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Science of Single-Wall Carbon Nanotubes: Purification, Characterization and Chemistry

by

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

Doctor of Philosophy

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ABSTRACTS

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Characterization of raw nanotube materials produced by different methods is demonstrated. Depending on the production methods, tubes of different diameters can be produced. Purification of single wall carbon nanotubes produced by laser-oven and HiPco process is also discussed. Metal catalyzed oxidation at low temperature has been shown to selectively remove non-SWNT carbon and permit extraction of metals with concentrated HCl. These multi-stage purification methods have been investigated and the sample purity is documented by EDAX, ESEM, TGA, Raman and UV-vis-Nir spectroscopy.

Covalent attachment of functional groups and molecules, including fluorine, methyl, n-butyl and n-hexyl groups, to the sidewalls of single wall carbon nanotubes has been achieved. Further fluorination study is done to investigate the effect of HF which is used as catalysts. Parallel fluorination experiments are performed on both laser-oven-grown and HiPco SWNTs. Larger diameter tubes, i.e. laser-oven-grown SWNTs, require higher fluorination temperatures. A limiting stoichiometry of C\textsubscript{2}F can be reach for fluorotubes. Quantitative measurement of the alkylation was done by thermal gravimetric analysis. A mechanism involving electron transfer and effects of reaction
temperature, solvents and steric effects of the alkyl groups are discussed. Prolonged exposure of small diameter SWNT ropes (diameters < 5 nm) to hot fuming sulfuric acid has been shown to grow super-ropes with approximately 10,000 tubes in cross-section from rope sizes of approximately 10 tubes. This represents the largest rope sizes ever seen. Examination of the spectral properties of the SWNTs indicates that the roping occurs without changing the chemical state of the nanotubes. Acid intercalation of single wall carbon nanotubes is examined. Several super acids and strong acids are used to study the charge transfer and protonation effects on SWNTs. The degree of charge transfer is clearly correlated with the ability of acid to intercalate into the nanotube packs.

A molecular mechanics calculation is used to optimize the proposed Fluorotube structures. This is the first theoretical work on the modeling of Fluorotubes. Results show that fluorine would like to add along the circumference of the tubes instead of going down the tube axis. The (1,4) isomer has the lower total steric energy (TSE) between the two proposed Fluorotube structures, but the energy difference is small. Scanning tunneling microscopy has been used for atomic scale imaging of the fluorotubes. Significant band features are seen on fluorotubes, not on pristine carbon nanotubes. Butylated tubes have also been investigated by STM imaging. Instead of bands, relatively large, distinct features with spacings of about 50 Å are observed. Both theoretical and experimental results indicated the (1,4) isomer with bands around the tubes should be the preferred structure.
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Chapter 1

PURIFICATION AND CHARACTERIZATION OF SINGLE-WALL CARBON NANOTUBES

1.1 INTRODUCTION OF SWNTS

Nanostructures offer a new paradigm for materials manufacture by utilizing submicron-scale assembly to create entities from the "bottom up" rather than the "top down" ultraminiaturation method of chiseling smaller structures from larger ones. In 1959, Richard Feynman delivered his famous lecture, "There is plenty of room at the bottom"\(^1\). He stimulated his audience with the vision of exciting new discoveries if one could fabricate materials and devices at the atomic/molecular scale. It was not until the 1980s that instruments were invented with the capabilities Feynman envisioned. Scanning tunneling microscopes\(^2\), atomic force microscopes\(^3\)\(^-\)\(^4\) and nearfield microscopes\(^5\)\(^-\)\(^6\) provide the "eyes" and "fingers" required for nanostructure measurement and manipulation. Traditional models and theories for material properties and device operations involve assumptions based on "critical scale lengths" that are generally larger than 100 nanometers. Under this critical scale, distinct behaviors often emerge that cannot be explained by traditional theories and models. Thus, scientists from many disciplines are avidly fabricating and analyzing nanostructures seeking to discover novel phenomena at the intermediate scale between individual atoms/molecules. Researchers are just beginning to understand some of the principles to use in creating "by design" nanostructures and how to fabricate nanodevices and systems economically. The ability
to synthesize nanoscale building blocks with precisely controlled size and composition and then to assemble them into larger structures with unique properties and functions will revolutionize segments of the materials manufacturing industry. In short, nanostructuring can bring lighter, stronger, and programmable materials, reduction in life-cycle costs through lower failure rates, innovative devices based on new principles and architectures, and the use of molecular/cluster manufacturing which takes advantage of assembly at the nanoscale level for a given purpose.

One of these amazing nanomaterials is called the “carbon nanotubes”\( ^{7,8} \). They are effectively buckyball\( ^{9,10} \) structures played out as long strands rather than spheres (Figure 1-1). Their strength as structural supports comes from their sturdy molecular structure, which looks like what one would get if one could roll a two dimensional sheets of graphite into a three dimensional cylinder. The properties of carbon nanotubes as new materials are remarkable, a fact that was evident almost as soon as they were first discovered in 1991\(^1\), turning up in the soot and dirt piles that fill chambers where scientists produce fullerenes, large geometric carbon molecules. Nanotubes can be fabricated into two forms: single-wall carbon nanotubes (SWNTs)\(^8\) or multi-wall carbon nanotubes (MWNTs). While a SWNT consists of only a single cylinder, a MWNT consists of several concentric tubes, each with a specific diameter.

Carbon nanotubes are great molecular cylinders, in which every two carbons are connected by a strong covalent bond, and every atom accommodates exactly three neighbors. No dangling chemical bonds are on the end since a nanotube is ultimately sealed on the ends. The strength of these bonds and their clever organization makes nanotubes highly resistant to failure in tension. The limit of how long they can be is
Figure 1-1  Structures of carbon nanotubes

Nanotubes can be derived from the buckyball molecule $C_{60}$ by adding belts of atoms (a), or by rolling a two-dimensional graphene sheet cut at various angles with respect to the hexagonal lattice. The angle determines which helicity will characterize the resulting nanotubes: armchair (b), zigzag (c) or an arbitrary chiral angle between the two (d). During their formation nanotubes acquire caps with fullerene geometries. (adapted from drawings by Riichiro Saito et al. 1996.)
unknown, thus aerospace scientists have proposed using them as cables extending into space (Figure 1-2). In addition, nanotubes can easily be cut into sections as small as a few nanometers. One of the first important applications of carbon nanotubes has been in the fabrication of sharp, strong and functionalized AFM probe tips (Figure 1-3)\textsuperscript{12}. The hollow nature of nanotubes allows them to function as pipes for transporting and molding atoms and molecules. Furthermore, the tubes come in semiconducting and conducting form (Figure 1-4), meaning that they can also be used as molecular wires and circuits. The electronic properties of carbon nanotubes are directly related to their shape, making them an important Nano-Eletromechanical System (NEMS) \textsuperscript{13-15}.

1.2 QUALITY OF SINGLE-WALL CARBON NANOTUBES

1.2.1 Introduction

The development of nanotechnology with respect to devices and the new materials and processing methods necessary for the construction of these devices is growing rapidly worldwide. Nanotechnology is expected to impact space activities because of the potential for lightweight strong materials and nano/micro scale devices. As a result there is a growing need to characterize the quality of materials used in the fabrication of devices and high strength materials as well as the performance and reliability of nanotechnology-based devices and materials. A promising new material
Figure 1-3  Nanotubes as nanoprobe in scanning probe microscopy

Multiwalled nanotubes (MWNT) were prepared in the optimized DC carbon arc apparatus reported previously. In order to use a nanotube as a robust probe, a MWNT was bonded to the side of the tip of a conventional silicon cantilever using a soft acrylic adhesive 1-10 nm thick (a). This permits the nanotube to bend away from its connection whenever the tip is inadvertently "crashed" into a hard surface, and then to snap back to its original straight position when the tip is withdrawn. Effectively the nanotube is then "spring loaded" much like the side view mirror of an automobile. (b) and (c) show the tip of the probe and the MWNT on the tip, respectively.
Figure 1-4  Nanotube shape and structure
A rollup vector \((n,m)\) specifies the oriented width, recording the number of steps along the \(a\) and \(b\) directions. The ability of carbon atoms to assemble in these structures results from the fact that each atom's four electrons can form three in-plane bonds, slightly bent, in so-called sp²-hybridization; the fourth electron is shared, delocalized, making fullerenes aromatic and allowing for electrical conductance in nanotubes. As follows from elementary geometry and an assumption that the C-C bond has its normal length of 0.14 nanometers:

\[d \text{ (tube diameter)} = 0.078n^2 + nm + m^2 \text{ (nanometers).}\]

\[\theta \text{ (chiral angle)} = \arctan[3m/(m+2n)].\]

(adapted from drawings by Dresselhaus et al. 1996.)
with great potential for new sensor and composite materials applications is that of single wall carbon nanotubes (SWNTs).

SWNTs typically consist of tubes with diameters from 0.7 to 1.5 nanometers with lengths of the order of half a micron but much shorter and longer tubes are also present. When they are made, SWNTs are usually accompanied by nanometer-sized graphitic or amorphous carbon, and metallic nano-sized particles, which must be separated from the SWNTs. It will be necessary in the future applications of SWNTs to have standard analytical methods that provide quantitative measurements of the quantity and size distributions of SWNTs. Raman spectroscopy has been extensively used to identify SWNTs since both theory\textsuperscript{16-25} and experiments \textsuperscript{26-37} have predicted and shown that SWNTs exhibit unique and intense Raman spectra. In addition, UV-Vis-nir gives us the electronic states of SWNTs, which correspond to the type (i.e. semiconducting vs. metallic etc.) and the size of tubes.

The use of Raman and UV spectra for characterization of SWNT samples as obtained from production and in the more purified state is illustrated by the following examples. The effects of heating and exposure to acidic and basic solutions on SWNT is also demonstrated.

1.2.2 Results and Discussion

Six samples of unpurified nanotube soot from their respective SWNT production equipment have been examined with Raman spectroscopy. The Raman instrument is a
Renishaw System 1000 micro-Raman spectrometer with an 1800 line/mm grating. It was used with their standard 780 nm diode laser with a laser power of \(-10\) mw through a X10 objective. Samples were pressed between a glass slide and a cover slide. Two of the samples were grown in laser vaporization apparatus (Figure 1-5) located at Rice, Tubes@rice\textsuperscript{38}, and NASA Johnson Space Center, JSC \textsuperscript{39}. Three of the samples where grown in arc vaporization apparatus located at NASA-JSC \textsuperscript{40}, Montpelier, France \textsuperscript{41} and Carbolex \textsuperscript{42}. One was grown in a high-pressure carbon monoxide organo-metallic apparatus located at Rice, HiPCO@rice \textsuperscript{43}. Processed and purified samples where obtained from Tubes@Rice.

Figure 1-6 shows the Raman spectra for each of the samples. For all samples, peaks characteristic of SWNTs near 1590 cm\(^{-1}\) and in the 100-300 cm\(^{-1}\) region dominates the spectra. Spectra in the 1590 cm\(^{-1}\) region are seen to be quite similar in frequency for all the samples and represent modes where the carbon moves in the surface of the SWNTs. Spectra in the 150 to 300 cm\(^{-1}\) regions show much more variation with sample. Vibrational modes in this region are assigned as radial breathing modes of the SWNT and are quite sensitive to the diameter of the SWNTs. Theory has shown that the breathing mode of SWNTs is to a good approximation inversely proportional to the diameter of the SWNT. This expression \(\omega = A/d\) has been calculated by a number of investigators \textsuperscript{17, 18, 20, 21, 29, 32} where \(A\) is predicted to range from 224 to 234 and \(d\) is given in nanometers and \(\omega\) in wavenumbers. The values given in Figure 1-7 were calculated with a value of 234. One sees that the diameter distribution of SWNTs varies significantly for the different preparation methods. It is interesting to note that most of these nanotube soot samples are thought to contain less carbon as SWNTs than as other forms of carbon. The Raman
Figure 1-5  Apparatus for laser-ablation production of single wall carbon nanotubes

Single-walled nanotubes are produced in a quartz tube heated to 1,200°C. Nanotubes grown this way self-organize into ropes with promise for engineering applications. In the techniques used at Rice University, a laser is aimed at a block of graphite, vaporizing the graphite. Contact with a cooled cooper collector causes the carbon atoms to be deposited in the form of nanotubes. The nanotube "felt" can then be harvested. (Illustration by Aaron Cox.)
Figure 1-6  Raman spectra (laser - 780 nm) of unpurified nanotube soot
Figure 1-7  Raman spectra (laser - 780 nm) of unpurified nanotube soot at the breathing mode region
spectra, however, exhibit spectra dominated by SWNTs without strong peaks due to the other forms of carbon. The weak peak at 1290 cm\(^{-1}\) is generally assigned to amorphous carbon and is typically accompanied by a broad peak in the 1600 cm\(^{-1}\) region. One might use the intensity of the 1290 cm\(^{-1}\) peak as a measure of the non-SWNT carbon. However, it is known that the intensity of this peak relative to the peak in the 1600 cm\(^{-1}\) range varies widely with the graphitic ordering of the carbon. This makes it difficult to quantify the amount of non-SWNT carbon based on peak intensity of the 1290 cm\(^{-1}\) peak. The strong overlap of SWNT features and those for non-SWNT carbon in the 1600 cm\(^{-1}\) region and the much greater intensity of the SWNT peaks also make it difficult to extract quantitative information from relative intensities in this region.

The effects of exposure to concentrated sulfuric acid followed by neutralizing in ammonium hydroxide and subsequently heating to 200° C are shown in Figure 1-8 and 1-9. One clearly sees large changes in both the UV-vis-near-IR and Raman spectra of the SWNT. Thus one can conclude that quantitative comparisons of SWNT samples must ensure that all samples are processed in the same manner particularly when they are processed in acidic or basic conditions.

1.2.3 Conclusion

Thus it seems best to view Raman spectroscopy, with aid from UV-vis-near-IR spectra, as a sensitive method for determining the presence of SWNTs among other forms of carbon as well as providing an approximation of the average SWNT diameter and
Figure 1-8  UV-VIS-NIR spectra of HiPCO SWNT

(a) Original  
(b) $\text{H}_2\text{SO}_4$  
(c) $\text{NH}_4\text{OH}$  
(d) Heated
Figure 1-9  Raman spectra of HiPco SWNTs using 780 nm laser
(a) Untreated SWNTs
(b) SWNTs soaked in sulfuric acid
(c) (b) neutralized with NH4OH
(d) (c) heated in Ar @ 200°C for 1 hr
distribution of diameters rather than a quantitative measure of SWNT content. In addition one must keep in mind that only certain SWNT sizes are sensitive to a specific laser wavelength, thus the size distribution may appear discontinuous although there is, in fact, a smooth distribution of sizes.

1.3 PURIFICATION BACKGROUND

Since their discovery in 1990, carbon single-wall nanotubes (SWNTs) have attracted considerable interest because of their unique physical, chemical and mechanical properties. Carbon SWNTs are expected to be useful in many different fields, such as field emission displays, super-capacitors, molecular computers and ultrahigh strength materials. However, in order to obtain the optimal performance of SWNTs in various applications, high-purity carbon SWNTs will be required.

The impurities typically found in as-prepared carbon single-wall nanotubes (SWNTs) are the metals that were used as catalysts for growth and amorphous carbon. Metals are present as nanoparticles and typically encased in carbon outer layers that make them impervious to dissolution in an acid. All purification methods attempt to remove the metal and unwanted carbon without affecting the carbon SWNTs. Different purification methods have been reported to-date. The purity of the SWNTs is typically reported in terms of the metal content and apparent particle content relative to SWNTs.
Carbon single-wall nanotubes are typically accompanied by other carbonaceous materials when synthesized using the laser oven method or arc discharge evaporation method. A number of purification methods have been developed to date. They can be categorized into four major methods: acid oxidation, gas oxidation, filtration and chromatography. The acid reflux procedure was first described by Rinzer et al.\textsuperscript{33} in which raw nanotube materials are refluxed in nitric acid to oxidize the metals and impurity carbons. Other groups have employed different reaction times, temperatures, and acid concentrations, with similar results. Acid treated nanotubes are thought to have carboxylic acid groups at the tube ends and, possibly, at defects on the sidewalls. Since functionalized SWNTs will have considerably different properties than those of pristine tubes, the extent of chemical modification achieved through the acid purification route must be carefully evaluated.

Gas-phase oxidation is commonly used as the purification method for MWNT.\textsuperscript{51-55} However, Dujardin et al. have suggested that the same purification process would destroy single-wall carbon nanotubes. Dillon et al.\textsuperscript{56} have described an oxidation process that produces > 98 wt % pure SWNTs. In their purification process, raw nanotube soot first undergoes a nitric acid refluxing process. Oxidation of the acid treated product is then carried out in air at 550 °C for 30 minutes, leaving behind SWNTs having a weight of ~ 20% of the initial raw material. TGA studies indicate that these purified tubes can withstand temperatures up to 600 °C in air. Zimmerman et al.\textsuperscript{37} have discussed an oxidation with a mixture of HCl, Cl\textsubscript{2} and H\textsubscript{2}O to remove unwanted carbon in raw nanotube materials. Only a small quantity (~5 mg) of nanotubes was purified each time, and no large scale purification by this method was demonstrated.
Bandow et al.\textsuperscript{27} have reported a procedure for a one-step SWNT purification by micro-filtration in an aqueous solution in the presence of a cationic surfactant. Konstantin et al.\textsuperscript{58} developed an ultrasonically assisted filtration method which allows the purity of nanotubes to reach $> 90\%$. Highly pure and length-selected SWNTs in aqueous solution can be obtained by column chromatography, according to Duesberg et al.\textsuperscript{59} Limited solubility of nanotubes is the major disadvantage of size-exclusion chromatographic methods.

This study defines a cleaning procedure that provides additional removal of metal and non-nanotube carbon from SWNT samples that have been grown with the laser oven method and initially cleaned with nitric acid. The process is similar to that suggested by Dillon et al.\textsuperscript{56} with the difference that this gas phase oxidation process is carried out at successively higher temperatures, with each step followed by an acid wash. We believe this approach preserves a larger fraction of the SWNT component of the sample.

\subsection*{1.4 LASER-GROWN SWNTS}

In the course of working with SWNTs, it became obvious that there is a clear correlation between the temperature at which air oxidation of SWNTs begins and the metal content of the sample. The metal is typically present as nanoparticles with a carbon coating that varies from disordered carbon layers to graphitic shells. It is thought that low temperature oxidation can remove the more disordered carbon layer which permits
removal of this metal with an acid wash. We believe it is important that this metal be removed before going to high temperature oxidation since metal nanoparticles are likely to catalyze the oxidation of SWNTs. Higher temperature oxidation removes the more stable carbon layer on the remaining metal particles thus permitting their removal with an acid wash.

A limiting temperature near 500 °C exists where the rate of removal of the carbon layer on the metal particles is similar to the uncatalyzed, gas phase oxidation of SWNTs. At this point, any further metal removal by oxidative removal of the metal particle carbon coatings results in a large loss of SWNTs.

Sample purity is documented with SEM, TEM, and electron microprobe elemental analysis. Raman and UV-vis-near-IR spectra are also reported for the different stages of the cleaning procedure.

1.4.1 Experimental Procedure

The starting SWNT samples were obtained from Tubes@Rice\textsuperscript{33, 60, 61} as a suspension in toluene. This suspension was filtered and washed with methanol to remove additional soluble residue left from the initial nitric acid cleaning carried out by Tubes@Rice. This left a black puffy paper (buckypaper). This paper was then refluxed in water\textsuperscript{62, 63} for approximately 2-5 h, depending on the amount of starting material. The water becomes yellowish which suggests further removal of aromatic carboxyl acids.

Two sets of metal removal studies were carried out with successive gas phase oxidation at increasing temperatures. Each oxidation was followed by a wash in
concentrated HCl solution. In the first study, the temperature at which the sample was oxidized was raised in small increments in order to determine the temperatures at which the carbon-encased metal is exposed for subsequent reaction with HCl. Typically, the sample was heated in a 5% O₂/Ar, 1 atm mixture, for 1 h at selected temperatures and subsequently sonicated in concentrated HCl for 10 min. The green color that develops in the concentrated HCl provides an indication of the dissolution of cobalt and nickel metal oxides that form during oxidation of the sample. Weight loss after each procedure was determined after drying the samples in vacuum at 150 °C. The temperatures at which gas phase oxidation was carried out and the respective weight loss values are given in Table 1-1. In the second study, the oxidation procedure was reduced to a water reflux and a two-step oxidation process to produce the best results for metal removal with minimum weight loss of nanotubes. In this case, we expose the samples first to 300 °C, then to 500 °C temperature oxidation with an HCl extraction step after each oxidation. Table 1-2 provides the weight loss and metal concentration data for the two-temperature process. When heated to 500 °C, metal loss is more dramatic, and the final metal content is about 0.1 atomic percent relative to carbon.

In these studies, Raman spectra were obtained with a Renishaw micro-Raman spectrometer operating with a 780 nm laser. UV-vis-near-IR spectra were obtained with a Shimadzu-UV-3101 PC spectrometer. Transmission electron microscopy (JEOL 2010 TEM) was obtained using 100 kV beam energy. Thermogravimetric (TGA) data were obtained with a TA Instruments model 2960 system. Elemental analysis was obtained with a Cameca SX 50 electron microprobe equipped with four wavelength dispersive X-ray spectrometers. Raman, IR, and TGA were carried out with SWNTs in the form of
<table>
<thead>
<tr>
<th></th>
<th>Metal at. %*</th>
<th>Weight loss</th>
</tr>
</thead>
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<td>(a)</td>
<td>1.71</td>
<td>******</td>
</tr>
<tr>
<td>(b)</td>
<td>1.56</td>
<td>9.2%</td>
</tr>
<tr>
<td>(c)</td>
<td>1.44</td>
<td>8.7%</td>
</tr>
<tr>
<td>(d)</td>
<td>1.41</td>
<td>8.8%</td>
</tr>
<tr>
<td>(e)</td>
<td>1.43</td>
<td>12.2%</td>
</tr>
<tr>
<td>(f)</td>
<td>0.17</td>
<td>18.9%</td>
</tr>
</tbody>
</table>

Table 1-1  Weight loss and metal concentration in SWNTs after purification process  
(a) as-purified tubes@rice SWNTs  
(b) (a) after water reflux  
(c) (b) heated in 300°C, 5% O₂/Ar  
(d) (c) heated in 400°C, 5% O₂/Ar  
(e) (d) heated in 450°C, 5% O₂/Ar  
(f) (e) heated in 500°C, 5% O₂/Ar

- Mₓ/Mₓ*100 (in terms of percentage), where M=atomic %, X=Co + Ni, C = Carbon
- Total weight loss from the process is 57.8 %
<table>
<thead>
<tr>
<th></th>
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<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
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<tbody>
<tr>
<td>Co</td>
<td>0.97*</td>
<td>0.88</td>
<td>0.85</td>
<td>0.10</td>
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<tr>
<td>Ni</td>
<td>0.84</td>
<td>0.68</td>
<td>0.59</td>
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<tr>
<td>Metal at. %</td>
<td>1.81</td>
<td>1.56</td>
<td>1.44</td>
<td>0.17</td>
</tr>
<tr>
<td>Weight loss</td>
<td>4.25%</td>
<td>17.07%</td>
<td>22.94%</td>
<td></td>
</tr>
</tbody>
</table>

Table 1-2  Weight loss after each process and metal concentration in SWNTs
(a) as-purified tubes@rice SWNTs
(b) (a) water refluxed
(c) (b) heated at 300°C in 5% O₂/Ar
(d) (c) heated at 500°C in 5% O₂/Ar

- \( \text{M}x/\text{M}c \times 100 \) (in terms of percentage), where \( \text{M} = \text{atomic} \% \), \( \text{X} = \text{Co, Ni} \), \( \text{C} = \text{Carbon} \)
- Total weight loss from the process is 44.3 %
buckypaper. Samples for UV-vis-near-IR were prepared by sonicating SWNTs for \( \approx 10 \) min in 0.15 wt % Triton-X/D\(_2\)O solution in a cup sonicator at 55 kHz. TEM samples were prepared by sonicating SWNTs in methanol and drop drying them onto lacy carbon TEM grids.

### 1.4.2 Results and Discussion

The rate of oxidation of SWNT samples held at 425 °C in air for 6 h was used as a test of sample purity in the first study. These results are shown in Figure 1-10. One sees large changes in the rate of oxidation when the sample is refluxed in water and after gas phase oxidation at 300 °C followed by an HCl wash. The next largest change in oxidation rate occurs after gas phase oxidation at 500 °C and an HCl wash. The largest changes in the metal-to-carbon ratio occur after the water reflux, oxidation at 300 and at 500 °C gas phase treatments respectively, and these correlate with the largest changes in the rate of oxidation shown in Figure 1-10. This clearly suggests that SWNT oxidation at 425 °C is metal catalyzed. From the result in the first study, we adopted the two temperatures, 300 °C and 500 °C, as the oxidation temperatures for the two-stage gas-phase purification process in the second study.

Figure 1-11 illustrates the oxidative behavior of a sample that has been cleaned with the two-stage process. This sample appears to be stable in air at temperatures as high as 550 °C. It is likely that oxidative stability up to 600 °C can be achieved with more metal removal. However, the higher temperature oxidation treatments will also result in the loss of a larger percentage of SWNTs. To verify the catalytic oxidation
Figure 1-10  TGA of SWNTs in the corresponding order of purification stages
(a) as-purified tubes@rice SWNTs
(b) (a) after water reflux
(c) (b) heated in 300°C, 5% O₂/Ar
(d) (c) heated in 400°C, 5% O₂/Ar
(e) (d) heated in 450°C, 5% O₂/Ar
(f) (e) heated in 500°C, 5% O₂/Ar
Figure 1-11  TGA of metal effects on oxidation

(a) Co added (to purified SWNTs)

(b) 2-stage purified SWNTs
effects of the metal present in a nanotubes sample we added Co from a Co(NO₃)₂ aqueous solution to the cleaned sample. Its oxidative behavior in air is also shown in Figure 1-11. A reduction in air stability is clearly seen for the Co-doped sample, thus proving that metal catalyzed oxidation of SWNTs occurs at temperatures below 500 °C.

Figures 1-12 and 1-13 show SWNT samples before and after the purification process with SEM and TEM, respectively. The bright areas are thought to be due to agglomerated metal particles. They are clearly removed by the cleaning process. In the TEM images shown in Figure 1-13, metal particles are identified as the dark particles. They appear to be gathered into groups and associated with a nodular form of carbon. In the cleaned sample most of the metal is gone, however some of the nodular carbon is still present.

Figure 1-14 shows Raman spectra of SWNTs as raw material, nitric acid treated, purified through the two-stage oxidation process, and purified SWNTs annealed at 900 °C. Typical SWNT features are observed for the tangential and radial modes near 1590 and 180 cm⁻¹ respectively. The most noticeable effect of cleaning and annealing is the increased intensity of the Raman features when the cleaned sample is annealed at 900 °C. The radial modes present near 180 cm⁻¹ can be correlated with SWNT diameters.²¹, ²⁸, ³¹, ⁶⁴, ⁶⁵ The peaks present for the annealed sample suggest that the nanotube diameter in the sample range from 1.13 to 1.53 nm, with an average size of 1.33 nm. This is calculated with \( d = \frac{234}{\nu^2} \), where \( d \) is the tube diameter in nanometers and \( \nu \) is in wavenumbers.

Figure 1-15 presents UV-vis-near-IR spectra of SWNTs suspended in a 0.15 wt % Triton-X/D₂O solution. All of the spectra have been normalized to the annealed sample spectral intensity at 1200 nm. Well-spaced and symmetric structures, called van Hove
Figure 1-12   SEM images of SWNTs
(a) Before purification (as-purified tubes@rice SWNTs)
(b) After 2-stage purification process, unannealed
Figure 1-13  TEM images of SWNTs
Before Purification (as-purified tubes@rice SWNTs):
(a) magnification = 25K
(b) magnification = 100K
After 2-stage purification process
(c) magnification = 25K
(d) magnification = 100K
Figure 1-14   Raman Spectra of SWNTs
(a) Tubes@rice SWNTs raw materials
(b) As-purified tubes@rice SWNTs
(c) After 2-stage purification process
(d) After 2-stage purification and annealing at 900°C

- Inset is the expanded Raman spectra of (d), showing the breathing modes of nanotubes. Diameter value is calculated as \( d = \frac{234 \text{ nm}}{\nu} \), where \( d \) is the tube diameter in nm and \( \nu \) is the wavenumber for the peak.
Figure 1-15  UV-Vis-Nir of purified SWNTs
(a) raw soot
(b) as-purified tubes@rice SWNTs
(c) after 2-stage purification process
(d) after 2-stage purification process and annealing at 900°C
- Spectra have been normalized at 1200 nm
- Scale bar shows adjusted tube diameter
\[ d = \frac{2 \gamma_0 \alpha_\infty}{E_g} \]

\[ E_g \] is the semiconducting energy gaps of SWNTs, \( a_\infty \) is 0.142 nm, and \( \gamma_0 \), the best-fit parameter from experimental STM data, is 2.7 eV. We have converted \( E_g \) to \( \lambda \) for the convenience of calculating tube diameter directly from UV-vis-NIR spectra, and multiply the equation by 1.3 to give the correct average diameter of tubes as determined by X-ray diffraction data. The final form of equation that we use to calculate tube diameters is \( d = 8.041 \times 10^{-4} \lambda \), where \( d \) and \( \lambda \) are in nm.
singularities, appear in the local density of states of nanotubes due to the one-dimensional nature of the conduction electron states in nanotubes. The one-dimensional nature of the energy bands has been illustrated previously by observation of the van Hove singularities with STM studies. UV-vis-near-IR spectra provide additional evidence of this phenomenon.

The peak centered at 1700 nm is due to the first van Hove singularity in semiconducting nanotubes while the second Van Hove singularity is seen centered at 900 nm. A third set of peaks centered near 650 nm is assigned to the first van Hove transition of metallic SWNTs. The van Hove peaks are superimposed on a background that decreases smoothly from the ultraviolet to the near-infrared.

The location of the van Hove peaks is a sensitive function of the SWNT diameter. Smaller diameter tubes exhibit van Hove transitions at shorter wavelengths. The observed peaks are due to overlapping van Hove transitions from all nanotube sizes that are present. The dependence of the band gap of semiconducting SWNTs on diameter has been measured with STM by Lieber. This information permits the prediction of the location of the first van Hove transition in the near-infrared for semiconducting SWNTs. The position is determined by the band gap and the width of the van Hove singularity peak in electron density as a function of energy. Because of the finite width of the van Hove singularity, the optical peak position will appear at a higher energy than the measured band gap.

Thess et al. in 1996 showed that the average diameter of SWNTs produced by Tubes@Rice is 1.38 nm, as determined from X-ray diffraction. In order to correlate the average diameter (1.38 nm) measurement for these laser-oven-grown samples as obtained
by X-ray diffraction, we have increased the predicted diameter from band gap information of Lieber at. el. by 30% to account for the width of the van Hove singularity. The adjusted scale is shown in Figure 1-15.

It is interesting to note that the first van Hove transition for the material taken directly from the laser-oven-grown raw soot, appears quite different from the other spectra. Its appearance suggests that two distributions of nanotube diameters are produced in the Tubes@Rice growth process. We note that the relative intensities of the breathing modes in Raman spectra do not show the same relative intensities for different tube diameters. (Figure 1-16). We attribute this to differences in resonant enhancement behavior for different SWNT diameters. In fact, Raman spectra do not appear to track relative changes in concentration accurately for different diameters during the cleaning process. We believe that UV-vis-near-IR spectra are a more reliable measure of SWNT size distributions since the transition moments of the van Hove singularities for different diameters are likely to be similar and only weakly dependent on tube diameters.

Subsequent oxidative cleaning with nitric acid and gas phase oxidation appears to remove smaller diameter tubes preferentially. This is evidenced by a shift of the first van Hove peak to longer wavelengths with each cleaning step. It is also seen that the intensities of the van Hove transitions increase with cleaning and annealing of the nanotubes. In fact, the absorbance values at 1700 nm for the cleaned and annealed sample are almost equal to the absorbance at 400 nm. It is interesting to speculate that the relative intensity of the first van Hove transition to the continuum absorbance value at 400 nm in the ultraviolet provides a useful measure of the perturbation of the HOMO π-electron density of SWNTs due to sidewall substitution and/or oxidation. For instance.
Figure 1-16 – Raman breathing modes of raw and purified single wall carbon nanotubes

(a) after 2-stage purification process and annealing at 900°C

(b) raw soot
other studies have shown that the van Hove features are completely absent for partially alkylated SWNTs with retention of the continuum background. 72

1.5 HIPCO SWNTS

A high pressure CO disproportion process has recently been shown to produce nanotubes of high purity, with current yields of > 90% atomic percent SWNT carbon73. This production method has been labeled as the “HiPco” (high pressure CO) process. A small amount of Fe(CO)₅ is injected to a stream of CO gas flow at high temperature and pressure. The iron from the carbonyl decomposition forms metal clusters that act as catalytic sites to promote the Boudard reaction: CO + CO → C(s) + CO₂(g). It is believed that once the growing metal clusters achieve a size near that of C60 that they will nucleate and grow SWNTs. A SWNT is the most stable form of carbon that can be catalytically grown from metal clusters near 1 nm diameter. Once the SWNT has started to grow, it continues to grow until the metal cluster which is also growing with addition of iron atoms not originally involved in the initial metal cluster formation, reaches a size which favors formation of a carbon shell around the cluster. This ends the growth of the SWNTs. The average diameter of HiPco SWNTs is about 1.1 nm, which is smaller than its laser counterpart, 1.3 nm60. The dominant impurity in HiPco nanotubes is the metal catalyst which is encased in thin carbon shells and distributed throughout the sample as 3-5 nm size particles. Four to five atomic percent of Fe is typical in current raw HiPco materials. The concept of this purification is based on the previous purification study of
laser-oven-grown tubes\textsuperscript{74}. As suggested previously, metal catalysts from the production accelerate the oxidation rate of carbon at low temperature. We have found that metal catalysts can be exposed with a low temperature oxidation step. This appears to breach the carbon shell and convert the metal catalysts to an oxide and/or hydroxide. This causes an expansion of the metal particle due to the lower density of the oxide, as shown in the schematic of Figure 1-17, that breaks the carbon shells open. This is evidenced by the inability of concentrated HCl acid to extract Fe before oxidation of the nanotube samples. Below we will describe and discuss a purification procedure for HiPco SWNTs. Sample purity is documented with SEM, TEM, and EDAX. Raman and UV-vis-near-IR spectra are also reported.

1.5.1 Experiments

Raw HiPco tubes were subjected to oxidation in a wet Ar/O\textsubscript{2} environment at various temperatures. The addition of water is believed to enhance the low temperature ocatalytic oxidation of carbon as shown by TGA in Figure 1-18. Thus we have added water in all low temperature oxidation steps. Figure 1-19 shows the sample behavior as function of time at different temperatures. Weight gain was observed during the early period of heating due to the oxidation of iron metal catalysts. Subsequent weight loss of carbon occurs via metal catalyzed oxidation. The carbon that is first consumed is believed to be the carbon shells that are in direct contact with the metal. No weight loss is seen for low temperature oxidation (e.g. 150°C or below) after 20 hours of heating. At
Figure 1-17  Oxidation of Metals during purification step
Figure 1-18  TGA plot of raw HiPco tubes heated at 225°C for 18 hours in Ar
(a) Dry Ar
(b) Wet Ar
Figure 1-19  TGA of raw HiPco tubes heated at various temperatures in wet Ar/O₂ for 18 hours:

(a) Temp = 150 °C
(b) Temp = 200 °C
(c) Temp = 225 °C
(d) Temp = 250 °C
(e) Temp = 325 °C

- Gas mixture = 20% O₂ in Ar flowing through water bubbler before entering the furnace
temperature 225°C and higher, carbon shells which encase the metal catalysts can be removed with an extended oxidation period. Sonication or extended stirring in concentrated HCl solution after oxidation removes metal oxides from the processed samples.

All purified HiPco SWNTs in this study were processed as follows: Low-density raw HiPco tubes were physically compressed onto a dry filter paper by adding SWNTs to a filter holder while pulling a vacuum. SWNTs (typically ~ 100mg) were placed in a ceramic boat and inserted into a quartz tube furnace. A gaseous mixture of 20% O₂ in Ar (air may also be used) was passed through a water bubbler and over the sample at a total flow rate of 100 sccm. Nanotubes were heated at 225°C for 18 hours followed by sonication or prolonged stirring in concentrated HCl solution for ~ 15 minutes. The color of the solution was typically yellow due to dissolved Fe²⁺. HiPco tubes in the acid solution were then filtered onto a 47 mm, 1.0 µm pore size Teflon membrane (Cole-Parmer) and washed several times with deionized water and methanol. They were dried in a vacuum oven at 100°C for a minimum of two hours and weighed. The oxidation and acid extraction cycle was repeated at 325°C for 1.5 hours and 425°C for 1 hour. After drying in the vacuum oven, the HiPco tubes were annealed at 800°C in Ar for 1 hour.

Thermogravimetric (TGA) data were obtained with a TA instrument model 2960 system. Raman spectra were obtained with a Renishaw micro-Raman spectrometer operating with a 780 nm laser. UV-vis-near-IR spectra were obtained with a Shimadzu UV-3101 PC spectrometer. Transmission electron microscopy (JEOL 2010 TEM) was obtained using 100 kV beam energy. Raman, IR, and TGA were carried out with SWNTs in the form of solids. Samples for UV-vis-near-IR were prepared by sonicating
SWNTs for ~ 10 min in 1,2 dichlorobenzene solution in a bath sonicator (Cole-Parmer). TEM samples were prepared by sonicating SWNTs in methanol and drop drying them onto lacey carbon TEM grids.

1.5.2 Results and Discussion

It is important to weigh the sample before and after each cleaning step to get a measure of how much metal and carbon has been removed. Typical weight loss and metal concentration after each purification step are shown in Table 1-3. The Fe atomic percentage drops from ~3.5% to 0.02%, as obtained from the calculated TGA measurements. However, the weight loss increases dramatically from the 325°C to the 425°C step. UV-vis-near-IR indicate a loss of smaller diameter tubes during the 325°C and 425°C process (Figure 1-20). A majority of the nanotube ropes in cleaned HiPco samples are bigger in size when compared to the raw samples (Figure 1-21). Capillary forces from the liquids (water in the gas phase oxidation and HCl solution) might have pulled the tubes together to form bigger ropes. Purified HiPco SWNTs are able to withstand oxidation temperatures as high as 500°C (Figure 1-22). With less metal present in the nanotubes, the onset oxidation temperature is seen to increase along each purification step. The small changes between the 325°C and 425°C oxidation stpes suggests that oxidation at 325°C is sufficient for most purposes. TEM images show a large reduction of metal and non-SWNT carbon (Figure 1-23).
<table>
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<th>Metal %*</th>
<th>Weight loss</th>
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</tr>
<tr>
<td>225°C</td>
<td>0.67</td>
<td>33.7%</td>
</tr>
<tr>
<td>325°C</td>
<td>0.05</td>
<td>8.3%</td>
</tr>
<tr>
<td>425°C</td>
<td>0.03</td>
<td>22.9%</td>
</tr>
<tr>
<td>Annealed</td>
<td>0.03</td>
<td>4.2%</td>
</tr>
</tbody>
</table>

Table 1-3 Weight loss and metal concentration after each purification step
(a) raw HiPco tubes heated at 225°C in wet Ar/O2 for 18 hours
(b) (a) heated at 325°C in wet Ar/O2 for 2 hours
(c) (b) heated at 425°C in wet Ar/O2 for 1 hour

- Total weight loss = 69.1%
  Total weight loss excluding the 425°C step = 46.25%

- Each oxidation step is followed by sonicating in concentrated HCl solution for 10 – 15 min. Tubes were then filtered and dried from the acid solution in the vacuum oven at 100°C for minimum of two hours
- Mx/(Mx+Mc)*100 (percentage), where M=atomic %, X=Fe and C=Carbon
Figure 1-20  UV-vis-near-IR spectra of HiPco SWNTs

(a) Raw HiPco tubes

(b) After 225°C oxidation step

(c) (b) after 325°C oxidation step

(d) (c) after 425°C oxidation step

- Spectra have been normalized at 925 nm and scale bar shows the adjusted tube diameter
Figure 1-21  SEM images of HiPco SWNTs before and after purification

(a) Before purification

(b) After purification
Figure 1-22  TGA of purified HiPco SWNTs
(a) Raw HiPco
(b) After 225°C step*
(c) After 325°C step*
(d) After 425°C step*

- Each step is completed after HCl extraction of metals and vacuum dried. All samples were subsequently annealed at 800°C in Ar for 1 hour
- TGA experiments were done in Air
Figure 1-23  TEM images of HiPco SWNTs

Raw HiPco tubes

(a) Magnification 100K
(b) Magnification 500 K

Purified HiPco tubes

(c) Magnification 100K
(d) Magnification 500K
We have found that clean HiPco tubes annealed in wet Ar are hard to disperse into a 1,2 dichlorobenzene solution. Dry Ar annealed tubes are more dispersible in 1,2 dichlorobenzene. At such an annealing temperature, 800°C, water could be catalyzed by residual metal catalysts and thus react with sidewalls of nanotubes to form hydroxyl attachments. The same wet Ar annealed samples are observed to disperse better in 0.15 wt. % Triton-X water solution. However, raw HiPco tubes are more dispersible in either 1,2 dichlorobenzene or Triton-X water solution than either the wet or dry annealed cleaned samples. Facilitation by the presence water at 800°C could mobilize the tubes to form bigger ropes so the tubes become less dispersible in solutions. Figure 1-24 shows the UV-vis-near-IR spectra of wet vs. dry annealed clean HiPco SWNTs. It has been proposed that the perturbation of the HOMO π electron density (van Hove singularity) could be due to the sidewall substitution (hydroxyl attachments), which lead to a decrease in van Hove intensity. It could also be explained as the broadening of the van Hove signatures, due to the roping phenomenon of nanotubes.

Cleaned HiPco SWNTs after HCl sonication and vacuum oven drying (before annealing) have relative lower intensities of van Hove peaks. After neutralization in 2 M NaOH solution, these peaks increase (Figure 1-25). Dispersibility of cleaned HiPco tubes before annealing is observed to be just as good as the raw HiPco SWNTs.

1.6 CONCLUSION
Figure 1-24  UV-vis-near-IR spectra of purified HiPco SWNTs annealed at 800°C in Ar
(a) in wet Ar
(b) in dry Ar
Figure 1-25  UV-vis-near-IR spectra of purified HiPco SWNTs

(a) Raw HiPco SWNTs
(b) (a) after 225°C oxidation, HCl sonication and vacuum dry
(c) Neutralized (b) with 2 M NaOH solution

- Spectra have been normalized at 925 nm and the scale bar shows the adjusted tube diameter
The currently limitation on nanotube research and/or applications are the production cost and rate. SWNTs by HiPco process could be produced at a rate of hundreds of grams a day. This study has demonstrated that the purification of HiPco SWNTs leads to 99.97% pure nanotubes. The purification procedure can be easily scaled up in term of grams, even kilograms. With the production and purification of HiPco tubes, both high quality and large quantities of SWNTs can be provided for further research and applications.
Chapter 2

CHEMISTRY OF SINGLE-WALL CARBON NANOTUBES

2.1 FLUORINATION OF SINGLE-WALL CARBON NANOTUBES

2.1.1 Background

Since the initial discovery in 1991\textsuperscript{11}, and subsequent development of large-scale syntheses of buckytubes,\textsuperscript{75, 76} various methods for their synthesis, characterization, and potential applications have been pursued. Depending on their diameter and the degree of helicity, carbon nanotubes can exhibit variations in electronic properties, ranging from semi-conducting to metallic structures\textsuperscript{30}. After years of researching, people understand more about nanotubes\textsuperscript{18, 31}. However, chemical derivatization of this novel carbonaceous material is still in its early stages. Only in 1998 the first sidewall functionalized carbon nanotubes were reported when Mickelson et. al\textsuperscript{77, 78} were able to fluorinate the sidewalls of carbon nanotubes. After that astonishing preparation of fluoronanotubes, several derivatizations of carbon tubes were reported earliest this year\textsuperscript{12, 72, 79} and more are waiting to be published\textsuperscript{80}. 
2.1.2 Experimental procedure

Precursor nanotubes used in this study are laser-grown-oven SWNTs from tubes@rice, or HiPco SWNTs also from Rice University. The single-walled carbon nanotubes, about 1 nm in diameter, were produced by the dual laser vaporization of Co/Ni doped graphite rods at tubes@rice\textsuperscript{33, 58} or by the high pressure CO gas phase disproportionation reaction at Carbon Nanotechnology Inc\textsuperscript{81}. Fluorination details can be seen elsewhere\textsuperscript{78}. Based on Mickelson’s study, we have varied some parameters within the procedures to produce the desired fluorinated carbon nanotubes which will be described later.

Nanotubes from tubes@rice were obtained as a suspension in toluene solution. Filtering the nanotube solution through a PTFE filter membrane and washing with methanol to remove unwanted residues leaves a black, puffy film on the surface. Unlike the buckypaper made from tubes in N,N-dimethylformamide (DMF) or Triton-X (polyoxyethylene isoctylcyclohexylether) solution (surfactant manufactured by Aldrich), these films, or buckypapers are believed to have a “3-D network” structure. The tubes are not as tightly packed and fluorine should be able to penetrate into the nanotubes ropes more easily. Laser-oven-grow tubes were then subjected to the 2-stage oxidation process to further remove the metal catalysts and amorphous carbon presented in the samples. HiPco tubes were obtained as-produced from the reactor. They underwent gas-phase purification procedures as described in Chapter 1 to remove unwanted carbon shells and Fe catalysts in the raw materials. In both cases, the purified laser-grown tubes and HiPco SWNTs serve as good precursors for fluorination.
Several reactions were carried out to establish optimal fluorination conditions (i.e. temperatures and reaction times). The goal is to reach saturation, C\textsubscript{2}F, without destroying the tube structure. A fluorine/HF/He mixture (2 cc/min, 0.2 cc/min and 100 cc/min respectively) was passed through a temperature-controlled Monel flow reactor containing the SWNTs samples. HF gas was turned off immediately after the reaction, while fluorine gas was kept flowing until the chamber temperature for the fluorination reactor dropped below 100°C to avoid the additional HF adsorption onto the nanotubes.

2.1.3 Result and Discussion

2.1.3.1 Laser-oven-grown SWNTs

HF has known as a catalyst for fluorination of graphite. It is also suggested that with the addition of HF in the fluorination, C-F bonds which are more covalent in nature will be produced. Figure 2-1 shows the FTIR spectra of nanotubes fluorinated with or without HF addition at 200°C. Apparent upshift of the C-F stretching frequency is observed with HF addition to the fluorine atmosphere. Higher degree of fluorination is also observed with higher relative C-F intensity. Same shifting effect is also seen when raising the fluorination temperature (Figure 2-2).

Because of the nature of the nanotubes, black in color, light does not transmit through them and therefore we could not take IR spectra of tubes in transmission modes. The initial FTIR spectra were taken using the diffuse reflectance accessory. No peaks
Figure 2-1 FTIR spectra of fluorinated carbon nanotubes (T=200°C)
(a) With HF addition
(b) Without HF addition

- Negative absorptions at 2000 cm\(^{-1}\) and 2200 cm\(^{-1}\) are due to the diamond crystal on the ATR accessory
Figure 2-2  FTIR spectra of fluorinated laser-grown-SWNTs
(a) Fluorinated at 200°C
(b) Fluorinated at 250°C

- Negative absorptions at 2000 cm⁻¹ and 2200 cm⁻¹ are due to the diamond crystal on the ATR accessory
were observed. However, a new peak shows up at ~1100 cm\(^{-1}\) (Figure 2-3). When mixing Fluorotubes with KBr and subsequently heating on the hot plate at ~120°C, one can immediately see the evolution of a gas which is yellow. KBr has reacted with Fluorotubes: \(n\text{KBr} + (\text{C}_2\text{F})_n \rightarrow n\text{KF} + n/2 \text{Br}_2 + 2\text{C}_n\). This also indicates the weakness of the C-F bond on fluorotubes. C-F bonds in fluorofullerenes or fluoronanotubes are significantly weaker than the C-F bonds in traditional alkyl fluorides. Similar KBr tests were done on fluorinated C\(_{60}\) and fluorinated graphite. While heating, fluorinated C\(_{60}\) changes its color from white to yellow, indicate the loss of fluorine. FTIR spectrum also shows the disappearance of C-F bonds after heating (Figure 2-4). C-F bonds in fluorographite, "CFx", are much stronger. Under the same experimental conditions, fluorine remains attached to the graphite. The same set of experiments was repeated using NaI instead of KBr. A purple gas, I\(_2\), is evolved during heating Fluorotubes with NaI (Figure 2-5).

Table 2-1 shows the results from several fluorination experiments for laser-oven-grown SWNTs. At temperature higher than 150°C with proper reaction times, a C/F ratio of ~2 can be reached. At temperatures lower than 150°C, however, a C-F peak is not clearly observed in the IR spectrum. At higher reaction temperatures, a well-defined, but broad C-F peak can be seen around 1210 cm\(^{-1}\) in the FTIR spectra taken with the ATR (Attenuated Total Reflectance) accessory (Figure 2-6). Peaks with higher wavenumbers correspond to stronger covalent bonds. Lowering the temperature might induce the creation of ionic C-F bonds, or weaker covalent bonds. This phenomenon was also observed in fluorinated graphite. In the current study, C/F ratio for tubes fluorinated at 150°C as high as 3 were found, depending on the duration of the reaction. Buckypaper
Figure 2-3  FTIR spectra of the products of KBr + Fluorotubes reaction at 120°C

(a) Fluorotubes
(b) After the KBr reaction
Figure 2-4  Fluorinated C<sub>60</sub> reacted with KBr
(a) Fluorinated C<sub>60</sub>
(b) After reaction with KBr
Figure 2-5  FTIR spectra of Fluorotubes after reaction with KBr or NaI
(a) Fluorotubes
(b) After reaction with KBr
(c) After reaction with NaI
<table>
<thead>
<tr>
<th>Reaction Temp (C)</th>
<th>Reaction Time (hrs)</th>
<th>C/F</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
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<td>5</td>
<td>2.2</td>
</tr>
<tr>
<td>290</td>
<td>2</td>
<td>1.92</td>
</tr>
</tbody>
</table>

Table 2-1  Reaction Temp and Time vs. C/F
Figure 2-6  FTIR-ATR spectrum of laser-oven-grown nanotubes that are fluorinated at 250°C

- Negative absorptions at 2000 cm⁻¹ & 2200 cm⁻¹ are due to the diamond crystal in the ATR accessory and at 2300 cm⁻¹ due to CO2 background absorption
made from the toluene suspension has a "network" structure, i.e. the nanotubes are loosely bound in the buckypaper. Fluorine thus can diffuse into the inner structure of the ropes easier and find more reaction sites on the surface. Nanotubes filtered from DMF suspension are more tightly packed by van der Waals interactions. If annealed at high temperature, which was done with Mickelson's nanotube samples, this effect could increase dramatically. In his fluorination study, Mickel found no evidence of fluorination at 150°C. The tubes he used were obtained from Tubes @ Rice which underwent the nitric acid cleaning procedures. Elemental microprobe analysis shows ~3 atomic percent of metal (Ni and Co). Before fluorination, all purified tubes have been subjected to anneal at 800°C. We have shown previously that metal presence at high temperature could induce cross-linking. Bucky paper is also more tightly packed once it's annealed. At a low fluorination temperature, such as 150°C, fluorine apparently does not diffuse through the nanotubes packs. From TEM examination, tubes started to disintegrate around 350°C. Figure 2-7 and Figure 2-8 shows the FTIR and Raman spectra of defluorinated nanotubes that were originally fluorinated under different temperatures. At temperature above 250°C, the intensity of defects/disorder, as indicated by the 1298 cm⁻¹ peak, is almost the same intensity of the nanotube tangential modes at 1592 cm⁻¹. In order to keep the tube structure and obtain a saturated C/F ratio (~2) at the same time, we decided to use 250°C as our optimal fluorination temperature. The minimum reaction time to reach C₂F is ~5 hours at 250°C. Electron microprobe analysis (EMPA) and IR indicated the desired carbon-fluorine ratio and C-F stretching frequency. These fluorinated tubes are soluble in THF, DMF and alcohol solvents.
Figure 2-7  FTIR of defluorinated SWNTs

(a) Fluorotubes
(b) (a) after defluorination
Figure 2-8  Raman spectra of defluorinated carbon nanotubes

(a) Pristine nanotubes

(b) Fluorinated at 250°C

(c) Fluorinated at 315°C

(d) Fluorinated at 350°C

(e) Fluorinated at 375°C
2.1.3.2. HiPco SWNTs

SWNTs produced by HiPco process have smaller diameters, 1.1 nm, when compared to laser grown SWNTs, 1.3 nm. Therefore HiPco tubes are energetically more favorable to the fluorination. A lower fluorination temperature was used to fluorinate HiPco nanotubes. Figure 2-9 shows the IR spectra of HiPco tubes fluorinated at various temperature. These spectra are taken with the ATR (Attenuated Total Reflectance) accessory. Under the same fluorination condition, we can attach more fluorine onto the sidewalls of nanotubes with HiPco tubes. Fluorination at 250°C apparently has caused major destruction of the tubes. Figure 2-10 shows the Raman spectra of defluorinated HiPco tubes. The peak at 1298 cm⁻¹, which corresponds to the sp³ carbon, or the defects/disorder, has the intensity as high as the tangential modes of nanotubes. Physical observation also indicate the discoloration of nanotube samples, i.e. SWNTs become yellowish when fluorinated at 250°C. These Fluorotubes are also soluble in alcohols, DMF and THF. Overall, lower temperature should be used when fluorinating HiPco tubes.

2.1.4 Future Work

The nature of the C-F bond in Fluorotubes should give us an insight to the temperature effects on the fluorination, and could lead to successful characterization
Figure 2-9  FTIR spectra of fluorinated HiPco carbon nanotubes

(a) Fluorinated at 100°C
(b) Fluorinated at 150°C
(c) Fluorinated at 200°C
(d) Fluorinated at 250°C

- No C-F bond is observed at 100°C
Figure 2-10 Raman spectra of defluorinated HiPco SWNTs

(a) Fluorinated originally at 100°C

(b) Fluorinated originally at 150°C

(c) Fluorinated originally at 200°C

(d) Fluorinated originally at 250°C

- Spectra were normalized at the tangential modes of nanotubes, which is at ~1592 cm⁻¹
of further derivatization, such as alkylation. It can also provide for selective functionalization with different types of C-F bonds. De-fluorination and partial fluorination are currently being pursued in order to create active sites for further reaction and defect studies. In short, gas phase fluorination processes have been explored. Solid phase reactions of nanotubes with reactive metal fluorides (AgF₂, MnF₃, PtF₆, etc.) are also interesting routes for producing fluorotubes which need to be investigated in the future. The reaction chemistry of solvated Fluorotubes could be an important route for preparation of various functionalized tubes with a variety of useful properties. In addition, fluorotubes can be used in several applications, including battery and composite formation.

2.2 COVALENT SIDEWALL FUNCTIONALIZATION OF SINGLE WALL CARBON NANOTUBES

2.2.1 Introduction

Nanometer scale structures have become the focus of considerable interest since they represent ideal systems for testing fundamental ideas about the roles of dimensionality and confinement in materials, and represent potential building blocks for nanostructured materials, composites and novel electronic devices of greatly reduced size. Among the wide range of nanometer scale structures prepared to date, carbon
nanotubes and, in particular, single-wall carbon nanotubes (SWNTs) stand out as unique materials for fundamental research and emerging applications\textsuperscript{8, 11, 60, 75, 82, 83}. For example, carbon nanotubes are the stiffest known materials\textsuperscript{84}, exhibit novel electronic properties that bridge the bulk and molecular states\textsuperscript{85-87}, and represent a flexible starting point for preparing new nanomaterials\textsuperscript{88, 89}. A major factor driving interest in this area has been the ability to synthesize gram quantities of purified single-wall nanotubes (SWNTs) by laser-vaporization of a metal-doped graphite target\textsuperscript{33, 60}. X-ray diffraction, electron microscopy and electron diffraction indicate a remarkable uniformity of diameter and self-organization into two dimensional "rope" crystallites consisting of hundreds of 13.6 \AA{} diameter close packed tubes at the van der Waals separation of 3.2 \AA{}.

In some cases, chemical modification will be required if these materials are to reach their full potential. However, this area of research presents enormous challenges and results have been slow to emerge\textsuperscript{53, 90-92}. Haddon\textsuperscript{93} has reported that nanotubes may be solvated by reacting octadecyl amines with the carboxylic acid groups that are bound to the ends of the tubes. Addition of dichlorocarbene to the sidewalls of tubes was also reported. Lieber\textsuperscript{12} and his co-workers demonstrated that carboxyl acid groups attached to the ends of the nanotubes function as AFM tips. Mickelson demonstrated a high degree of sidewall derivatization by fluorination\textsuperscript{78, 94}. The fluorinated materials can be further functionalized by attaching alkane chains to the sidewall of SWNTs\textsuperscript{72}. In this paper, we present an up-to-date account of recent results on the use of fluorinated SWNTs as intermediates for sidewall derivatization\textsuperscript{95}. 
2.2.2 Experiments

General. Single wall carbon nanotubes produced by the laser oven method were obtained from Tubes @ Rice\textsuperscript{60, 96}. After purification by conventional acid treatment\textsuperscript{33}, the tubes were subjected to a further 2-stage purification process\textsuperscript{74}. SWNTs with residual metal less than 0.1 atomic percent and impurity carbon less than 1 wt. percent were obtained after purification. Thermogravimetric (TGA) data were obtained using a TA instrument model 2960 system. Raman, IR, Mass spectra and TGA experiments were carried out with SWNTs in the form of buckypaper. Samples for UV-Vis-Nir were prepared by sonicating SWNTs for ~ 10 min in 0.15 wt % Triton-X D2O solution with a cup sonicator. Raman spectra were obtained with a Renishaw micro-raman operating with a 780 nm laser. UV-Vis-Nir spectra were obtained with a Shimadzu UV-3101 PC spectrometer. FTIR spectra were obtained using a Nicolet spectrometer with the ATR accessory.

Fluorination. Fluorination was carried out following the procedure described earlier. In this case, HF (2.0 sccm) was introduced as a catalyst into the F2/He (2.0 sccm, 20 sccm respectively) mixture during fluorination. Nanotubes were fluorinated at 250°C.

Alkylation. 10 mg of the fluorinated tubes were added to a flame dried 100 ml three necked round bottomed flask under an atmosphere of argon. Dry hexane (5ml) was then added and the contents were sonicated for 5 min. Alkyllithium (methyl-, butyl- and hexyl-lithium) in hexane (8 ml) was added dropwise to the resulting suspension and the mixture was sonicated (VWR scientific model 50 HT) for 20 min. The solution was
stirred overnight under argon and then cooled in ice. The unreacted hexyllithium was quenched by the slow addition of ethanol with stirring. After quenching, water (50 ml) was added and the solution was stirred to dissolve salts formed. Nanotubes were then filtered on a PTFE filter paper (0.45 μm) and washed with water. Collected nanotubes were again suspended in 3 N HCl, sonicated for 15 min and again filtered and washed with plenty of water. Finally the tubes were placed in hot ethanol and sonicated for 15 min and filtered. Final products were dried under vacuum overnight.

2.2.3 Result and Discussion

UV-Vis-Nir serves as an excellent monitor for sidewall perturbation of nanotubes. This may be attributed to rehybridization at carbon (sp2 to sp3) since the π electrons in the highest occupied molecular orbitals (HOMOs) that are used to form new bonds are no longer available, and the van Hove transitions characteristic for unperturbed SWNTs vanish. The UV-Vis-Nir spectra of pristine and hexylated SWNTs are displayed in Figure 2-11. Thus, the absence of electronic transitions for the hexylated SWNTs supports the assumption that sidewall functionalization by n-hexyl groups has occurred.

Infrared spectra of SWNTs alkylated by different groups are shown in Figure 2-12. n-hexyl- and n-butyl substituents exhibit typical C-H stretching absorptions at 2957, 2924 and 2855 cm\(^{-1}\). The relative intensity of the C-H stretching absorptions is higher when the SWNTs are functionalized by n-hexyl groups. Each material exhibits a peak at ~ 1578 cm\(^{-1}\) that can be assigned as the active carbon stretching mode of the nanotubes.
Figure 2-11  UV-vis-Near-IR spectra of SWNTs

(a) Pristine SWNTs

(b) Hexylated SWNTs
Figure 2-12  ATR-IR spectra of alkylated SWNTs

(a) Methylated SWNTs

(b) Butylated SWNTs

(c) Hexylated SWNTs
Assignment of infrared bands in the 1000 cm\(^{-1}\) to 1500 cm\(^{-1}\) region may arise from the bending modes and umbrella (rocking) modes of the -CH\(_3\) groups.

Thermal gravimetric analysis of degassed (80°C) derivatized SWNTs was used to evaluate the extent of sidewall functionalization. Figure 2-13 shows the typical TGA data from alkylated SWNTs. One can clearly notice a loss of weight over two temperature ranges. Region 1 corresponds to the loss of alkyl groups. The calculated carbon-to-alkyl group ratio (C/R) for methyl, n-butyl and n-hexyl SWNTs from TGA weight loss data are listed in Table 2-2. The C/R ratio of n-hexyl-SWNTs to n-butyl-SWNTs is about 1.2, similar to their molar mass ratio of 1.5. Similar studies indicate a higher degree of functionalization when methyl lithium is used as the alkylating reagent.

The loss of weight associated with region 2 is less clear. In this regard, the FTIR spectra recorded after heating at 250°C still shows the presence of n-hexyl groups. However, the overall intensity of the C-H peaks decreases to about 1/3 of the original value. Theses absorptions disappear after heating at 500°C. This indicates a more stable, different type of alkyl attachment to the sidewall of the nanotubes. Fluorinated SWNTs that have been defluorinated by hydrazine exhibit similar TGA plots (Figure 2-14). The mass spectrum indicates that CF\(_x\) species are evolved when samples have been heated about 350°C. This phenomenon is under investigation currently.

The spectral signatures of pristine SWNTs return after heating n-hexyl-SWNTs in Ar at 800°C, demonstrating that at the higher temperature, the alkylation is completely reversible (Figure 2-15). Further support for reversibility is provided by Raman spectra. Thus upon heating, the relative intensities of the tangential and breathing modes return and increase. Steric effects were evaluated by comparing the relative reactivites of n-
Figure 2-13  Weight loss after heating functionalized SWNTs under Ar

(a) Methylated SWNTs

(b) n-butyl-SWNTs

(c) n-hexyl-SWNTs

- Weight losses were obtained by thermal gravimetric analysis. It was programmed in three segments: (1) ramping from room temperature to 80°C and hold for 30 min (2) ramping from 80°C to 250°C and hold for 30 min (3) ramping from 250°C to 500°C and hold for another 30 min
<table>
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<td>Methyl</td>
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<td>27</td>
</tr>
<tr>
<td>n-Butyl</td>
<td>9.16</td>
<td>36</td>
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<tr>
<td>hexyl</td>
<td>11.64</td>
<td>42</td>
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Table 2-2  Weight % of alkyl groups (R) on the sidewall of nanotubes

- R % is obtained from thermal gravimetric analysis. The sample was heated up to and held at 250°C in Ar. C/R = carbon to alkyl group ratio by weight
Figure 2-14  TGA plot of hexylated SWNTs vs. defluorinated SWNTs

(a) Defluorinated SWNTs

(b) Hexylated SWNTs

- Weight losses were obtained from thermal gravimetric analysis. It was programmed in three segments as described earlier
Figure 2-15  (A) UV-vis-Near-IR spectra of Ar-heated hexylated SWNTs

(a) Hexylated SWNTs

(b) Hexylated SWNTs heated in Ar @ 500 °C for 1 hour

(B) Raman spectra of Ar-heated hexylated SWNTs

(a) Hexylated SWNTs

(b) Hexylated SWNTs heated in Ar @ 500°C for 1 hour
butyl lithium and tert-butyl lithium. Whereas the van Hove transition totally disappears for the products from the reaction using n-butyl lithium, it is somewhat lower in relative intensity, yet observable, for tert-butyl lithium reaction (Figure 2-16). As expected, the weight loss of t-butyl SWNTs is much less than n-butyl SWNTs after heating SWNTs in argon, confirming that tert-butyl is not effectively reacted with SWNTs since both groups have the same molecular mass.

The effect of solvent on these alkylation reactions was also investigated. Fluorotubes are soluble in THF, but not in hexane or ether. Table 2-3 shows the weight % gain when SWNTs were reacted with n-hexyl lithium at room temperature in various solvents. The effect of temperature is illustrated in Table 2-4. The effect is negligible in THF, whereas a significant increase of alkyl attachment is observed with n-hexane. Overall, we can obtain an optimized yield of alkyl-SWNTs by lowering the reaction temperature in hexane solution.

These results are consistent with a multi-step process that is initiated by one-electron transfer from the alkyl lithium reagent to the nanotube. Expulsion of fluoride from the resulting radical anion would lead to a radical site on the SWNT. Recombination of the alkyl radical from the lithium reagent with the SWNT would lead to the alkylated nanotube. Crowding of alkyl groups suggests that not every fluorine would be replaced by an alkyl group. Steric effects probably account for the observation that more extensive alkylation occurs when the sterically less demanding methyl lithium is used. Additional strong support for the electron transfer process comes from the fact that phenyl lithium which is known to react by a two-electron process does not react with fluorinated SWNTs.
Figure 2-16  UV-vis-Near-IR spectra of butylated SWNTs

(a) SWNTs reacted with t-Butyl lithium
(b) SWNTs reacted with n-Butyl lithium
<table>
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<th>Solvent</th>
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<tr>
<td>Ether</td>
<td>7.01</td>
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<tr>
<td>Hexane</td>
<td>11.74</td>
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<tr>
<td>TMEDA</td>
<td>6.57</td>
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Table 2-3  Weight % of attached n-hexyl groups with reactions done in various solvents

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<tr>
<th>Room T</th>
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<td>THF</td>
<td>10.19%</td>
</tr>
<tr>
<td>Hexane</td>
<td>11.74%</td>
</tr>
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</table>

Table 2-4  Weight % of n-hexyl groups on SWNTs with different reaction temperatures and solvents

- R% is obtained from thermal gravimetric analysis. The samples were heated up to and held at 250°C in Ar
2.2.4 Conclusion

We have demonstrated that alkyl lithium reagents may be used to attach alkyl groups to the sidewalls of nanotubes. Thermal gravimetric analysis combined with UV-Vis-Nir spectroscopy provides a quantitative measurement of the degree of functionalization. The pristine nanotubes can be recovered after thermolysis demonstrating that the alkylation is reversible. Evidence suggests that some of the alkyl groups are attached to sites forming less stable C-R bonds. C-F bonds are not completely lost during the alkylation. Defluorination studies suggest that about five atomic percent of the fluorine remains after the SWNTs have been subjected to alkylation. They could be located either inside or ends of the nanotubes, or attached to defects on the nanotubes. Chemical modification on the sidewall by alkylation leads to derivatives that are soluble in common organic solvents such as tetrahydrofuran and chloroform. Future studies will focus on cross-linking of SWNTs as a route to new materials that might be useful in the manufacture of nanotube fibers and composites.
2.3 SUPER-ROPING OF SINGLE WALL CARBON NANOTUBE

2.3.1 Introduction

Development of more productive methods\textsuperscript{61, 97} for growing single wall carbon nanotubes (SWNTs), most recently the HiPco process developed by Smalley et al.\textsuperscript{73, 81} at Rice University is making it potentially cost effective to consider their use in a variety of applications. As a result, attention is increasingly focused on developing methods for processing SWNTs into unique new materials\textsuperscript{98} such as highly ordered fibers, composites and membranes\textsuperscript{98, 103}.

When they are first formed, SWNTs rapidly assemble into rope-like structures. A rope consists of interleaved aligned\textsuperscript{104} SWNTs that are weakly van-der Waals bonded to each other\textsuperscript{60, 105-107}. SWNT material made by the laser-oven method typically has ropes of 100-1000 tubes\textsuperscript{60}, and readily makes papers that can easily be peeled off a filter. After refluxing in 2.6 M nitric acid for 12 hrs, there is a clear indication of some super-roping\textsuperscript{108} to make ropes of typically 1000 tubes.

SWNT material made from the HiPco process starts out with much smaller ropes, typically 10 tubes in cross-section and does not make a peelable buckypaper. With small tube diameters typically made in the HiPco process, treatment with nitric acid is not possible because the small diameter tubes are too readily oxidized by the refluxing nitric acid treatment; however sulfuric acid is fine.
This study has investigated the formation of super-ropes in sulfuric acid at elevated temperatures. Enhanced roping is expected as a result of increased mobility of SWNTs in the ropes due to sulfuric acid intercalation of the ropes.

2.3.2 Experimental Procedure

Four hundred milligrams of as produced HiPco SWNTs$^{73}$, a very low density high surface area material (~600 m$^2$/g) was added to a 250 ml round bottomed flask equipped with a condenser and magnetic stirrer. Fuming sulfuric acid (125 ml, 27-33% free SO$_3$) was added to the flask and stirred. After mixing was complete, the paste was thick and difficult to stir at room temperature. The paste was subsequently heated to 90°C and stirred for 48 hours. The cooled contents of the flask were added dropwise to ether (500 ml) cooled in an ice bath with vigorous stirring. This was allowed to sit for 15 minutes and then filtered through a PTFE (0.5 micron) filter paper. The SWNTs where again suspended in acetonitrile/ether (50:50, 250 ml), sonicated for 15 min and recovered by filtration.

2.3.3 Results and Discussion

The fuming sulfuric acid processed SWNT material easily forms a defined filtrate paper in marked contrast to the initial HiPco SWNT material that forms a particulate-like
material. This difference in behavior is attributed to the formation of SWNT ropes in the heated fuming sulfuric. The result is the most dramatic super-ropeing we have ever seen, easily 10,000 tubes per rope. The ropes are now long and strong enough to intertwine and make a quite robust paper.

The rope diameters are the largest observed to date (~ 100 nm) and are shown in Figure 2-17. We suggest that this is due to the mobility of SWNTs and ropes in the heated sulfuric acid that results from the protonation of rope surfaces and intercalation of sulfuric acid into the lattice of the ropes. This is expected to lower energy barriers to individual SWNT and rope movement thus enabling smaller ropes to coalesce into larger ropes. It is likely that other acids that are known to intercalate graphite will also facilitate the formation of super-ropes.

Exposure of SWNTs to fuming sulfuric may also cause sulfonation of the sidewalls as was found to for C_60. This is not the case for SWNTs as both electronic and Raman spectra, shown in Figure 2-18, indicate that the SWNTs remain unaltered after exposure to fuming sulfuric acid. Both electronic and Raman spectra of SWNTs have been previously shown to be quite sensitive to sidewall functionalization.

2.3.4 Conclusion

Facilitating the movement of SWNTs and ropes in a hot liquid is expected to impact future efforts to create highly aligned SWNT fibers and membranes. For instance, the growth of large ropes in the presence of aligning forces such as occur in high
Figure 2-17  SEM images of super-size nanotubes after oleum treatment
(a) Raw HiPco tubes
(b) After oleum treatment
Figure 2-18  Spectra of super-rope nanotubes
(A) UV-vis-near-IR spectra of nanotubes
   (a) Raw HiPco tubes
   (b) After oleum treatment
(B) Raman spectra of nanotubes
   (a) Raw HiPco tubes
   (b) After oleum treatment
magnetic fields\textsuperscript{104} is likely to lead to better alignment of SWNT within fibers and membranes that are formed in the presence of the field. New strength measurements of highly aligned super-ropes are expected to provide a database useful for extrapolation to the ultimate strength of perfectly aligned SWNT fibers. Similar measurements will permit the investigation of the effects of chemical modification, cross-linking, and high/ultrahigh temperature annealing on the ultimate strength of SWNT fibers.

2.4 ACID INTERCALATION OF SINGLE WALL CARBON NANOTUBES

2.4.1 Introduction

The research activities in the field of graphite intercalation compounds (GIC) has been tremendous\textsuperscript{115-121}. GIC represent a class of materials that not only can be used for testing a variety of condensed-matter concepts but also stimulates new ideas and approaches. Application of GIC is in various areas, such as batteries\textsuperscript{122}. Intercalation of carbon fibers was reported as early as 1969\textsuperscript{100, 123}. Because of the large aspect ratio (length/diameter) greatly improves the sensitivity of transport property measurements such as resistivity, magnetoresistance, thermopower and thermal conductivity, it is possible for systematic investigations of these properties to be made. From the application standpoint, many of the applications\textsuperscript{99, 124} of intercalated carbon fibers exploit
the high specific conductivity of GICs, acting as fillers for conducting polymers with high mechanical performance requirement and so on. With the discovery of single wall carbon nanotubes\textsuperscript{11}, which have greater mechanical strength and better thermal and electrical conductivities, the application of GIC have been brought to a new level. Bower et al.\textsuperscript{125} demonstrated the intercalation and partial exfoliation of SWNTs by nitric acid in 1998. In the same year, Eklund et al.\textsuperscript{126} calculated the charge-transfer in the sulfuric acid-nanotube intercalation system. In this study, we investigate the intercalation ability of different acids, including super acids.

2.4.2 Experimental Procedure

Two types of single-wall carbon nanotubes were used in the study: laser-oven-grown SWNTs (l-SWNTs) and HiPco SWNTs (h-SWNTs), from Tubes@Rice and HiPco reactors at Rice University, respectively. All SWNTs were purified as described previously. Seven acids were used and they are: concentrated hydrochloric acid (Fisher, 12.1N), concentrated nitric acid (Fisher, 15.8N), concentrated sulfuric acid (Fisher, 36N), oleum (Acro, 20% free SO\textsubscript{3}), fluorosulfonic acid (Fluka, >97%), trifluoromethane sulfonic acid (Acro, 99%), methansulfonic acid (Acro, 99%). Super acids are defined by Gillespie as any acid system that is stronger than 100% sulfuric acid, i.e., Ho (acidity function) ≤ -12. Oleum (Ho=-13.76), fluorosulfonic acid (Ho=-15.1), Trifluoromethane sulfonic acid (Ho=-14.1) and methan sulfonic acid (Ho < oleum) are the super acids used
here in this study. Raman spectra were obtained with a Renishaw micro-Raman spectrometer operating with 780 nm laser and 514 nm laser.

2.4.3 Results and Discussion

Raman breathing modes of purified single-wall carbon nanotubes are distinct in the region of 150 – 200 cm\(^{-1}\), depending on the diameter of nanotubes. HiPco tubes tend to have smaller diameter tubes than those produced by laser-ablation methods (Figure 2-19). It has been shown recently that the high frequency tangential replacement SWNT modes near 1593 cm\(^{-1}\), which are related to the C' interlayer modes in GIC, were found to be sensitive to the charge exchange between the nanotube and the guest ions that have intercalated into the interstitial channels in the tube bundles\(^{26}\). Figure 2-20 shows typical Raman spectra of SWNTs after soaking in acids for 24 hours. One can immediately notice the shifts on the tangential mode of nanotubes. These effects are similar to that of acids intercalated into graphite, exhibiting upshifts in the frequency associated with the donation of electrons from nanotubes to the acids in the case of acceptors. The presumption for all single wall carbon nanotubes charge transfer processes is that the dopant resides as ions (and also possibly as neutral atoms) in the interstitial channels between the tubes in the triangular nanotube lattice. A shift will be different with respect to the acids that were used in the study (Figure 2-21). Sulfuric and nitric acids are known to intercalate nanotubes, while oleum is part of the sulfuric acid family. The degree of charge transfer is clearly correlated with the ability of acid to intercalate into the
Figure 2-19  UV-vis-near-IR spectra of nanotubes
(a) Raw HiPco tubes
(b) Raw laser-grown tubes
Figure 2-20  Raman spectra of acid-soaked SWNTs
(a) Pristine, purified SWNTs
(b) Fluorosulfonic acid
(c) Nitric acid
(d) Oleum
* Laser-grown SWNTs are used
* This is done with 780 nm Raman laser
* All nanotubes have been soaked in the respective acids for 24 hours
Figure 2-21  \( \Delta \) Raman shifts of acid-treated nanotubes
* Taken with 780 nm laser
* \( \Delta \) Raman shifts are calculated as follows:
  Raman frequency of tangential modes of nanotubes of the acid-treated tubes
  minus that of pristine tubes
nanotube packs. Although fluorosulfonic acid is more acidic (-15.1) than oleum (-13.8), it is oleum which produced the larger if not the largest Raman shifts on both laser-grown or HiPco tubes. With ability to migrate into nanotube bundles and form charge transfer species inside, acids that are capable of intercalation thus will be able to create larger total charges on the acid-nanotube system. Addition of oleum to fluorosulfonic acid increase the Raman shifts on nanotubes relative to using fluorosulfonic acid alone. Because of their smaller diameters, HiPco tubes will be more reactive to nitric acid oxidation than laser-grown tubes and oxidation, a chemical reaction, will cause larger shifts in the Raman spectra. Therefore, nitric acid or its mixture with sulfuric acid in this study creates the largest Raman shifts on HiPco tubes among all the acid or acid mixture tested here. Because of the resonance effects between Raman laser and single wall carbon nanotubes, one can expect to see different distributions of nanotubes dominate with different Raman lasers. Rao's study shows that the 514 nm Raman laser resonates with metallic SWNTs, while the 780 nm laser resonances with semiconducting tubes. Both lasers were used for the Raman spectra obtained for the acid soaked SWNT samples (Figure 2-22). Metallic tubes, either HiPco or laser-grown tubes, show larger Raman shifts than the semiconducting tubes. It is suspected that metallic tubes are more sensitive to the acidic environment. In addition, HiPco tubes have larger shifts in general than laser-grown tubes with all the acids tested. Again HiPco tubes are smaller in diameter and their curvature create a more active site for charge-transfer or even reactions (oxidation or sulfonation) to occur.
Figure 2-22  Δ Raman shifts of acid-treated nanotubes
(a) Laser-grown SWNTs
(b) HiPco SWNTs
* Taken with 780 nm and 514 nm laser
* Δ Raman shifts are calculated as follows:
  Raman frequency of tangential modes of nanotubes of the acid-treated tubes
  minus that of pristine tubes
2.4.4 Conclusion

We have found that nanotubes are sensitive to the chemical environment in which they are surrounded, in this case an acid bath. There's a question of the role of water in the intercalation of nanotubes. Most of the acids used here are sensitive to moisture, although superacids are water-free. More studies will need to be done to investigate this effect. It will also be interesting to find out the time needed to saturate the intercalants or protons in the nanotube bundles. The initial evidence shows the oxidation and possible sulfonation of HiPco tubes by nitric acid and fluorosulfonic acids, respectively. This might lead to several possible routes of functionalizing HiPco tubes. In addition, because of the different reaction to acids by metallic and semiconducting nanotubes, acid protonation with Raman resonance spectra could lead to a possible way of separating different types of nanotubes according to their electronic properties.
Chapter 3

THEORETICAL MODELING OF FLUORINATED CARBON NANOTUBES

3.1 MOLECULAR MECHANICS METHODS

3.1.1 Introduction

Research on carbon nanotubes has attracted increasing interest in the recent years due to their unique characteristics as a member of the carbon family. In order to understand the chemical and physical properties of nanotubes, theoretical modeling is often used to explain some observed phenomenon\textsuperscript{124,127-129}. Although quantum mechanics calculations of molecular electronic structure\textsuperscript{95,130} can be highly accurate, they are also costly in computational time. Simulation of large molecules and biological macromolecules can therefore only be performed with classical mechanics. With these empirical methods, one calculates the mechanical and electrostatic interaction energies between bonded and non-bonded atoms. Any manufacturing technology must move atoms from where they are to where we want them to be. How atoms move and the forces that act upon them during their motion are therefore critical areas of study in nanotechnology. Molecular mechanics explains this field.
3.1.2 Background

Molecular mechanical force fields use the equations of classical mechanics to describe the potential energy surfaces and physical properties of molecules. Early reports on molecular mechanics date from the seventies, such as Allinger\textsuperscript{131} in 1973 and Hagler\textsuperscript{132} in 1974. Molecular mechanics treats molecules as arrays of hard, impenetrable balls connected by springs. The molecular energy is calculated by summing the potentials for bond distances, bond angles, and torsion angle deformations between 2,3, and 4 bonded atoms and the dispersion and electrostatic potentials between non-bonded atoms. All potentials are based on structural parameters and empirically derived constants.

3.1.3 Individual energy components

A Morse function best approximates a bond potential energy as a function of distance. Only a Morse potential can accurately describe a dissociating bond, compared to harmonic potentials, but force fields use the harmonic potential since (1) it is faster to compute and parameterize, and (2) Morse and harmonic functions are similar at the potential minimum (Figure 3-1). Most molecular mechanics programs approximate the Morse curve with a mathematically simpler Hooke's Law function, which reproduces the bottom of the well pretty well, but fails at long bond lengths:

\[ V_{\text{stretch}} = \sum K(r-r_0)^2 \]
(Graph generated by O.S. Smart, U. of Birmingham, 1995)

Figure 3-1  Morse potential vs. Harmonic function

(Graph generated by O.S. Smart, U. of Birmingham, 1995)
\[ V_{\text{bend}} = \sum K_{\theta}(\theta - \theta_0)^2 \]

where \( r \) is the bond distance, and \( \theta \) is the bond angle. The torsion function represents the energy arising from bonds not fully staggered. It is best characterized as a periodic function, which is often implemented as a truncated Fourier series:

\[ V_{\text{torsion}} = \sum V_n/2 \left\{ 1 + \cos(n\phi - \phi_0) \right\}, \]

where \( V_n = \) torsion force constant, \( n = \) periodicity of the Fourier term, \( \phi_0 \) is the phase angle, and \( \phi \) is the torsion angle. A Van der Waals interaction refers to attraction and/or repulsion between non-bonded atoms. It is constructed as a 6-12 function:

\[ V_{VDR} = \sum \left\{ A_{ij}/R_{ij}^{12} - B_{ij}/R_{ij}^6 \right\}, \]

Where \( R_{ij} \) is the nonbonded distance between two atoms, and \( A_{ij}, B_{ij} \) are the Van der Waals parameters for the interacting pair of atoms. The dipole energy is the energy of interaction of bond dipoles and any point charges. It can be derived from classical electrostatics:

\[ E_{\text{dipole}} = k \varepsilon \sum \mu_{i\mu_j} \left[ \cos \chi - 3 \cos \alpha_i \cos \alpha_j \right]/R_{ij}^3, \]
where $\varepsilon$ is the dielectric constant, $\chi$ is the angle between the bonds and $\alpha$'s are the angles made by the bond dipoles with a line joining their midpoints.

3.1.4 Force field – mm +

A force field describes a molecule as a collection of atoms that interact with each other by simple analytic functions. It will give the best results for molecules similar to those used to develop its parameters. MM+ is unique among the force fields in the way it treats bonds and angles. Both bond and angle terms can contain higher order terms than the standard quadratic. MM+ is an extension of MM2, which was developed by Allinger and co-workers$^{133}$ in 1977 and was originally designed for small organic molecules$^{134-137}$, although it has been expanded to peptides. Carbon nanotubes and peptides are similar in their relatively large, repeatable basic units, and experimental data can be found for carbon materials. Thus, mm+ is an ideal force field to be used in our molecular mechanics calculation.

3.1.5 Geometry Optimization

A starting structure is defined for MM+ as a list of atomic Cartesian coordinates and a connectivity table that define the bonds between the atoms. Typically the user
specifies the positions of only the heavy atoms and the program adds hydrogens and unshared pairs in standardized locations, to make each atom tetrahedral, trigonal, or linear, as appropriate. The method of defining a minimum is crucially important. The energies of the individual bonding components are functions of deviations of a molecule from a hypothetical compound that has bonded interactions at minimum values. The force fields are applied to the input geometry and a total steric energy (TSE) is calculated. The molecular geometry can then be altered and the TSE is recomputed; the process is repeated until a minimum TSE is found. Once the energy and structure remain constant from iteration to iteration, computation ceases. Further evidence that a minimum has been found can be obtained by computing the normal-mode vibrational frequencies of the molecule. Since any distortion of a molecule from the geometry at a stationary point on the potential energy surface will lead to an increase in energy, the computed frequencies will all be positive (real) for a molecule in such a state. If the molecule lies at a first-order saddle point (transition state), one and only one frequency, corresponding to motion along the reaction coordinate, will be negative (imaginary). Two or more imaginary frequencies imply location at a maximum. The absolute energy of a molecule from a molecular mechanics calculation has no physical meaning. Rather, it's very useful for comparing energies between two or more molecules. Unlike quantum mechanics, molecular mechanics does not treat electrons explicitly. However, it evaluates steric effects for a molecular system from a database of desired parameters.
3.2 BACKGROUND

Single-wall carbon nanotubes have been the subject of a large number of studies since their discovery in 1991. One of the novel and promising avenues in SWNT research is the synthesis of new compounds, arising from the addition of atoms or radicals to the exterior. The derivatization of C$_{60}$ (buckminsterfullerene)$^{138-146}$. SWNT's other famous family member has been worked on extensively in recent years. Because of the similarity between the two, researchers have applied the same types of functionalization used with C$_{60}$ to SWNT's. By using the technology developed in the fluorination of graphite and C$_{60}$, Mickelson et al.$^{77}$ have reported the fluorination of high purity SWNT's. They have demonstrated via gravimetric and electron microprobe analysis that large amounts of fluorine can be added to SWNT's and that there is a limiting stoichiometry of C$_2$F at which the fluorinated tube can still remain in its tube-like structure. Several theoretical studies have recently appeared in the literatures dealing with different aspects of carbon nanotubes.$^{95, 147-150}$ We have investigated some possible mechanisms for fluorine addition to the SWNT's and conceptualized some possible structures consistent with C$_2$F stoichiometry with molecular mechanics and semi-empirical methods. Since then, several modeling studies of functionalized SWNTs have been published using higher level of theory.$^{95, 151-153}$
3.3 COMPUTATIONAL DETAILS

Two computational methods have been used in this work. To get a fundamental idea about the fluorine addition mechanism and fluorotube structures, we started with a molecular mechanic calculation as implemented in the Hyperchem\textsuperscript{154} software package. A MM+ force field was used for the calculation. Fluorine addition was modeled for (10,10) single wall nanotubes. In the first part of the computation, we investigated the possible addition sites for two fluorine atoms. Calculations were done on (1,2) and (1,4) fluorine additions to the nanotube system. We also looked at 4-F and 6-F addition to the sidewalls of nanotubes to get a perspective on the addition mechanism of fluorine to the sidewalls of carbon nanotubes. Finally, we propose two possible fluorotube structures based on the experimental result. Total steric energies were calculated for the proposed isomers and individual energy components: stretching, bending and torsion energies were also obtained. The nanotubes assumed in the calculation consisted of 200 fluorines and 600 carbons with end caps. All geometries were optimized before energy calculations were performed. The hyperchem molecular mechanics calculation was run on a Pentium I computer, and Hyperchem version 4.0 was used. A semi-empirical method was also applied for calculating similar structures. This work was primarily done by Wang\textsuperscript{155}, preceded by the molecular mechanics results. Here I will report mainly the results from the molecular mechanics calculation, and the comparison with the semi-empirical calculation.
3.4 RESULTS & DISCUSSION

3.4.1 Two-fluorine addition

There are three possible ways of adding one fluorine molecule to the sidewalls of SWNT: (1,2), (1,3) and (1,4) additions within a hexagonal ring (Figure 3-2). (1,3) addition of fluorines would introduce radicals to the nanotube environment. Radicals would be very reactive and are not favored. The molecular mechanics calculations were done only for the (1,2) and (1,4) additions. According to the calculated total (steric) energy of system, (1,2) addition to the sidewalls of nanotubes has a lower energy, though the difference between the two isomers is not large.

3.4.2 Addition Mechanism

Once the fluorination is initiated, incoming fluorines will have multiple addition sites to choose from. Figure 3-3 shows the possible addition sites for incoming fluorines. Fluorines will add to the nearest neighboring carbons to the initiation sites, as seen in Figure 3-4. The semi-empirical calculation also produced a similar result. As the reaction continues, fluorines have two possible routes to attach themselves to the tubes: along the tube axis or around the tube circumference (Figure 3-5). The calculated results suggest that fluorines will prefer to add along the tube axis once the fluorination is initiated. However, a different result was found through the semi-empirical calculation.
Figure 3-2 - Possible fluorine initiation sites. The arrow indicates the direction of the nanotube axis relative to blue sphere, which represents a F atom,

Position 1 — 1,2 addition
Position 2 — 1,3 addition
Position 3 — 1,4 addition
Figure 3-3  The addition of four fluorines to a nanotube

Shaded circles represent the 1st \( F_2 \) molecule;

Empty circles represent the incoming \( F_2 \) molecule after initiation;

Numbers represent possible sites for addition (1,2 or 1,4) on the six-membered rings
Figure 3-4  Energy comparison of the addition of four fluorines to a nanotube at different positions

(a) (1,2) isomer energy vs. fluorine position
(b) (1,4) isomer energy vs. fluorine position

* "Down" – adding fluorine along the circumference of tubes
* "Right" – adding fluorine along the tube axis
Figure 3-5 Some possible fluorine addition sequences

(i) Adding along the tube axis
(ii) Adding around the tube circumference

(a) (1,4) addition
(b) (1,2) addition

Arrows indicate the nanotube axis
In Wang's calculation, she applied AM1 & CNDO, two of the more popular semi-empirical methods, for the fluorine addition model. She found that addition around the tube circumference is the preferred fluorination sequence. In the molecular mechanics calculation, total energy is the sum of stretching, bending, torsion, van der Waals and stretching-bending individual energy components. In addition to the total steric energy, electronic effects are also included in the semi-empirical methods. Since both steric and electronic effects are major contributions to the stability of the fluorotubes, it appears that fluorine addition could be dominated by the electronic effects, i.e., formation of strong, polar bonds.

3.4.3 C₂F Fluorotubes

Previously, Mickelson et al have shown that there is a limiting stoichiometry of C₂F for which fluorinated tubes can still maintain at their tube-like structures, according to EMPA, gravimetric and TEM analysis. Here, we have proposed two possible Fluorotube structures: 1,2 (conjugated) & 1,4 (parallel) isomers. In the (1,2) isomer, the double bonds in the hexagonal rings are in a conjugated structure, while they are parallel to each other in 1,4 isomer (Figure 3-6). For a 600 F addition, the 1,4 isomers are more stable with lower total steric energy. Figure 3-7 shows the optimized Fluorotube structures in ball-and-stick images. Their total steric energy and individual energy components are shown in Table 3-1. All of the fluorines seem to line up in the (1,4) isomer when viewed from the end of the nanotubes, whereas in the (1,2) isomer, the tube
Figure 3-6  Proposed fluorine addition patterns on the fluorinated carbon nanotubes

(a) (1,2) addition - also described as "conjugated"
(b) (1,4) addition - also described as "parallel"
Figure 3-7  Optimized fluorotube structures

(a) (1.2) isomer
(b) (1.4) isomer

Both end views (on the left) and side view
(on the right) are shown
<table>
<thead>
<tr>
<th></th>
<th>(1,2)</th>
<th>(1,4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stretching</td>
<td>168.5</td>
<td>136.5</td>
</tr>
<tr>
<td>Bending</td>
<td>936.1</td>
<td>740.8</td>
</tr>
<tr>
<td>Torsion</td>
<td>1285.3</td>
<td>912</td>
</tr>
<tr>
<td>VdW</td>
<td>461.4</td>
<td>530.4</td>
</tr>
<tr>
<td>S-B</td>
<td>17.9</td>
<td>6.2</td>
</tr>
<tr>
<td>Total E</td>
<td>2883.4</td>
<td>2313.4</td>
</tr>
<tr>
<td>Energy / F</td>
<td>14.2</td>
<td>11.6</td>
</tr>
</tbody>
</table>

Table 3-1 Total steric Energy vs. C$_2$F isomers

Energy is represented in kcal/mol
looks twisted. This can be explained by the fluorine-fluorine repulsion in the fluorotube system. In (1,2) isomer, fluorines are closer together and this leads to a larger steric energy for the system, making this type of Fluorotubes more unstable than the other. The (1,4) isomer is also more stable from Wang's semi-empirical results. Short Fluorotubes were modeled due to the limitation on size for semi-empirical calculation.

3.5 SUMMARY

Our calculation provides an insight to the possible Fluorotube structures. Based on a limiting stoichiometry of C₂F from previous experimental results, we proposed two Fluorotube isomers, with fluorine addition in either (1,2) or (1,4) positions within a hexagonal ring in a nanotube system. From a molecular mechanics calculation with mm+ force field, we found that the 1,4 Fluorotube isomer is more stable, though the difference of the total steric energy between the two isomers is not very large. It is our belief that the two isomers could coexist from the fluorination of the nanotubes. By comparing the calculation results from molecular mechanics and semi-empirical methods with respect to stability, it appears that steric effects dominate the electronic effects in fluorinated carbon nanotubes. Further purification and characterization of fluorotubes, if possible, will have to be done to verify any preferred existence of one isomer. In addition, because of the arrangement of the bonds in hexagonal rings, fluorotubes can be either insulators or conductors. Electrons can hop through conjugated bonds in (1,2) isomers thus makes this
type fluorotubes conducting, whereas (1,4) isomers have their double bonds perpendicular to the electron flow through the conducting direction, along the tube axis, creating insulating fluorotubes.

3.6 CONCLUSION

After this initial molecular mechanics and semi-empirical works on the structures of fluorinated carbon nanotubes, few more results have been published on the modeling of Fluorotubes using higher level of theory. Seifert et al.\textsuperscript{156} investigated fluorinated carbon nanotubes using density functional parametrized tight-binding approximation on (10,10) SWNTs. The fluorination of a (10,0) SWNT model by four fluorine atoms was investigated by Bauschlicher\textsuperscript{151} using the ONIOM method to combine quantum-mechanical density functional theory with empirical molecular force fields. Most recently, Kudin et al.\textsuperscript{153} calculated the energies and band structures of (10,10) and (18,0) fluorinated nanotubes using density functional theory and periodic boundary condition which is the most sophisticated calculation methods up-to-date on nanotube modeling. Bettinger et al.\textsuperscript{152} further investigated the thermochemistry of Fluorotubes and the nature of the C-F bond. The discrepancy between our initial, lower level molecular mechanics / semi-empirical calculation and Kudin's sophisticated density-functional theory with periodic boundary condition might arise from the small model system as well as from the level of theory employed in our study. Nevertheless, our theoretical models of
Fluorotubes have provided the ground-work for the further, more advanced theory work on functionalized nanotubes. In addition, the importance of involving electronic interaction in the nanotube system is also demonstrated by comparing our work to the later study. In short, with all the possible theoretical results on the fluorinated single-wall carbon nanotubes, the mystery of the Fluorotube structure will not completely resolve until the better atomic imaging of it can be achieved with scanning tunneling microscopy.
4.1 STM THEORY

4.1.1 Background

Scanning tunneling microscopy, or "STM", is a method for imaging the surface of solid materials with "atomic" resolution. It was invented in the early 1980's by Gerd Binning and Heinrich Rohrer\(^2\)\(^{157}\) from the IBM Zurich Research Laboratory in Switzerland. Our understanding of electron tunneling begins in the early 1920s with the advent of quantum mechanics. In the 1960s, Giaver\(^158\) used tunneling to measure the superconductor energy gaps in metals, and in the 1970s, Young, Ward and Scire\(^159\) observed tunneling and transition to field emission in the point-plane geometry that presaged the STM. Binning and Rohrer received the Nobel Prize in Physics in 1986 for their invention of the STM (Figure 4-1). This instrument is not a true microscope, which gives a direct image of an object. Rather, the structure of a surface is studied using a stylus that scans the surface at a fixed distance from it.
Figure 4-1 Basic STM design
4.1.2 Theory

The most extensively used theoretical method for understanding the tunneling junction is the time-dependent perturbation approach developed by Bardeen\(^{160}\) (1960). The scheme for Bardeen's approach is shown in Figure 4-2. He obtained the electronic states for the separated subsystems by solving the Schrödinger equations. Time-dependent perturbation theory is used to calculate the rate of electronic transfer from one electrode to the other. Bardeen showed that the amplitude of electron transfer, or the tunneling matrix element \(M\), is determined by the overlap of the surface wavefunctions of the two subsystems at a separation surface:

\[ M = \hbar/2m \int (\chi^{*} \delta\Psi/\delta z - \Psi \delta\chi^{*}/\delta z) \ dS \]

where \(\Psi\) and \(\chi\) are the wavefunctions of the two electrodes. The tunneling current can be evaluated by summing over all the relevant states. At any finite temperature, the electrons in both electrodes follow the Fermi distribution. With a bias voltage \(V\), the total tunneling current is:

\[ I = 4\pi e/\hbar \int \{ f(E_{T} - eV - E) - f(E_{T} + e) \} \times \rho_{S}(E_{T} - eV + \epsilon) \rho_{T}(E_{T} + \epsilon) |M|^{2} \ d\epsilon \]

where \(f(E) = (1 + \exp((E - E_{T})/K_{B}T))^{-1}\) is the Fermi distribution function, and \(\rho_{S}(E)\) and \(\rho_{T}(E)\) are the density of states (DOS) of the two electrodes. Bardeen further assumed that the magnitude of the tunneling matrix element \(|M|\) does not change appreciably in the
interval of interest. Thus the tunneling current is determined by the convolution of the DOS of two electrodes:

\[ I \propto \rho_s(E_F-eV+\varepsilon)\rho_T(E_F+\varepsilon)d\varepsilon; \]

Clearly, according to Bardeen’s formula, the electronic structures of the two participating electrodes are interchangeable. If the goal is to obtain the DOS of the sample, one requires a tip with constant DOS, or a free-electron metal tip. In this case:

\[ \frac{dI}{dV} \propto \rho_s(E_F-eV). \]

Therefore, with a free-electron metal tip, the dynamic tunneling conductance is proportional to the DOS of the sample. However, because of the close proximity of the tip and the sample, Bardeen’s original approach is not appropriate. The perturbation theory approach that Bardeen used is uniquely applicable for the expression of the tunneling current. Holstein \(^{161}\) (1955) and Herring \(^{162}\) (1962) proposed improvement to the original Bardeen theory by including modifications of the wavefunctions of one object due to the existence of another object (Figure 4-3). In spite of its simplicity, the modified Bardeen theory provides the backbone for much of the physics in scanning tunneling microscopy.

### 4.1.3 Atomic Scale imaging

The basic idea of the modern STM is shown in Figure 4-4: A metallic tip, usually transition metals or semiconductors, is sharpened so that it ends in a small cluster of
Figure 4-2  Bardeen's approach to the tunneling theory

Figure 4-3  Modified Bardeen's approach to the tunneling theory
Figure 4-4 STM operation scheme
atoms. If the tip is brought to within a few atomic diameters of a sample that is under investigation, electrons can go back and forth between the tip and the sample by a tunneling mechanism. The flow of tunneling electrons is very sensitive to the separation between the sample and the tip. In use, the tip is mounted on a three-dimensional positioner that raster scans the tip above the sample, with feedback and control electrons to make sure that the tip doesn't actually touch the surface. As the tip is moved across and above the surface, a computer records the height at each point, and turns the result into an image of the surface. The invention of the STM realized a dream of physicists and chemists which was to visualize individual atoms and molecules, and their arrangement in real space. A large number of organic molecules have been imaged by STM, in particular, with atomic resolution. STM opens a new era of organic chemistry, and leads to a nanoscale view of the physical world.

4.2 BACKGROUND

The fundamental chemistry of single walled nanotubes (SWNTs) is still in its infancy. Initial speculation suggested that chemical functionalization of SWNTs would be most favorable at the ends\textsuperscript{79} of nanotubes, and that functionalization of SWNT sidewalls might be difficult to achieve. Successful controlled fluorination of the SWNT sidewalls leading to soluble products has recently been reported\textsuperscript{78}, providing a vital precursor for the subsequent attachment of a wide variety of functional groups to the exterior of the SWNTs. Various techniques have been used to image nanotubes:
scanning electron microscopy\textsuperscript{163} (Figure 4-5(a)), atomic force microscopy\textsuperscript{109, 164} (Figure 4-5(b)), and scanning tunneling microscopy\textsuperscript{66, 67, 70, 165, 166} (Figure 4-5(c)). Scanning probe microscopes are proximity probes. They can provide three-dimensional topographic images, and, in addition, can give the atomic structure of the surface. They can also be used to measure the electronic (STM) and elastic (AFM) properties of small structures. STM is restricted to electrically conducting objects, but AFM does not have this restraint. The unique characteristics of SWNTs that make them ultimately attractive for application also limit our ability to study their chemical derivatives with conventional chemical methods. As seen in Figure 4-6(a) and Figure 4-6(b)\textsuperscript{167}, AFM and SEM images of fluorinated carbon nanotubes do not tell us much about their structures. Here, we show that scanning tunneling microscopy (STM) images of fluorinated SWNTs provide a crucial starting point for developing a detailed understanding of SWNT sidewall chemistry. We have also obtained STM images of butylated SWNTs for which the fluorinated tubes\textsuperscript{78} were used as precursor. This substitution chemistry gives rise to electronic modulation in the vicinity of the attached butyl group, analogous with similar observations on graphite surface\textsuperscript{168-170}. One can also prepare “solvated” fluoronanotubes in a variety of alcohol by forming R-O-H... F-(C\textsubscript{n}F)- bonds\textsuperscript{77}.

4.3 EXPERIMENTAL PROCEDURE
Figure 4-5  Microscopic images of nanotubes
(a) SEM image of carbon nanotubes
(b) AFM image of carbon nanotubes
(c) STM image of a section of carbon nanotubes
Figure 4-6  Fluorinated carbon nanotubes
(a) SEM image
(b) AFM image
The synthesis of single-walled nanotubes has been described previously. SWNTs in "bucky paper" form were fluorinated by passing a dilute fluorine gas helium mixture (3% \( \text{F}_2 / 97\% \text{ He} \)) through a Monel flow reactor containing the SWNT sample. By varying the sample temperature and reaction time, various degrees of fluorination up to the saturation condition, \( \text{C}_2\text{F} \), can be obtained. This procedure is described in detail elsewhere. Following fluorination, the SWNT material can be removed from the reactor and analyzed with electron microprobe analysis to determine the exact product stoichiometry, i.e., the C/F ratio. Butylation of the sidewall-fluorinated tubes were accomplished by reactions with alkylithium species or via Grignard reagents.

Solvation of Fluornanotubes has also been achieved. Approximately 1 mg of the fluorinated SWNT material was placed into a vial containing approximately 10 ml of either isopropanol or dimethyl formamide. Sonication of SWNTs in either solvent for approximately five minutes results in the selective solubilization of highly fluorinated (isopropanol) or sparsely fluorinated (DMF) samples. The solvated Fluorotubes were then dispersed on a Au (111) on mica substrate by means of a rotary spinner and examined with STM. All STM images were obtained using a homebuilt STM instrument with commercial electronics under ambient conditions. In addition to Pt/Rh STM tips, \( \text{C}_{60} \)-adsorbed Pt/Rh STM tips were selectively utilized to provide enhanced atomic resolution and to image electronic modulations on the SWNT. Butylated tubes were solvated in a manner similar to the solvation of fluorinated SWNTs, except that chloroform was used as the solvent rather than DMF or isopropanol.
4.4 RESULT AND DISCUSSION

4.4.1 Fluorinated carbon nanotubes

Figure 4-7 shows some STM images of pristine carbon nanotubes. This image was taken with a C_{60} platinum tip. Some multiple imaging was seen here due to the tip artifacts. If we zoom in on the bottom part of the image, one can see an atomically resolved image of the carbon nanotube. However, in Figure 4-8, striking features were observed in the STM images of fluorinated tubes: there are narrow, abrupt, dark bands formed around the circumference of the tube upon fluorination. While similar scanning parameters were used in both pristine and fluorinated nanotubes, atomic resolution is not readily observable for the latter. Figure 4-9 shows STM images of fluorotubes prepared under different fluorination conditions. In addition to the strongly banded regions shown in Figure 4-9, long uninterrupted regions of the tube are also observed in Figure 4-10. Images of partially fluorinated SWNTs shows that the darker narrow regions remain abruptly terminated but typically form significantly broader bands. From a comparison between the STM images obtained for fluorinated SWNTs and the corresponding elemental analyses, we conclude that the narrower, darker bands correspond to unfluorinated regions of the nanotube. Even in the case of partial fluorination, the transition between the fluorinated and unfluorinated bands typically remains quite abrupt and orthogonal to the SWNT axis. In Figure 4-10, we also see that partially fluorinated nanotubes under high resolution exhibit this observed variation at atomic resolution: the
Figure 4-7  STM image of bare tube taken with C60 tips
(a) Scan parameters: bias voltage = 0.5 V.
tunneling current = 1.0 nA
(b) Zoomed in on the bottom of the tubes in (a)
Figure 4-8  - Carbon nanotubes fluorinated at 150 °C for 10 hrs; 
Spin-dried from IPA soln
Figure 4-9  Fluorinated carbon nanotubes:
they were fluorinated at 250°C for 12 hrs
(a) Visible bands can be seen
(b) Another fluorinated tube
Figure 4-10  Fluorinated carbon nanotubes:
Fluorinated at 150°C for 12 hrs
(a) Three fluorotubes are seen on the gold steps
(b) Zoomed in on the top tube in (a). Dark section
    is relatively large and believed to be unfluorinated
Figure 4-10

(c) Atomic resolution of tubes is seen in this section of tubes. The shadow areas are believed to be fluorinated. Atomic resolution of carbon is seen at the unfluorinated sites.
narrower regions of the tube correspond to regions where atomic resolution is obtainable under these scanning conditions.

A comparison of these STM images with theory provides insight into a likely geometry and functionalization mechanism for fluorinated SWNTs. Two possible isomers for fully fluorinated C$_2$F nanotubes are proposed in the previous chapters. In one case, the fluorine atoms occupy the 1,4 positions on every other row of hexagons; we call this the 1,4 isomer. The fluorine atoms can also occupy the 1,2 positions of the hexagons of alternate rows while the double bonds form a conjugated system along the tube axis. This is the 1,2 isomer.

When looking into the semi-empirical calculation results, from the CNDO optimized geometries obtained using the capped model, the calculated C=C bond length for the conjugated chain of the 1,2 isomer was approximately 1.37 Å, and the C-C bond length was approximately 1.45 Å. For the 1,4 isomer, the C=C bond length obtained was 1.35 Å. The C-F bond length of the two isomers is approximately 1.377Å, which is quite close to the C-F bond length of C$_{60}$F$_{60}$\textsuperscript{172}. The AM1 single point energy calculations based on the CNDO optimized geometries showed that the energy differences between the 1,2 and 1,4 isomers are very small: 76.02 kcal/mol, 25.22 kcal/mol and 64.30 kcal/mol for C$_{360}$F$_{20}$, C$_{360}$F$_{40}$, and C$_{360}$F$_{60}$ respectively. For the greatest degree of fluorination studied, C$_{360}$F$_{60}$, there is only 1 kcal/mol difference per fluorine atom. All results support the 1,4 as the more stable isomer, but the energy difference between the two isomers is actually quite small, and it would be realistic to anticipate that both isomers may coexist.
In the STM images, the fluorinated regions typically appear to terminate abruptly, forming bands around the circumference of the tube. This feature allows us to infer that the addition of fluorine to the pristine SWNT may occur more favorably around the circumference of the tube, not down the tube axis. We have, therefore, performed an AM1 calculation in order to ascertain the most energetically favorable sequence for multiple fluorine addition. This is shown schematically in Figure 4-11. First, a single fluorine atom is added to a $C_{160}H_{40}$ molecule (shown as position 1). Making the assumption that the second fluorine atom chooses an active position near the first, three potential active positions exist for the second fluorine atom (position 2, 4, and 4'). AM1 Results for $C_{160}H_{40}F_2$ show that for the 1,2, 1,4, and 1,4' isomers, the energy difference is negligible: all are candidates for the starting point of multiple fluorine addition. We then placed the second pair of fluorine atoms close to the first pair as either a (1,2), (1,4) or (1,4') isomer, and calculated the addition energy for the second pair of atoms as a function of the relative separation between fluorine atom pairs. Relative energies corresponding to fluorine addition at positions around the circumference of the tube $C_n$ (n=0-4) and along the tube axis $A_n$ (n=1,2) relative to the position of the first pair of fluorine atoms were calculated. These results are shown in Table 4-1. The energies of the isomers where the two pairs of fluorine add directly adjacent to each other are referenced as 0. It is quite clear that for the 1,2 isomer, if the four fluorine atoms are allowed to add around the circumference of the tube, they will try to stay as far away from each other as possible to minimize fluorine-fluorine repulsion. By comparison, addition along the axis of the tube for the 1,2 isomer is about 30 kcal/mol more exothermic than circumferential 1,2 addition. This is a strong indication that the 1,2
Figure 4-11  Geometry denotes the secondary fluorine addition sites
<table>
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<th></th>
<th>C0</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>A1</th>
<th>A2</th>
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</thead>
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<td>~0</td>
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<td>-2.1</td>
<td>-2.8</td>
<td>10.8</td>
<td>9.5</td>
</tr>
<tr>
<td>1,4'</td>
<td>0</td>
<td>-4.7</td>
<td>-5.4</td>
<td>-6.5</td>
<td>-6.9</td>
<td>9.5</td>
<td>6.5</td>
</tr>
</tbody>
</table>

C denotes fluorine addition around the tube circumference;
A denotes growth along the tube axis;
0-4 denotes the interval between the two pairs of fluorine atoms

Table 4-1  Relative energies (Kcal/mol) of four fluorine atom addition
isomer, if allowed, would form via fluorine addition along the tube axis. In the case of the 1,4 isomer, the calculations indicate that addition around the circumference of the tube is approximately 10 kcal/mol more energetically favorable than growth along the tube axis.

The circumferential growth mechanism of the 1,4 fluorination isomer would explain the abrupt bandlike boundaries ubiquitously observed in our STM images of fluorinated SWNTs. It is interesting to note that even under saturation fluorination conditions, some dark bands are still observable. This would be consistent with the 1,4 isomer being initiated at multiple sites along the tube, as shown in Figure 4-12(a). Since fluorination occurs on alternate pairs of rows of the 1,4 isomer, one can image the existence of adjacent 1,4 isomeric domains where the fluorinated rows of one domain lie in registry with the double bond row of a neighboring domain. This would result in full fluorination of the nanotubes but with abrupt boundaries and may be the origin of the observed structures. Since the calculated energy difference between the (1,2) and (1,4) isomers is small, one can expect to have both types of fluorine addition occur during the fluorination process. Discrete regions of (1,2) isomer may also be present on the nanotubes (Figure 4-12(b)). Defects (Figure 4-12(c)), such as introduction of ring types other than hexagon, rehybridization of carbon atom between $sp^2$ and $sp^3$, or incomplete bonding defects (vacancies, dislocation etc.) in the tubes might also play a role in either initiating or terminating the various isomeric domains.

### 4.4.2 Butylated carbon nanotubes
Figure 4-12  Gap formation in STM images: Lattice mismatching or defects

(a) Multiple fluorine initiation sites
(b) Mixture of both (1,2) and (1,4) additions
(c) Defects - example shown here is a 5-7 defect
Since the C-F bonds in fluorofullerenes are significantly weaker than the C-F bonds in traditional alkyl fluorides, sidewall fluorinated SWNTs can serve as a chemical starting point for subsequent addition of a variety of moieties. We have also imaged, via STM, sidewall butylated SWNTs which utilize fluorinated SWNTs as a precursor. STM images of butylated SWNTs are shown in Figure 4-13(a). One immediately notices that the banded morphology of fluorinated SWNT is no longer visible. Instead, relatively large (~ 10 Å) bright features with an average spacing of 50 Å are distinctly apparent as one scans along the butylated nanotubes. In higher resolution, the apparent atomic periodicity appears to be 2.46 Å (Figure 4-13(b)). This supperlattice feature is an electronic modulation of the nanotubes induced by the presence of the attached butyl group, and has been studied both experimentally and theoretically on graphite. Using a modified version of the LCAO method with periodic boundary conditions, we have calculated the density of states at $E_f$ for a (10,10) nanotube perturbed by a strongly bound carbon atom (Figure 4-13(c)). This is a simple one π electron per carbon atom, 2401 atom model with the appropriate boundary condition for a (10,10) nanotube in which the resulting surface charge density is "warped" into a cylindrical shape. Both the sizes of the modulated region and the supperlattice periodicity are in good agreement with the experimental image.
Figure 4-13  STM images of butylated tubes

(a) Visible "band" structures (indicated by arrows) are believed to be butyl groups
(b) Atomic resolution of carbon can be seen on the tubes (indicated by the arrow). Lattice spacing also supports it
(c) LCAO theory prediction
4.5  CONCLUSION

We have obtained the first STM images of sidewall functionalized SWNTs, particularly fluorinated and alkylated tubes. This powerful local probe, in combination with theoretical analysis, yields detailed new insights into how addition and substitution chemistry may be occurring on nanotubes sidewalls.
Reference


27. Bandow, S., A.M. Rao, K.A. Williams, A. Thess, R.E. Smalley, and P.C. Eklund, 


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


34. de la Chapelle, M.L., C. Stepan, T.P. Nguyen, S. Lefrant, C. Journet, P. Bernier, 
E. Munoz, A. Benito, W.K. Maser, M.T. Martinez, G.F. de la Fuente, T. Guillard, 


38. The operating conditions at which the sample from Tubes@rice was produced were as follows: Target composition-2% Ni, 2% Co, balance carbon by weight. Two Nd/Yag lasers were operated at 30 Hz with a 42 ns delay, laser wavelength-1064 nm, 1.1 J/pulse, energy density of ~5 J/cm2, system pressure of 500 torr Ar, gas flow of 750 sccm, furnace temperature of 1100 C and a quartz furnace tube with an inner diameter of 4 inches. Runs typically went for 24 hours.

39. The laser apparatus is described by S. Arepalli and C. D. Scott, C.P.L., 302, 1390, 1999. The operating conditions at which the sample was produced are as follows: Target composition-1% Ni, 1% Co, balance carbon by weight, Two Nd/Yag lasers were operated at 15 Hz at 12W with a 50 ns delay. The first laser pulse was green and the second infrared. Energy densities of both lasers were 1.6 J/cm2 at the sample, System pressure of 500 torr Ar, gas flow of 100sccm, furnace temperature of 1200 C and a quartz furnace tube of 1 in outer diameter. Product weight ~ 0.5 g, Run time 2 hours. The information and sample were provided by S. Arepalli, and P. Nikolaev, NASA-JSC.

40. The operating conditions at which the arc sample from Nasa-JSC was produced are as follows: anode diameter of 0.25 inches, cathode diameter of 0.75 inches, electrode gap width of 6-8 mm, current of 100 amps, and pressure of 500 torr of He. The apparatus was modeled after that described by C. Jounet, W.K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapelle, S. Lefrant, P. Deniard, R. Lee and J.E. Fisher, Nature, 388, 756, 1997. The information and sample were
provided by C.D. Scott, NASA-JSC.

41. The operating conditions at which the Monpellier arc sample was produced are similar to that for the NASA arc sample. The apparatus is described in the reference listed in reference 0. In this sample, significant variation in SWNT tube size was observed for different locations in the sample. The information and sample were provided by C.D. Scott, NASA-JSC.

42. This sample was obtained commercially from Carbolex as unpurified nanotube soot, C.A.-g., purity stated to be 50-70% nanotubes based on Raman and SEM analysis. Carbolex Inc., ASTEC CCC Bldg. Rm. A157, University of Kentucky, Lexington, KY 40506, U.S.A., Ph. 606-257-9488, e-mail sales@carbolex.com. The sample was provided by R. Barrera, Rice Univ.

43. The operating conditions at which this sample, HiPco@rice was produced were as follows: 70 mtorr of Fe(CO)5 in 300 psi of CO injected into the furnace at 10 slm, furnace temperature 850 °C, furnace tube-4 inch inner diameter quartz tube, actively cooled injector for CO/Fe(CO)5 mixture, sample collected on a cooled exit flange. The sample and information was provided by M. Bronikowski and R.K. Kelley, Rice Univ.


