Magnetic Purification and Spectral Dependence on pH of Surfactant Suspended Single Wall Carbon Nanotubes

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

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April, 2003
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Abstract

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Many properties of single wall carbon nanotubes (SWNTs) are unique and advantageous. The electrical, thermal, and strength properties of SWNT are highly desirable for many applications. To take advantage of these properties it is necessary to remove the impurities that are inevitably produced during the growth of the nanotubes. High gradient magnetic separation techniques have been used to separate the magnetic catalyst particles from the nanotubes.

Even if all the impurities were removed there would still be many different types of SWNTs in a sample. For the first time, different types of SWNTs have been observed acting as individual chemical species by changing the pH of surfactant stabilized suspensions of SWNTs. In the future, one can expect this scheme to play an important role in the separation of SWNTs by type.
Acknowledgments

Throughout my graduate career, there have been many people that have helped and supported me along the way.

My research adviser, Dr. Smalley, has made it possible for me to work in an area that I love, and for giving me the opportunity to make real contributions to the field. I would also like to acknowledge the other members of my committee, Dr. Andrew Barron and Dr. Alexander Rimberg and thank them for their patience.

I would also like to thank Dr. Andrew Rinzler, Pavel Nickolaev, and Andres Thess for showing me the ropes and getting me started in the lab. Dr. Bob Hauge and Ken Smith have been instrumental in many of my endeavors. Carter Kittrell is a never ending resource for parts and supplies, and Bruce Brinson is one of the best microscopists I know.

I need to thank Mary Wilder, Leah Benard-Boggs, Susan Norman, Kristina Ericson, Diana Gomez, Yvonne Creed and especially Beau Carpenter. They made things run smoothly over the years.

I also want to thank the other graduate students and post-docs that have helped me throughout my time at Rice: Mike Bronikowski, Hongjie Dai, Deron Walters, Jie Lu, Michael Strano, Jake Schmidt, Ramesh Sivarajan, Jason Hafner, Michael O’Connell, Lars Ericson, Yuhuang Wang, Fernando Rodriguez, Michael Casavant, Peter Boul, Valerie Morre. Kristy Rialon and Eric Haroz are two very hard working and competent undergraduates that have helped quite a bit in the lab.

The biggest thanks I can ever give go out to my family. My daughter Rachel; you have given me more help than you can ever realize. My mom and dad have always encouraged me and had confidence in me even when I questioned my own abilities. They symbolize what I aspire to be. Finally, my wife deserves a huge amount of thanks for putting up with me when I’m grouchy because I’ve stayed up too late the night before. She has been a never ending source of encouragement, support, and sanity.
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List of Abbreviations

A . . . amp
cm . . . centimeter
CNT . . . carbon nanotube
CVD . . . chemical vapor deposition
DMF . . . N,N-dimethylformamide
EDAX . . . energy dispersive X-ray analysis
HiPco . . . high pressure CO
K . . . Kelvin
M . . . molar
MWNT . . . multi-wall carbon nanotube
NdFeB . . . neodymium iron born
NIR . . . near infrared
NMR . . . nuclear magnetic resonance
PLV . . . pulsed laser vaporization
rpm . . . revolutions per minute
SDS . . . sodium dodecyl sulfate
SWNT . . . single wall carbon nanotube
UV . . . ultraviolet
V . . . volts
Vis . . . visible
W . . . watts
YAG . . . yttrium aluminum garnet
1. Introduction

Carbon nanotubes are tubular structures composed solely of carbon which have unique physical and electronic properties that could have a profound effect on a variety of technologies that range from macroscale composites to nanoscale electronics [1]. Because of these unique properties, interest in carbon nanotubes has increased extraordinarily since their discovery in 1991 [2]. There are two very general types of carbon nanotubes, single wall carbon nanotubes (SWNTs), and multi wall carbon nanotubes (MWNTs) [1].

2. Background

To understand the general structure of nanotubes, it is best to start with the structure of graphite. Graphite consists of multiple layers of carbon atoms. The layers of carbon atoms are held to neighboring layers by relatively weak Van der Waals forces, but each layer is made of carbon atoms that bound together with the carbon-carbon double bonds. The double bond is one of the strongest bonds in nature. The carbons in each layer are $sp^2$ hybridized and so are bound to the three closest carbon atoms in the same layer creating a hexagonal lattice. The in-plane strength of this hexagonal carbon layer is large because of the strength of the carbon-carbon double bonds.

SWNTs resemble one plane of the hexagonally arranged carbon atoms (also known as a graphene sheet) that has been rolled up onto itself with the resulting edges joined, thus forming a seamless tube. The positions of the carbon atoms that make up SWNTs are precisely defined, and this creates a tube with sides of hexagonally arranged carbon atoms (Figure 1). SWNTs have diameters on the order of one to five nanometers,
but can have lengths over several microns. There is no theoretical reason that their lengths can not be kilometers or longer.

![Graphene Sheet to SWNT](image)

Figure 1: Rolling up a graphene sheet to form a SWNT [3].

Because the structure of SWNTs are made of sp² hybridized carbons, the strength and stiffness of SWNTs are unequaled by any known material [1]. The thermal conductivity is very high along the axis of the tube yet much lower perpendicular to the axis of the SWNTs. One of the most interesting properties of carbon nanotubes is the ability of different SWNTs to be either metallic or semiconducting. This unique electronic property is not based on dopants that may be added to the carbon structure as in the case of silicon and other semiconductors; both metallic SWNTs and semiconducting SWNTs are still made of the same element, carbon, with no change in the local bonding of the carbon atoms. The differences in the electronic behavior of SWNTs depend solely on the structure (diameter and the helicity) of the individual nanotubes [4, 5].
MWNTs can be thought of as being constructed by taking SWNTs of smaller and smaller diameters and placing them inside each other. Ideally, they resemble several SWNTs nestled inside each other. This can be deceptive, because one of the most touted properties of carbon nanotubes is their exceptional strength. Initially, one may imagine that MWNTs would be superior to SWNTs, especially in mechanical strength. After all, MWNTs have more graphene sheets in their structure, so their strength should increase as the number of tubular graphene sheets increases. However, defects can be formed during the growth phase of MWNTs. The formation of defects in SWNTs is much less likely.

The problem arises during the initial formation of nanotubes. If a defect occurs during the growth phase, the final conclusion of the defect will be one of three things:

1) Under the high temperature of the growth conditions, the defect can be annealed out and the hexagonal array of the nanotube is maintained.

2) The defect causes the tube to close, thus stopping the growth process.

3) In MWNTs, a defect within an individual rolled up graphene sheet can be stabilized and can be incorporated in the total structure by interacting with the open end of one of the other concentric tubes within the MWNT.

SWNTs do not have concentric walls that can stabilize a defect that may form. Thus any defects are either annealed out, or the SWNT simply closes at the defect site. There is no way that a defect can be stabilized by interaction with an adjacent layer. This makes SWNTs much more likely to be defect free on an atomic scale than their cousins the MWNTs. The work of this thesis deals only with the single wall variety.
2.1 Brief History of SWNTs

The history of SWNTs begin in 1985 with the discovery of a novel class of carbon by Dr. Richard Smalley, Dr. Robert Curl, and Sir Harold Kroto [6] for which they won the 1996 Nobel Prize in chemistry. The new forms of carbon were spherical caged structures which were given the name of buckminsterfullerenes because the structures of these new compounds were reminiscent of the geodesic domes built by the inventor Buckminster Fuller. C\textsubscript{60} is probably the best known of the fullerenes. C\textsubscript{60} has 60 carbon atoms arranged in a spherical structure that resembles a soccer ball. The next larger fullerene is C\textsubscript{70}. It can basically be envisioned by taking a C\textsubscript{60} cutting it in half and inserting 10 carbons into the structure.

In 1990, at a workshop organized by the Air Force Office of Scientific Research, Dr. Smalley posed the question as to whether C\textsubscript{60} could be extended in one dimension by adding countless numbers of carbons to the structure, in much the same way that C\textsubscript{70} can be thought of as adding a “ring” of 10 carbon atoms to a C\textsubscript{60} (Figure 4).
Figure 4, C\textsubscript{60} (left) and C\textsubscript{70} (right). The "ring" of ten atoms in C\textsubscript{70} is highlighted.

The first nanotubes observed were MWNTs which were reported by Ijima in 1991 [2]. He had produced MWNTs by using the carbon arc technique which was a technique which had been developed earlier to produce large amounts of fullerenes. Two years after the discovery of multi-wall nanotubes, Ijima and Ichihashi at NEC [7] and Bethune \textit{et al.} at IBM [8] independently reported the preparation of single wall carbon nanotubes.

In 1995 Guo \textit{et al.} reported a process to produce SWNTs by using high powered lasers to ablate a carbon target that had been impregnated with cobalt and nickel catalysts [9]. This technique produced SWNTs with higher yield and quantity than previously available and was later improved by Thess \textit{et al.} [10].

In 1999 an all gas phase method of producing SWNTs was reported by Nikolaev \textit{et al.} [11]. This method uses the decomposition of CO to CO\textsubscript{2} and carbon to produce SWNTs. This all gas phase method has the potential to produce SWNTs on a truly industrial scale.
2.2 General Properties of Single Wall Carbon Nanotubes

Carbon nanotubes have been touted as the “Ultimate Carbon Fiber”: with good reason. Walters et al. [12] measured the strength of a bundle of SWNTs by pinning a bundle on a silicon substrate and etching a trench underneath the bundle by lithographic means [12]. They then used an AFM to test the strength of the bundle by applying lateral forces on the midpoint of the bundles. They found the strength to be at least 45 GPa. Steel can be in the range of 0.5 - 1.5 GPa [13], so SWNT bundles are 30 - 90 times stronger than steel. Though impressive, this measured value for the strength of SWNT bundles is only a lower limit. This is because during the experiment it could not be determined if the failure was due to SWNTs breaking, the bundle unraveling, or the bundle simply pulling out of the metal pads that held the ends in place [12].

Because of their amazing strength, research into using SWNTs in high strength composites has been underway for several years. An increase in strength of these SWNT/polymer composites has been observed, but the main failure mode is that during stress, the SWNTs are pulled out of the epoxy at the fracture. This does not make full use of the strength of the nanotubes, but only the strength of the adhesion of the nanotubes to the polymer matrix.

The idea of making cable solely out of SWNTs is an intriguing concept. Such a cable would be strong enough to support its own weight (plus some) from geosynchronous orbit. This is the origin of the concept of the “space elevator”. Briefly, the space elevator would consist of a platform in geosynchronous orbit around the earth and above the equator. A cable made at least in part of SWNTs would connect the orbiting platform to the earth. Vehicles would then be able to climb the cable. The
vehicles would be electrically powered, thus alleviating the necessity to carry fuel into orbit, which is a large amount of the cost of sending up rocket powered craft.

More modest technological advances of materials made entirely out of SWNTs could include advanced construction materials, light weight aerospace components, automotive parts, and even sports equipment like tennis rackets and golf clubs. These applications would benefit by an increase in strength and decrease in weight.

Amazing strength is not the only benefit that SWNTs have to offer. Thermal management applications would also be transformed by the fabrication of materials that contained aligned SWNTs. The thermal conductivity of SWNT has been calculated to be 9.5 W cm\(^{-1}\) K\(^{-1}\) along the tube axis and 0.056 W cm\(^{-1}\) K\(^{-1}\) perpendicular to the axis. This is close to the thermal conductivity of graphite along the graphene sheet (10 W cm\(^{-1}\) K\(^{-1}\)) and perpendicular to the graphene sheet (0.055 10 W cm\(^{-1}\) K\(^{-1}\)) [14].

This anisotropy in the thermal conductivity would mean that a macroscopic rod made from aligned SWNTs would have a much higher heat transfer from one end of the rod to the other than from the sides. This rod would feel very much like the graphite in a pencil along the sides, but the ends would feel cool, because the heat from the fingers would be quickly transported away from the hand. Heat pipes made of aligned SWNTs (or composites with aligned SWNTs) in contact with a heat generating source (such as a microprocessor) could shuttle heat away keeping the source from overheating.

Also, SWNTs have unique electronic properties associated with them. Depending on their structure, or chirality, SWNTs can be either metallic or semi conductive [5, 6]. Metallic SWNTs would enable the fabrication of nanoscale wires that would be smaller than current silicon technology can achieve. Devices (diodes, transistors) could be
constructed out of the semiconducting nanotubes as well. Field effect transistors using SWNTs have already been demonstrated [15]. Devices have even been seen along an individual SWNT [16]. In the future it may be possible to create a computer architecture that is composed solely of SWNTs; the devices would be made out of the semiconductors, and connections would be made out of metallic SWNTs.

Finally it can be envisioned that some or all of the properties of SWNTs can be combined into one multifunctional unit. For example, assuming sufficient control over the manufacturing process, the hull of an airplane could be made of SWNTs. The SWNTs would not only provide structural strength and integrity, but channels of metallic SWNTs could distribute electricity throughout the airplane, and embedded electronics could provide computational power.

There is still a long way to go before any of these dreams can be achieved, but research into better understanding the properties and production of SWNT continues to grow at a fast pace.

2.3 Nomenclature and Helicity of SWNT

The helicity of SWNTs has been mentioned a few times and the fact that the electronics of an individual SWNT depend on the structure of the SWNT. But what is helicity, and how do we define it? Earlier it was mentioned that SWNTs can be viewed as a graphene sheet that has been rolled into a tube, but there are many different ways to roll a graphene sheet into a tube.

Below is a graphical representation of a graphene sheet and the resulting SWNTs from different ways of rolling them up. Rolling the graphene sheet up from left to right
would result in what is known as a "Zigzag" SWNT. Rolling the sheet up at a 30° angle results in what is known as an "Armchair" SWNT. These two types of SWNTs are the two achiral types of SWNTs. Rolling the sheet up at an angle less than 30° and more than 0° results in a chiral tube that has helical structure along the axis of the SWNT.

The way that a graphene sheet is rolled up to form a SWNT can be described by the chiral vector, \( C_h \), and is defined as:

\[
C_h = na_1 + ma_2
\]  

(2.3.1)

Where \( n \) and \( m \) are integers and \( a_1 \) and \( a_2 \) are the primitive vectors [17]. The graphene sheet is rolled up in such a way that the tail \( C_h \) touches the head of the vector, thus the circumference of the SWNT formed will be the length of \( C_h \).
Figure 6. The top half shows $5a_1$ and $5a_2$ being added together to form the chiral vector $C_h$ for a (5,5) SWNT. The lower part shows the labeling of the points in a hexagonal sheet. Starting at (0, 0) the vectors na$_1$ and ma$_2$ are added together to form $C_h$. The point that the chiral vector $C_h$ points to is labeled (n, m).

The vector $C_h$ uniquely describes the structure of a SWNT, so the vector can be used to name SWNTs. The convention is (n, m). By this convention, all zigzag tubes have $m = 0$; for example a (9, 0) and (11, 0) tubes are zigzag tubes. Armchair SWNTs have $n = m$; (5, 5) and (10,10) are examples of armchair tubes.

The different ways of “rolling up” a graphene sheet doesn’t only affect the atomic structure of the SWNT, but also the electronic properties of an individual SWNT [18,
19]. Earlier it was stated that SWNTs can be either metallic or semiconducting. The difference comes from band theory of graphite and quantization due to the small diameter of the SWNT. Briefly, a SWNT will be metallic if \((n - m)/3\) is an integer or zero; if this requirement is not met then the SWNT will be semiconducting [1].

2.4 Production Techniques of SWNTs

There are four main production methods of SWNTs; the carbon arc technique, the laser vaporization technique, chemical vapor deposition (CVD) and the high pressure CO (HiPco) process. Although in practice each technique is quite different, the basic principle is the same; to deposit carbon onto nanometer sized metal catalyst particles which catalyzes the formation and growth of SWNTs.

2.4.1 Carbon Arc Technique

The carbon arc technique uses an electrical arc passing between two graphite electrodes to generate the high temperatures needed to sublimate carbon at the anode. A current and voltage of about 100 A and 30 V is typically used during the process in an inert atmosphere of 500 Torr of helium or argon [7, 8].

The carbon arc method was originally described by Kratschmer and Huffman as a way to produce large amounts of fullerenes [20]. In 1993, Bethune et al. [8] and Ijima and Ichihashi [7] independently reported using this technique to produce SWNTs. The main difference between making SWNTs and making fullerenes is the incorporation of a metal catalyst. To incorporate metal catalysts, the anode is typically drilled out and the metal catalysts are placed in the hollow anode. The best know catalyst so far is a 1:4.2 atomic percent mixture of yttrium and nickel [21].
To start the growth process, an electric arc is struck between the electrodes. Under the high temperatures produced by the electric arc, the carbon and the metal catalysts are vaporized at the anode. The anode is moveable so that as the carbon from the tip of the anode is sublimed, the anode can be advanced to keep the same gap distance between the anode and cathode.

Although SWNTs can be found throughout the growth chamber, the highest purity of SWNTs occurs within a collar or “collarette” that forms around the anode. The mass of the collarette is about 20% of the total material produced. By volume, the collarette is about 80% SWNTs [21].

Figure 7. Block diagram of the design of the carbon arc technique. The vacuum chamber is filled with ~500 Torr of helium. An arc is struck between the electrodes, and a distance of a few millimeters is maintained by adjusting the position of the anode.
2.4.2 Laser Vaporization

The Laser Vaporization technique utilizes a carbon target that has been impregnated with the metal catalysts (typically nickel and cobalt). The target is placed in an oven and heated to 1200 °C in an atmosphere of argon at 500 Torr. The target is then vaporized with successive pulses from a high powered laser. The vaporized metal catalysts condense to form catalyst particles in the nanometer range. The carbon condenses on these catalyst particles and produce SWNTs [10].

The target is formed from carbon black, metal salts, and a binder. The metal salts and the binder are dissolved in acetone, and the carbon black is added to create a slurry. The solvent is then evaporated. This process ensures homogenous distribution of the metal catalyst and the binder. The resulting powder is then placed in a mold and heated under pressure to cure the binder. The target is then placed in an inert atmosphere and heated to 1100 °C. This carbonizes the binder and reduces the metal salts. The target is placed in a quartz tube and sealed with water cooled flanges. The tube is then placed in a furnace and heated to 1200 °C in a flowing argon atmosphere. The target is ablated with a Nd:YAG laser [9]. (In later designs two Nd:YAG lasers were used to increase production rates[10].) The vaporized carbon and metals are entrained in the argon flow and begin to condense. The metal condenses to metal catalyst particles and these in turn catalyze the formation of SWNTs.
2.4.3 Chemical Vapor Deposition

With CVD, the catalyst particles are usually formed by impregnating a catalyst support (fumed alumina, silica or a zeolite) with a solution of metal salts. During drying, the support keeps the metals from agglomerating and forming larger metal particles. The nanometer sized catalyst particles on their support are heated to a temperature of about 900°C. Hydrocarbons are then passed over the catalyst where the hydrocarbons decompose to hydrogen gas and carbon, forming SWNTs [22, 23, 24].
2.4.4 HiPco Process

The HiPco (so named because it uses High Pressure carbon monoxide (CO)) uses volatile metal precursors (metal carbonyls) that decompose to form metal clusters at high temperature. The decomposition of the metal carbonyl and the subsequent formation of catalyst particles occur in an atmosphere of carbon monoxide. The catalyst particles facilitate the decomposition of CO to CO$_2$ and carbon to produce SWNTs [11].

The metal precursors are carried to the reaction chamber by a relatively cool carrier flow of CO. The precursor is kept below its decomposition temperature by the use of a water cooled injector. The nozzle of the injector is located within the interior of the reaction chamber where the temperature of the surrounding CO atmosphere is well above the decomposition temperature of the metal precursors. After the metal precursors leave the water cooled injector, they are injected into the hot CO atmosphere where they quickly become heated above their decomposition temperature. The newly formed metal atoms cluster together, and condense into metal clusters (catalyst particles) which catalyze the Boudouard reaction;

$$2 \text{CO} \xrightarrow{\text{metal catalyst}} \text{CO}_2 + \text{C}_{(s)} \quad (2.4.4.1)$$

The reaction happens on the surface of the metal catalyst. CO is adsorbed by the surface of the metal catalyst and the CO molecules diffuse along the surface until two CO molecules come in contact and react. The resulting CO$_2$ is desorbed, and the C$_{(s)}$ is incorporated into the growing SWNT.
2.5 Magnetic Impurities

Regardless of the way single walled nanotubes are produced, metal catalyst particles are typically used in the growth process. A wide variety of metals have been used, but the most commonly used metals are iron, nickel, cobalt, (all ferromagnetic) or mixtures that contain at least one of these metals. After the growth and deposition of the SWNTs has ended, the metal catalyst particles remain entangled in the material and can hinder further analysis and processing. For example, NMR analysis can be rendered useless with significant amounts magnetic particles in the sample [25, 26]; theoretical packing density of aligned nanotubes won’t be achieved if catalyst particles are embedded between adjacent tubes; fluorescence of nanotubes (a technique that is proving to be very valuable) [27] may be partially quenched if metallic catalyst particles are present and in contact with the fluorescing SWNTs.

Removal of these metals from the final product has been problematic. The main reason for this is that the majority of the metal particles are not exposed to the environment, but have a fullerene like carbon layer protecting them [28]. During the growth phase the catalyst particles can incorporate more and more metal atoms and grow to the point that it is thermodynamically more favorable for incoming carbon to overcoat the metal particle as opposed to grow nanotubes. Once the metal particle is covered with carbon it is essentially isolated from the reactants, thus ending the growth of any nanotube that had been associated with it.

Any attempt of direct chemical attack to the metal catalyst particle must penetrate the carbon overcoating. The overcoating of carbon is strained because of curvature. However, the radius of curvature is at least the same as the nanotube that was produced
by the catalyst particle, and most likely larger. The larger radius of curvature means less 
strain energy in the overcoating as compared to the SWNT, and so the carbon 
overcoating will be less chemical reactive.

What this means is that any direct attack that can etch away the overcoating and 
expose the metal catalyst is likely to attack the SWNT as well. There are variations on 
this, for example; most of the catalyst particles are probably not coated with truly 
fullerene type structures, and would leave edge carbons open to attack. This approach of 
only attacking edge carbons is useful because the carbon overcoating can be etched away 
from the non-fullerene type “defect”. Of course this would also mean that the open ends 
of SWNTs would also be attacked. However, if the amount of time was limited, then the 
amount lost at the open ends of the SWNT could be minimized while exposing the 
(previously) encapsulated metal particle.

The only caveat to this technique is that the process depends on defects occurring 
in the carbon overcoating of the metal catalyst particle. If there are no defects, then any 
chemical attack that would attack the truly fullerene-type overcoating would likely attack 
the sidewalls of the SWNT as well. At present, the “soft bake” approach [28] to 
purification of HiPco material removes about 90% of the metal contaminants, which 
would indicate that 90% of the overcoatings are not truly fullerene-like.

As research continues to improve the yield and production rate of SWNTs, the 
time that catalyst particles remain in the “hot zone” during the growth phase of SWNT 
may also increase. This would increase the probability that the catalyst particles would 
grow larger. In addition to larger catalyst particles, any overcoated particle would spend 
more time in the “hot zone” which would anneal out many defects in the carbon
overcoating. This would lead to a higher percentage of catalyst particles that contain a true fullerene like carbon overcoating. Thus, the utility of chemical attack on the metal particles and their carbon overcoatings may be diminished in the future.

3. Magnetic Separation

The catalysts used in most production techniques incorporate at least one of three ferromagnetic elements (cobalt, iron, or nickel). If one could use the magnetic properties of the particles to remove them from a suspension of the nanotube material, then any further chemical processing of the raw material that may affect the structure of the SWNTs could be avoided.

Magnetic separation techniques are well understood and used in numerous areas including clay processing [29], desulfurization of coal [30], water treatment [31,32,33] treatment of radioactive wastes [34], separation of mining ores [35], and filtration of cooling water in nuclear reactors [36].

Separation of magnetic particles from a suspension is simple in concept. A suspension is placed in a magnetic field, and the magnetic particles within the suspension are attracted to the magnetic field, leaving the bulk of the suspension free of magnetic particles. The strength of the magnetic field is important, but equally important is the gradient of the magnetic field [37].

For example, an idealized solenoid has a uniform magnetic field in the interior, and a gradient near the ends. A magnetic particle placed near the ends of the solenoid would be attracted toward the solenoid because of the gradient that exists at the end.
Once inside the solenoid, the particle would feel no net force toward one end or the other because the magnetic field is homogenous.

Figure 10. A magnetic object in the interior of the solenoid would not feel any net force because the magnetic field is homogenous. As the moves toward the open ends of the solenoid, the magnetic field becomes inhomogenous, and the object would feel a restoring force toward the center of the solenoid.

One way to imagine this is that a sphere is within a magnetic field of varying gradients (Figure 11). Magnetic flux lines can be drawn to represent the magnetic field. If the particle is magnetic the particle will become magnetized, and there will be local attractive forces on the particle. In a homogenous magnetic field, the forces created on one side of the particle exactly cancel out the forces on the other side, with no overall net force. However, if there is a gradient, then the forces do not cancel each other out, and there is a net force. In the second illustration, we see that the magnetic flux lines are not linear, but curved. To make matters easy, assume that the flux lines coming out of the
particle on the right are parallel. If we divide the forces into their component vectors, then we see that the forces in the y direction do cancel each other out, but the forces in the x direction do not, creating a net force to the left. In the extreme case, the flux lines enter the particle along the y direction and leave the particle in the x direction. We can see that the higher the gradient the particle experiences, then the higher the force on the particle. Also, if the gradient isn’t linear, a smaller particle will see a smaller gradient across its volume, and will experience a smaller overall force.

![Diagram](image)

Figure 11. a) A particle in a homogenous magnetic field feels no overall force due to the magnetic field. b) In an imhomogenous field, there is a net force on the particle. c) Even in the same gradient, a smaller particle will feel a smaller net.
3.1 Checkerboard Array

Magnetic separations have been carried out on Tubes@Rice with limited results using a magnet array made of 32 (1" X 1" X 0.25") NdFeB magnets arranged in a 6X6 array (minus the corner magnets). The magnets were face polarized, and they were positioned in a “checker board” pattern so that a “south face” was directly above, below, left and right of a “north face”. This produced gradients that were higher than could be obtained with individual magnets.

Suspensions of SWNTs in 1%Triton X-100 in water were made by placing Tubes@Rice material (purified by Tubes@Rice by nitric acid reflux) into a 1%Triton X-100/water mixture. The SWTN/TRITON X-100/water mixture was homogenized for two hours and sonicated at 540 W for 10 minutes.

The suspension to be treated was placed in a Petri dish and the dish placed on the magnetic array. Within minutes aggregation of material could be seen at the edges of magnets. The material was allowed to set on the magnetic array for two hours. After this time, the material that was still in suspension was very gently removed, leaving the material that had been attracted to the magnetic field gradient at the bottom of the Petri dish. This magnetic treatment procedure was usually done a total of three times for one batch.

It would take approximately seven hours to treat 100ml by this method. The magnetically treated suspension could be filtered to form a bucky paper. EDAX results indicated that the concentration of Ni and Co had dropped by an order of magnitude. However, the most immediate test was to simply take one of the NbFeB magnet used in the magnetic array, and bring it close to the bucky paper. It was possible to move the
Figure 12. Magnet array. Grey and white squares indicate opposing polarity, and the black areas indicate the areas of highest gradient, and the deposition pattern of magnetic particles.

bucky paper with the magnet, but it was not attracted so much that the paper would lift off a surface and “stick” to the magnet. This is in stark contrast to papers made with the untreated material. Bucky papers made with the material as received from Tubes@Rice were so attracted to the magnet that they would lift off a surface when a NdFeB magnet was brought within two or three centimeters of it.

This magnetic process was time consuming, and still left magnetic particles in the material. Later, NMR analysis was needed for experiments relating to polymer wrapping [38]. NMR on the material treated in this way was impossible because the remaining magnetic particles perturbed the homogeneity of the magnetic field of the NMR so much that the NMR couldn’t lock on the standard signal from D2O. Obviously another
technique was needed to remove so that even more of the magnetic material could be removed from the SWNT suspensions.

3.2 High Gradient Magnetic Separation

High Gradient Magnetic Separation (HGMS) is a technique that has been applied to various industries including the beneficiation of kaolin clay to remove iron and iron oxides [37]. Here we report on the use of this technique for the separation magnetic catalyst particles from surfactant stabilized aqueous suspensions of both Tubes@Rice produced material and HiPco produced material.

The properties that lie behind the success of HGMS are that the magnetic gradient near the surface of a magnet is dependent on the radius of curvature, and that a wire placed within a magnetic field will have an induced magnetic field associated with it. If a suspension of magnetic particles is passed over the wire, then the suspended magnetic particles will be attracted to the wire, and be held there. Once the suspension has passed, the external magnetic field can be removed, and the particles can easily be flushed from the wire.

So, the basic idea behind HGMS is to pack a column with a stationary ferromagnetic matrix and then place this packed column in a magnetic field. The suspension to be separated is then allowed to flow through this column. Suspended magnetic particles are then attracted to the stationary magnetic matrix and held there by the magnetic forces. The magnetic particles that have been trapped by the magnetic
Figure 13. Induced magnetic field of a magnetic matrix particle in an external magnetic field.

matrix can easily be recovered by removing the magnetic field and flushing the column with clean solvent.

3.3 Design of the HGMS Apparatus

The HGMS apparatus used was constructed from a 14 mm (ID) thick walled glass column. The magnetic matrix was held in place by using glass wool at the exit of the column. When using metal wools, a 200 μm, track etched polypropylene filter was placed at the exit of the column to trap any large bundles of SWNT that may have passed. After the first few runs, it was apparent that no bundles large enough to be trapped on the filter were making it through the magnetic column, and the filter membrane was removed. The bottom of the column was fitted with a stopcock to regulate the flow. Magnetic matrix materials consisted of #00 (400 series) Stainless Steel wool (~200 μm diameter), #0000 Steel wool (~100 μm diameter), and 300 mesh nickel powder (~45 μm diameter).
Figure 14. Design of magnetic column. The 1 micron filter was used initially to see if any bundles got through the magnetic matrix. None were detected initially, so it was later removed. For clarity, the plastic magnet holders are not shown. They are placed between the magnet assemblies and the glass column.

The external magnetic field was supplied by eight 1" x 1" x 0.25" face pole NdFeB magnets. Four magnets were placed on a 1.5" x 1.5" x 0.25" plate of Armco Magnet Steel. All four magnets on one plate had the same magnetic orientation. The remaining four magnets were placed on a second steel plate with the opposite magnetic orientation as the magnets on the first plate.
To keep the magnets assemblies from breaking the glass column, and to hold the magnets in place, two plastic separators were constructed. The measured magnetic field in the center of the column was 0.5 Tesla without the magnetic matrix.

Figure 15. Left, arrangement of magnets on steel plates. In this orientation, the column would be horizontal between the plates. Right, plastic magnet holder used to protect the glass column and to hold the magnetic array in place. The magnets fit in the top channel, and the column would fit in the lower semicircular channel.

3.4 Sample preparation for HGMS Treatment

In these experiments both Tubes@Rice material and HiPco material was used. Tubes@Rice material was received “as purified” by nitric acid reflux and subsequent washing [39, 40]. The received Tubes@Rice material was in a water slurry. HiPco material was received dry, as prepared with no previous processing.

3.4.1 Tubes@Rice Sample Preparation

The Tubes@Rice material was filtered using a 5 μm polypropylene track etched membrane. The filer cake (which consisted of ~5 mg of SWNT material and 50 mg of
water) was then washed three times with 50 mL portions MeOH to remove any trace amounts of toluene that may have remained from the purification process. It was then rinsed three times with 50 mL portions of water, and subsequently washed with dimethyl formamide (DMF). The wet filter cake was then placed in a 150 mL beaker and 5 mL of DMF were added to the beaker. The filter cake was broken up with a glass stir rod and mixed well with the stir rod until a slurry of nanotubes and DMF was obtained. The slurry was diluted to 100 mL and divided between two 250 mL Erlenmeyer flasks. The two suspensions were further diluted to 100 mL each.

The two suspensions were then sonicated for two hours in a 50 kHz cup sonicator. The resulting suspension was clear with a greenish-gray color. There were no visible flocks (visible aggregates of SWNTs) in the suspension.

3.4.2 HiPco Sample Preparation

The raw HiPco material (5mg) was placed in 200 mL of 1% SDS/water mixture. The SWNT/SDS/water mixture was homogenized for two hours using an Ultra Turrax homogenizer. For the first five minutes of homogenization, pieces of the material would clog the blades of the homogenizer. So every couple of minutes the homogenization was stopped, the blades were removed from the mixture and cleaned with a stainless steel spatula. The homogenizer was then replaced into the mixture, and homogenization was continued. After about five minutes (two or three cleanings) the blades of the homogenizer no longer became clogged and homogenization continued for the remainder of the two hour time period.
After homogenization, the mixture appeared dark with a high concentration of aggregates. The mixture was then transferred to a cup-horn sonicator and sonicated for 10 minutes at 95% power (570 Watts). After sonication, the mixture appeared dark and homogenous, without the appearance of aggregates. After sonication, the temperature of the suspension was approximately 60 °C. The mixture was then transferred to a 200ml flask, covered and allowed to cool to room temperature.

3.5 Operation of the HGMS column

To avoid the formation of “air pockets” in the magnetic column, the column was filled with water/SDS from the bottom by opening the stopcock, and placing the bottom of the column in a beaker filled with the same solvent that was used to suspend the SWNTs. The solvent was pulled up through the column using a rubber pipette to supply vacuum at the top of the column. Typically, the top of the magnetic matrix would be covered with approximately 2.5 cm of water/surfactant mixture at this point. The stopcock was then closed, and the column was transferred to a ring stand and held in place with two clamps.

Once the column was secured, the magnets were CAREFULLY put into place. The safest way to place the magnets on the column was to hold the magnetic plates, with the plastic separators attached, at about a 60° angle from vertical on either side of the column and slowly bring them together by decreasing the angle. The magnetic attraction to the column matrix and the opposing magnets were sufficient to hold the magnets in place.
The column was then flushed with approximately 100 mL of the solvent to remove any contaminants in the column that may have come out later during the treatment of the SWNT suspension. It is important not to let the DMF or water/surfactant level get below the top of the magnetic matrix to avoid the formation of air pockets in the magnetic matrix.

Just before adding the sample to be treated, the upper level of the solvent was lowered to the top of the matrix material. The sample to be treated was then slowly pored in the column. Then stopcock was then opened and the flow rate adjusted to the desired flow rate.

When the level of the sample had reached the top of the matrix, additional clean solvent was added to the column to again avoid the formation of air pockets in the matrix, and to avoid the possibility that surface tension would dislodge any trapped magnetic particles and carry them through the magnetic matrix. Flow was continued through the column until the effluent ran clear. The collection flask was then changed, and the magnets around the column removed. Often the effluent would turn black immediately after the removal of the magnets. The flow was continued until the effluent was again clear.

Samples of the effluent were then analyzed with UV-Vis-NIR to determine SWNT concentration. The SWNT were then flocked out of the suspension by the addition of approximately 10 mL of 1M HCl. The flocked suspension was then filtered with 5um pore size polypropylene membranes. The metal content of the resulting filter cake (known as a bucky paper) was measured using EDAX.
3.6 HGMS Results

The HGMS apparatus was tested with three magnetic matrix elements; grade #00 stainless steel wool (400 series) which is nominally 170 µm in diameter; grade #0000 steel wool, which is nominally 80 µm in diameter; and 300 mesh nickel powder, approximately 45 µm in diameter. The packing densities of the metal wools were between 5%-7%. The packing density of the nickel powder was approximately 25%.

The first matrix material was the stainless steel wool. Although it has a larger diameter and a lower magnetization, the corrosion resistance makes it the material of choice for many applications.

The SWNT suspension was Tubes@Rice material prepared as detailed above. The material was passed through the column with the magnets attached, and the treated material was collected.

By visual inspection, the concentration of the treated material did not appear to have diminished from the original concentration. Removal of the magnets did not reveal magnetic material that had been trapped in the matrix. Additionally, flushing the demagnetized column with DMF did not produce any material that may have been trapped in the matrix. No further analysis of the material was done.

The stainless steel wool was removed from the column and replaced with the steel wool. Again the packing density was about 6%. As the magnetically treated suspension was collected, it was apparent that the concentration of carbon material was lower than the original suspension.

Once the level of the untreated SWNT suspension reached the top of the steel wool matrix, the column was filled with DMF. When the suspension coming out of the
magnetic column became clear, the collection flask was exchanged with an empty flask and the magnets were removed.

Upon removal of the magnets, the clear suspension coming through the column immediately became black. The flow of DMF through the column was continued until the suspension once again became clear.

Below is the spectra of the original suspension, the material that came through the magnetic column, and the material that stayed behind when the magnets were in place.

Figure 16. UV-Vis-NIR spectra of Tubes@Rice (laser material) treated by HGMS using steel wool matrix.

The steel wool was removed from the column and replaced with nickel powder. The same procedure that was used for the steel wool packing was followed to treat
another batch of SWNT suspension. The results and observations were similar to those observed with the steel wool matrix.

Figure 17. UV-Vis-NIR spectra of Tubes@Rice (laser material) treated by HGMS using nickel matrix.

The magnetically treated suspensions were allowed to flocculate by adding 10ml of 1M HCl and then vacuum filtered using a 5 um filter membrane. The resulting bucky paper was then analyzed by EDAX to determine the metal content in each.

EDAX of the original material showed it to be 0.43 atomic percent nickel and 0.53 atomic percent cobalt. EDAX of both of the treated bucky papers did not show any nickel or cobalt. However, iron was detected in the material that had been treated with the steel wool matrix. It was suspected that the iron that was detected was due to leaching of
iron from the steel wool during treatment. If this were true, then the iron should be easily washed away with a hydrochloric acid solution.

The treated bucky paper was homogenized with the Ultra Torrax for 15 minutes in 1M HCl. The suspension was filtered to form a bucky paper. EDAX of the washed bucky paper did not indicate that iron was present.

Because of the iron that had leached out of the steel wool, and because of the similar results from the original experiments, nickel powder became the material of choice for the magnetic matrix.

The results for HiPco material were not as encouraging as the Tubes@Rice material. The spectra was taken of the original suspension of SWNT in 1% SDS/water. The suspension was magnetically treated the same way that the Tubes@Rice material was treated using nickel powder. The spectra of the magnetically treated suspension, and the spectra of the material that remained on the nickel matrix until the magnets were removed were taken. Figure 18 shows the UV-Vis-NIR spectra obtained.

EDAX analysis of a bucky paper that was made the same way as the magnetically treated Tubes@Rice material showed that the iron content was 1.3 atomic percent. Although this is a decrease from the 4.3 atomic percent of the original material, the concentration of iron was still higher than the original metal concentration of the Tubes@Rice material. Furthermore, from the spectra of the material that stayed in the magnetized column, it was apparent that SWNTs were held in the column.

Briefly, the results showed that for Tubes@Rice material the catalyst particles can be easily removed from a suspension by the use of this technique with both steel wool
Figure 18. UV-Vis-NIR spectra of HiPco material treated by HGMS using nickel matrix and nickel powder used as the magnetic matrix. The iron catalyst particles in HiPco material are not as easily removed.

The reason for the difference between the two may be that the catalyst particles produced by the HiPco process are smaller than those produced by the Tubes@Rice process. Because of their smaller size, the HiPco particles would not see as strong a force as the larger Tubes@Rice particles.

Another, more probable, explanation is that the metal catalyst particles are still attached to a large majority of the SWNTs. The fact that SWNTs were captured by the magnetic matrix supports this theory. If this is true, then magnetic catalyst particles could also be dragged through the magnetic matrix by the nanotubes to which they are attached.
4. UV-Vis-NIR Spectral Dependence on pH of SWNT

During the experiments with the HGMS column, UV-Vis-NIR spectra were routinely taken to determine the concentration. After doing a control run without the magnets but still using nickel powder matrix, it was noticed that the spectra of the SWNT suspension had changed. Specifically the absorbance of several features in the IR region had increased. This increase in spectral intensity was traced to a change in pH.

Figure 19. UV-Vis-NIR spectra of HiPco SWNTs in 1% SDS/water before and after running through the magnetic column without the magnetic field present.
4.1 Density of States and the Spectra of SWNTs

The UV-Vis-NIR spectra of SDS suspended SWNTs exhibit several peaks that are attributed to transitions in the DOS called Van Hove transitions (Figure 20). The DOS and the corresponding energy gap of an individual SWNT depends on if the SWNT is metallic or semiconductive. At the Fermi energy, the DOS of semiconducting SWNTs is zero. Metallic SWNTs have a small but nonzero DOS at the Fermi energy. The DOS also depends on the diameter of the SWNT. Larger diameter tubes have a smaller energy gap than larger tubes. The optical absorptions in the NIR region of the spectra are a result of lowest energy transitions of semiconducting tubes and are called “The first Van Hove peaks”.

To investigate the pH dependence of the spectra, suspensions of SWNT’s in 1% SDS in water were prepared. The pH was varied using standardized solutions of HCl and NaOH. The spectra of the samples were taken using a Shimadzu 3100PC spectrometer. 10mm path length quartz cells were used for the sample holder. The reference cell contained a 1% SDS/water mixture. Scan rate was approximately 200 nm/min., spectral resolution was set at 2 nm, and data interval was set at 1nm.

4.2 Sample preparation

To make a standard starting mixture, 100mg of raw HiPCO (61CE) material was placed in a 300 mL beaker. 200 mL of 10% (w/w) SDS/water solution was added to the beaker. The material was wetted by the water/SDS solution, and the mixture was homogenized for 2 hours at low speed (13,000 rpm) using an Ultra Turrax homogenizer.
Figure 20. DOS of (7,6)(semiconductor), (7,7)(conductor) and (13,7) (conductor) SWNT’s. [3]

Unless otherwise noted, this starting mixture was used for the following experiments by removing 20 ml of the mixture and diluting to 200 mL with DI water. The resulting mixture was then sonicated for 10 minutes in a cup-horn sonicator at 95% power (approximately 540 watts). This resulted in a suspension that was 50 mg/L SWNT and 1% SDS in water. The mixture appeared to be well suspended with no visible flocks in the mixture. The sonicated mixture was then covered with parafilm and allowed to cool to room temperature for 2 hours.
4.3 Dependence of Spectra on pH.

10ml aliquots of a 50mg/L SWNT/SDS/water suspension were placed in seven 20ml scintillation vials. The initial pH of the mixture was 6.07. HCl (0.01M) and NaOH (0.01M) were added in 1 mL, 0.1 mL, and 0.01 mL volumes to the individual vials. The mixtures were allowed to equilibrate for 2 hours before the pH and the spectra were recorded.

The pH of the mixtures are as follows:

<table>
<thead>
<tr>
<th>Acid/Base</th>
<th>volume added (mL)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01M NaOH</td>
<td>1.00</td>
<td>9.76</td>
</tr>
<tr>
<td>0.01M NaOH</td>
<td>0.10</td>
<td>7.43</td>
</tr>
<tr>
<td>0.01M NaOH</td>
<td>0.01</td>
<td>6.31</td>
</tr>
<tr>
<td>NA (initial)</td>
<td>0.0</td>
<td>6.07</td>
</tr>
<tr>
<td>0.01M HCl</td>
<td>0.01</td>
<td>5.63</td>
</tr>
<tr>
<td>0.01M HCl</td>
<td>0.10</td>
<td>3.72</td>
</tr>
<tr>
<td>0.01M HCl</td>
<td>1.00</td>
<td>2.38</td>
</tr>
</tbody>
</table>

Table 1. Addition of HCl and NaOH SWNT suspensions.

As the pH of the solution is decreased, the Van Hove peaks diminish and around pH 4 the first Van Hove peaks are completely gone. Most significantly, they do not decrease equally at the same pH intervals. The peaks of the larger diameter tubes (longer
Figure 21. UV-Vis-NIR spectral dependence of Van Hove peaks with pH in 1% SDS/water.

wavelength) begin to reduce in size at a higher pH than the peaks of the smaller diameter tubes (shorter wavelengths). This means that the larger tubes are becoming “protonated” at a higher pH than the smaller diameter tubes. This is the first time that a difference in the chemical behavior of different diameter tubes has been observed. This could prove useful for the separation of nanotubes by diameter and type.

4.4 Acid-Base Cycling

One can wonder if upon the addition of acids or bases, the nanotubes are undergoing an irreversible process. It may be that the change in the spectra is indicating that a reaction is occurring that permanently destroys the band gaps of the SWNTs and making them unsuitable for certain (mainly electronic) applications.
To check to see if the effect of pH on the optical spectra was reversible, 10ml of a sample was placed in a scintillation vial and 0.1M NaOH and 0.1M HCl were added sequentially. After each addition of either acid or base, the suspension was mixed thoroughly, and allowed to equilibrate for 2 hours before spectra were taken.

In the following figure, Base 1 is the spectrum taken after addition of 10ul of 0.1M NaOH; Acid 1 is the spectrum that was taken after addition of 20ul of 0.1M HCl (10ul to neutralize the 10ul of NaOH added previously and 10ul to make it acidic). The remaining spectra were taken after addition of 20ul of either 0.1M NaOH or 0.1M HCl. With these additions, the pH should be ~4 for the acidic spectra, and ~10 for the basic spectra.

![Graph](image_url)

Figure 22. Cycling a SWNT/1%SDS/water suspension between acidic and basic conditions.
By cycling between acidic and basic conditions, it can be seen that the Van Hove peaks can be restored to their original shape and intensity under basic conditions. So the effect of the acid on the Van Hove peaks is reversible and the associated band gaps are preserved.

4.5 Time Evolution of Spectra

To check the evolution of the spectra over time, 10ul of a 0.1M NaOH solution was added to 10ml of a SWNT/SDS/water suspension. The spectra was taken at 1.5, 3.25, 5.0, 6.75, 8.5, 10.08, 11.67, 13.5, 15.67, 18, 19.75, 22, 27, 32, 37, 42, 47, 52, 57, 62, 67, 77, and 87 minute intervals. In Figure 23, increasing absorbance correspond to increasing time.

![Graph showing absorbance over wavelength](image)

Figure 23. Change of the UV-Vis-NIR spectra over time after the addition of 10 µL of NaOH.
According to this series of spectra, it takes about 2 hours for the spectra to stabilize at room temperature. A similar amount of time is needed to stabilize the spectra when changing to acidic conditions using HCl.

5. Conclusions

5.1 HGMS

Removal of the magnetic catalyst particles by high gradient magnetic separation has been successfully achieved with laser material and has been applied with limited success with HiPco material. The reasons for limited success of the HiPco material are most likely the smaller size of the catalyst particles, and that some of the catalyst particles are still attached to the SWNTs. It should be possible to remove the smaller catalyst particles by using a higher applied external magnetic field and smaller diameter magnetic matrix.

Increasing the external magnetic field would be useful to the point of magnetic saturation of matrix material (which is around 2 Tesla for nickel). Operations could be simplified by the use of an electromagnet so that the magnetic field could be varied, and easily removed without having to physically take away permanent magnets.

Decreasing the diameter of the magnetic matrix would increase the gradient of the induced magnetic field around the matrix material. However, decreasing the diameter of the nickel powder would decrease the diameter of the fluid path. Higher pressures would be necessary to force the suspension through the column. By using smaller diameter metal wools or metallic wires, packing density (and thus the pore size of the column) can be better controlled.
5.2 Spectral Dependence on pH

The spectral features of SWNTs in a water suspension have been shown to depend on the pH of the suspension. Furthermore, it has been shown that the spectral features of large diameter of SWNTs diminish at a higher pH than smaller diameter SWNTs. This is the first time that SWNTs of different diameters have been shown to behave as distinct chemical species. The process has been shown to be reversible by alternatively acidifying and basifying a SWNT suspension multiple times. The spectral features are recovered after each cycle. This means that acidification does not produce a permanent change in the electronic properties of SWNTs. The results presented here show promise for separation and differential chemical functionalization of SWNTs.
Bibliography


