionalization reactions. The NMR results also suggest that there are no other meaningful reaction products.

As shown in Figure 2, the spectra of the sample solutions in the UV/vis region are generally featureless curves of gradually decreasing absorbivity with increasing wavelength, without any fundamental differences between the different soluble samples. The near-IR spectra were obtained for the samples in the solid state, a thin film on glass substrate (Figure 2). For all five fractions and the purified starting SWNT sample, there are the near-IR absorption bands at ~5400 cm⁻¹ (0.78 eV) and ~9700 cm⁻¹ (1.26 eV), which may be assigned to transitions corresponding to the first and second van Hove singularities in the electronic density of states for semiconducting SWNTs. However, the absence of the electronic transition peak around 14 000 cm⁻¹ (1.86 eV), corresponding to the absorption of metallic SWNTs, in the spectra of the soluble samples can hardly be considered as evidence for any selection against the metallic nanotubes in the functionalization reactions. It is known that the chemical modification of metallic SWNTs could significantly change their absorption properties.
There have been several reports on the dependence of the near-IR absorption spectral feature on the SWNT diameter. For example, Jost et al. suggested that the band-gap transition energy is proportional to the inverse of the nanotube diameter. Ruoff and co-workers also suggested that the shift of the near-IR absorption band around 6000 cm$^{-1}$ with the dispersion of SWNTs could be explained by different solubilities for SWNTs of different diameters, among other effects. Banerjee and Wong reported that the resolution of the near-IR spectral peaks in the solubilized SWNT sample could be explained by suggesting that certain discrete diameter distributions of nanotubes might be preferentially solubilized. The near-IR absorption spectra reported here (Figure 2) are apparently broad and show no obviously systematic changes in spectral features that might differentiate the soluble fractions. On the other hand, the absorption spectra do not exclude the possibility of selective solubilization of SWNTs in the sequential functionalization reactions. In fact, Raman spectroscopy is a more sensitive technique for an evaluation of the different soluble fractions.

The SWNTs in the solubilized fraction are well-dispersed, which makes it essentially impossible for direct Raman measurements because of overwhelming luminescence interference. Thus, Raman measurements of the different fractions were carried out after the thermal defunctionalization of the samples. The principle and practice for the thermal defunctionalization of functionalized carbon nanotubes via slow TGA scans have been reported previously. In the TGA scans, the organic functional groups are selectively evaporated, leaving behind defunctionalized SWNTs. As compared in Figure 3, the Raman spectra of the soluble fractions have similar features, except for changes in the radial breathing mode structure around 170 cm$^{-1}$. A closer look at the changes is provided in Figure 4. First of all, the radial breathing mode peaks of the final solid residue left from the repeated functionalization reactions are shifted to lower wavenumbers from those of the starting SWNT sample. The relative intensities of the two peaks are also reversed in the two samples (Figure 4). For the soluble fractions, the radial breathing mode peak profiles are between the two extremes of the starting sample and the final residue,
Table 1. Results from Dynamic Light Scattering Analyses of the Soluble Fractions in Homogeneous Solutions

<table>
<thead>
<tr>
<th>fraction</th>
<th>90° scattering angle</th>
<th>30° scattering angle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>avg sizea (nm)</td>
<td>avg sizeb (nm)</td>
</tr>
<tr>
<td>1</td>
<td>1115</td>
<td>1020</td>
</tr>
<tr>
<td>2</td>
<td>791</td>
<td>1225</td>
</tr>
<tr>
<td>3</td>
<td>597</td>
<td>1011</td>
</tr>
<tr>
<td>4</td>
<td>859</td>
<td>1382</td>
</tr>
<tr>
<td>5</td>
<td>1034</td>
<td>1410</td>
</tr>
</tbody>
</table>

* Obtained from the histogram in terms of Gaussian distribution analysis. * Standard deviation.

Figure 5. TEM images of the different soluble fractions deposited on a holey carbon-coated copper grid (all scale bars 100 nm).

consistent with the changes from one extreme to the other. Since the radial breathing mode frequency is correlated with the SWNT diameter in an inversely proportional relationship, the Raman results in Figure 4 suggest that the functionalization reactions are selective, resulting in preferential solubilization of SWNTs of smaller diameters.

An attempt was made to apply the sizing technique based on dynamic light scattering to the characterization of SWNTs in aqueous solutions of the soluble fractions.

Figure 6. High resolution TEM image of the soluble fraction 4 deposited on a holey carbon-coated copper grid.

Table 2. SWNT Contents in the Soluble Fractions

<table>
<thead>
<tr>
<th>fraction</th>
<th>SWNT content (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>4.7</td>
</tr>
<tr>
<td>3</td>
<td>8.1</td>
</tr>
<tr>
<td>4</td>
<td>9.1</td>
</tr>
<tr>
<td>5</td>
<td>17</td>
</tr>
</tbody>
</table>

In the measurements, the solution concentration was adjusted according to the scattering intensity for readings in the range between $5 \times 10^4$ and $1 \times 10^5$ counts. As shown in Table 1, the average sizes thus obtained are similar for different fractions, all around $1000$ nm, with generally broad size distributions. In principle, the dynamic light scattering is not a technique suitable for rod-shaped objects, especially for the nanotubes of such a large aspect ratio. The manufacturer of the particle size analyzer suggests that a lower scattering angle should be considered as a more favorable option for sizing rod-shaped objects. However, the results obtained by measuring the soluble fractions at different scattering angles show no meaningful difference (Table 1).

The functionalized SWNTs were analyzed by TEM. A specimen for analysis was prepared by using an inoculating loop to place a drop of a diluted solution of the functionalized SWNTs onto a holey carbon-coated copper grid, followed by the solvent evaporation. As shown in Figure 5, the TEM images for the five soluble fractions from sequential functionalization reactions exhibit no systematic changes, though the nanotubes in the first fraction appear somewhat shorter. The functionalized SWNTs in the images are apparently bundled. The bundling is due at least in part to the TEM sample preparation process. In fact, TEM images at a higher resolution, such as the one shown in Figure 6, confirm the aggregation of functionalized SWNTs.

The nanotube contents in the soluble fractions were estimated in TGA measurements with a slow scan rate of $5 ^\circC/min$ in nitrogen atmosphere. As shown in Table 2, the different soluble fractions contain different weight percentages of SWNTs, with a general trend of higher nanotube contents in later fractions. This might be rationalized by assuming that the SWNTs containing an average more defect sites (thus for the attachment of more functional groups) are preferentially solubilized in the
The presence of organic functionalities makes the direct SEM characterization of the soluble fractions difficult because of the severe surface-charging interference. The SEM imaging condition is significantly improved upon removal of the functional groups in the thermal defunctionalization. Shown in Figure 7 are some SEM images of the defunctionalized soluble samples. There are still surface-charging effects, probably due to residual functional groups that are not completely removed in the thermal defunctionalization. This is consistent with what has discussed above: that the nanotube contents in the soluble fractions are probably slightly overestimated in TGA analyses. A comparison between SEM images of the starting and final SWNT samples (Figure 7) seems to suggest that the final residue obtained after the five repeated functionalization reactions may be somewhat cleaner than the starting SWNT sample.

In summary, the direct heating of SWNTs with PEG$_{2000}$ is an effective way to functionalize and solubilize the nanotubes. The different soluble fractions obtained from the sequential functionalization reactions are generally similar, showing no obviously systematic changes from one reaction to the next. However, one clear exception is the solubilization of SWNTs of different diameters, with the reactions preferentially solubilizing the nanotubes of smaller diameters. Strong experimental evidence for the selectivity is primarily from Raman spectroscopy, though other experimental results are not inconsistent with the explanation. The mechanism behind the selectivity is not clear. It is possible that the preferential solubilization is related to the fact that carbon nanotubes of much smaller diameters are somewhat soluble even without the functionalization. In addition, the nanotube contents in different soluble fractions obtained from the sequential functionalization reactions are apparently different with higher nanotube contents in later fractions. Further investigations on other functionalization reactions for SWNT samples produced by other methods will be pursued.

Acknowledgment. We thank Professor A. M. Rao for supplying the carbon nanotube samples. Financial support from NSF, NASA, and the Center for Advanced Engineering Fibers and Films (NSF-ERC at Clemson University) is gratefully acknowledged. We also acknowledge the support by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, as part of theHTML User Program, managed by UT-Battelle LLC for DOE under Contract DE-AC05-000R22725.

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Quantum-Sized Carbon Dots for Bright and Colorful Photoluminescence

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Fluorescent semiconductor quantum dots have generated much excitement for a wide variety of applications, especially those in biology and medicine. For both in vitro and in vivo uses, however, the known toxicity and potential environmental hazard associated with many of these materials may represent serious limitations. Therefore, the search for benign nanostructured materials is of utmost importance. In particular, the discovery of new systems that can be used to deliver and sense small molecules has become an important area of research. We have previously reported the use of carbon nanotubes as a means of delivering small molecules to biological systems. In this report, we describe the use of carbon nanodots as a new class of materials for this purpose.

The carbon nanodots were synthesized via a laser ablation of a carbon target in the presence of water vapor with argon as carrier gas. The carbon target was prepared by hot-pressing a mixture of graphite powder and cement, followed by stepwise boiling, curing, and annealing in argon flow. A Q-switched Nd:YAG laser (1064 nm, 10 Hz) was used for the ablation, during which the carbon target was in a flow of argon gas carrying water vapor (through a water bubbler) at 500°C and 75 kPa. The so-produced sample, according to electron microscopy analysis, was dominated by nanoscale carbon particles in aggregates of various sizes. There was no detectable photoluminescence from the sample and its aqueous suspension. The sample was treated with a sub-nanomolar acid solution (up to 2.6M HCl) with refluxing for up to 12 h. The treated sample still exhibited no detectable photoluminescence. However, upon the surface passivation by attaching simple organic species to the acid-treated carbon particles (Scheme 1), bright luminescence emissions were observed (Figure 1).

Many organic molecules could serve as the purpose of surface passivation. For example, diazine-terminated condopic polyethylene glycol (H2NCH2COCH2CH2O)nCH2CH2CH2NH2 (average n = 35, PEG35) was used to react with the carbon nanoparticles (Scheme 1). In a typical reaction, PEG35 (200 mg, 0.13 mmol) was mixed with an acid-treated particle sample, and the mixture was heated to 120°C for 72 h. After the reaction, the mixture was cooled to room temperature and dispersed in water, followed by centrifugation (~14,000 g) for 30 min. The colored but homogeneous suspension contained the carbon dots with PEG35 species attached to the surface (Scheme 1). A small fraction of the supernatant was diluted for the preparation of microscopy specimens, deposited on a carbon-coated copper grid for scanning transmission electron microscopy (STEM) and on a mica surface for atomic force microscopy (AFM). The results suggest that these carbon dots are around 5 nm in diameter (Figure 2).

Other molecules or polymers, such as poly(propylene)ammonium-hexylamine (PPE-HA), could also be used in largely the same procedure for surface passivation to achieve similar results (Figure 3).

The passivated carbon dots with organic moieties attached to the surface are strongly photoluminescent both in the solution-like...
rescence emission is the radiative recombination of excitons. For the photoluminescent carbon dots reported here, however, there must be a quantum confinement of emissive energy traps to the particle surface, namely, that a large surface-to-volume ratio in a particle is necessary in order for the particle upon surface passivation to exhibit strong photoluminescence. There has already been experimental evidence supporting such a mechanistic argument. Larger carbon particles (30–50 nm in average diameter, for example) with the same surface passivation were found to be much less luminescent. Conversely, it might be expected that even higher photoluminescence quantum yields be achieved in smaller carbon dots with the same or similar surface morphology and passivation.

As in their silicon counterparts, the carbon dots may, in principle, be separated or manipulated such that some of the inhomogeneity in photoluminescence is removed. On the other hand, the inhomogeneity may be exploited in the use of the surface-passivated carbon dots for optical labeling to allow the selection of different emission colors with different excitation wavelengths (confocal microscopy, for example). The versatile surface functionalities as required for passivation will also be very useful for the carbon dots in bioimaging applications. The reagents, such as PEGylated, are not only aqueous compatible but also readily conjugated with antibodies or other bioactive molecules. Preliminary results on the optical imaging of biological species with the emissive carbon dots are provided in the Supporting Information.

Supporting Information Available: Additional characterization results, and preliminary results on the optical imaging of biological species. This material is available free of charge via the internet at http://pubs.acs.org.

References

NMR Detection of Single-Walled Carbon Nanotubes in Solution
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Xin Wang, Liangwei Ou, Balin Chen, and Ya-Ping Sun

Abstract: The detection of nanotube carbons in solution by 13C NMR is reported. The highly soluble sample wasfrom the functionalization of 13C-enriched single-walled carbon nanotubes (SWNTs) with diamino-
tetraacetic acid (DTPA) and polyethylene glycol (PEG-cool). The ferromagnetic impurities due to the residual
metal catalysts were removed from the sample via repeated magnetic separation. The nanotube carbon
signals are broad but partially resolved into two overlapping peaks, which are tentatively assigned to
nanotube carbons on semiconducting (sp2) and metallic (downfield) SWNTs. The solid-state NMR signals
of the same sample are similarly resolved. Mechanistic and practical implications of the results are discussed.

Introduction
There have been extensive recent investigations on the functionalization of single-walled carbon nanotubes (SWNTs)1–3
The functionalization typically renders solubilities of the nanotubes, enabling their characterization in homogeneous organic
and/or aqueous solutions. NMR is obviously one of the most desirable instrumental methods for studying the structures and
properties of functionalized carbon nanotubes. However, a number of technical difficulties have probably hindered a direct
13C NMR probing of the functionalized nanotube itself in solution, such as limited sample solubility and the presence of ferromagnetic impurities, among others. Thus, the available solution-phase NMR results are centered on the characterization of the functional groups. For example, Chen et al. reported the use of 1H NMR results to validate their proposed noncovalent π-stacking mechanism for the functionalization of SWNTs with poly(ethylene glycol) polymers.4 Holzinger et al. used 13C
NMR to characterize their soluble SWNT samples functionalized by various substituted oxycarbonyl nitrene compounds.6 The
NMR signals from the functional groups on SWNTs are often broader than those from the free functionalization agent, with generally similar patterns but sometimes shifting to the upfield.2

Solid-state 13C NMR has been applied to the characterization of nanotube carbons in the functionalized SWNT samples.6,7
The signals of the nanotube sp2 carbons are generally broad, centered around 120–130 ppm, similar to those for unfucntionalized SWNTs.8,9 In a recent study of polymer-functionalized SWNTs, solid-state 2D 1H–13C heteronuclear correlation spectroscopy was employed for evidence of significant interactions of the functional groups with the nanotube.7 Even for solid-state NMR, however, it is widely acknowledged that NMR measurements and results can be strongly affected by the presence of substantial ferromagnetic impurities from the residual metal catalysts used in the nanotube production.10,11 Despite the development of various purification methods,2 the catalyst residues can often survive some of the rather harsh chemical and thermal treatments of carbon nanotube samples. As a result, SWNTs produced by using catalysts of nonferromagnetic metals (Ni/Pd or Pt/Rh, for example) have been used in some recent NMR studies.10,11

Here, we report results from the first attempt of a solution-phase 13C NMR study of nanotube carbons in functionalized SWNTs. The nanotube sample was produced with 13C isotope enrichment. The high nanotube equivalent solubility was

achieved via the known functionalization of SWNTs with diamino-terminated oligomeric poly(ethylene glycol). The ferromagnetic impurities due to the residual metal catalysts were effectively removed from the functionalized nanotube sample in solution via repeated magnetic separation. The solution-phase NMR results are compared with those from solid-state NMR measurements. The partially resolved resonant carbon signals in the NMR spectra are discussed in terms of theoretically predicted differences in chemical shifts between semiconducting and metallic SWNTs.9

Experimental Section

Materials. Amorphous 13C powder (99.99% carbon, IC content >98%) and graphite powder (CVI grade) were supplied by Itoh Industries and Bucky carbons, respectively. Carbon cement was obtained from Daulo Industries. Powdered NBS (2–3 mm, 99.5%) and Cu (1–3 mm, 99.9%) were purchased from Alfa Aesar. D.C.H-(3-aminopropyl)poly(ethylene glycol) of average molecular weight, Mw 1500 (PEG250), and KCl (~99%) were obtained from Aldrich and denatured cellulose from Cambridge Isotope Laboratories. Cellulose amine dicyano butyric acid with a molecular weight cutoff (MWCO) of 12000 was supplied by Sigma.

The SWNT sample without 13C enrichment was purchased from Carbon Solutions. For the purification, raw material (1.2 g) was heated in air at 300 °C for 30 min. followed by refluxing in HNO3 (2 M, 500 mL) for 24 h. The mixture was then cooled to room temperature and subjected to centrifugation (~14000 g). Fisher Scientific, Scientific 228 Centrifuge. The sediment was repeatedly washed with deionized water and dried under vacuum to yield a purified SWNT sample (356 mg).

Raman spectra were obtained on a Renishaw Raman spectrometer equipped with a 0.06 m double laser source for 785 nm excitation and a CCD detector. Thermogravimetric analysis (TGA) experiments were carried out on a Mettler Toledo TGA-DSC1 system with a heating rate of 5 °C/min. Electron microscopy imaging was conducted on a Hitachi HD-2000 scanning transmission electron microscope (STEM) operated at 200 kV with digital imaging capability. The atomic absorption analysis service was provided by Goldie and Associates (Sanera, South Carolina). Samples for the analysis were digested by using hot HNO3/HCl mixture in ac- cordanv with the EPA 200.2 method.

NMR measurements were performed on a Bruker Avance 500 NMR spectrometer equipped with a 4 mm magic angle spinning (MAS) probe head and a 5 mm nano-mate probe head for solution. For every broad signals, experimental multiplicity with a line broadening up to 500 Hz was applied for every carbon FID (free induction decay), coupled with user-defined spine baseline correction in the data processing. The spin–lattice relaxation times of both solid and solution samples were measured with the inversion recovery pulse sequence. Since the solution- and solid-state NMR experiments showed that the nanotube carbon signals were not affected by the proton decoupling, the reported NMR spectra were collected without the decoupling (to avoid overemphasizing the sample and potential damage to the equipment in solid-state experiments).

13C-Enriched SWNTs. The laser ablation method14 was used for the synthesis of 13C-enriched SWNTs. The laser source was a Spectra Physics Quantel 530-YAG laser operated at 10 Hz (2 J/ pulse at 1064 nm and 9 mm beam diameter). In a typical experiment, the ablation target was prepared by mixing powdery 13C (0.8 g), graphite (1.25 g), Ni (0.126 g), and Cu (0.126 g) with graphite cement (2–40 g) for hot-pressing (130 °C) into a pellet (about 10 mm thick and 15 mm in diameter), followed by boiling at 180 °C for 5 h in air, stirring at 810 °C for 8 h, and annealing at 1200 °C for 30 h in an argon flow (50 scmm, atmospheric pressure). The furnace temperature was set at 1150 °C, with a steady argon flow (62 scmm, 75 kPa), in the ablation experiment. The laser-irradiated carbon from the laser ablation was characterized by Raman, and the results were consistent with the expected substantial presence of 13C-enriched SWNTs in the target. According to the characteristic O-band shift, the atomic content of 13C in the nanotubes was estimated as 16%.14

The purification of the 13C-enriched SWNT sample was similar to that discussed above for the regular SWNT sample.

Functionalization and Magnetic Separation. In a typical experiment, a purified 13C-enriched SWNT sample (60 mg) was mixed with PEG2000 (1.2 g), and the mixture was heated at 120 °C. After 2 days at this temperature, the reaction mixture was cooled to room temperature for repeated extraction with water. In each extraction, the soluble fraction containing PEG2000-functionalized nanotubes was separated from the insoluble residue via centrifugation (~4100g for 15 min). Typically, these procedures were performed with the supernatant in the last repeat being colorless. The aqueous solutions from the repeated extractions were combined for further isolation.

The magnetic separation to remove residual metal catalysts in the solubilized sample was accomplished by using a commercially available magnetic separator (Dynal Biotech, Model MPCL)16 Each magnetic separation experiment was for 2 days, and the experiments were repeated three times to ensure maximal precipitation of all magnetically responsive species. The final supernatant was recovered, followed by dialysis (MWCO ~ 12000) against fresh deionized water for 3 days (removing free PEG2000) to yield a colorless aqueous solution of PEG2000-functionalized 13C-enriched SWNTs (PEG13C)2/SWNT.

The same procedure was applied to obtain a magnetically purified 13C-functionalized SWNT sample without 13C enrichment for the nanotubes.

Results and Discussion

The properties (appearance, solubility, nanotube content, 1H NMR, microscopy images, etc.) of the PEG13C/SWNT sample are similar to those of their counterpart without 13C enrichment already reported in the literature.14 The high solubility of these functionalized nanotubes15 coupled with the 13C enrichment, made it possible to probe nanotube carbons in solution-phase NMR measurements. As shown in Figure 1 for PEG13C/SWNT in D2O (solution concentration ~ 50 mg/mL SWNT equivalent), the nanotube 2p carbons exhibit a broad central feature at ~132 ppm (4 (Hm) ~ 28 ppm), which is consistent with theoretical predictions17 and close to those observed in solid-state NMR.4,22 Obviously, nanotube carbons can be detected by NMR in solution.

The broadness in the signals reflects the chemical shift dispersion of nanotube carbons, which are likely homonuclear due to different nanotube chiralities, lengths, adjacent defects, etc.6,18 Interestingly, however, there are some distinctive features in the broad signals, which through deconvolution (resolving the curve into underlying peaks) can be represented by two Lorentzian peaks of similar line-widths (~20 ppm, Figure 1). The ratio of areas under the peak centered at 128 ppm to that at 144 ppm is ~1.8. A variation of relaxation delay time from 5 to 0.4 s had little effect on the signal shape, with similar line-widths and chemical shifts. We tentatively assign the two peaks

to semiconducting (upfield) and metallic (downfield) SWNTs. In fact, the observed difference in their chemical shifts (~15 ppm) is in reasonable agreement with what has been predicted by recent theoretical calculations. These calculations suggested that there should be an approximately ~12 ppm upfield shift for the semiconducting nanotube carbons from their metallic counterparts due to the localized ring currents.

There was also suggestion that the broad solid-state NMR signals of nanotube carbons could be deconvoluted into two peaks corresponding to semiconducting and metallic SWNTs, despite the fact that these signals were not resolved at all. The peak shoulder structure shown in Figure 1 represents the first experimental confirmation that there is indeed a pair of broad signals associated with the sp² carbons in SWNTs. The acquisition of the partially resolved ¹³C NMR benefited significantly from the effective removal of residual metal catalysts via repeated magnetic precipitation in solution. It is well-known that the ferromagnetic residuals associated with the Ni–Co catalysts interfere with NMR measurements. These residuals are often encapsulated in carbon cages or structural cavities and are thus, impossible to remove completely in the chemical purification. The solidification of the nanotube sample enabled the solution-phase magnetic separation. The separation was effective, as confirmed by STEM analyses of the separated samples (Figure 2) and by TGA analysis (negligible residuals), and also was reflected in the NMR results (diminished spinning sidebands in the solid-state NMR spectrum, for example). According to the atomic absorption analysis of the PEG₉₅₀–¹³C–SWNT sample, the Ni content was <0.057 wt % and the Co content was much lower (below the detection limit).

The solid-state ¹³C MAS NMR spectrum of the PEG₉₅₀–¹³C–SWNT sample was acquired for comparison with the solution-phase result. The nanotube carbon signals in the solid-state spectrum are equally broad, with no obvious overlapping peaks at ~126 and ~136 ppm (Figure 3). Similar to the solution-phase signals, these two peaks may also be assigned to semiconducting and metallic SWNTs. The relative intensities
of the two peaks are somewhat different in solid state versus in solution. Additionally, the overall intensity of the nanotube carbon signals in reference to that of PEG15000 functional groups is significantly higher in solid state than in solution. These two differences between solid-state and solution-phase NMR results may share the same cause. As in other soluble functionalized SWNTs, the PEG15000-^{13}C—SWNT sample contains bundled nanotubes in solution. The bundling of larger bundles may proceed too slow to eliminate such orientation-dependent contributions to the NMR line-width as chemical shift anisotropy and dipolar coupling. These species are essentially NMR "silent" in solution, corresponding to a lower effective nanotube carbon concentration to result in their relatively weaker overall signal intensity in the solution-phase NMR spectrum. The functionalized semiconducting SWNTs disperse better in solution, as made evident by recent experimental results. Therefore, their NMR signals relative to those of their metallic counterparts are stronger in solution (Figure 1) than in the solid state (Figure 5).

There are apparently significant interactions between the nanotube carbons and the PEG moieties in the solid state, with the latter serving as spin—lattice relaxation centers. The relaxation time (T1) of the nanotube carbons was estimated by using the null-point approach based on the inversion recovery sequence. Both nanotube components effectively "disappeared" at the same point, τnull = 0.16 s, corresponding to T1 ~ 0.2 s. Despite the absence of ferromagnetic impurities in the PEG15000-^{13}C—SWNT sample, the estimated T1 is up to 2 orders of magnitude shorter than those of similarly^{13}C-enriched SWNTs without functionalization.8,11 The interactions are also reflected in the NMR results of the PEG carbons. For PEG15000-^{13}C—SWNT in D_2O solution, the spin—lattice relaxation time of PEG carbon signals (500 ms) is close to that in free PEG15000.

(710 ms). However, in solid state, the relaxation time of PEG carbons in the PEG15000—^{13}C—SWNT sample is more than an order of magnitude shorter (37 ms) than that in free PEG15000 (430 ms). It seems that the segmental mobility of PEG moieties in PEG15000—^{13}C—SWNT in the solid state is low, presumably with the motion of PEG moieties restricted by their proximity to the nanotubes. Such significant difference of the relaxation times for the nanotube-bound functional groups in solution phase versus in solid state is interesting. It may be exploited for potential applications in the NMR characterization of nanocomposite materials, such as probing interactions of carbon nanotubes with the polymeric matrix.

In summary, we demonstrated that the nanotube carbons in solution could readily be detected in ^{13}C NMR by using highly soluble functionalized SWNTs. The ferromagnetic impurities in the sample for NMR measurements were effectively removed via repeated magnetic separation. The nanotube carbon signals are broad, but partially resolved into two adjacent features, probably corresponding to nanotube carbons in semiconducting (upfield) and metallic (downfield) SWNTs. The solid-state NMR signals of the same sample are similarly resolved. These results suggest that ^{13}C NMR may be explored to serve as a useful tool in the characterization of SWNTs of different electronic structures.8,15

Acknowledgment. Financial support from NSF, NASA, and Center for Advanced Engineering Fibers and Films (NSF-ERC at Clemson University) is gratefully acknowledged.

Supporting Information Available: Raman spectra of ^{13}C-enriched SWNTs and SWNTs without enrichment. This material is available free of charge via the Internet at http://pubs.acs.org.

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Solubilization of boron nitride nanotubes

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A successful attempt in the functionalization and solubilization of boron nitride nanotubes (BNNTs) for their electronic, thermal, and mechanical properties, which are in many cases different from and/or superior to those of carbon nanotubes. For example, BNNTs are semiconductors with a wide band-gap (4–5 eV) independent of the nanotube chirality or morphology. The thermal conductivity, oxidation resistivity, thermal and chemical stability, and yield resistance of BNNTs are higher than those of their carbon analogs. Among widely discussed unique applications of BNNTs are their use as nanoscale semiconductors operating in oxidative environments at high temperatures and as insulating nanocomposites of high thermal conductivity.

Most investigations in the literature were focused on BNNTs in the solid state, because these nanotubes, like their carbon counterparts, are generally insoluble in common organic and aqueous media. For carbon nanotubes, the research efforts on their functionalization and solubilization have stimulated and enabled the exploitation of the properties and applications that are not accessible in the solid state, such as the dispersion of carbon nanotubes in polymeric nanocomposites and the compatibilization with biological systems. Similarly significant effects on the research of BNNTs may be expected from the introduction of the nanotubes into homogeneous solution. We report here a successful attempt in the solubilization of BNNTs. The functionalization was based on interactions of amino groups in oligomeric diamine-terminated poly(ethylene glycol) (PEG) with the BNNT surface, conceptually similar to those proposed in the solubilization of carbon nanotubes. The solubilization procedure and results from the characterization of BNNTs before and after the solubilization are presented and discussed.

BNNTs were synthesized by the carbon nanotube substitution reaction, in which purified multi-walled carbon nanotubes (MWNTs, Nanostructure & Amorphous Materials, Inc.) were used as a template to react with boron oxide (powder, 99.8%, Alfa Aesar) and anhydrous ammonia (National Welders Supply Company) in a quartz chamber at high temperature (1200 °C), followed by thermal treatment (780 °C) in low-pressure air to remove the residual carbon from the sample. The X-ray photoelectron spectroscopy (XPS, Kratos AXIS 165) analysis of the sample yielded a B:N ratio of 1.05:1, with the slight excess of boron due to residual boron oxide. Upon further purification by repeated washing with hot water to remove boron oxide, the content of BNNTs in the sample was at least 75% by weight, comparable with those reported in the literature.

The thermogravimetric analysis (TGA, Mettler-Toledo TGA/SDTA851e) result of the sample in air is shown in Fig. 1. The weight loss at high temperatures was due to the oxidation of boron in the BNNTs, and the amount of increase (~25%) was consistent with the estimated BNNT content in the sample. The presence of BNNTs in the sample was confirmed by scanning electron microscopy (SEM, Hitachi S-4700) and transmission electron microscopy (TEM, Hitachi HD-2000) characterization. The SEM image in Fig. 2 (top) shows abundant nanotubes. The TEM results suggest that the BNNTs are mostly long tubes of around 20 nm in diameter (Fig. 2, bottom), with generally thinner walls than those in the starting MWNTs and also with a distorted layer structure in the wall.

The BNNTs were solubilized via functionalization with amine-terminated oligomeric poly(ethylene glycol) (PEG) in a typical experiment, a sample of BNNTs (42 mg) was mixed with PEG1000 (890 mg), and the mixture was heated to 100 °C and kept at that temperature for 3 days under nitrogen protection. Upon cooling to ambient temperature, the reaction mixture was extracted repeatedly with deionized water, coupled with centrifuging at 3000 g. According to the weight of the solid residue, the majority (more than 55%) of the starting BNNTs were solubilized in water as a result of the functionalization with PEG1000 (Scheme 1).

The functionalized BNNTs are soluble in water and organic media compatible with PEG1000. While BNNTs are colorless, the attachment of PEG1000 to the functionalized BNNTs changed the sample color to brown (Fig. 3). Both the functionalization and

![Fig. 1](A TGA trace of the BNNT sample (air, 10 °C min⁻¹), where the weight increase is due to the addition of oxygen.)
the solution color are likely due to interactions of the PEG$_{1000}$ amino groups with nanotubes, as proposed in Scheme 1. According to results from control experiments, the amino moiety in the functionalization agent is necessary for the functionalization and solubilization of BNNTs. In fact, there was no solubilization at all when the nanotube sample was simply heated in neat deionized water under the same experimental conditions. Similarly, no meaningful solubilization was found with the use of alcohol-terminated or methoxy-terminated PEG (PEG$_{1000}$OH and PEG$_{1000}$OCH$_3$, respectively) as the functionalization agent.

![Fig. 2 SEM (top) and TEM (bottom) images of the purified BNNTs.](image)

Scheme 1

![Fig. 3 (a) An aqueous solution of the PEG$_{1000}$-functionalized BNNTs. (b) The suspension from the dialysis of the solution in (a) against water. (c) The supernatant from the low-speed centrifuging of the suspension in (b).](image)

The functionalization of BNNTs with PEG$_{1000}$ was reversible. The brown-colored solution of PEG$_{1000}$-functionalized BNNTs was placed in a membrane tubing (molecular weight cutoff ~12000) for dialysis against fresh deionized water. In less than 3 days, the color disappeared and the solution turned into a suspension (Fig. 3), from which colorless BNNTs were recovered almost quantitatively via simple low-speed centrifuging. As shown in Fig. 4, the FT-IR (Thermo-Nicolet Nexus 670) spectral features of the recovered BNNTs are generally the same as those of the starting BNNTs (except for several small peaks due to residual PEG$_{1000}$OH, with the characteristic peaks at 1380 cm$^{-1}$ and 800 cm$^{-1}$ due to B-N vibrations parallel and perpendicular to the nanotube axes, respectively).

Additional experiments were performed to confirm that the solution color was indeed associated with the PEG$_{1000}$-BNNT interactions. One was to precipitate the PEG$_{1000}$-functionalized BNNTs from the brown-colored solution via high-speed centrifuging. At 25000 g for 30 min, brownish precipitates were observed, and the solution became only slightly yellowish, suggesting that the color was attached to the nanotubes.

![Fig. 4 The FT-IR spectra of the starting (a) and recovered (b) BNNT samples in a KBr matrix.](image)
another experiment, the PEG$_{1000}$-functionalized BNNTs were diazylized against an aqueous solution of the PEG$_{1000}$ with matching concentration. No meaningful precipitation or change in solution color were observed after the diazlysis. Thus, the color must be a part of the functionalization, as proposed in Scheme 1.

The dispersion of the PEG$_{1000}$-functionalized BNNTs was examined by both TEM and AFM (Molecular Imaging PicoPlus). For the TEM specimen, a small drop of an aqueous solution of the functionalized BNNTs was placed on a holey-carbon-coated copper grid, followed by solvent evaporation. As shown in the TEM image in Fig. 3, the nanotubes are well-dispersed. The sample for AFM measurement was deposited on a mica substrate. However, the presence of abundant functional group PEG$_{1000}$ made the imaging somewhat difficult. Thus, the specimen was treated at 400 °C in air for 1 h to remove some of the functionalized molecules from the sample. The subsequent AFM image of the thermally treated specimen exhibits island-like structures on the nanotube surface (Fig. 3), which may be attributed to the remaining PEG$_{1000}$ functional groups.

In summary, BNNTs could be introduced into homogeneous aqueous and organic solutions via the functionalization with oligomeric PEG molecules bearing amino moieties. The color change of the sample from colorless to brown upon the functionalization was identified as being associated with interactions between the PEG amino groups and the nanotube surface. Both the solubilization and the color change were found to be reversible, which could be interpreted mechanistically as being due to the formation and dissociation of amine-boron ionic bonds. The solubilization via functionalization may add a new dimension in applications of BNNTs, such as their homogeneous dispersion in nanocomposite materials for unique thermal and optical properties.

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Notes and references

14. The functionalization of BNNTs with stannic oxide nanoparticles has been reported (W. Q. Han and A. Zettl, J. Am. Chem. Soc., 2002, 124, 2001), but no solubilization.
Separation of metallic and semiconducting single-walled carbon nanotubes

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1. INTRODUCTION

Carbon nanotubes are one-dimensional carbon allotropes. They are cylindrical hollow structures, with the conjugated carbon network forming one or multiple concentric atomic layers of thin walls, known as single-walled carbon nanotubes (SWNT) or multi-walled carbon nanotubes (MWNT), respectively. An SWNT (or an MWNT layer) may be formed conceptually by rolling up a graphene sheet into cylindrical structure [1-3]. This requires a chiral vector \( \mathbf{C}_h \) consisting of two primitive vectors \( \mathbf{C}_h = n \mathbf{a}_1 + m \mathbf{a}_2 \), to match the graphitic carbon atoms from edge to edge (Fig. 1). The chiral vector, often referred to as the chiral index \( (n,m) \) (or chirality, helicity), uniquely defines the diameter \( d \) and the chiral angle \( \theta \) of the SWNT:

\[
d = \frac{\sqrt{3}a_c}{\pi} (n^2 + mn + m^2)
\]

\[
\theta = \tan^{-1}\left(\frac{3m}{2n + m}\right)
\]

where \( a_c \approx 0.142 \text{ nm} \) is the nearest-neighbor C-C distance.

It is now well established, both theoretically and experimentally, that a SWNT can be either semiconducting or metallic (including semi- or quasi-metallic) in nature, which is referred to as "metalliclicity". The SWNT metalliclicity depends upon its chirality: if \( n - m = 3q \) (\( q \) is an integer), its electronic density of states (DOS) exhibits a significant band-gap near the Fermi level, and the SWNT is semiconducting; if \( n - m = 3q \), the conductance and valence bands overlap, and the SWNT is metallic (semimetallic when \( n \neq m \)). Thus, the ratio of semiconducting and metallic SWNTs in a statistically as-grown mixture is 2:1. In fact, a tiny difference in the nanotube chirality could result in distinctively different properties. For example, (10,10) and (11,9) SWNTs have almost identical diameters (1.358 \text{ nm} vs. 1.358 \text{ nm}) and minor differences in their chiral angles (30° vs. 26.7°), but they are metallic (continuous DOS near Fermi level) and semiconducting (a band-gap of -0.64 \text{ eV}) respectively.
Figure 1. The conceptual SWNT formation by rolling up a graphene sheet. As an example, the dashed lines represent the two edges that will merge in the rolling up of a (7,3) semiconducting SWNT.

There have been many reports and predictions on the superior materials properties of carbon nanotubes, including those relevant to their potential electrical, mechanical, thermal, optical, and other applications [4,5]. Many of these applications depend strongly on the metallic and semiconducting characteristics of carbon nanotubes. For example, semiconducting SWNTs are necessary in field-effect transistor (FET) devices [6] (including those for chemical [7] and biological sensors [8]) and electroluminescent and photovoltaic materials [9–11]. Metallic SWNTs are required for nano-circuitry [12], transparent conductive coatings, and polymeric nanocomposites of unique electrical properties [13,14]. Therefore, the availability of SWNT samples of desired metallic or semiconducting characteristics for their respective applications is of paramount importance.

Semiconducting and metallic SWNTs differ not only in their electrical conductivities but also in other physical and chemical aspects, such as static polarizability, doping properties, chemical reactivities, and some other electronic structure-induced characteristics. Conversely, the different properties between the two types of SWNTs make possible their identification and separation. As first reported by the IBM group in 2001 [15], metallic SWNTs could be selectively eliminated via current-induced electrical breakdown to leave behind semiconducting...
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SWNTs for FET devices. Since then, there has been great interest in the research community in preparing nanotube samples containing only metallic or semiconducting SWNTs. Significant progress has been achieved in the development of methodologies and merits for metallic/semiconducting enrichment in nanotube production or post-production separation, projecting a promising future for the research field.

In this chapter, we will review most of the currently available strategies and experimental methods for enriched metallic or semiconducting SWNTs and provide a perspective on the further development. We will begin with a brief introduction on the techniques that are commonly used or required for the differentiation and characterization of metallic and semiconducting SWNTs.

2. IDENTIFICATION AND CHARACTERIZATION

A number of micro- and macroscopic techniques have been used for the characterization and differentiation of semiconducting vs. metallic SWNTs in a given sample. Qualitative information on whether a sample is enriched with one kind of SWNT could usually be obtained rather conveniently. However, despite much effort and recent advances, a quantitative evaluation of either mixed or enriched samples is by no means a trivial task. Summarized here are some commonly used characterization techniques. Their advantages and disadvantages, especially with respect to the more challenging quantitative evaluation, are discussed.

2.1. Microscopic techniques

Microscopic techniques are those based on "counting" individual nanotubes, in which the semiconducting or metallic SWNTs are identified one by one to build a data set for statistical analysis. Among the most sophisticated are the uses of microscopy methods to image each SWNT at atomic resolution to determine its chirality (Fig. 2). Unfortunately, this is hardly straightforward experimentally for routine practices, even in light of the recent rapid advances in scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS) [16,17], and high-resolution transmission electron microscopy (HR-TEM) [18,19] instrumentation. High-resolution electron diffraction technique has been used in the characterization of bundled SWNTs, but its applicability to the determination of nanotube chirality is probably limited [20,21].

Other methods in this category include those based on direct electrical measurement of individual nanotubes. For example, the I-V relationship of nanotube devices can be determined, with the assistance of atomic force microscopy (AFM), to identify the metallic or semiconducting nature of the underlying nanotube [22]. Alternatively, selective current-induced electrical breakdown could be used [22] (Sec. 3.2). In this method, the electrodes are bridged with multiple SWNTs. By ramping the current at controlled gate voltage (so that no current is passed through semiconducting SWNTs), metallic SWNTs are burned off one by one, providing individual abrupt changes (counts) in the electrical signal. The semiconducting SWNTs are then turned on and similarly burned off one by one, providing the other data set of counting (Fig. 3).
Figure 2. High-resolution STM (left) and TEM (right) images of SWNT.
(Reproduced from Refs. [3] and [19], respectively, with permission. Copyright © 1996 American Chemical Society and 2003 The Royal Microscopical Society.)
Figure 3. (a) Schematic drawing of a five-SWNTs-in-parallel transistor device. (b) $I_d$ vs. $V_g$ showing sequential electrical breakdown of the SWNTs in the device. (Reproduced from [22] with permission. Copyright © 2004 American Chemical Society.)

In the use of electrical counting methods, especially those based on the electrical breakdown, the controlled fabrication of microelectrodes that are in excellent contact with the nanotubes is a significant technical challenge. Other issues also include the presence of semi-metallic SWNTs in the sample [23], the interference owing to strong current oscillations for semiconducting SWNTs at current saturation and high source-drain biases [22], and the bundling of nanotubes [15]. For bundling, in particular, it is inevitable that some of the semiconducting SWNTs will be sacrificed in the devices containing bundled SWNTs before metallic SWNTs can all be destroyed (counted) [15]. Therefore, when the counting technique is applied to a bulk sample, exhaustive solution processing is often required to exfoliate the nanotube bundles [24].
2.2. Macroscopic techniques

Macroscopic characterization techniques measure the properties of an assembly of nanotubes. These include various spectroscopic methods, and certainly, bulk electrical conductivity measurements.

2.2.1. Optical Absorption

Both semiconducting and metallic SWNTs have optical signatures in the visible and near-IR wavelength regions, corresponding to their respective electronic transitions. Because of the quantum confinement effect, the DOS of SWNT is characterized by well-defined spike-like features, known as van Hove singularities [1,2]. In a simple tight-binding model, the energy separation of each van Hove singularity pair is inversely related to the nanotube diameter \( d \) and weakly dependent upon the chiral angle \( \theta \). The energy gaps in semiconducting \( (S_j) \) and metallic SWNTs \( (M_j) \) can be approximately expressed as follows [20]:

\[
S_j = \frac{2 \hbar \nu_r}{d}, \quad S_2 = \frac{4 \hbar \nu_r}{d}, \quad \ldots
\]

\[
M_j = 6 \hbar \nu_r, \quad M_1, \quad \ldots
\]

where \( \nu_r \) is C-C tight-binding overlap energy (~2.4-3.0 eV), \( a_{nn} \) is the nearest neighbor C-C distance (~0.142 nm), and \( d \) the nanotube diameter. The inverse relationship between the band-gap energies and the tube diameter was concisely presented as a comprehensive plot by Kataura and coworkers ("Kataura Plot", Fig. 4) [27]. The plot has subsequently been modified on the basis of available experimental energy gap data for semiconducting SWNTs [28-32].

According to the tight-binding approximation (Formulas (3) and (4)), the diameter of SWNTs is in the range of ~0.7-1.8 nm, such that \( S_1 \) of 1-0.4 eV (1240-3100 nm), \( S_2 \) of 2-0.8 eV (620-1550 nm), and \( M_j \) of 3-1.2 eV (410-1030 nm). For currently available samples from different production methods, these optical absorption features are distinctive without severe overlapping if SWNTs in the sample are in a relatively narrow diameter range (Fig. 5). The optical density of each nanotube transition obeys Beer's Law [33]. However, the relationship between the absorption cross-sections of different SWNTs and their chiralities is still unclear. Experimentally, technical issues, such as the necessary corrections for the effect of light scattering (due to the aggregation of nanotubes) and for the plasmon background, should be carefully considered when optical absorption is used in the quantitative evaluation of metallic and semiconducting SWNTs [33,34]. The doping of nanotube surface (either covalently or non-covalently) may significantly suppress or diminish \( S_j \) and in some cases \( S_2 \) transitions [35-39].

The DOS of metallic ("armchair", \( n = m \)) SWNTs in bundles and semi-metallic \( (n - m = 3q, n \neq m) \) ones exhibit only a small gap at millielectronvolt level, and thus optical transitions in the far-IR region [40]. This small energy gap in the metallic SWNTs may disappear upon chemical alteration of the conjugated carbon structure, such as in carbene addition [41,42], in addition to its extreme sensitivity toward various doping effects. The far-IR absorption feature may serve as a
Figure 4. The original Kataura plot: the relationship of SWNT band-gap energies with the nanotube diameter (•: metallic SWNTs; ○: semiconducting SWNTs). Arrows indicate the diameter distribution of SWNTs produced from two different catalysts. Two horizontal lines in each catalyst area define the "metallic window" in which the optical transitions are from the metallic SWNTs only. (Reproduced from Ref. [27] with permission. Copyright © 1999 Elsevier Science B. V.)

Qualitative tool in the probing of reactions with metallic SWNTs, as demonstrated by Haddon and coworkers [40–42]. Its potential in quantitative evaluations is yet to be explored.

2.2.2. Fluorescence Spectroscopy

Well-dispersed semiconducting SWNTs exhibit weak but distinctive band-gap fluorescence (Fig. 6) [24]. The excitation and emission energy contour plot follows a characteristic pattern, making it possible to directly determine the (n,m) values of semiconducting SWNTs present in the sample [28]. Conversely, the S_{1} and S_{0} energies have been determined from the experimental excitation–emission data [29]. Metallic SWNTs are practically non-fluorescent, which somewhat limits the applicability of the characterization technique. The fluorescence in semiconducting SWNTs is vulnerable to quenching associated with inter-tube interactions in
bundled nanotubes. A sample preparation procedure involving ultrasonication and ultracentrifugation in the presence of surfactant is typically required [24]. Since only a tiny fraction of the bulk sample under consideration is “extracted” in the procedure, there is need for caution in the extrapolation of the observed fluorescence properties to the entire sample.

2.2.3. Raman Spectroscopy

In Raman measurements of SWNTs, the nanotube signals are resonantly enhanced when the excitation wavelength is close to the optical transitions (usually S_2, S_3, M_1) [43,44]. In other words, metallic or semiconducting SWNTs of certain diameters are sensitive only to selected Raman excitation wavelengths. There are three sets of Raman signals for SWNTs that reveal the most information: G-band at ~1550–1600 cm^{-1} from vibrations of graphitic sp^2 carbons (tangential and parallel to the tube axis), D-band at ~1350 cm^{-1} from disordered sp^2 carbons, and radial breathing mode (RBM, tubular carbon vibrations in the radial direction) peaks in the low-frequency region of ~100–200 cm^{-1}. The G-band and RBM peaks are more useful to both qualitative and quantitative evaluations of metallic and semiconducting SWNTs.
The two kinds of SWNTs have different $G$-band line-shapes [45,46]. The two components of the $G$-signal, $\omega_{G}$ at lower frequency ($\sim 1500$ cm$^{-1}$) and $\omega_{G}'$ at higher frequency ($\sim 1550$ cm$^{-1}$), are related to vibrations at the tangential direction and parallel to the tube axis, respectively. The $\omega_{G}$ component is similar in both metallic and semiconducting SWNTs, a sharp Lorentzian peak narrow in line width. The $\omega_{G}'$ component in semiconducting SWNTs is also Lorentzian in shape, but the same component in metallic SWNTs is asymmetrical and much broader, known as Breit-Wigner-Fano (BWF) lineshape (Fig. 7). Thus, at a given Raman excitation wavelength, the observation of BWF lineshape for the $G$-band is commonly used as a qualitative indicator for the presence of metallic SWNTs.

The position of a nanotube Raman signal is inversely proportional to its diameter:

$$\omega_{\text{signal}} = c_{1}/d + c_{2}$$

where $d$ is the diameter of the SWNT and $c_{1}$ and $c_{2}$ are empirical parameters available in various reports [28,30,44,47,48]. Thus, by using the BWF region in a Raman spectrum, one can easily estimate the diameter distribution of the SWNTs that are in resonance with the excitation wavelength. In single-molecule Raman spectroscopy,
Figure 7. Raman tangential mode spectra of SWNTs obtained with several different laser lines. The BWF G-band features (in the dashed ellipse) are obvious at laser energies of 1.89–2.14 eV. The inset shows low-resolution Raman spectra in 1300–2800 cm\(^{-1}\) in the critical range of laser energies 2.00–2.18 eV. (Reproduced from Ref. [45] with permission. Copyright © 1998 The American Physical Society.)

where only one SWNT is detected, it is possible to assign the nanotube chirality [42,54]. There have also been similar chirality assignments based on Raman results of surfactant-assisted individual SWNT dispersions [28,30].

In the evaluation of metallic and semiconducting SWNTs, it is important to know the electronic types and diameters of SWNTs that are resonant with the given
Raman excitation wavelength. A particularly useful guide is the Kataura Plot, which visually depicts the relationship between the nanotube diameters and their corresponding transition energies [27-32]. Several precautions are also advised with respect to the use of Raman RBM modes in determining the metallic or semiconducting enrichment in a sample. First, multiple excitation wavelengths are always necessary to obtain overall information on a given sample because of the resonance effect. The construction of total RBM maps is helpful if (quasi-) continuous Raman excitations are available (Fig. 8) [51]. Second, RBM is very sensitive to the nanotube morphology, namely that the same SWNT sample with a distribution of chiralities (diameters) after different processing procedures could have different relative RBM intensities for the various tubes that are in resonance [52,53]. Third, the relative RBM intensities of different nanotubes in a Raman spectrum do not quantitatively represent their relative abundance because of the resonance

![Graph](image)

Figure 8. A Raman RBM "map" obtained with 76 different laser lines for HiPco-SWNTs dispersed in aqueous SDS solution. (Reproduced from Ref. [51] with permission. Copyright © 2004 The American Physical Society.)
effect, although each signal itself may be comparable in different samples providing the sample morphology is strictly controlled. Recently, several comprehensive and quantitative evaluations of nanotube diameter selectivity and metallic/semiconducting enrichment in SWNT samples have been reported [54, 55].

2.2.4. NMR spectroscopy

As predicted theoretically, the chemical shifts of nanotube carbons in metallic and semiconducting SWNTs are different, with the latter ~12 ppm up-field shifted (lower in chemical shift value) owing to the effect of localized ring current [56]. In a recent NMR investigation of functionalized SWNTs (13C enriched) in both solution and solid state, Klzyhorodskiy et al. [57] observed two resolved nanotube carbon signals (Fig. 9). The two signals are separated by 10–15 ppm, consistent with those of metallic and semiconducting SWNTs. Separately, the relaxation times of the carbons in metallic and semiconducting SWNTs are known to be different, with the former being much shorter [58]. Thus, the carbon NMR technique based on more accurate determination of chemical shifts and/or relaxation times may find increasing applications in qualitative and quantitative evaluations of metallic and semiconducting SWNTs in mixed or enriched samples.

Figure 9. The 13C NMR spectrum of a functionalized 13C-enriched SWNT sample in D2O solution. Shown in the inset is a deconvolution based on two Lorentzian peaks, tentatively assigned to metallic (higher δ) and semiconducting (lower δ) SWNTs. (Reproduced from Ref. [57] with permission. Copyright © 2005 American Chemical Society.)
2.2.5. Bulk Conductivity

The electrical conductivity of bulk SWNT samples is commonly measured by using the classical four-point probe technique [59]. However, the absolute values of electrical conductivity thus measured are easily affected by some external factors in the experiments, so that caution is necessary in the data interpretation. On the other hand, the relative conductivity values for different samples are generally comparable if measured under the same conditions, which thus allows for a meaningful evaluation of samples enriched with metallic or semiconducting SWNTs at different levels [60,61]. Terahertz conductivity measurements have also been applied for similar purposes [62-64].

3. ENRICHMENT AND SEPARATION

Three major production methods for SWNTs are arc-discharge [66], laser ablation [25], and chemical vapor deposition [66-68] (CVD, including the HiPco or high-pressure carbon monoxide disproportionation method [69]). The nanotube samples from these production methods are widely considered as containing the statistical distributions of metallic (1S) and semiconducting (2S) SWNTs. There have been claims for enriched content of armchair nanotubes in the laser ablation samples, but the available experimental evidence is hardly conclusive. The nanotubes produced by the arc-discharge and laser ablation methods have relatively narrower diameter distributions, with means at ~1.5 and 1.4 nm, respectively. The nanotubes from the HiPco process have smaller but broadly distributed diameters (0.7–1.3 nm).

The arc-discharge and laser ablation methods are similar in the way that SWNTs form as a result of the organization of gaseous carbon atoms in the presence of proper metal catalysts, where the carbon evaporation is achieved in the high-energy bombardment of graphite targets by arcing and laser, respectively. In the CVD production, SWNTs are grown on catalyst nanoparticles (floating or on substrates) in a flow of precursor gas. Thus, the CVD method generally allows more flexibility in the experimental configuration and control over the conditions for the nanotube formation. Discussed next are reports on the use of CVD for selectivity in the growth of a certain nanotube type or nanotubes of metallic or semiconducting characteristics.

3.1. Selective Growth in Production

Buchholz et al. [70] reported that a narrow chirality distribution of SWNTs could be achieved by using silica-supported Co-Mo catalysts in carbon monoxide CVD (CoMoCAT SWNTs). The distribution was visualized in terms of a contour excitation-emission spectrum of the as-produced sample (Fig. 10), which suggested significant enrichment in (6,5) and (7,5) SWNTs (semiconducting). Interestingly, Miyazaki et al. [71] used a completely different combination of carbon source and catalyst (alcohol CVD with zirconium-supported FeCo catalysts) to produce samples of similar chirality selectivity, enriched in near-armchair tubes, especially (6,5) and (7,5) SWNTs. These CVD conditions are apparently in favor of small-diameter armchair-like nanotubes, but their selectivity toward metallic vs. semiconducting SWNTs was not reported.
Figure 10. Contour plots of (top) normalized fluorescence intensities and (bottom) the corresponding \((n,m)\)-abundance map for the CoMoCAT-SWNTs. Only semiconducting SWNTs are showed. For the \((n,m)\) map, the thickness of each hexagon cell is proportional to the observed fluorescence intensity for that structure. (Reproduced from Ref. [79] with permission. Copyright © 2003 American Chemical Society.)
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The selective growth of semiconducting SWNTs has been reported by Li et al. [32]. These authors used plasma-enhanced methane CVD with uniform iron catalysis to synthesize SWNTs on silica substrates. According to evaluations of direct electrical measurements by APM and the current-induced electrical breakdown method, the sample was found to contain almost 100% semiconducting SWNTs. The diameter distribution in these nanotubes was relatively broad (0.7–1.5 nm), and the average diameter could be altered by tuning the plasma power. The samples with smaller average diameters were found to be richer in semiconducting SWNTs [72]. According to their density functional theory calculation, semiconducting SWNTs may have lower formation energies per unit length than metallic SWNTs of similar diameters, and the difference may be more pronounced in the smaller-diameter regime [72].

There have been reports on utilizing atomically ordered structure of substrates to template the nanotube formation for aligned SWNTs or MWNTs with some chirality selectivity [73, 74], suggesting a possibility that SWNTs of a desired chirality might be prepared by engineering the substrate [75].

External electric field has also been used to influence the growth of one kind of SWNTs [76, 77]. For example, the axial polarizability values of semiconducting SWNTs (inversely proportional to the square of tube diameter) are much smaller than those of metallic SWNTs (infinitely large) [78]. In addition, the static polarizability of SWNTs in the axial direction is much higher than that in the transverse direction. Thus, when the nanotubes were allowed to rotate freely during growth (not in contact with substrate), short metallic SWNTs could be preferentially aligned in an external electric field during growth, as observed by Jaiswal and Lieber [79]. The merit of such an in situ differentiation method is somewhat similar to the post-production separation methods discussed below in that the strategy is to differentiate one electronic type from the other by taking advantage of their difference in properties.

3.2. Post-production enrichment

The post-production enrichment and separation methodologies developed in the past few years took advantage of the different physical (different conductive behavior and static polarizability) or chemical (preferential non-covalent and covalent reactions) properties of metallic and semiconducting SWNTs. Some of the methods allow the collection of one type of SWNTs by physically altering (or even destroying) the other type, while others facilitate the enrichment or separation of both types of SWNTs. Some are not scalable (sub-milligram quantity or less) and might be only applicable at device level, while others have been practiced at bulk level from milligrams to grams. Because of their more significant practical implications, the bulk separation methods will be discussed separately in Sec. 3.3.

3.2.1. Current-induced electrical breakdown

Current-induced electrical breakdown was first used by Collins et al. [10, 70] as a post-production method to selectively obtain semiconducting SWNTs for FEI devices. In the practice, bundled SWNTs were deposited across the source/drain microelectrodes. On the basis of the assumption that metallic and semiconducting SWNTs in the
bundle were in equally efficient contact with the electrodes, electrical current was applied at controlled gate voltage \( V_g \) such that the current could pass through metallic but not semiconducting SWNTs. At high enough current level, defects formed and propagated along the metallic SWNTs because of self-heating-induced oxidation (in air), eventually leading to their breakdown (Fig. 11). Semiconducting SWNTs, on the other hand, remained insulating at the applied \( V_g \) and thus left behind. The same strategy was applied to the fabrication of FET devices from SWNTs, whose metallic layers could be stripped off until a semiconducting one became available for transport [15].

Recently, it was demonstrated that the current-induced electrical breakdown could also be applicable to devices containing multiple individual SWNTs bridging the electrodes. According to Li et al. [22] (see also Secs. 2 and 3.1), wide source/drain electrodes were fabricated on top of individual SWNTS grown on SiO\textsubscript{2}/Si substrate from plasma-enhanced CVD. The \( V_g \) was held at + 10 V to deplete the semiconducting SWNTs (predominantly \( p \) type). When the bias was increased, the individual bridging metallic SWNTS preferentially failed, sending abrupt changes in the electrical output (Fig. 3).

The electrical breakdown mechanisms is not unique to metallic SWNTs. It works for semiconducting SWNTs as well if there is sufficiently high current passing through the nanotubes with the control of \( V_g \) sign (usually negative) and bias magnitude. In fact, this is the basis for the statistical counting of SWNTs in terms of their electrical type, as discussed earlier (Sec. 3.1).

3.2.2. Alternating Current Dielectrophoresis

The initial purpose of alternating current dielectrophoresis (ac DEP) was to deposit suspended carbon nanotubes between electrodes for their alignment [80,81]. Because of their much higher polarizability, metallic SWNTs could be preferentially aligned under ac field [82], an effect somewhat similar to the electric

![Figure 11. An SEM image, overlaid by a schematic drawing, illustrates the partial electrical breakdown of a SWNT bundle. (Reproduced from Ref. [15] with permission. Copyright © 2001 The American Association for the Advancement of Science.)](image-url)
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Figure 12. Rayleigh scattered light from the dielectrophoretically deposited SWNTs and the electrodes, recorded with an incident-light dark-field microscope. The scattered light from the aligned SWNTs appears green to the eye (A) and is polarized perpendicular to the electrodes (B). (Reproduced from Ref. [82] with permission. Copyright © 2003 The American Association for the Advancement of Science.)

field-induced alignment of metallic SWNTs during their growth [76] (see Sec. 3.1). As reported by Krupke et al. [82], a drop of a surfactant-assisted individual SWNT dispersion was placed on an ac DEP chip operated at 10 MHz. Directional nanotube deposition between the electrodes was observed (Fig. 12). When compared to the sample of SWNTs deposited on Si without ac DEP, the results from Raman characterization seemed to suggest that the electrode-deposited SWNTs were enriched with metallic SWNTs.

Baik et al. [83] essentially repeated the same experiment and found similar changes in Raman features. However, they suspected that the morphological difference of the samples contributed, at least in part, to the observed Raman signal profile "change." For example, the Raman profile in the spectrum of the sample from ac DEP (supposedly with enriched metallic SWNTs) was almost identical to that of a sample without ac DEP (Fig. 13). Therefore, it might make more sense to compare Raman spectra of the nanotube dispersion before and after ac DEP (enriched with semiconducting SWNTs) as a result of preferential deposition of metallic SWNTs [84] since fewer morphological problems are expected.

The preferential deposition of metallic SWNTs occurs only at certain frequencies where semiconducting SWNTs experience negative DEP force (repelled by electrodes) while metallic ones experience positive DEP force (attracted toward electrodes) [82,85,86]. At low enough ac frequency, semiconducting SWNTs can also be attracted toward the electrodes, although with a somewhat less positive DEP force.
Figure 13. Raman spectra (the RBM region, 632.8 nm excitation) of specimens starting from an SDS-assisted HiPco-SWNT dispersion: (a) material dried on a glass slide; (b) dielectrophoretically deposited material; and (c) acetone-induced precipitates. (Reproduced from Ref. [86] with permission. Copyright © 2000 American Chemical Society.)

compared to that for metallic SWNTs [85,87], Donald and Bagdhi suggested that even under such conditions, reasonably enriched deposition of metallic SWNTs could be expected if a microfluid device was used [87]. The crossover frequency for semiconducting SWNTs (DEP force = 0) was found to be around 10 MHz at a surfactant concentration between 0.1 and 1% [85]. In other words, only at frequencies above 10 MHz, metallic SWNTs can be selectively attracted toward the electrodes.

The quantities of the separated samples by ac DEP are currently at nanogram level at best [82], since an individual SWNT dispersion is necessary to achieve enough differentiation between the two nanotube types. The deposition efficiency
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from a single ac DEP experiment is also low, in which only \(-0.1\%\) of the starting SWNT material is collected at electrodes [82]. Thus, recycling the SWNT dispersion for deposition is definitely needed for improved separation [86,87].

3.2.3. DNA-Assisted Separations

Zheng et al. [88] found that single-stranded DNAs (ssDNAs), such as those with enriched thymidine (T) units (polyT) and specially alternative guanine (G) and T units (poly(GT)) [89], readily adsorb onto the nanotube surface and efficiently disperse SWNTs upon ultrasonication. After ultracentrifugation, dispersions enriched with individual nanotubes could be obtained, as evidenced by the presence of well-resolved bands in their absorption and fluorescence spectra. ssDNAs are negatively charged species and thus express linear negative charge on the wrapped SWNTs. Based on the theoretical conclusion that metallic and semiconducting SWNTs have different polarizabilities, resulting in different linear charge densities in the ssDNA-wrapped SWNTs, Zheng et al. injected the dispersion into an anionic exchange column for separation. The optical absorption (Fig. 14) and Raman results were consistent with the expectation that the early fractions were enriched with metallic SWNTs.

The elution in ion-exchange chromatography is based on charge density, not the total charge. Therefore, unlike other chromatography techniques [90-97], this method is not suited for sorting in terms of nanotube lengths. On the other hand, smaller-diameter semiconducting SWNTs are of higher polarizability and thus relatively lower charge density when wrapped by ssDNAs [89,98,99]. Therefore, these SWNTs are also eluted in early fractions (Fig. 14). Since the diameter effect is more pronounced for smaller-diameter nanotubes, the ssDNA-assisted ion exchange chromatography technique is a principle more suitable for starting SWNTs of a larger average diameter. Nevertheless, the diameter selectivity did allow the isolation of predominantly (6,5) semiconducting SWNTs from the nanotube sample produced by the CoMoCAT method [100-102].

Arnold et al. [103] recently used centrifugation to separate ssDNA-wrapped SWNTs in solutions with a density gradient media. Upon the centrifugation, the nanotubes formed discrete colored bands in the centrifuge tubes. Optical absorption spectroscopy showed that these discrete bands were due to ssDNA-wrapped SWNTs of different average diameters. It seemed that the larger the diameter of the semiconducting nanotube, the higher the hybrid density (in the range of 1.11-1.17 g/mL). A (6,5)-enriched fraction was also obtained from CoMoCAT SWNTs.

For either ion-exchange chromatography or density gradient centrifugation, the use of ssDNAs for preparative separation is probably cost prohibitive. In fact, ssDNAs have no preferential interactions with different types of SWNTs, serving only as an effective nanotube dispersion agent in the separation method. In principle, it may be possible to replace ssDNAs with other molecules as dispersion agents for the same functions. For example, polyelectrolytes that can non-covalently disperse SWNTs and express uniform charge density on the nanotubes might be used in the ion-exchange chromatography. Many surfactant-assisted SWNT dispersion [24,104,105] or different soluble functionalized SWNTs [106-112] might be explored in the separation based on density gradient centrifugation.
Figure 14. Absorption spectra of starting DNA-wrapped HiPco-SWNTs and fractionated samples from anionic exchange chromatography. The dashed rectangles define approximate regions for metallic and semiconducting optical transitions. (Reproduced from Ref. [86] with permission. Copyright © 2003 The American Association for the Advancement of Science.)

3.2.4. Preferential Doping

Halogens, such as bromine, are known to readily complex with carbon nanotubes [85,96,115,114]. Furthermore, theoretical calculations suggested that the binding energies of bromine with metallic SWNTs are larger than those with semiconducting ones [115,116]. Chen et al. [115] added diluted bromine solution to a surfactant-assisted individual SWNT dispersion, stirred vigorously, and separated immediately in ultracentrifugation. If the same density (1.0 g/cm³) for all of the initial surfactant-coated individual SWNTs is assumed, the preferential doping of bromine on metallic SWNTs should result in higher relative densities of the
corresponding complexes. It was found that the sediment was enriched to some
degree with metallic SWNTs according to optical absorption characteristics after
the de-doping via annealing at a high temperature (Fig. 15). The supernatant, on the
other hand, was enriched with semiconducting SWNTs.

![Graph showing absorption spectroscopic analysis for Br-assisted enrichment of metallic SWNTs.](image)

Figure 15. An absorption spectroscopic analysis for the Br-assisted enrichment of metallic SWNTs. (A) Absorption spectrum for a Br-separated supernatant sample overlaid fit to free Lorentzians. The two Lorentzians corresponding to the metallic (M, M') and semiconducting (SCI, SCI') bands are highlighted. (B) The same for the corresponding sediment sample. (C) Comparison of the Lorentzians from A and B normalized to the same underlying metallic band areas. (D–F) Corresponding spectra, fits, and comparison for a control sample (no Br). (Reproduced from Ref. [15] with permission. Copyright © 2003 American Chemical Society.)
For semiconducting SWNTs, many doping reactions are in fact band-gaps dependent. Dopants such as protons [24,88] and some small inorganic and organic molecules [109,117] preferentially interact with larger-diameter semiconducting SWNTs, which have smaller band-gaps, according to optical absorption and fluorescence studies. However, no related fractionation or separation effort has been reported.

3.2.5. Preferential Covalent Functionalization

Covalent sidewall chemistries of SWNTs have been attributed largely to the curvature-induced pyramidalization and with an orbital misalignment [100]. The nanotube functionalization strategies reported so far resemble those of either fullerene or graphite [106-111]. Some of these reactions were recently found to be in favor of metallic SWNTs over their semiconducting counterparts, which have been rationalized by considering the metallic nanotubes as better electron donors [112,113].

Tour and co-workers applied diazonium chemistry, previously known for graphite derivatization, to the sidewall functionalization of SWNTs [37,107]. Recently, Strano et al. [129] treated a surfactant-assisted SWNT aqueous dispersion with an aryl diazonium reagent, 4-chlorobenzenediazonium tetrafluoroborate and found a gradual decrease in the $M_2$ band in the optical absorption spectra (Fig. 16). Raman results also supported that the metallic SWNTs were preferentially reacted with the diazonium compound [32,129]. However, whether the reaction involves a charge-transfer mechanism (aryl cations) seems still a subject of debate [121].

Semiconducting SWNTs are also reactive with diazonium compounds, though with a lower reactivity, which makes the separation less effective at least at the bulk level. Dyke et al. [122] carefully derivatized SWNTs with the controlled addition of diazonium compounds containing different polar and non-polar addends for the purpose that the functionalized metallic and semiconducting SWNTs would have polarity difference due to the different addend composition and/or density. The solvable product was then separated via silica gel chromatography according to the polarity difference, but the resulting enrichments in the separated metallic and semiconducting fractions were marginal.

Preferential sidewall addition of nitric acid cations to SWNTs, similarly derived from graphite chemistry, were also evaluated in terms of the selectivity toward metallic and semiconducting nanotubes and the nanotube diameters. An et al. [64] used rather extreme reaction conditions (50% HNO3 for 4 weeks or sonication for 24 h) in the reaction of a nitromethane compound with SWNTs. According to Raman (Fig. 17) and optical absorption results, most metallic SWNTs (smaller diameter in particular) were destroyed to become soluble carboxenous species, whereas the reaction for semiconducting SWNTs was to a considerably lesser extent so that their tubular structures were largely preserved and could be recovered upon thermal defunctionalization. A sample enriched in semiconducting SWNTs could thus be obtained by simple filtration to remove soluble carboxenous species (from destroyed metallic SWNTs) followed by heat removal of functional groups [64].

Banerjee and Wong suggested that metallic SWNTs are more reactive than their semiconducting counterparts in another type of covalent SWNT functionalization reaction—the solution-phase carboxylation reaction with CaO, under narrow UV
For semiconducting SWNTs, many doping reactions are in fact band-gap dependent. Dopants such as proton 24,38 and some small inorganic and organic molecules 190,177 preferentially interact with larger-diameter semiconducting SWNTs, which have smaller band-gaps, according to optical absorption and fluorescence studies. However, no related fractionation or separation effort has been reported.

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Yoon and co-workers applied the diazonium chemistry, previously known for graphite derivatization, to the sidewall functionalization of SWNTs 37,107. Recently, Strom et al. 129 initiated a surfactant-assisted SWNT aqueous dispersion with an aryl diazonium reagent, 4-chlorobenzene substituted tetrafluoroborate and found a gradual decrease in the M_{\pi} band in the optical absorption spectra (Fig. 16). Raman results also supported that the metallic SWNTs were preferentially reacted with the diazonium compound 32,120. However, whether the reaction involves a charge-transfer mechanism (aromatic cations) seems still a subject of debate 121.

Semiconducting SWNTs are also reactive with diazonium compounds, though with a lower reactivity, which makes the separation less effective yet at the bulk level. Dike et al. 123 carefully derivatized SWNTs with the controlled addition of diazonium compounds containing different polar and non-polar addends for the purpose that the functionalized metallic and semiconducting SWNTs would have polarity difference due to the different added compound and/or density. The soluble product was then separated via silica gel chromatography according to the polarity difference, but the resulting enrichments in the separated metallic and semiconducting fractions were marginal.

Preferential sidewall addition of nitrobenzene cations to SWNTs, similarly derived from graphite chemistry, were also evaluated in terms of the selectivity toward metallic and semiconducting nanotubes and the nanotube diameters. An et al. 64 used rather extreme reaction conditions (92% EtOH for 3 days) in the reaction of a nitrobenzene compound with SWNTs. According to Raman (Fig. 17) and optical absorption results, most metallic SWNTs (smaller diameter in particular) were destroyed to become soluble carbonaceous species, whereas the reaction for semiconducting SWNTs was to a considerably lesser extent so that their tubular structures were largely preserved and could be recovered upon thermal defunctionalization. A sample enriched in semiconducting SWNTs could thus be obtained by simple filtration to remove soluble carbonaceous species (from destroyed metallic SWNTs) followed by heat removal of functional groups 64.

Storzer and Wong suggested that metallic SWNTs are more reactive than their semiconducting counterparts in another type of covalent SWNT functionalization reaction—the solution-phase acetylation reaction with Gd, under narrow UV
Figure 17. Raman spectra (the RBM region) of pristine SWNTs, the residual sample on the fiber after the nitroen treatment (NRFA), and the residual sample with further heat treatment at 1000°C in vacuum (NHFA-HTT) with excitations of (A) 514, (B) 785, and (C) 633 nm. The resonantly enhanced RBM regions are enclosed with rectangles and denoted to be corresponding to the respective absorption features. (Reproduced from Ref. [64] with permission. Copyright © 2006 American Chemical Society.)
Figure 18. Schematic illustration of the laser resonance chirality selection method. The SWNTs with specific chirality that are at resonance with the energy of the excitation laser beam (indicated by color match) are selectively removed after the intense laser irradiation. (Reproduced from Ref. [139] with permission. Copyright © 2004 American Institute of Physics.)
In most of the sidewall covalent reactions, that the reactivity is curvature-induced and diameter-dependent (more reactive for the smaller-diameter SWNTs) is a significant issue. It complicates the use of such reactions for the purpose of metallicity separation. For example, in the nitronium addition, only small-diameter metallic SWNTs were destroyed in the process [61]. In some cases, the diameter-selectivity could be predominant, as found in the solution-phase ozonolysis [126].

3.2.6. Other Merits

There are theoretical calculations suggesting that some other chemical processes may be selective toward one chirality/metallicity. For example, according to the density functional calculations of Seo et al. [129], CO should selectively be adsorbed on the open edge of semiconducting zigzag SWNTs (m = 3, e.g. (10,0)) over that of metallic armchair tubes (s = m, e.g. (5,5)). Such CO adsorption will eventually etch away the carbons from the zigzag tubes, while armchair ones remain intact. Similar selective adsorption will not happen with the use of other oxygen-containing gases, such as O2, CO, NO, and NO2, also according to the calculations [129].

Several uncommon experimental methods and criteria have been reported for selectively obtaining or eliminating certain types of SWNTs. For example, Hassassian et al. [130] claimed that hydrogen plasma was selective toward metallic SWNTs according to Raman and TEM studies. In another report, Tan et al. [131] applied optical tweezer technology to trap SWNTs at the center of the laser beam. The electric field component of the laser induces a dipole in a nanotube, which pushes the nanotube in the direction of optical density gradient toward the center of the laser beam. The authors suggested that semiconducting SWNTs are more prone to such optical trapping force, which may result in a minor enrichment in semiconducting nanotubes in the isolated trapping sample. Separately, Mashashi et al. [132] proposed an interesting method to use a high-energy laser beam to selectively eliminate SWNTs of certain chiralities. As discussed earlier, when the bandgap transition energies of SWNTs match with the laser excitation wavelengths, the Raman signals for the respective nanotube vibration modes are resonantly enhanced [44]. Similarly, the resonance with the high-energy laser irradiation may result in the depletion of the corresponding types of nanotubes. This could apparently be achieved at moderate laser power (10 kW/cm²) according to Raman characterization of the affected sample [132].

3.3. Toward bulk separation

Most of the available methods for the post-production separation of metallic and semiconducting SWNTs are limited by their ability to handle only a very small quantity of sample. The methods based on covalent functionalization have additional issues of being invasive, and thus there are concerns about the potential for damage to the nanotube electronic structures. To achieve effective separation for samples in bulk quantities, highly selective but less invasive techniques are obviously more desirable. In addition, the final products should also be easily distinguishable by their relatively simple physical characteristics. Several methods satisfying some of these requirements have been developed, which show promise of being scalable toward bulk separation.
3.3.1. Separation with amines

Prolonged heating of a mixture of nitric acid-treated SWNTs and octadecylamine (ODA) melt, first reported by Cho et al. [135], is a simple functionalization reaction for the nanotube solubilization. Mechanistically, it was proposed that the interaction is primarily zwitterionic between the amine and the nanotube broken end/surface defect-derived carboxylic acids [136]. However, Chattopadhyay et al. [60] noticed that after a thorough washing to remove free unbound molecules, the amount of ODA functionalities incorporated was much larger than what would have been possible even if all carboxylic acid moieties on acid-treated SWNTs (usually <5%) were converted into amine groups with the amines. In light of the reports on surface self-organization behavior of ODA [134,135] and the ready amine physisorption on SWNTs [136], these authors made an intuitive suggestion that there was massive ODA physisorption on the nanotube surface and the adsorption was stable enough to sustain the solvent extraction [60]. Separately, it was demonstrated that the adsorption of small amine molecules on semiconducting SWNT FET devices could change the nanotube transport properties from p- to n-type, while the metallic nanotube devices were not sensitive to the amine exposure [7,157]. According to Kong et al. [157], the wide energy continuum of DOS near the Fermi level in metallic SWNTs likely made them insensitive toward the charge-transfer effects induced by amine species. On the basis of these experimental facts and their own observation, Chattopadhyay et al. [60] suggested that the massive ODA functionalities on the nanotube surface beyond the zwitterionic interaction would apply only to semiconducting SWNTs (Fig. 19). As a result, ODA-functionalized semiconducting SWNTs should possess much higher solubility than their metallic counterparts, allowing the separation of the two types of nanotubes in terms of their solubility difference in a solvent like THF.

The Raman spectroscopy and electrical conductance results were supportive of the conclusion that the two separated samples were each enriched with either metallic (the less soluble fraction) or semiconducting SWNTs (the more soluble fraction). In a more quantitative evaluation of the enrichment in the separated fractions, Surmach et al. [51] carried out Raman measurements by using two laser wavelengths, with one (2.33 eV, or 532 nm) exciting small-diameter metallic (resonant with higher-energy $M_2$) and large-diameter semiconducting (lower-energy $S_2$) SWNTs (from HiPco method) and the other (1.96 eV or 642 nm) for the opposite resonance with lower-energy $M_1$ and higher-energy $S_2$. The spectral deconvolution of the Raman Raman peaks (Fig. 20) allowed the identification of the metallic and semiconducting nanotube signals according to the Kataura plot (energy-diameter dependence). By assuming a starting metallic-to-semiconducting ratio of 1:2, the same ratios for the separated less- and more-soluble fractions were 1.14:2 and 1:1.64, respectively, further supporting the enrichment conclusion. The separation method is in principle scalable to larger sample quantities.

For SWNTs produced from the HiPco process, there is a wide distribution of nanotube diameters. ODA was found to be highly selective toward smaller-diameter SWNTs (average ~0.9 nm) [54,65]. Poor enrichment result was also obtained for SWNTs produced from the laser-ablation method (average diameter ~1.4 nm). Therefore, the ODA separation of metallic and semiconducting SWNTs is more
suitable for smaller-diameter nanotubes. One may speculate that the curvature in smaller-diameter semiconducting SWNTs enhances the amine adsorption.

3.3.2. Separation with planar aromatic molecules

The non-covalent attachment of planar aromatic molecules like pyrene to SWNTs has been well established. It was proposed that the pyrene molecules readily anchor on the nanotube graphitic surface via π–π stacking interactions [138]. For the
Figure 20. A Raman analysis (based on RSM features) of the ODA-assisted enrichment of the ODA-assisted enrichment by using two excitation wavelengths: (top: 2.33 eV, and bottom: 1.66 eV). Each spectrum was deconvoluted into Lorentzians that were individually assigned to IBM features from either metallic (red) or semiconducting (white) SWNTs, according to Kataura Plot. (Reproduced from Ref. 74 with permission. Copyright © 2004 American Institute of Physics.)

Functionalization and solubilization of carbon nanotubes based on the non-covalent interactions, various oligomeric and polymeric compounds containing pyrene [98,139–143] and tetraazaisavelenes [144,145] (including porphyrins [61,146–148] and phthalocyanines [149,150]) or even some rigid conjugated polymers [151] have been used successfully.

Li et al. [61] employed a free-base porphyrin compound with four tethered long alkyl chains, 5,10,15,20-tetrakis(hexadecylphenyl)21H,23H-porphine (THPP), for the solubilization of SWNTs via the non-covalent interactions. Interestingly,
however, the experiments yielded a considerably more significant finding that the solubilization was selective toward semiconducting SWNTs—namely that the soluble fraction was enriched with semiconducting SWNTs and the insoluble residue was enriched with metallic SWNTs (Fig. 21). The conclusion was supported by all of the results from optical absorption, Raman, and bulk conductivity measurements [51]. The fact that the porphyrins in the soluble fraction could readily be removed via simple solvent extraction for the recovery of clean semiconducting SWNTs was consistent with the interactions being non-covalent in nature. The separation method is simple, amenable to scale-up, and also effective. In addition to porphyrins, other planar aromatic molecules, such as those containing pyrene moieties (for example, 1-docosyloxyphenylpyrene or DOPP [152]), were also found to be effective in selectively solubilizing semiconducting SWNTs. According to the subsequent experimental results, sample fractions containing at least 80% metallic or 80% semiconducting SWNTs can be obtained from the separation (Fig. 21) [152].

Mechanically, Li et al. [51] proposed that the two types of SWNTs, those with intrinsic defects or those from the oxidative treatment in their purification, should have different surface properties. The surface of a semiconducting SWNT in the

Figure 21. A schematic illustration for the selective interactions of porphyrin with semiconducting SWNTs for the semiquantitative separation [51,152].
Figure 22. Absorption (A) and Raman spectra (B) of samples enriched with metallic (red) and semiconducting (blue) SWNTs from the separation with DomP [162].

The presence of solvent might be viewed as being similar to those of radical ion pairs, favorable to interactions with relatively large planar aromatic molecules. The presence of such interactions, strong in some respect, was reflected by the dramatic changes in the optical absorption of the semiconducting SWNTs upon the attachment of the aromatic moieties. As shown in Fig. 23, while the attachment of DomP made the nanotubes soluble, it also diminished both \(S_1\) and \(S_2\) transitions characteristic of semiconducting SWNTs [59]. In this sense, the non-covalent interactions between pyrene moieties and the nanotube may be considered as complexion. The
Figure 23. (A) Absorption spectra of the DomP-stabilized SWNT sample in THF (---) and in SDS-assisted D_{2}O suspension after the removal of DomP via dialysis (---), with the nanotube-equivalent concentration in the former being at least five times higher than that in the latter. (B) Similarly, absorption spectra of the sample in the solid state before (---) and after (---) the removal of DomP. (Reproduced from Ref. [39] with permission. Copyright © 2004 American Chemical Society.)

nanotube-complexed pyrenes could be removed via non-invasive means, such as dialysis or solvent extraction, and the removal of pyrene moieties from the nanotube surface resulted in the recovery of the characteristic S_{1} and S_{2} absorption features (Fig. 23). The complexation of porphyrins with semiconducting SWNTs resulted in the same diminishing of optical absorption bands, which similarly recovered upon the removal of the porphyrins [192]. The effects on optical absorption associated with the complexation of the planar aromatic species with semiconducting SWNTs are different from those with the covalent modification of the nanotube sidewalls [27] or the doping by halogens or protox (affecting only S_{1}) [35,36,38]. As proposed by Fernando et al. [39], the complex of a semiconductor SWNT with (a monolayer of) pyrenes may be viewed as a double-walled carbon nanotube (Fig. 24) [39], whose outer layer is not only highly defected (incomplete surface coverage) but also of mixed chiralities (different pyrene starting configuration). The SWNT-pyrene complex may in fact be analogous to a MWNT, which has featureless absorption because of broad hybridizations of different band-gap transitions.

Bisnath [146] suggested on the basis of computational results that Co(II)-complexed terzaaza[14]annulene adopts bent structures when approaching the SWNT surface and that it is more affinity toward a zigzag (8,0) SWNT than an armchair
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Figure 24. A schematic representation of a semiconducting SWNT covered by a monolayer of pyrenes, which is conceptually similar to a double-walled carbon nanotube.

(5,5) SWNT, with formation energies of $-54.7$ and $-7.9$ kcal/mol, respectively (Fig. 20). These results are, to some extent, consistent with the experimental observation on selective interactions of THPP or other similarly large planar aromatic molecules with semiconducting SWNTs [81,102]. Budić [145] also suggested that Co-complexed tetramethylenes should have more efficient adsorption on SWNTs than their free-base forms. However, the experimental results reported by Li et al. [81] have proven otherwise. In fact, the Zn-complexed THPP was found to be incapable of solubilizing SWNTs via the non-covalent interactions. On the other hand, there was a report on another Zn-complexed acidic porphyrin (porphyrin IX zine (II) complex, or 9,10,17,18-tetramethyl-9,10,17,18-divinyl-2,3,18-porphine(2-propionic acid) solubilizing SWNTs [146]. Further investigations are required to resolve such discrepancies.

The starting sample typically contains severely bundled SWNTs. The separated fractions from the non-covalent interactions with porphyrins, pyrenes, or other planar aromatic molecules are probably composed of individual nanotubes as well as thin bundles (from partial exfoliation). These bundles may in principle contain mixtures of metallic and semiconducting nanotubes, responsible in part for the incomplete separation. Therefore, repeated functionalization/separation experiments on the separated fractions [133,154] to further exfoliate the bundled SWNTs represent a strategy to obtain samples of better metallic or semiconducting purity. The effectiveness of such a strategy was demonstrated preliminarily in the report of Li et al. [81]. Subsequent experiments to use the repeated non-covalent functionalization strategy confirmed that improved separation of metallic and semiconducting for their respective better-enriched samples could be achieved [156].

4. OUTLOOK

There is some excitement in the nanotube research community associated with the recent development of methodologies for separated metallic and semiconducting SWNTs [155-169]. Despite some success with the approach of in-production
Figure 23. Optimized structures of a (8,0) semiconducting SWNT (ZNT) and a (5,5) metallic SWNT (ANT) complexes with Co-complexed tetraaza[14]annulene. The closest distances (in angstroms) between the annulene molecule and SWNT side-walls are shown in red. trans-N-Co-N and βC-Co-βC angles and their values in the NT complexes are shown in blue and green, respectively, with the corresponding values for isolated optimized Co-complexed tetraaza[14]annulene in parenthesis. Binding energy values (in bold italics) are in kcal/mol. (Reproduced from Ref. [145] with permission. Copyright © 2004 American Chemical Society.)
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control, selective production of a specific type of SWNTs may prove to be a very difficult task. The post-production separation appears more promising and realistic, at least in the near term. However, a number of issues, some of which are common to most available methods, remain to be addressed: Some examples are: (1) Impurity: The typical starting nanotube sample contains impurities such as amorphous carbons and carbon particles (also with embedded metal residues from the catalysts), which may interfere with the separation that is based on small difference in interactions. The likely presence of defective and "mutated" SWNTs (those containing multiple metallicity/chirality segments connected with kinks or defects) should also be considered. (2) Diameter selection: The diameter selection accompanying the metallic-semiconducting separation represents a complication, sometime a rather troublesome one. For SWNTs of a wide diameter distribution (such as those produced from the HiPCO process), some methods may be applicable only to a certain diameter range. Thus, possible distortions to the quantitative relationships between nanotubes of different diameters should be considered. (3) Quantification: Relatively simple and reliable analytical techniques to directly quantify the separated samples are still in demand. Among the most promising in the near term are probably significant improvements in Raman and optical absorption spectroscopy techniques. (4) Mechanism: The mechanistic understanding of a separation method is critical to its optimization experimentally. This will be particularly valuable to the methods that are promising for bulk separation.

The available experimental results have already demonstrated that substantially enriched metallic and semiconducting SWNTs can be obtained. We are optimistic that better and wider users of the currently most promising post-separation methods will result in enriched samples in larger quantities, from which exciting technological breakthroughs at the nanotube-based device level may be expected.

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REFERENCES
Separation of metallic and semiconducting single-walled carbon

 Separation of metallic and semiconducting single-walled carbon  

79. P. G. Collings, M. Hersam, M. Arnold, R. Martel and P. Avouris,  
80. K. Yamamoto, S. Akita and Y. Nakayama,  
81. X. Q. Chen, T. Saito, H. Yamaoda and K. Matsuoh,  
82. B. Krakow, H. C. Lohneysen and M. M. Kappes,  
83. S. Bai, M. Urey, L. Rottkina and M. Strano,  
85. B. Krakow, P. Hornschuch, M. M. Kappes and H. v. Lohneysen,  
86. S. W. Lee, D. S. Lee, H. Y. Yu, E. E. B. Campbell and Y. W. Park,  
Diner, M. S. Dresselhaus, R. S. Mclean, G. B. Onoaa, G. G. Samsoondre, E. D.  
90. G. S. Duesberg, J. Muster, V. Kostic, M. Burghard and S. Roth,  
91. S. Nyogi, H. Hu, M. A. Hamon, P. Bhunwir, B. Zhao, S. M. Rezende,  
J. Chen, M. E. Ikiz, M. S. Meier and R. C. Haddon,  
92. B. Zhao, H. Hu, S. Nyogi, M. E. Ikiz, M. A. Hamon, P. Bhunwir, M. S. Meier  
93. D. Chattopadhyay, S. Lastella, S. Kim and F. Papadimitrakopoulos,  
94. B. Chen and J. P. Selegue,  
95. S. K. Doorn, R. E. Fields, H. Hu, M. A. Hamon, R. C. Haddon, J. P. Selegue and  
Flashe and R. E. Smalley,  
98. S. R. Lustig, A. Jagota, C. Khrapin and M. Zheng,  
and M. L. Urey,  
100. M. Zheng and B. A. Diner,  
Samsoondre, C. Faetini, M. A. Pimenta, A. Jorio, P. P. Filho, M. S. Dresselhaus,  
G. Dresselhaus, R. Saito, M. Zheng, G. B. Onoaa, E. D. Semke, A. K. Swan, M. S.  
Urdal and B. B. Goldberg,  
Separation of metallic and semiconducting single-walled carbon