RICE UNIVERSITY

Controlled Synthesis of Single-Walled Carbon Nanotubes

by

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The chemistry and applications of carbon nanotubes are critically dependent on nanotube chirality. To date, no one has demonstrated chirality-selective synthesis of single-walled carbon nanotubes from pre-synthesized catalyst nanoparticles. A proposed chemical approach to the mass production of chirality-selective SWNTs is their "cloning" by chemical cutting, decoration with catalyst nanoparticles, and continued growth. The progress of this process will be reviewed. Purified HiPco nanotubes were sidewall functionalized to allow suspension in water and organic solvents. Methods were developed to end-functionalize suspended nanotubes with linkers used to attach pre-formed catalyst particles. SWNT-catalyst complexes (SWNTcats) were deposited on a surface and exposed to hydrogen to show the feasibility of controlled etching of a single nanotube resulting in removal of the functional linker. To orient the nanotubes for growth, SWNTcats were assembled into open structures on a carbon fiber grid.

Vertically oriented carbon nanotube carpets grown by catalytic CVD have received enormous attention because of their suitability in a growing number of important technological applications. An area of concern is the sudden termination of growth that occurs after micron heights are attained. A previously unexplored factor in this termination is the coarsening of the catalyst particles used for growth by Ostwald ripening. The coarsening behavior of Fe catalyst films supported on alumina deposited
by atomic layer deposition as a function of thermal annealing in H2 and H2/H2O is demonstrated. The results reveal that the addition of water in water assisted growth of single-walled carbon nanotube carpets may be a means of inhibiting Ostwald ripening through the ability of oxygen and hydroxyl species to reduce diffusion rates of catalyst atoms and thus delay the termination of growth.
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Chapter 1: Overview of Single Walled Carbon Nanotubes

Introduction

In recent years the concept of nanotechnology – designing structures on the nanometer scale has become a major focus in research. One of the hot topics in scientific journals, it has grown to spawn journals all on its own. One of the most famous molecules in this phenomenon is the nanotube, which has graced the cover of numerous scientific journals with promises of remarkable applications. As research has continued, the nanotube has become the focus of vast research efforts and commercial endeavors. In this chapter we look at the unique structure of these molecules and the remarkable properties that arise because of this structure. We explain the typical ways of characterizing SWNTs and some of the spectral features used to identify SWNT characteristics. We look at the methods currently used to produce SWNTs, and at the difficulties these techniques face. Finally, we discuss the purpose of the research detailed in this thesis and how this work ties in with the broader scheme of SWNT production.

Structure of SWNTs

Although nanotubes were arguably first synthesized in the 1960’s [1-3], they were not rediscovered until 1991 when Iijima analyze the product of fullerenes synthesized by arc discharge using transmission electron microscopy (TEM) [4]. TEM images revealed long, nested cylinders 2-50 walls deep comprised of carbon hexagons in a graphene lattice structure. In 1993, Iijima [5] and Bethune [6] formed single-walled carbon nanotubes by adding transition metals to the graphite anode before arc discharge.
Single walled carbon nanotubes are structurally equivalent to a single perfect graphene sheet rolled into a seamless tube, often capped at one or both ends with the structural equivalent of half a buckyball. The diameter can range between 0.7 to 10 nm, although the majority of SWNTs have diameters below 2 nm. Although the tubes range broadly in length due to synthesis and purification techniques, most are greater than 300 nm and many are as long $10^5$ nm, making SWNTs essentially one dimensional.

Although the basic form of a nanotube is always a cylinder, the local form of a nanotube can differ. The local differences in form can be visualized by imagining the rolling of a graphene sheet. Depending at what angle the sheet is rolled, the nanotube can either be achiral, or chiral. There are two types of achiral tubes, zigzag and armchairs, and they are named after the shape of the nanotube edge. When the nanotube structure is recreated by rolling a graphene sheet, the edge of the nanotube has either a cis, trans or mixed structure. When the edge of the nanotube has a cis structure (Fig. 1.1(A)), the bonds are shaped like an armchair. Armchair nanotubes have a chiral angle of 30 degrees and indices $(n, n)$. When the edge of the nanotube has a trans structure, the tube is called a zigzag nanotube (Fig. 1.1(B)). These zigzag tubes have a chiral angle of zero degrees and indices of the form $(n, 0)$. The third kind of tube, the chiral tube, has both cis and trans forms at its edge and makes up the remainder of the nanotubes (Fig. 1.1(C)) [7].
Mathematically, the chiral vector of the nanotube formed is given by the roll-up vector

\[ C_h = n\hat{a} + m\hat{b} \]

where \( \hat{a} \) and \( \hat{b} \) are unit vectors in the graphene lattice and \( n \) and \( m \) are integers. Tubes are indexed by \( n \) and \( m \), which determine both the diameter and chirality of the tube. The diameter of a nanotube can be calculated using these indexes.

\[
D_t = \frac{C_h}{\pi} = \frac{\sqrt{3}}{\pi} a_{e-e} \sqrt{n^2 + mn + m^2}
\]
where $a_{cc} = 0.142$ nm, the carbon-carbon bond length.

The chiral angle of a nanotube is given by

$$\alpha = \tan^{-1} \left( \frac{\sqrt{3n}}{2m+n} \right)$$

Fig. 1.2 relates the chiral angle and roll-up vector to the nanotube indices $(n,m)$ [7]. With relatively few indices we can calculate most of the important characteristics of the tube.

**Figure 1.2.** A nanotube may be thought of as a graphene sheet rolled into a cylindrical structure. A graphene sheet with indexed lattice points displays the relationship between the chiral angle, roll-up vector, and lattice index [8-9].
The three types of nanotubes have different electronic properties due the electronic bands of graphene [8-9]. Graphene has conducting states only at certain points on the Fermi surface and in certain directions in $k$-space (Fig. 1.3). Hence, graphene is metallic at room temperature in some directions and semiconducting in others. When the nanotube is rolled along one of the metallic directions, a metallic nanotube is formed, while in all other directions the band gap is $0.9 \text{ eV}/D_t(n,m)$. Armchair nanotubes are the only truly metallic nanotubes; all others are semiconductors at 0 K. For certain chiral tubes, however, the band gap is small enough that the conduction band is partially filled at room temperature. Despite a trend in the literature to call these nanotube metallic, they are most properly called semimetals and occur when $[(n - m) \mod 3] = 0$ [10].
Figure 1.3. The band structure of graphene, as calculated plotted versus wavevector. The valence and conduction bands meet at each $k$-point. SWNTs are metallic if their one-dimensional Brillion zone intersects a $k$-point of graphite.

Properties of SWNTs

The unusual structure of carbon nanotubes gives rise to a host of unusual traits with potential uses in a variety of applications. These traits can roughly be organized into three categories – electrical, thermal, and mechanical – and are due to the band structure, one dimensional nature, and carbon-carbon bond strength of the atoms in the carbon nanotube.
Electrical

SWNTs display near-ballistic conduction due to reduced phonon scattering in its one-dimensional structure. This conduction causes a room temperature resistivity that exceeds copper, measured as low as $1 \mu \Omega \cdot \text{cm}$ [11-13]. Nanotubes have also been shown to carry a current density over 100 A/cm$^2$ before electrical breakdown [14]. Semiconducting nanotubes also have astounding properties – the charge carrier mobility is higher than any known semiconductor at 79 k$\cdot$cm$^2$/V [15].

Thermal

Although the thermal conductivity across a nanotube is expected to be poor, the thermal conductivity down the length of the tube was predicted to rival diamond at 2000 W/K$\cdot$m due to the efficient transfer of phonons down the nanotube [16]. The thermal conductivity of a single multi-walled nanotube exceeded this prediction and was measured at 3000 W/K$\cdot$m [17]. Due to the greater structural perfection, single-walled nanotubes were predicted to have a thermal conductivity even greater than MWNTs. This prediction was realized in 2006 when the thermal conductivity was extracted from its high bias electrical characteristics at nearly 3500 W/K$\cdot$m [18].

Mechanical

Carbon nanotubes were expected to have high mechanical strength due to the overlapping sp$^2$ bonds that formed the uniform structure of the carbon lattice. Individual
nanotubes were predicted to have Young's modulus close to 1 TPa [19-20]. SWNTs exceeded this prediction with a measured value of 1.25 TPa [21]. The strain to failure was predicted to fall in the range of 5-30% for individual carbon nanotubes [22]. Although not yet measured in individual SWNT, the strain to failure of SWNT ropes was observed to be ~5% [23]. The tensile strength of SWNT ropes was measured at ~47 GPa [24].

**Characterization of SWNTs**

Single walled carbon nanotubes have spectroscopic and visual features that reflect their properties. The techniques used for characterization are roughly divided into those that probe the physical characteristics by use of electron or force microscopy and spectroscopic techniques that look for chemical or electronic signals. Those in the first category include transmission electron microscopy, scanning electron microscopy, and atomic force microscopy. Those probing the spectroscopic response of nanotubes include fluorescence, ultraviolet-visible, and Raman measurements. We will briefly discuss the basics of the primary techniques used in this thesis and how they apply to single walled carbon nanotubes.

In Transmission Electron Microscopy (TEM) an electron beam is focused on the sample and the transmitted electrons measured and reconstructed into an image of the sample. Denser areas of the sample transmit fewer electrons and appear darker in the image. TEM has sub-nanometer resolution, and so is useful for determining the diameter and number of walls in a nanotube sample. Because of the high density of metal particles, it is also easy to distinguish metals from nanotubes and other carbon material.
Scanning electron microscopy (SEM) also utilizes an electron beam focused on the sample. In this technique, however, the electron beam interacts with the sample and causes the sample to emit electrons and electromagnetic radiation. In secondary electron mode, low energy species of the emitted sample electrons, called secondary electrons, are detected and mapped as a two-dimensional intensity distribution. This distribution is used to produce a digital image of the surface.

Atomic force microscopy (AFM) or scanning force microscopy used in tapping mode consists of a small tip at the end of a cantilever that oscillates near the surface being imaged. Interactions with the surface cause the amplitude of the oscillation to decrease when the tip comes close to the surface. The deflection of the tip off the surface is measured using a laser spot focused on the tip. The amount of force needed to keep the oscillation amplitude constant is used to produce the image. The lateral resolution of an AFM is very high – theoretically angstrom resolution. The horizontal resolution, however, is limited by the diameter of the tip and is typically on the order of 10 nm.

Resonant raman spectroscopy of carbon nanotube detects plasmons caused by the vibrational modes of tubes. A typical nanotube spectrum contains several features. The first is the G peak at 1590 cm\(^{-1}\), which is the result of graphene in-plane stretching. A peak at 1390 cm\(^{-1}\) is known as the disorder mode and increases in size as the number of functional groups or empty lattice sites increase in the carbon nanotube. The most interesting peaks occur between 100 cm\(^{-1}\) and 300 cm\(^{-1}\). These peaks are the breathing modes and are due to the tubes radially expanding and contracting. Because each tube has a different diameter, the frequency at which this occurs is different for each species of tubes. Different lasers enhance the breathing mode signatures of different chirality nanotubes, and so probe different species of tubes.
Production of SWNTs

There are three basic methods of SWNT production – arc discharge, laser ablation, and chemical vapor deposition. In arc discharge, a current is generated between a cathode and anode formed by graphite rods imbedded with transition metal catalysts. The high temperature created by the arc results in SWNTs with few defects, but the high temperature gradient around the arc causes a variety of impurities. The SWNTs produced tend to be well aligned due to the electric field gradient between the graphite rods, and are narrowly distributed around 1.2 nm. Unfortunately, scaling production to commercial
levels is difficult, if not impossible, due to the geometry necessary to produce the arc [26].

Laser ablation uses a neodymium-yttrium-aluminum-garnet laser to vaporize a Co/Ni graphite composite target held at 1200 °C in the tube furnace. The nanotubes grow off the evaporated metal – carbon mixture and are carried by Ar gas to the end of the tube where they are collected by a cooled copper piece. The SWNTs grow in ropes, and TEM of the product reveals no associated catalyst particle. This led to the development of the scooter mechanism theory; this mechanism suggests that a single Ni or Co atom can stabilize the open end of a SWNT and scoot along the growing edge adding carbon atoms in its wake. Analysis of samples by x-ray and electron diffraction suggest that the ropes formed favor the (10,10) arm chair structure [27], although SWNTs of varying diameters and chiralities have been observed [28]. Unfortunately, this method of production is also limited in the quantity of tube that can be practically produced.

Chemical vapor deposition (CVD) synthesis of SWNTs occurs when a carbon-rich feedstock gas encounters a transition metal nanoparticle at elevated temperatures. The metal acts as a catalyst to decompose the feedstock and becomes saturated with carbon. This carbon adds to the growing edge of the nanotube in contact with the catalyst particle. At some point, the growth terminates and the catalyst becomes overcoated with carbon. CVD growth has been observed both in the gas phase and off catalyst particles on a surface. Because of the inherent scalability of this method, it is the subject of the majority of nanotube growth studies.

Current nanotube production has several difficulties. First and foremost, nanotubes of a certain type can not be produced singly – all production methods yield a mixture of various chiralities. Second, production yield is still relatively low, with much
of the carbon feedstock converted into non-nanotube carbon. Third, nanotube growth terminates and the mechanism is still poorly understood.

In this thesis we study the growth of carbon nanotubes in an effort to understand the causes of two of the largest problems facing nanotube synthesis today – the chirality control of single walled carbon nanotube, and the termination of growth during synthesis. In Part I, we go over the basic premise of seeded growth for chirality control as designed by Richard Smalley. Next, we explain how we formed a seed. We explain how we etched the carbon nanotube by exposing the nanotube-catalyst compound to a reducing environment and what it reveals about SWNTs. Finally, we comment on a few examples of seeded growth on a surface.

In Part II, we summarize Richard Smalley’s Snag and Drag model for the scale up of seeded growth. We show that it is possible to nebulize SWNTs, and highlight the importance of this discovery in the respiratory toxicity studies of carbon nanotubes. We show that these nebulized nanotubes can be electrostatically collected on a carbon fiber to form self-assembled SWNT-carbon fiber structures. We show that nanotubes nucleated in growth gasses can be electrically collected on a carbon fiber and grown into long loosely aligned fibers. We summarize various growth conditions and highlight trends in the growth data.

In Part III, we propose Ostwald ripening as a mechanism for SWNT growth termination on a surface. We show data supporting Ostwald ripening as an explanation for increase yield and length observed by water assisted growth.


Chapter 2: Seeded Growth Overview

Single walled carbon nanotubes show great promise in an array of applications. Since the electronic and spectroscopic response of SWNTs is largely based on SWNT chirality, the procurement of chirality specific SWNTs, either by sorting or controlled growth, is highly desirable. One of the most studied methods is the use of a narrow distribution of diameter catalyst particles, as the synthesized nanotube diameter has been shown to largely correlate to the catalyst diameter [1-3]. Unfortunately, although the diameter distribution of the produced tubes is narrow, even the ideal case of identical metal clusters produces a variety of chiral structures in the SWNTs produced [4].

Smalley proposed the use of short segments of nanotubes chemically docked to metal catalyst particles as precursors for diameter-specific CVD growth. In this method, a metal catalyst particle is attached to the end of a SWNT. This SWNT-catalyst is subjected to CVD growth conditions where the nanotube acts as a template, allowing carbon atoms to add to the edge without changing chirality. There are two main implementations of seeded growth – continued growth and SWNT amplification. Continued growth takes a spun SWNT fiber made from armchair nanotubes and uses it to template growth for a long metallic wire. The second, called SWNT amplification, uses small amounts of individual chirality sorted SWNTs to produce greater amounts of single chirality tubes. Although this thesis is about SWNT amplification, because the processes are related we give a brief overview of continued growth.

In continued growth, a spun nanotube fiber is treated to create a flat, open ended surface at the top. Catalyst is deposited on the open ends and treated to form discrete
nanoparticles intimately attached to the open ends. The catalyst is activated and exposed
to carbon feedstock, which adds carbon atoms to the preexisting nanotube structure
causing epitaxial growth. (Fig. 2.1)

Figure 2.1. Continued growth scheme. (A) Nanotubes in a SWNT fiber are
etched to reveal open ends. (B) Metal is deposited to form catalyst particles on the
open ends. (C) Carbon feedstock is introduced at elevated temperature and carbon
added epitaxially to the SWNT fibers. In this case, ethanol is converted to water,
hydrogen, and nanotube carbon. [5].

In the continued growth effort, a spun nanotube fiber was cut and polished using a
focused ion beam and impurities removed with an acid wash. The ends of the fiber were
opened using an inductively coupled oxygen plasma. A 0.2 nm layer of Fe/Ni was
deposited on the open ends using e-beam evaporation. Ethanol feedstock was introduced
to the catalyst docked fiber and the temperature ramped to 800 C. After 30 minutes, a 2
μm extension of the fiber was observed using a real time image in a CCD camera. SEM (Fig. 2.2) suggests that the tubes grow seamlessly out from the nanotube fiber substrate and a Raman comparison (Fig. 2.3) between the extended part and the original fiber shows radial breathing modes consistent with continued growth [5-6].

Figure 2.2. (A) SEM image taken from nanoscopically flat SWNT substrate by FIB cutting, (B) SEM image taken after the growth experiment. (C), (D) High magnification images taken from the edge of the fiber after growth experiment [5].
Figure 2.3. Raman data taken before and after growth experiment with three different lasers. Black line is from before growth, red line is from after growth, and green line is from controlled experiment. [5]

The results from the continued growth study strongly suggest chiral specific growth was achieved, and so we kept the techniques in mind when expanding the processes which allow seeded growth. Although encouraging, because the same tube can
not be imaged before and after growth, it is not possible to prove seeded growth occurs using continued growth.

The SWNT amplification production model differs from continued growth in that it seeks to prove chiral specific growth and provide a method of producing individual chiral specific nanotubes for a variety of applications. In SWNT amplification, chirality sorted SWNTs are cut into small segments, docked to a catalyst particle and exposed to a growth environment (Fig. 2.4). The nanotubes multiply in length and some are fed back into the process, while others are retained for applications.
Figure 2.4. SWNT amplification scheme. A small amount of presorted single-walled carbon nanotubes are purified and cut into small segments to serve as templates for chirality specific growth. A catalyst is attached to the end of each SWNT and feedstock introduced to multiply the length of each SWNT, yielding an increase in SWNT material. These nanotubes are fed back into the SWNT amplification cycle.

The following chapters explore the SWNT amplification method of chirality specific growth. We seek to show the feasibility of this approach for obtaining chiral specific growth by examining growth of a single nanotube on a surface. Individual SWNTs on a surface can be tracked throughout the entire growth process, allowing both length and diameter to be monitored. If a nanotube appears in a new location on the
substrate, the growth is assumed to be new nucleation. If a nanotube already present on
the substrate lengthens while its diameter remains constant down its length, chiral
specific growth is the most obvious explanation. With a vertical sensitivity of ±0.1 nm,
AFM can reveal slight changes in diameter. Horizontal growth on surfaces thus provides
an ideal proof of concept for seeded growth.

There are two basic possibilities for nonchiral specific growth: newly nucleated
growth off of the backside of the catalyst particle and a change in the chirality of the tube
when the growth is reinitiated off the front. There are two possibilities in the case of
nonchiral specific continued growth: a 7-5 defect producing a kink and a 7-5 defect
producing a diameter change (Fig. 2.5).
Seeded Growth

Chiral specific continued growth

Nonchiral specific growth

Newly nucleated growth

Kink inducing continued growth

Diameter increasing continued growth

Figure 2.5. Model of newly nucleated growth from a catalyst particle.
In newly nucleated growth, the additional nanotube adds to the side of the nanotube opposite the original tube. Since the nanotube location can be tracked by AFM, it is possible to determine where SWNT length is added relative to the catalyst particle. Also, since the catalyst particle is generally larger than the HiPco seed, newly nucleated growth would probably cause a change in the size of the nanotube produced and a changing diameter down the length of the tube (Fig. 2.5). Another possible outcome of new nucleation is a second, larger nanotube nucleated around the original seed nanotube producing a multiwall. To occur, this process would need to overcome the attractive forces between the original nanotube and the substrate and would lead to a noticeable diameter increase. A third possible outcome is nonchiral specific growth. In order for nonchiral specific continued growth to occur, a 7-5 defect would need to add to the site of regrowth. Along with a change in chirality, this defect would introduce either a kink in the structure of the nanotube (Fig. 2.5, 2.6) [7] or a noticeable diameter change (Fig. 2.5) [8-9].
Figure 2.6. (A) AFM and (B) model of a SWNT with a 7-5 kink inducing defect.

Since all cases of non-chiral specific growth lead to either diameter or location changes distinguishable by AFM, a careful analysis of the SWNTs before and after growth provides the evidence necessary to determining whether seeded growth is chirality specific.

Before growth, a number of steps were developed including catalyst attachment, surface deposition, and reductive docking (Fig. 2.7).
Figure 2.7. Diagram of proof of concept steps. Single-walled carbon nanotubes are purified of metal impurities, individualized by functionalization or polymer wrapping, and attached to catalyst particles to form SWNT-catalyst complexes. These SWNT-catalyst complexes are deposited on a surface where the catalyst is reductively docked to the nanotube carbon followed by exposure to carbon feedstock.

In preparation for seeded surface growth, raw HiPco SWNTs are purified to remove large fullerenes, amorphous carbon, and old catalyst particles. The SWNTs are then cut into multiple small template seeds. After cutting, the SWNTs are altered to yield suspensions as individuals in a suitable solvent, and a catalyst particle is attached to the end of each nanotube. Once catalyst attachment is completed, the SWNT-catalyst complex (SWNTcat) is deposited on a surface and imaged by AFM. The nanotube is exposed to hydrogen to reduce the metal catalyst, burn away the SWNTcat linkers, and etch into a small section of the SWNT leaving the catalyst particle in direct contact with the SWNT. Finally, the SWNT undergoes growth experiments and the previously imaged nanotube is re-imaged for comparison.
The next few chapters explain our work towards observing chiral specific growth on a surface. In chapter 3, we explain how we prepared the SWNTcat — the first half of the process. In chapter 4 we show that we can successfully dock a catalyst particle to the nanotube putting it in direct contact with the templating carbon atoms. Finally, we show two cases suggestive of seeded growth.


[6] Kim MJ,


Chapter 3: Functionalization of SWNTs to Facilitate the Coordination of Metal Ions, Compounds and Clusters

The formation of a SWNT-catalyst complex is a necessary precursor to chiral specific growth using the Smalley seeded growth model. In this chapter we elucidate the chemistry developed to form the SWNT-catalyst complex (SWNT-cat). There are two issues to address in choosing a SWNT-cat for large-scale SWNT amplification; these include maximizing the percentage of SWNT converted to SWNT-cat, and the formation of SWNT-cat with the best pro-catalyst possible for growth.

While the yield of SWNT-cat formed from any given batch of SWNTs is obviously dependent on the ability to maximize the attachment of the pro-catalyst to the SWNT, there are really two components to this reaction. The first is to ensure that a maximum number of SWNTs have ends suitable for the attachment of the pro-catalyst. Second, the efficiency of the coupling reaction between the SWNT and the pro-catalyst must be optimal. We first show the formation of coupling groups to allow the attachment of metal containing species specifically to the ends of SWNTs. We next optimize the efficiency of the coupling reaction between the pro-catalyst and SWNTs by varying the reaction conditions.
Figure 3.1. All reaction schemes developed to prepare SWNTs for catalyst attachment. Products 1-15 are referenced below.

Methods

Solvents were purchased from Fisher Scientific. Isonicotinic acid, benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBOP), N,N-diisopropylethylamine (DIEA), cysteamine, 4-dimethylaminopyridine, 4-hydroxyphenyldiphenylphosphine, dicyclohexylcarbodiimide, thionyl chloride, FeCl₃, Na₂MoO₄, and HPMo₁₂O₄₀ were purchased from Aldrich Chemical and used as received. 4-hydroxypyridine was purchased from Aldrich Chemical and recrystallized.
from water [1]. 4-tert-butylphenol was purchased from Fisher Scientific and recrystallized from hexanes. All reagents were ACS grade or better.

The molecule \([H_xPMo_{12}O_{40}<H_4Mo_{72}Fe_{30}(O_2CMe)_{15}O_{254}(H_2O)_{98}]\) (FeMoC) was prepared by a modification of literature methods [2]. Aryl sulfonic acid functionalized SWNTs (ASA-SWNTs), aryl-tert-butyl side-walled functionalized SWNTs (ATB-SWNT), and dodecyl side-walled functionalized SWNTs (DD-SWNTs) were prepared according to the literature [3-4]. Methods preceded by an asterisk (*) were developed for this thesis. All others were pioneered by the Barron laboratory and included for completeness.

*Reaction of ASA-SWNTs or ATB-SWNTs with FeMoC.* A solution of functionalized-SWNT in CHCl₃ or EtOH was heated to 55 °C while stirring. A 3-fold molar excess of FeMoC (60 mg, 0.003 mmol) was added and the solution reacted at 55 °C for 4 h. The reaction was also carried out with ATB-SWNTs in CHCl₃ at room temperature. A drop of the solution was then spin coated onto a fresh mica surface for AFM characterization at 3,000 rpm for 40 sec.

**DD-SWNT-CO₂-py (1).** 1,3-dicyclohexylcarbodiimide (DCC, 269 mg, 1.30 mmol), 4-hydroxypyridine (126 mg, 1.32 mmol), and 4-dimethylaminopyridine (DMAP, 12 mg, 0.10 mmol) were dissolved in CHCl₃ (10 mL). Piranha etched DD-SWNTs (100 mL, 200 mg L⁻¹) was added to the solution. The reaction was stirred overnight at room temperature. The SWNTs were filtered over a 0.2 μm PTFE membrane and resuspended in CHCl₃ (100 mL).
**DD-SWNT-CO_{2}-py (2).** Isonicotinic acid (40 mg, 0.32 mmol), DCC (67 mg, 0.32 mmol), and DMAP (5 mg, 0.04 mmol) were dissolved in CHCl\textsubscript{3} (10 mL). Piranha etched DD-SWNTs (25 mL, 200 mg.L\textsuperscript{-1}) in CHCl\textsubscript{3} was added to the solution. The reaction was stirred overnight at room temperature. The SWNTs were filtered over a 0.2 \textmu m PTFE membrane and resuspended in CHCl\textsubscript{3} (100 mL).

**DD-SWNT-N-py (3).** Piranha etched purified DD-SWNTs (77.4 mg) were added to DMF (200 mL) and bath sonicated for 5 min. PyBOP (239 mg, 0.46 mmol) was added to the solution followed by DIEA (40 \mu L, 0.23 mmol). After 5 min, 4-aminopyridine was added (200 mg, 2.12 mmol) and the reaction stirred for one hour at room temperature. The SWNTs were filtered over a 0.2 \textmu m PTFE membrane and resuspended in DMF with light bath sonication (3 min). The SWNTs were again filtered over a 0.2 \textmu m PTFE and suspended in CHCl\textsubscript{3} by light bath sonication.

**PVA-PVB/SWNT-N-py (4).** Piranha etched purified SWNTs (77.4 mg) were added to DMF (200 mL) and cup sonicated for 15 min. PyBOP (239 mg, 0.46 mmol) was added to solution followed by DIEA (40 \mu L, 0.23 mmol). After 5 minutes, 4-aminopyridine was added (200 mg, 2.12 mmol) and the reaction stirred for one hour at room temperature. The SWNTs were filtered over a 0.2 \textmu m PTFE membrane, rinsed with acetone, and resuspended in DMF with bath sonication (10 min). The SWNTs were again filtered over a 0.2 \textmu m PTFE and rinsed with acetone. The functionalized SWNTs were added to PVB-PVA (154.6 mg) in EtOH (200 mL) and bath sonicated for 10 min.
**DD-SWNT-SH (5).** DCC (200 mg, 0.97 mmol) and 2-aminoethanethiol (100 mg, 1.3 mmol) were dissolved in dry CHCl₃ (10 mL). The ligand/catalyst mixture was slowly added, with stirring, to Piranha etched DD-SWNTs (20 mg) resuspended in CHCl₃ (80 mL), and the reaction was stirred overnight at room temperature. The SWNTs were filtered over a PTFE membrane (0.2 μm) and dried under vacuum.

**DD-SWNT-PPh₂ (6).** DCC (168 mg, 0.81 mmol), DMAP (5 mg, 0.04 mmol) and 4-hydroxyphenyldiphenylphosphine (132 mg, 0.47 mmol) were dissolved in CHCl₃ (10 mL). The ligand/catalyst mixture was slowly added, with stirring, to piranha etched DD-SWNTs (28 mg) suspended in CHCl₃ (80 mL), and the reaction was stirred overnight at room temperature. The SWNTs were filtered over a 0.2 μm PTFE membrane and dried under vacuum.

**DD-SWNT-C₆H₄Bu⁺ (7).** DCC (420 mg, 2.0 mmol), 4-t-butylphenol (300 mg, 2.0 mmol), and DMAP (14 mg, 0.11 mmol) were dissolved in CHCl₃ (10 mL). Piranha etched DD-SWNTs (22 mg) were added to the solution. The reaction was stirred overnight at room temperature. The SWNTs were filtered over a 0.2 μm PTFE membrane and dried under vacuum.
SWNT-py (8). DCC (269 mg, 1.30 mmol), 4-hydroxypyridine (126 mg, 1.32 mmol), and DMAP (12 mg, 0.10 mmol) were dissolved in CHCl₃ (10 mL). Piranha etched SWNTs (100 mL, 200 mg L⁻¹) in CHCl₃ was added to the solution. The reaction was stirred overnight at room temperature. The SWNTs were filtered over a 0.2 μm PTFE membrane and resuspended in CHCl₃ (100 mL).

SWNT-SH (9). Piranha etched SWNTs (20 mg) were suspended in CHCl₃ (80 mL). DCC (200 mg, 0.97 mmol) and 2-aminoethanethiol (100 mg, 1.3 mmol) were dissolved in dry CHCl₃ (10 mL). The ligand/catalyst mixture was slowly added, with stirring, to the SWNTs, and the reaction was stirred overnight at room temperature. The SWNTs were filtered over a 0.2 μm PTFE membrane and dried under vacuum.

SWNT-PPh₂ (10). Piranha etched SWNTs (28 mg) were suspended in CHCl₃ (80 mL). DCC (168 mg, 0.81 mmol), DMAP (5 mg, 0.04 mmol) and 4-hydroxyphenyldiphenylphosphine (132 mg, 0.47 mmol) were dissolved in dry CHCl₃ (10 mL). The ligand/catalyst mixture was slowly added, with stirring, to the SWNT suspension, and the reaction was stirred overnight at room temperature. The SWNTs were filtered over a 0.2 μm PTFE membrane and dried under vacuum.

US-SWNT-C(O)Cl (11). In a typical reaction, US-SWNTs [5] (100-200 mg) were added to a Schlenk flask under N₂ with SOCl₂ (50 mL) and DMF (2 mL). The reaction mixture was stirred at 60 °C for 48 h under N₂. After decanting off the excess SOCl₂, the SWNTs were washed 3 times with dry CHCl₃ and then dried in vacuo.
US-SWNT-py (12). 4-hydroxypyridine (140 mg, 1.47 mmol) was dissolved in CHCl₃ (~20 mL) and the solution slowly added via cannula to US-SWNT-C(O)Cl (prepared fresh from 80 mg US-SWNTs) dispersed in CHCl₃ (25 mL). The reaction mixture was stirred at 50 °C for 48 h. The SWNTs were then filtered over a 0.2 µm pore PTFE membrane and washed 3 times with dry CHCl₃. Finally the product was dried in vacuo overnight.

US-SWNT-SH (13). 2-aminoethanethiol (130 mg, 1.69 mmol) was dissolved in dry CHCl₃ (~20 mL). The solution was slowly added via cannula to US-SWNT-C(O)Cl (prepared fresh from 80 mg US-SWNTs) dispersed in CHCl₃ (25 mL) and the reaction mixture was stirred at 50 °C for 48 h. The SWNTs were then filtered over a 0.2 µm pore PTFE membrane and washed 3 times with dry CHCl₃. The sample was dried in vacuo overnight.

US-SWNT-P(0)Ph₂ (14). CHCl₃ (25 mL) was added via cannula to the dried US-SWNT-C(O)Cl (prepared fresh from 110 mg US-SWNTs). 4-hydroxyphenyldiphenylphosphine (180 mg, 0.65 mmol) was dissolved in CHCl₃ (30 mL). The ligand solution was slowly added via cannula to the SWNT-C(O)Cl dispersion and the reaction mixture was stirred at 50 °C for 48 h. The SWNTs were then filtered over a 0.2 µm pore PTFE membrane and washed 3 times with dry CHCl₃. The product was dried in vacuo overnight. ³¹P MAS NMR: 20.4 (W₁/₂ = 1990 Hz).
US-SWNT-PPh_2 (15). US-SWNT-P(O)Ph_2 (250 mg), P(OEt)_3 (2 mL, 11.6 mmol) and HSiCl_3 (5 mL, 49.5 mmol) were added to degassed toluene (75 mL) under nitrogen. The reaction mixture was heated with stirring to 100 °C for 24 h. At that time the reaction mixture was allowed to cool and a portion (ca. 0.75 mL) of the supernatant was removed and placed into an NMR tube with C_6D_6 (ca. 0.2 mL). A solution 31P NMR spectrum was collected and the relative peak areas of P(OEt)_3 (δ = 138.7) to O=P(OEt)_3 (δ = -1.4) were determined. The reaction was then resumed with periodic NMR monitoring until there was no more increase in O=P(OEt)_3. The total reaction time was 48 h. MAS 31P NMR: 5.25 (W_1/2 = 1830 Hz).

Results and Discussion

For our SWNT amplification methodology to succeed the catalyst cluster must be able to preferentially dock to the SWNT at cut ends; any other configuration precludes continued growth. To that end we chose to use sidewall functionalized SWNTs in order to prevent sidewall-metal complexation, as well as limit bundling and allow for reactivity in organic solvents such as CHCl_3 [3]. The sidewall substituted SWNTs have carboxylate residues at any open end as a consequence of piranha (H_2SO_4:H_2O_2) etching of the SWNTs prior to functionalization [6]. Given the suitability of carboxylic acids for complexation of FeMoC [7], we investigated the conditions for complexation of FeMoC directly to the ends of sidewall functionalized piranha acid etched SWNTs.

The choice of solvent was found to be important for the reaction of sidewall functionalized SWNTs with FeMoC. DMF is usually an effective solvent for suspending
organic functionalized SWNTs, however, for the iron-based pro-catalysts (including FeMoC) DMF shows good coordination strength and thus competes for binding with the carboxylate groups resulting in no SWNT-FeMoC complexation. In contrast, as a non-coordinating solvent, CHCl₃ did not compete, and it is also a moderately good solvent for the dispersal of organic functionalized SWNTs, e.g., aryl-tert-butyl side-walled functionalized SWNTs (ATB-SWNT, Fig. 3.2 (A)) [4]. Given the ability to disperse arylsulfonic acid side-wall functionalized SWNTs (ASA-SWNT, Fig. 3.2 (B)) in water, this was considered, however, FeMoC compatibility is poor due to decomposition [8].

The FeMoC cluster is stable in both EtOH and MeOH and ASA-SWNTs also show modest solubility in alcohols [4]. We thus examined the feasibility of docking the catalysts to tubes in chloroform, ethanol, and methanol.

Figure 3.2. (A) ATB-SWNT, (B) ASA-SWNT, (C) DD-SWNT
A molar excess of FeMoC was added to the SWNT solution and after 4 hours the
samples analyzed by TEM and AFM. In each case analysis demonstrated the attachment
of the pro-catalyst to the SWNT. The TEM image of ASA-SWNT-FeMoC, in Fig. 3.3,
clearly shows the presence of a 2-3 nm spherical feature on the tip of a single SWNT.
FeMoC has been reported to be 2.1 nm in diameter [9]. In a similar manner, AFM
measurements (Fig. 3.4) show individual ASA-SWNT 0.7-1.0 nm in height, while the
particles on the ends are 2.1-2.4 nm in height, consistent with the attachment of FeMoC
to the ends of the SWNT. It is important to note that FeMoC complexation appears to be
exclusively at the ends of the tubes, and no complexation is observed on the side-walls of
the SWNTs.

![TEM image of a FeMoC pro-catalyst attached to the end of an arylsulfonic acid side-walled functionalized SWNT (ASA-SWNTs) (courtesy of Valerie Moore).](image_url)

**Figure 3.3.** TEM image of a FeMoC pro-catalyst attached to the end of an arylsulfonic acid side-walled functionalized SWNT (ASA-SWNTs) (courtesy of Valerie Moore).
Figure 3.4. AFM image (1.8 × 1.8 µm) of FeMoC pro-catalyst attached to the ends of arylsulfonic acid sidewall functionalized SWNTs (ASA-SWNT-FeMoC).

A docking comparison shows that the reaction proceeds better with heat, and that ASA-SWNTs in EtOH yield results superior to those of ATB-SWNTs in CHCl₃ (Table 3.1). Tubes in MeOH docked similarly to SWNTs in EtOH, although percentages were not determined.
Table 3.1. Percent docking of FeMoC pro-catalyst to carboxylate termini of sidewall functionalized SWNTs.$^a$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp. (°C)</th>
<th>Solvent</th>
<th>SWNT-FeMoC (%)</th>
<th>SWNT-(FeMoC)₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATB-SWNTs</td>
<td>25</td>
<td>CHCl₃</td>
<td>13</td>
<td>0</td>
</tr>
<tr>
<td>ATB-SWNTs</td>
<td>55</td>
<td>CHCl₃</td>
<td>50</td>
<td>6</td>
</tr>
<tr>
<td>ASA-SWNTs</td>
<td>55</td>
<td>EtOH</td>
<td>83</td>
<td>20</td>
</tr>
</tbody>
</table>

$^a$ One hundred tubes were analyzed per sample.

This demonstrates that the linkage of a pro-catalyst to a sidewall functionalized SWNT is dependent on both the conditions of the reaction and the sidewall functional groups/solvent. However, the limiting factor may be the formation of carboxylate terminated SWNTs, i.e., the retention of a fraction of closed SWNTs in the sample. It should be noted that for both ATB-SWNTs and ASA-SWNTs there are tubes with FeMoC on both ends as well as on a single end. We presume that the yield, relative yield, and mono-di substitution ratio are functions of the presence of open or accessible ends. Given that the functionalized SWNTs were prepared from similarly etched samples the greater number of FeMoC complexed with ASA-SWNTs (as compared with ATB-SWNTs) may be due to the greater availability of suitable carboxylate functional groups after the sidewall reaction.
Alternative Linkage Groups for the Complexation of Pro-catalysts

Carboxylate groups (and other oxygen donor ligands) may not necessarily be the best donor ligands for metal catalysts. We next investigated SWNT end functionalization with donor ligands using amidation reactions. Coupling reactions are simpler in CHCl₃ than in alcohols because of difficulty excluding water; therefore dodecyl side-walled functionalized SWNTs (DD-SWNTs, Fig. 3.2 (C)) were used rather than ASA-SWNTs or ATB-SWNTs. The sidewall functionalized SWNTs have been compared to similar pristine-sidewall samples where certain forms of analysis are simplified by the absence of a high fraction of organic residues.

With FeMoC and iron carboxylate trimers in mind as growth catalysts, our initial studies focused on pyridine ligands. Etched DD-SWNTs were reacted with 4-hydroxypyridine in the presence of DCC/DMAP catalyst to yield DD-SWNT-py (1). There has been speculation that after sidewall alkylation there may be more hydroxyl groups than carboxyl groups at the SWNT ends. So, in addition to 4-hydroxypyridine, we also coupled isonicotinic acid with dodecylated SWNTs.

In order to demonstrate that non-covalent sidewall solubilization could be employed in combination with end functionalization and to avoid any potential poisoning of the catalyst by sulfonic acid side groups, piranha etched SWNTs were reacted with 4-aminopyridine with the PyBOP/DIEA catalyst in DMF. The resulting insoluble SWNT-N-py was then solubilized in methanol or ethanol by wrapping with polyvinyl alcohol/polyvinyl butyral copolymer (PVA-PVB) via cuphorn sonication to yield PVA-PVB/SWNT-N-py (4). A portion of this was centrifuged for 10 minutes at 12,000 rpm and analyzed by fluorescence and UV-vis absorbance. Fluorescence of PVB-PVA-PVA
wrapped nanotubes in methanol suggests some SWNTs are individuals (Figure 3.5(A)) while broadening of the structure in the E_{11} region of the UV-vis absorbance spectrum suggests the majority are bundles (Figure 3.5(B)) [10].

Figure 3.5. (A) Fluorescence of polymer wrapped nanotubes at 660 nm excitation (red) and 785 nm excitation (purple) in methanol (B) UV-vis of the same.

AFM shows small bundles or individuals wrapped in polymer. The solution was stable in ethanol and methol at concentrations in excess of 100mg/L.
Figure 3.6. (A) PVB-PVA coated FeMoC pyridine docked SWNT bundles on HOPG. (B) Pyridine attached FeMoC SWNT in methanol.

We have shown that ligand exchange offers a route to covalent attachment of a metal pro-catalyst such as FeMoC to the end of a SWNT-ligand via suitable pyridine or carboxylic acid end functional groups. We have also shown that functionalized SWNTs react more readily at 55 °C then room temperature with FeMoC and the resultant conjugates may be characterized by AFM. We have further shown that SWNT-procatalyst conjugates can be non-covalently solubilized as small bundles in methanol and ethanol.


Chapter 4: Surface Docking of Carbon Nanotubes

In the previous chapter we detailed the formation of SWNT-catalyst complexes by altering the ends of SWNTs and optimizing conjugation conditions. In this chapter, we examine how to remove the nanotube functional linkers to chemically dock the catalyst to the nanotube carbon. This allows for carbon addition to the template nanotube during CVD synthesis.

HiPco SWNTs were purified via oxidation and the addition of SF$_6$ at 600 °C followed by refluxing in hydrochloric acid [1]. The SWNTs were piranha treated for 4 h at room temperature in a 4:1 sulfuric to hydrogen peroxide room temperature solution. This treatment etches the ends of the tubes but does not cause sidewall damage, leaving open ends capped with hydroxyl groups and carboxylic acid groups [2]. The Billups functionalization method [3] was used to sidewall functionalize the SWNTs with aryl sulfonic acid groups so they could be suspended in ethanol. By heating a 1:1 stoichiometric ratio of SWNTs and FeMoC in ethanol at 55 °C, we complexed the carboxylic acid groups at the end of the SWNTs to the metal catalyst particle. Docking conditions were repeated for Fe$_3$O(O$_2$CCH$_3$)$_6$(EtOH)$_3$ iron triangles [4].

The ethanol suspended SWNT catalyst complex (SWNTcat) was electrodeposited (Fig. 4.1) on highly ordered pyrolytic graphite (HOPG). HOPG was chosen due to its relatively low interaction with deposited material.
Figure 4.1. Schematic of Ronco Deposition Apparatus

Because AFM does not have the lateral sensitivity to determine if the metal particle is bonded directly to a SWNT carbon atom, it was necessary to observe controlled etching of the nanotube – the SWNT visibly decrease in length. For the SWNT to decrease in length, the metal particles must be mobile on the surface. On HOPG, FeMoC clusters heated in argon to over 500 °C immediately migrate to the step edges and etch into the step edges when exposed to hydrogen. The SWNTcats on HOPG were heated to 500 °C under argon in a standard 1-in. quartz tube furnace to remove the functional groups. The argon prevents the vaporizing functional groups from increasing the SWNTcat mobility, allowing them to rope up on the HOPG step edge. The SWNTcats on HOPG were then pre-imaged by AFM in preparation for controlled docking.

Controlled reductive docking was observed by a shortening of an individual nanotube by at least 50 nm. The controlled reductive docking was performed in two separate systems – a standard one-inch quartz tube furnace and a cold wall button heater chamber (Fig. 4.2). These two systems were chosen as they represent two different
experimental setups – etching with a hot substrate and hot gas and etching with a hot substrate and room temperature gas.

Figure 4.2. Schematic of (A) tube furnace and (B) button heater

We etched the SWNTcats completely away on HOPG using 760 torr Hydrogen at 500 °C for 60 min in the tube furnace (Fig. 4.3). SWNTcat on sapphire and silicon oxide exposed to similar conditions were not visibly affected due to the strong particle-surface and SWNT-surface interactions.
Figure 4.3. SWNT cats etched away on HOPG (tube furnace, 760 torr H₂, 500 °C, 60 min)

We observed controlled reductive docking in both systems (Fig. 4.4 a,b), although the button heater etched more slowly at the same temperature and pressure (Table 1). At atmospheric pressure, this difference was not observed, most likely due to the high thermal conductivity of hydrogen. Interestingly, not all SWNTs etched at the same rate, possibly due to differences in stability of arm chair, zig zig, and chiral edges or differences in stability due to SWNT diameter. This is especially fascinating, as it may explain why the continued growth group was not able to create smooth top by different methods of chemically etching SWNT fibers.
Figure 4.4. (A) Pre and post images of controlled reductive docking on HOPG. SWNTs exposed to 100 torr of hydrogen at 700 for 20 min in the cold wall button heater apparatus. (B) Series of reductive docking steps taken with SWNTs exposed to 760 torr H₂ at 600 °C for 5 min between steps (courtesy of Sean Pheasant).
Table 4.1 Hydrogen reductive docking conditions. Note that the same conditions were explored in both systems.

<table>
<thead>
<tr>
<th>Pressure (torr)</th>
<th>Time (min)</th>
<th>Temperature (°C)</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube Furnace</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>700</td>
<td>controlled reductive docking</td>
</tr>
<tr>
<td>100</td>
<td>20</td>
<td>700</td>
<td>no tubes remain</td>
</tr>
<tr>
<td>760</td>
<td>5</td>
<td>600</td>
<td>controlled reductive docking</td>
</tr>
<tr>
<td>Button Heater</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>700</td>
<td>no change</td>
</tr>
<tr>
<td>100</td>
<td>20</td>
<td>700</td>
<td>controlled reductive docking</td>
</tr>
<tr>
<td>760</td>
<td>5</td>
<td>600</td>
<td>controlled reductive docking</td>
</tr>
</tbody>
</table>

Attempts at growth were not nearly as successful – whether this was due to improper catalyst attachment, improper growth conditions, or carbide formation due to the HOPG substrate is not clear. We did see two possible examples of seeded growth, detailed below.

**Example 1**

**Method**

Purified HiPco SWNTs were piranha treated and functionalized using the lithium ammonia process with dodecyl groups. The dodecylated tubes were suspended in DMF, DCC coupled to a pyridine linker, and attached with 3-4 nm Fe₃O₄ particles. An AFM image of a particle with an unusually small diameter of 1.8 nm is shown in Fig. 4.5(a). The smaller diameter almost certainly increases the odds of growth as the size of the
catalyst is better matched to that of the tube. After deposition and argon pinning, the tubes were imaged by AFM (Fig. 4.5(a)). The sample was mounted on the button heater and heated to 800 °C at $1 \times 10^{-5}$ Torr where 100 mTorr of C$_2$H$_4$ was added to the system for 10 minutes. The sample was re-evacuated, cooled, and the sample reimaged (Fig. 4.5(b)).

![Image](image.png)

**Figure 4.5.** (A) Before and (B) after images of growth (courtesy of Valerie Moore).

It appears that the tube increased in length by 70 nm. Analysis down the length of the tube suggests that it maintained a constant diameter of 0.6 nm while the catalyst particle decreased in size from 1.8 nm to 1.0 nm due to removal of the catalyst ligands. This diameter consistency points to seeded growth. An alternative explanation proposed is that the shadow below the step edge in the left image is a poorly imaged portion of tube
which shifted up during imaging or growth experiments. This seems unlikely on a number of grounds. First, the tube would need to slide exactly on the angle over a step edge. Since nanotubes tend to align with the step edge, this seems unlikely. An AFM tip images across the surface and hence should cause the tube to move or buckle horizontally. If the tube was mobile during the heating stages, it would more likely pivot to align with the step edge than shift up. Also, the location of the catalyst particle appears to have remained constant. The tube-shifting theory thus requires that the catalyst particle dock to the middle of the tube and migrate to the end of the tube as the tube migrates up. Although possible, the most obvious interpretation is seeded growth.

**Example 2**

**Method**

Purified piranha-treated SWNTs in chloroform were docked to iron nitrate (Fig. 4.6(a)). After deposition on HOPG, the sample was heated to 800 °C at $1 \times 10^{-5}$ Torr where an atmosphere of 1:9 H$_2$:C$_2$H$_4$ was isothermally flowed for 10 minutes. The sample was re-evacuated, cooled, and the sample reimaged (Fig. 4.6(b)).
Fig. 4.6 appears to depict individual growth off of a bundle. A proposed mechanism is a catalyst particle suspended in air allowed growth off the bundle before the tube bent down and touch the HOPG surface where interaction caused cessation of growth. Unfortunately, because the SWNTs are in bundles, it is impossible to show that the diameter did not change. Because of this, we can not prove that this is seeded growth and not newly nucleated growth, however in hundreds of the growth attempts most with excess catalyst, not once did we observe clearly nucleated growth on HOPG. This differs from what is observed on oxide surfaces and suggests that tubes may not nucleate on HOPG. Due to the similarity in structure, nucleation may not occur on the sidewalls of nanotubes either, suggesting that the observed growth is seeded growth.

In this chapter, we have show that reductive docking of a catalyst particle to SWNTs is possible under a variety of reducing conditions. The flexibility of temperatures, pressures, and gasses where we observed docking suggests it is possible to
tailor this step to various implementations of the Smalley seeded growth model. We were unable to show chirality controlled growth on an HOPG surface, although we found two cases that suggest it may occur.


Introduction

The last few chapters explained the basic principle of chiral specific synthesis of SWNTs by seeded growth. We developed methods to synthesize SWNTcat seeds by adding a functional linker to a nanotube and attaching a catalyst to the functional linker. We showed that we can remove the functional linker by controlled etching of the ends of the SWNTs with H2. Growth of these SWNTcats was rare and length increase was slight, possibly due to surface interaction. Since seeded growth depends on hundred fold increases in SWNT length, we sought to develop a system that would allow SWNTs exhibit this increase in length by minimizing friction and other interactions that may hinder growth on a surface. These next chapters explore "snag and drag" chiral specific growth. In this chapter, we first give an overview of the design of the system. We next explain the materials and apparatus built. Finally, we give an overview of the technological advances needed to explore chiral specific growth via snag and drag.

The driving consideration in the design the snag and drag system was the isolation of the ends of the SWNTs to allow the metal to catalyze growth indefinitely. To do this, we needed to design framework of SWNTcats with the ends free and a system of growth that would keep the growth aligned, preventing growing SWNTs from interacting and inhibiting further growth. In addition to allowing enhanced growth, this alignment also prepares the SWNTs to be used in a variety of applications. We considered alignment both electrically and from the gas flow. SWNTs grown by arc discharge are aligned due to the bias inherent in the system [1]. Jie Liu has shown that tubes grown by kite growth
out from a surface are aligned with the gas flow [2]. We sought to take advantage of these findings to design a system which would put the tubes under a voltage bias and allow the tubes to grow out from the surface free from each other where they could be picked up in the flow of the growth gas.

We designed a system employing a carbon fiber grid to create the field. The small diameter of the carbon fiber grid (7 μm) enables a large field to be produced around these fibers, providing a force to align the SWNTs growing off from the carbon fiber during growth. The spaces between the carbon fibers allow the gas to flow through the grid, picking up the SWNTs when they reach the boundary layer of the gas and working in tandem with the field to produce aligned growth between the growth grid, and the back grid. We considered depositing the SWNTcats on the carbon fibers a variety of ways, including dip coating and electrodeposition in liquids, however, we concentrated our efforts primarily on producing individuals or small bundles of SWNTs in the gas phase and electrostatically collecting them on the grid using an electric field.

**Apparatus**

The system consisted of a 2-inch horizontal tube furnace and gas introduction system (Fig. 5.1). The furnace is connected to a Welch Chemstar 1376 rough pump and turbo pump to allow the furnace to be purged before SWNT deposition or growth. UHP gasses were connected to the furnace using copper tubing and swagelock fittings to minimize introduction of oxygen and other impurities. An injector (either a TSI atomizer or electrospray) was connected to one end to inject the SWNTcat for deposition on the grid.
Figure 5.1. Schematic of horizontal ("snag and drag") reactor.

The tube has an inner diameter of 1.8 in (4.57 cm) and length of 40 in (101.6 cm). From this we calculated the tube volume and replacements per minute based on the gas flow (Table 5.1).

Table 5.1. Tube volume replacement per minute for typical gas flow.

<table>
<thead>
<tr>
<th>Flow (lpm)</th>
<th>Gas velocity (cm/s)</th>
<th>Tube volume replacements per min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.02</td>
<td>0.6</td>
</tr>
<tr>
<td>2</td>
<td>2.03</td>
<td>1.2</td>
</tr>
<tr>
<td>3</td>
<td>3.05</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Fig. 5.2 shows a close-up of the grid arrangement. The grid arrangement was designed to bias the sample relative to the back exit grid. A front grid was used in most runs to help stabilize the electric field.
Figure 5.2. Grid arrangement. Grids consist of carbon fibers suspended in a graphite holder.

The exit grid (Fig. 5.3A) and the sample grid (Fig. 5.3B) are pictured below.

Figure 5.3A

Figure 5.3B

Figure 3.8. Pictures of (A) exit grid and (B) sample grid.

The grids are formed by 7 μm carbon fibers held between two parts of a graphite holder (Fig. 5.4). Graphite rods run through quartz sheaves and connect the center grid to a power source. Quartz washers hold the grids at a constant distance of .08 in apart (~ 2 mm).
Process Overview

In snag and drag, SWNTs are aersolized by forming small droplets of liquid with a low concentration of SWNTs suspended. As the droplets are dried in the gas flow, the SWNTs contact each other. If the droplet is dried quickly enough, the SWNTs do not have enough time to align before they are in contact with each other. The result is SWNTs attached to one another at one point forming a thistle-like structure with SWNT ends exposed out from the contact point. This thistle is deposited on the surface allowing only a few of the nanotube ends to touch the grid leaving the remainder free to growth. A model of the entire process of thistle deposition and growth is outlined below (Fig. 5.5).
In step one SWNTcat is atomized into the carrier gas where quick drying action causes thistle formation. This thistle is carried down the quartz tube until it deposits on the substrate, here pictured as a grid fiber. This is the “snag”. The SWNTcat forming the thistle are next hydrogen activated and exposed to growth conditions. During activation and growth, the grid is biased setting up an electric field that causes the SWNTcat to grow out from the fiber until the elongated SWNTs are caught in the boundary layer of the gas flow. This causes the nanotubes to wrap back where they continue to grow until they make contact with the exit grid. This wrap and grow is called the “drag”. The wrapped SWNTs are kept aligned by the flow gas and field, and should be less likely to stop growing. The SWNTs are also aligned, making it easier to form an aligned fiber.

The electric field around the fibers creates a negative image charge on the thistles which are then attracted to the positively charged grid fibers. Since smaller diameter cylinders produce higher electric fields, small diameter fibers work best. As the thistle attaches to the grid, it becomes biased. Since a nanotube has such a small diameter, the
bias sets up a large electric field around the SWNT. The deposited thistle attracts other thistles forming the observed open structures (Fig. 5.6).

Figure 5.6. Schematic of thistle lattice formation.

In the next few chapters we outline our progress on the snag and drag model of seeded growth. We separate out on the two components of snag and drag – first concentration on producing and snagging thistles, and then concentrating on growing long SWNTs in yarns out from the grid fibers. In chapter 7 we explain how we injected individuals and small bundles into the gas phase. In the process, we highlight importance of this work respiratory toxicity studies of SWNTs. In chapter 8 we show the self-assembly of the SWNTs into open structures on the carbon fibers and give an overview of uses for a SWNT-carbon fiber electrode. In chapter 9 we examine the drag portion. We show how we nucleated SWNTs in the gas phase, collected them on the carbon fiber grid, and grew SWNTs across the gap between the sample and exit grids.

Chapter 6: Nebulization of Single-Walled Carbon Nanotubes

In this chapter, we show how we aerosolize carbon nanotubes to form our nanotube thistles. Although a minor step in our work to chirally amplify carbon nanotubes, we believe as a technique it could facilitate a significant breakthrough in how the respiratory toxicology of carbon nanotubes is studies. Because of this, we have chosen to shape this chapter around that theme.

As research on the use of single walled carbon nanotubes (SWNTs) in composites, chemical sensors, and nanoelectronic components progresses, the respiratory toxicity of SWNTs is rapidly becoming a safety concern in the manufacturing of SWNT-based materials. Current literature on the respiratory toxicity of nanotubes is inconclusive [1-5], as the apparent respiratory effects of SWNTs range from mild to severe in different studies. To date, no studies of SWNT inhalation from air have been reported, in large part due to the difficulty of producing ultrafine particles of airborne SWNTs [6]. However, inhalation of airborne SWNTs most closely resembles natural exposure, and hence is critical for resolving the respiratory toxicity of nanotubes.

Here we report a method to produce airborne ultrafine particles of functionalized and unfunctionalized SWNTs for use in toxicity studies. To date, no studies have been done on the pulmonary toxicity of functionalized SWNTs, despite research that suggests it may vary from that of unfunctionalized SWNTs [7]. Additionally, there are no reported comparisons between the respiratory toxicity of SWNTs and that of SWNT-metal conjugates, although the metal at the end of unpurified SWNTs may be a significant cause of toxicity [8]. We also produce ultrafine particles of SWNT-nanoparticle conjugates, allowing a comparative study of SWNT and SWNT-metal complex
toxicology. We anticipate that our techniques will enable these areas to be more carefully explored.

HiPco SWNTs were purified [9] and etched using a room temperature piranha solution [10]. Our procedure consisted of suspending purified SWNTs (100 mg) in concentrated sulfuric acid solution (100 mL) by stirring for 1 h. Hydrogen peroxide (25 mL) was then slowly added to the ice bath cooled solution to generate a 4:1 sulfuric acid to hydrogen peroxide piranha solution. The ice bath was removed and the solution left to react for 4 h at room temperature. This process opens the ends of SWNTs and leaves them capped with a mixture of hydroxyl and carboxylic acid groups without inducing sidewall damage.

The piranha-treated SWNTs were sidewall functionalized with aryl sulfonic acid groups using a Birch functionalization [11]. Briefly, 40 mg of piranha treated purified SWNTs were placed in a flame dried container and 60 mL of ammonia was condensed into the flask. Small pieces of sodium were added to flask, followed by 2.7 g of 1-iodobenzene. The reaction was stirred for 24 h under argon, allowing the ammonia to evaporate. The flask was cooled on ice and 10 mL of methanol and 20 mL water were added. The SWNTs were acidified with HCl and extracted into hexanes, filtered through a 0.2-μm PTFE membrane filter and washed with ethanol and chloroform. After drying, the phenylated SWNTs were dispersed in 20 mL of oleum. The mixture was heated to 80 °C under argon for 4 h to sulfonate the phenyl groups on the SWNT sidewall. The suspension was then poured into 100 mL of ice water and filtered through a 0.22-μm polycarbonate membrane.

We prepared both water and methanol suspensions of the aryl sulfonated SWNTs by bath sonication. Atomic force microscopy (AFM) analysis of the solutions suggested
that the average SWNT length was around 400 nm. SWNT-nanoparticle complexes were formed by stirring together SWNTs and 4-nm iron oxide nanoparticles at a 1:1 ratio in methanol for 4 h at 55 °C [12].

The water and methanol suspensions were diluted to 9 mg/L, and nebulized using a TSI-3076 constant output atomizer (Fig. 6.1) in recirculation mode [13]. The standard nebulizing airflow of condensed air was replaced with nitrogen. Nebulization occurred when the nitrogen coalesced into a high velocity jet that intersected the SWNT solution drawn up through the vertical passage of the atomizer. Fine spray left the atomizer through the top while large droplets collided with the wall opposite the jet and drained back into the bottle. We also attempted TSI-3480 electrospray in positive, negative, and neutral modes in water, but did not find this approach effective in depositing SWNTs on a biased silicon plate placed at the opening of the electrospray apparatus. Inspection of the electrospray tip revealed that the SWNTs collected at the opening of the electrospray nozzle.
Nebulizing nitrogen flow

Aerosol dryer

Mica plate

SWNT/methanol solution

Figure 6.1. Diagram of nebulization of SWNTs onto mica plate.

In our procedure, we used methanol instead of water due to the lower surface tension of methanol corresponding to smaller droplet size and faster drying. The TSI impact atomizer produces droplets in water that vary in diameter between 0.02 to 2.3 μm with most between 0.02 and 0.3 μm. Hence, while the 2.3-μm droplets may contain \( 6 \times 10^4 \) SWNTs, most droplets should contain 1 to 130 SWNTs.

To insure that we atomized SWNTs in an individual or bundled state, we analyzed the material deposited from the atomizer flow. Methanol dispersed SWNT-nanoparticle conjugates were bath sonicated for 5 min and loaded into the atomizer bottle. The solution was nebulized onto a mica plate held at the end of a copper tube (Fig. 6.1) for 30 min using a 1.5 lpm nitrogen flow. The mica was imaged by AFM while avoiding aggregates of SWNTs visible by optical microscopy. AFM images of the mica show the surface to be littered with individual functionalized SWNT and small bundles (Fig. 6.2)
suggesting that the nitrogen carrier gas contains ultrafine SWNCT particulate including a significant number of individuals and small bundles. Attachment of the nebulizer to an exposure chamber [14] would allow the area to be filled with airborne SWNTs.

Figure 6.2. AFM height data of SWNTs nebulized onto mica plate.

Defunctionalization of SWNTs by heating is well documented in literature, and Raman analysis (Renishaw micro-Raman System 1000, 780-nm diode laser) of tubes electrostatically collected\(^1\) in a 500 °C tube furnace reveals a small disorder mode, suggesting that most functional groups have been removed (Fig. 6.3). The D/G ratio of the integrated peaks shown in Fig. 3 is approximately 1/4, while that of Birch functionalized tubes (not shown) is close to 1 [15].

\(^1\) McJilton, internal report
Collectively, our work shows that functionalized SWNTs and functionalized SWNCT-metal complexes can be dispersed as airborne particles by nebulization from suspension in methanol. Furthermore, these particles can be defunctionalized by heating. Our approach can be easily applied to pulmonary toxicity studies, allowing SWNTs to be realistically administered to biological specimens by inhalation.


Chapter 7: Self-Assembled SWNT Thistles on Carbon Fibers

Introduction

In the previous chapter we showed how we aerosolized SWNTs to produce individuals and small bundles of SWNTs in the gas phase and explained how this technique could facilitate toxicology studies on carbon nanotubes and carbon nanotube – metal composites. Here we show how these airborne SWNTs are electrostatically collected onto a carbon fiber grid to form a carbon fiber / carbon nanotube structure. Although we formed these structures due to their suitability as a growth substrate for seeded growth of nanotubes, they have great potential for a number of other applications including reinforced composites, thermal sinks, microelectrodes, chemical sensing, and scaffolds for photoelectrochemical solar cells.

Methods

HiPco SWNTs were purified [9] and etched using a room temperature piranha solution [10]. Aryl sulfonic acid functionalized SWNTs (ASA-SWNTs), according to the literature.. SWNT-nanoparticle complexes were formed by stirring together SWNTs and 4-nm iron oxide nanoparticles at a 1:1 ratio in methanol for 4 h at 55 °C [12] (cf 3). The methanol suspensions were diluted to 9 mg/L, and nebulized into the horizontal reactor (cf 5) using a TSI-3076 constant output atomizer in recirculation mode with a nitrogen carrier gas at a flow rate of 1.5 lpm (cf. 6). During nebulization, the SWNTcat solution was bath sonicated to keep the solution well suspended. We also attempted thistle production out of water, but were unable to produce open structures.
Inside the horizontal reactor, we biased a collection grid at +100V to the exit grid. An entrance grid was included in most runs to help stabilize the field. We held the horizontal reactor at 500 °C during the collection period of 30 min. Although the grid was usually biased at +100V, individual runs were done with the grid biased at -100V and 0V.

Discussion

Biasing the grid either positive or negative allowed up to produce open lacy thistle structure on the carbon grid with thistles extending radially out from the carbon fibers. At no bias, we did not get any noticeable deposition, strongly suggesting that the SWNTs are electrodeposited. That deposition occurs with either positive or negative bias suggests that the SWNTs are able to pick up either image charge due to their complex electronic structure.

We believe that the electric field around the fibers creates a positive or negative image charge on the thistles which are then attracted to the oppositely charged grid fibers. Since smaller diameter cylinders produce higher electric fields, small diameter fibers work best. As the thistle attaches to the grid, it becomes biased. Since a nanotube has such a small diameter, the bias sets up a large electric field around the SWNT. The deposited thistle attracts other thistles forming the observed open structures (Fig. 7.1).
Figure 7.1. A) SEM image of a carbon fiber B) Schematic of thistle lattice formation.
A Raman analysis of the thistles shows signatures that match raw HiPco SWNTs (Fig. 7.4) although with an enhanced disorder mode, possibly due in part to the signature of the bare carbon fiber (Fig. 7.5).
Figure 7.4. Raman (514 cm\(^{-1}\) excitation) of thistles in three locations and of raw HiPco.

Figure 7.5. Raman of bare carbon fiber.

We also deposited thistles on nanotube fibers (Fig. 7.6). The thistles did not appear to collect as well on the SWNT fibers as the carbon fibers, possibly due to the larger radius of the fiber and corresponding lower electric field. These structures could be useful in thermal
management applications if the density of thistles could be raise by lowering the diameter of the SWNT fiber [1].

Figure 7.6. (A)-(C) SWNT thistles deposited on SWNT fibers.

During the course of our work, we also produced nanorings of SWNTs by adding a small amount of water to the methanol suspended SWNTs. A number of groups have reported the formation of these structures, and from the evaporation of solvents on a surface [2]. When we added 3% water to our 9 mg/L solution of SWNTs in methanol, we formed nanorings instead of thistles (Fig. 7.7). We believe this is due to the tendency of the alcohol component of the droplet to principally evaporate first [3-4] leaving a much smaller droplet of water behind. The high surface tension water would most likely then cause the SWNTs to curl and line up around the edge of the droplets where van der Waals force between the SWNTs would keep the rings together after evaporation of the water. This method of ring formation is unique in that it could be used to deposit nanotube rings in any location since the rings are formed in the gas phase.
Figure 7.7. A-B Nanotoriods formed by nebulizing 3% water in methanol solution containing 9mg/L SWNT.
Thistle deposited on carbon fibers should form a useful substrate for seeded growth. The SWNTs start in an open structure and the high electric field around the SWNTs should repel surrounding similarly biased SWNTs preventing death from roping. As the SWNTs are repelled from each other and attracted to the back plane, it should theoretically cause aligned SWNT growth, forming an aligned SWNT fiber.

Thistles deposited on carbon fibers have potential for other applications. The lacy structure affords a high surface area structure of SWNTs which could have uses in chemical detection. Electrodeposition or electrochemical templating of metal or deposition of a thin film of other material on the thistles could make them a substrate for catalytic reactions and sensors [5-6]. Others have shown that nanotubes used to graft carbon fibers into composites result in reinforcement [7]. Recently, researchers have shown that SWNT filters have antimicrobial properties [8]. Others have looked at using them to absorb organics and toxins in water [9-10]. Due to the open structure, thistles could be useful for these applications as well as biased for electrostatic filter.

One interesting point about our thistles – what we have done indirectly is to synthesize a carbon fiber/ SWNT nano-electrode. Carbon fiber nanoelectrodes modified by single-walled carbon nanotubes have shown an increased sensitivity in the detection and electrochemical behavior of neurotransmitters [11-12], in part due to the larger surface area. Due to the lacy nature of our SWNT thistles, thistle coated carbon fibers may perform better than the carbon fiber electrode wrapped in SWNT sheets currently under investigation for the study of brain chemistry [11].

Work done by Kamat suggests that SWNTs can be used as a scaffold on carbon fiber electrodes to double the efficiency of light - harvesting titanium dioxide nanoparticles by facilitating charge collection and transfer to the electrode. Interestingly, when the titanium
dioxide loading was too high, the photocurrent went down, an effect the authors suggested was due to much of the titanium dioxide not in direct contact with the SWNTs. Because most of the SWNTs deposited on the carbon fiber electrode in this study appear to be bundles, the use of thistles could increase the efficiency of these structures [13].
Figure 7.8. (A) Electron transport with and without SWNTs. (B) Photocurrent response as a function of TiO$_2$ loading. (C) SEM of SWNT modified carbon fiber electrode with TiO$_2$. (D) SWNT-CF thistle. (A-C from [13]).
To summarize, we have shown that aerosolized SWNTs can be electrostatically collected on carbon fibers to form open structures radiating out from the carbon fiber base. This radial structure is probably due to the high electric field around the tips of the deposited SWNTs. These structures show the same Raman signature as HiPco nanotubes. We deposited thistles on SWNT fibers and showed that adding 3% water causes the formation of SWNT nanorings. These structures should allow growth off the tips by holding the catalyst-docked end free and electrically repelling other growing nanotubes, allowing for long, aligned growth.


[12] Shelly

Chapter 8: Electrostatic Collection and Growth of Single-Walled Carbon Nanotubes

Introduction

In the previous chapters we showed that we can aerosolize nanotubes into ultrafine particles of individuals and thistles into the gas phase and electrostatically deposit them into open structures on carbon fibers. Taken together, this composes that “snag” portion of the “snag and drag” system. In this chapter, we present our work to test the “drag” portion of the “snag and drag” system by electrostatically collecting nanotubes nucleated in the gas phase and continuing growth between the sample and exit grids. We looked at growth of tubes from ferrocene leached from an iron tank with CO feedstock.

Hot Zone CO growth

Methods

The grid arrangement was installed in the hot zone and a CO scrubber on the CO inlet set to 505 °C. The sample grid was biased at +100 V relative to the exit grid. The furnace was heated to 900 °C. During the temperature ramp, the furnace was pumped to 300 °C. A 2 lpm Ar flow was introduced and allowed to purge the system for 7 minutes. Ar flow was increased to 4.9 lpm and a 0.1 lpm H₂ flow introduced to mimic hydrogen etching for seeded growth. After 11 min., the temperature was 900 °C and CO was introduced at 1 lpm, H₂ increase to 0.429 lpm, and Ar flow stopped. After 30 min., CO and H₂ flows were stopped and the furnace cooled in a 1 lpm Ar flow.
Discussion

SEM of the carbon fiber grid after growth conditions revealed long yarns of single walled carbon nanotubes. (Fig. 8.1 – 8.2) It appears that the electric field helped form these long strands of nanotubes. Raman of the grown yarn shows signatures similar to those of HiPco SWNTs (Fig. 8.3). The low disorder mode suggests that the growth is reasonably clean with low defect density.

Figure 8.1. SEM showing large amounts of nanotube yarn between carbon fibers.
Figure 8.2. SEM images of nanotube yarn on carbon fiber grid.
Cold zone CO growth

To show the SWNTs continued to grow in the furnace rather than forming long ropes of short tubes, we placed the grid setup outside of hot zone of the furnace. SWNTs nucleate in the gas phase, grow while flowing through the tube furnace, stop growth after exiting the furnace, and are then electrostatically collected onto the sample grid.
Methods

The grid arrangement was installed in the cold zone and a CO scrubber on the CO inlet set to 505 °C. The sample grid was biased at +100 V relative to the exit grid. The furnace was heated to 900 °C. During the temperature ramp, the furnace was pumped to 300 °C. A 2 lpm Ar flow was introduced and allowed to purge the system for 7 minutes. Ar flow was increased to 4.9 lpm and a 0.1 lpm H₂ flow introduced to mimic hydrogen etching for seeded growth. After 11 min., the temperature was 900 °C and UHP CO was introduced at 1 lpm, H₂ increase to 0.429 lpm, and Ar flow stopped. After 30 min., UHP CO and H₂ flows were stopped and the furnace cooled in a 1 lpm Ar flow.
Discussion

SEM images of the grid show nanotubes collected on the biased center grid. (Fig. 8.4)

Figure 8.4. SEM of SWNTs collected in the cold zone of the furnace.
The morphology of the SWNT growth is clearly different, leading us to believe that the nanotubes nucleated in the gas phase continued to grow into long yarns after collection on the carbon fiber grids when the grids remained in the hot zone of the furnace.

**UHP nucleation and semiconductor growth**

We next nucleated and deposited SWNTs with UHP CO and then switched to semiconductor grade CO in an aluminum cylinder. This allows us to nucleate tubes with the UHP CO and continue growth with the semiconductor grade. A growth run using only semiconductor grade CO produced no SWNTs due to the lack of iron pentacarbonyl as catalyst.

**Methods**

The grid arrangement was installed in the hot zone and a CO scrubber on the CO inlet set to 505 °C. The sample grid was biased at +100 V relative to the exit grid. The furnace was heated to 900 °C. During the temperature ramp, the furnace was pumped to $2 \times 10^{-4}$ Torr (7 minutes). At 300 °C, 2 lpm Ar flow was introduced and allowed to purge the system during the temperature ramp to 900 °C (14 min.). UHP CO was introduced at 1 lpm, $H_2$ at 0.429 lpm, and Ar flow stopped. After 30 minutes, UHP CO and $H_2$ flows were stopped and the furnace purged with Ar at 1.5 lpm for 2 minutes. Semiconductor CO and $H_2$ gas were introduced at 1 lpm and 0.429 lpm respectively and Ar flow stopped. After 30 min., CO and $H_2$ flows were stopped and the furnace cooled in a 1 lpm Ar flow. Current between the sample and exit grid was monitored.
Discussion

During growth, the current consistently rose, suggesting that nanotubes were growing between the sample and exit grid. Inspection of the grid arrangement after removal reveals black strings connecting the sample and exit grid. SEM images of the sample grid reveal large amounts of long yarn, some of which appears to have been broken when we separated the sample and exit grid (Fig. 8.5). SEM analysis of the exit grid also revealed yarn (not shown). Graphing the current evolution during growth (Fig. 8.6) suggests two different types of growth from the UHP CO and the semiconductor grade CO.
Figure 8.5: Yarn grown from UHP CO followed by semiconductor grade CO.
The graph of current vs. time reveals some interesting things about our growth. The nanotubes are growing between the entrance and exit grid and producing the current. When CO gas is not present, the current does not rise. The current increases differently with UHP CO, which contains metal for SWNT nucleation, and semiconductor, which does not contain metal. During UHP CO growth, the current increases linearly after a short ramp up period, as we might expect if nanotubes are continuously nucleating, snagging on the grid, and growing between the entrance and exit grid. For the semiconductor grade, CO, however, the current appears to be
approaching a limit, as we might expect if we are only growing SWNTs already nucleated from the UHP-grade CO. As these SWNT bridge the sample and exit grids, there are no new nucleated SWNTs produced to continue the processes. We would expect the current increase to stop when all tubes nucleated from the UHP CO either overcoat or complete growth between the exit and entrance grids.

Summary

In the past few chapters we have discussed the snag and drag model of seeded growth. We have shown it is possible to produce aerosols of ultrafine SWNT particulate, and to electrostatically collect these SWNTs onto a biased carbon fiber grid, suggesting that the snag element of this model is feasible. We have next shown that the bias and gas flow do cause the growth of nanotube yarns between the sample and exit grid where the growth can be monitored by watching the current rise. We have further shown that holding the SWNTs in the hot zone on the grid cause them to increase in length such that there is current rise (and presumably growth) as long as 20 minutes after the final nucleation off a metal catalyst particle.
Chapter 9: Ostwald Ripening Induced Termination of Carpet Growth

Introduction

The previous chapters focused on research to control the growth of carbon nanotubes by looking at implementations of seeded growth. In the next few chapters, we focus on controlling the growth of nanotubes by determining the forces that cause the termination of growth, specifically to determine the extent of Ostwald ripening of catalyst particles on a surface used to grow carpets of carbon nanotubes and the role this plays on the termination of carpet growth.

The objective of the research was to establish if Ostwald ripening is a primary mechanism for the termination of growth in catalytic chemical vapor deposition synthesis of single-walled carbon nanotube (SWNT) carpets. Specifically, we examined ways to produce longer carpet growth by deterring or limiting Ostwald ripening on a surface. Determining the mechanism of this sudden termination of growth would allow the development of controlled fabrication steps to allow increased length and yield in carpet growth. This in turn, would improve the performance of SWNTs in an array of technological applications and could lead to decreased production cost as well as provide a more fundamental understanding of factors influencing nanotube growth. As SWNTs are suitable for many applications including sensors [1], field emitters [2], composites [3], fuel cells [4], fibers, and microelectronic cooling devices [5], overcoming challenges in synthesis could affect a host of areas and devices.
Background

One of the greatest challenges facing the application of carpets is the termination of growth that occurs at the micron or millimeter scale [6-7]. The cause of this termination is unknown and carpet height is notably shorter than the lengths of nanotubes produced by kite growth from a surface, suggesting the termination is not inherent to SWNT growth [8]. Part of the difficulty in determining the mechanism of this termination is due to the incomplete understanding of many aspects of the growth mechanism. A review of literature reveals many different plausible mechanisms for this termination, but none explain all acquired data. Among the many theories proposed are termination due to the overcoating of catalyst particles by amorphous carbon [9] and the diffusion of growth gas through the carpet to the catalyst [10]. Recent calculations, however, suggest that growth gas diffusion does not explain some cases of growth termination [8]. Also, nanotubes cease growing collectively in patches. This observation of spatial correlation of growth termination suggests random catalytic deactivation is unlikely. The authors suggest that a mechanism which would explain this collective termination is the mechanical coupling of the top surface of the carpet produces an energetic barrier which terminates growth [8]. This mechanism, however, fails to explain why the introduction of oxidants such as $\text{H}_2\text{O}$ and $\text{O}_2$ enhance the activity and lifetime of catalysts resulting in the growth of dense SWNT carpet with heights up to 2.5 mm.

Ostwald ripening has not been studied as a cause for the growth termination, although it fits the above observations. Ostwald ripening is the observed phenomena where large particles increase in size while smaller particles decrease in size via atomic diffusion.
Figure 11.1. Basic schema of Ostwald ripening wherein atomic diffusion of metal catalyst particles leads to the increase in size of large particles and decrease or extinction of small. Figure from wikipedia.org.

Ostwald ripening in the context of a nanotube termination mechanism, would cause many of the particles acting as catalysts for nanotube growth to gradually lose catalyst atoms until there is no longer enough metal to sustain catalytic growth, causing termination. (Fig. 11.2) A similar process has already been observed for VLS growth of Si nanowires grown from Au/Si catalysts on a Si(111) surface. In the study, Au diffused from the smaller metal islands to the larger islands. The continuous growth of the nanowires was found to be critically dependent on the ability to limit the surface migration of the Au. [11]
Figure 11.2. Model of growth termination caused by Ostwald ripening. Atomic diffusion of metal cause nanotubes with small catalyst particles to lose their catalysts, terminating growth. Courtesy of Placidus Amama.

Another point of interest is that when Hata et al. introduced water into the CVD reactor during carpet growth [7], the water-assisted CVD growth revealed that the activity and lifetime of the catalysts are dramatically enhanced by introducing small and controlled amount of water into the growth chamber. The result was massive growth of highly dense, vertically aligned SWNT carpets of high purity with heights up to 2.5 mm after 10 min. Zhang et al. [12] also reported a molecular oxygen-assisted growth of ultra-high-yield of SWNT carpets with heights up to 10 μm after 10 min by plasma-enhanced CVD. These results suggest that oxidizers are capable of increasing the activity and lifetime of the catalyst. The catalyst activity of water-assisted CVD growth is estimated to be 84% (±6%), the highest ever recorded for nanotube growth, and it is expected that growth with oxidizers may allow for catalyst activity up to 100% in the future [13]. Although current belief is that the oxidizers operate as a protective agent against amorphous carbon coating allowing carpet growth to continue, the result is also consistent with an inhibition of Ostwald ripening.
The schematic in Fig. 11.3 illustrates the role we expect water to play in inhibiting the ripening of the catalyst. During carpet growth, metal catalyst atoms desorb from the catalyst particles and diffuse across the substrate. Larger particles are energetically favored over smaller particles due to the lower fractional surface energy, and therefore absorb more atoms than the smaller particles. The larger particles then grow and the smaller particles shrink. Ultimately, when too much catalyst is lost the nanotube stops growing. Water vapor or hydroxyl groups impede diffusion by temporarily complexing with the catalyst atoms. This reduces the ripening rate, thus extending the life of the catalysts.

Figure 3. Model of water retardation of the Ostwald ripening rate by temporary association with the moving catalyst atoms

The catalyst-substrate interaction also plays a role in carpet growth. One study reports that Al₂O₃ deposited by ion-beam deposition increased the lifetime of the catalyst [14]. The explanation given is that this deposition method results in a denser, more amorphous layer that enhances the uniformity of the iron film by increased wettability of the iron. Ostwald ripening, however, provides another explanation for why different deposition methods would cause different growth. Because Ostwald ripening is dependent on the movement of atoms across the
surface, anything that slows this migration should retard Ostwald ripening. Thus, we expect
defect density in the surface to affect the rate of ripening.

Proposed Work

The next few chapters outline our progress on work designed to investigate the role
Ostwald ripening plays in the termination of single-walled carbon nanotube carpet growth. We
used a thin film of iron on an oxide surface, since this is a typical substrate for carpet growth.
The substrate used is a boron-doped silicon (100) wafer with 100-nm Al₂O₃ film deposited by
various methods and topped with a 5-nm Fe film deposited by e-beam evaporation.

In our experiments, we examined the following issues:

1) The observance of Ostwald ripening in the presence of molecular hydrogen. In this step,
   we will seek to confirm that Ostwald ripening takes place in a hydrogen environment
typical of growth conditions and pre-growth annealing and reduction conditions. We will
do this by determining the particle size distribution of the treated samples over a time
series by analyzing the surface with AFM and SEM post treatment. We expect the size of
the particles to grow with time as the number of total particles decreases overall. We will
use the information collected to determine a rate equation for the ripening. We will not
include a carbon source in this work, as carbon deposition will obscure changes in the
particles.

2) The effect of different ambient conditions on the rate of Ostwald ripening, most notably
   the influence of water. In this step, we will examine what role Ostwald ripening has on
   the water assisted CVD of nanotubes. We will determine if the ripening rate of iron
nanoparticles formed from the iron layer decreases due to the hydroxyl interaction. We will repeat the time series used for the H₂ annealing with a small amount of water added and determine the rate equation for any observed Ostwald ripening. We will compare this to the rate equation determined in step 1. Information gleaned from this comparison will be used to analyze literature trends comparing SWNT growth with and without water. This step may be expanding to include the effect of other ambient conditions known to change the density and length of nanotubes produced (e.g. atomic hydrogen.)

3) The effect of surface defects (and hence roughness) on the rate of Ostwald ripening. A typical surface for nanotube growth is alumina. Substrates of similar chemical composition but different defect density can be made by depositing 100 nm Al₂O₃ film on boron doped silicon (Si) (100) wafers by various means including sputtering, e-beam deposition, and atomic layer deposition (ALD) followed by a thin Fe film. Since the defect density of the sputtered layer Al₂O₃ > e-beam deposited Al₂O₃ > ALD deposited Al₂O₃ > sapphire Al₂O₃, we would expect the rate of ripening to increase on the substrates as we go through the list from left to right when the substrate is annealed in a typical pre-growth hydrogen environment. We will test this by exposing these substrates to annealing conditions and comparing the particle size distributions of the samples. We will then compare the effectiveness of these substrates for carpet growth by looking at the density, length, and quality (estimated by defects) of nanotubes produced and estimate the catalyst activity. We expect that the more defects on the surface, the less ripening takes place and the longer and denser the nanotube growth will be. We will repeat this work with the addition of water to see how the ripening rate and nanotubes produced are affected.
4) *The effect of temperature on the rate of Ostwald ripening within the typical growth range of carpets* (i.e. 700-1000 °C). We will determine the rate equation for Ostwald ripening during hydrogen annealing for temperatures typically used for carpet growth on one or more substrates by once again analyzing the particle size distribution as a function of time. We will seek to apply this information to nanotube growth data already found in literature. We expect the rate of ripening to increase with temperature possibly putting limitations on surfaces and ambient conditions suitable for high temperature growth.

**Expected Outcomes**

The goal of this research is to provide strong evidence as to whether or not Ostwald ripening is a dominant factor on the termination of SWNT tube growth during various carpet growth experiments. The results will allow us to probe the kinetics of the ripening. In addition to yielding basic information about the growth and termination mechanisms of nanotube carpets, it will provide information on how to mitigate the effects of Ostwald ripening using temperature, surface, and ambient conditions to retard the rate at which it occurs. Information should explain previous results in the field and aid in the development of synthetic routes for the production of longer, denser carpets. The next few chapters go through the work we accomplished on this project during the course of the past few months and outline future directions. In chapter 10, we show that annealing in hydrogen at 900 °C produces catalyst particle coarsening that continues over 25 min. We also show that the process is temperature dependent, with coarsening more extreme at 900 °C than at 750 °C. In chapter 11 we show that the addition of water impedes catalyst coarsening, possibly explaining the efficiency of water-assisted carpet growth. In chapter 12 we show some preliminary results which suggest that atomic hydrogen impedes coarsening.
by a currently unknown mechanism. We also show that surfaces are important with smoother, lower defect density surfaces producing greater coarsening.
14. Li, Q; Zhang, X.; DePaula, R.F.; et al. PNAS 2005, 102, 16141.
Chapter 10: Ostwald Ripening of Hydrogen Annealed Iron

Introduction

In the previous chapter we explained the process of Ostwald ripening, why it could lead to the termination of carbon nanotube carpet growth, and the effects we expect if it is a primary influence in catalyst activity. In this chapter we show that iron catalyst coarsens over time on e-beam deposited alumina on silicon when exposed to hydrogen and that temperature greatly affects the degree of coarsening after 5 minutes, results consistent with an Ostwald ripening model.

Due to the applicability of carpets to next generation products, there has been much research on the effect of different conditions on the characteristics of the nanotube carpet formed. Dai’s group found that oxygen played a beneficial role in nanotube carpet formation while hydrogen treatment was deleterious [1]. This work showed that a small amount of oxygen added to reaction conditions greatly increases the SWNT yield, forming dense carpets. Hydrogen rich conditions, however, resulted in extremely low SWNT yields. The explanation given for this affect is the oxygen removes reactive hydrogen radicals which they suggest harmfully impact SWNT growth. This interpretation has come under question, however, as more recent work suggest that use of a hot filament to produce a controlled amount of hydrogen radicals is actually beneficial to carpet growth [2]. Dai’s work also shows that larger diameter nanotubes are produced with the addition of hydrogen [1] whereas Xu et al. reports that small diameter nanotubes are produced when atomic hydrogen is used with acetylene during growth at 750 [2]. This suggests that the ratio of atomic hydrogen to atomic carbon is not the only factor in the role of oxygen and hydrogen in growth.
The observations in the papers above are consistent with Ostwald ripening induced growth termination. Hydrogen is able to reduce metal oxides leaving the atoms free to diffusion along the surface and ripen. Oxygen impedes this movement. Our first step to investigate this model is to determine if catalyst ripening takes place when a metal film is annealed in hydrogen.

Methods

The substrate consists of boron doped silicon (100) wafers with 10-nm Al₂O₃ deposited by e-beam evaporation supporting a 0.5-nm Fe film deposited by e-beam evaporation. Thermal annealing studies were performed in a CVD chamber used for growth of SWNTs on spin-on glass. The substrate was inserted into the furnace and heated to 900 °C under 150 sccms Ar. At 900 °C, the samples were exposed to 250 sccms H₂ for 1,5, or 25 min. A control was instead annealed in Ar for 30 min. After thermal annealing, the samples were cooled under 150 sccms Ar.

Discussion

AFM clearly shows catalyst coarsening during the course of hydrogen annealing. (Fig. 10.1A-D). Annealing in argon did not show similar effects (Fig. 10.1E), suggesting that hydrogen plays a significant role in catalyst mobility. This catalyst ripening could prevent or terminate nanotube growth by robbing growing nanotubes of their catalyst and causing other catalyst particles to grow too large, causing carbon overcoating of the catalyst and death or multiwall formation.
Figure 10.1. (A) As deposited iron film on e-beam deposited alumina (B-D) Iron film annealed at 900 °C in hydrogen on e-beam deposited alumina for 1 min (B), 5 min (C), and 25 min (D). (E) Iron film on e-beam alumina anneal in argon 30 min. (Height scale is 10 nm, Length scale 1 μm × 1 μm)

**Temperature Effects**

One prediction of the Ostwald ripening model is that the effect should be more pronounced at higher temperatures. This is different than what we would expect if the deleterious effect of hydrogen is due to the ratio of hydrogen to carbon atoms, which would not necessarily scale with temperature. This is particularly interesting, since carpets have been grown at temperatures between 650 °C and 1100 °C. We then looked to compare annealing at a lower temperature, 750 °C to our findings at 900 °C.
Methods

Low-temperature thermal annealing was performed in the same CVD chamber used for the growth of SWNT carpets at Rice. A detailed description of the CVD chamber and reaction conditions for SWNT carpets is given elsewhere [3]. The substrate consists of boron doped silicon (100) wafers with 10 nm Al2O3 deposited by e-beam evaporation supporting a 0.5-nm Fe film deposited by e-beam evaporation. The furnace was preheated to 750 °C, and substrate rapidly inserted in the furnace and annealed in 400 sccm H2 for 5 min. Prior to carrying out thermal annealing of the substrates in H2, the incoming gas lines were resistively heated for 60 min at a background pressure of $1 \times 10^{-6}$ Torr to ensure the removal of any water. After thermal annealing, the samples were rapidly cooled.

Discussion

AFM shows that catalyst coarsen worsens at higher temperatures of hydrogen annealing. (Fig. 10.2) as an Ostwald ripening model predicts. This result explains observations by Resasco’s laboratory [4] that higher synthesis temperature lead to the production of larger diameter nanotubes and a greater prevalence of multiwalls because of the growing size of the catalyst particles. This effect has been confirmed by other groups using different growth gasses, catalysts, and substrates, a small subset of which are referenced [5-7].
Summary

Hydrogen annealing of an iron film of e-beam deposited alumina at 900 °C shows coarsening of particles with time, whereas similar annealing in argon does not. This is consistent with hydrogen reducing the metal oxide and increasing the mobility of iron on the surface, allowing Ostwald ripening. Hydrogen annealing at 900 °C shows a much greater effect than hydrogen annealing at 750 °C, which is consistent with temperature increasing the diffusion of iron atoms on the surface. These results are consistent with the model of Ostwald ripening and explain trends in the literature that show that the tube diameter and multiwall formation increase with temperature and hydrogen annealing and that the overall yield and quality of the SWNTs decrease in increased temperature and hydrogen annealing.


Chapter 11: The Role of Water in Super Growth of Single-Walled Carbon Nanotube Carpets

Introduction

In the previous chapter we presented evidence that hydrogen annealing at temperature and pressures commonly used in carpet growth caused ripening of a thin iron film on e-beam deposited alumina. We believe that this may be the cause of the effects of hydrogen and temperature on carpet growth observed in literature. In this next chapter we examine the role of Ostwald ripening in the observed increase in growth of carbon nanotube carpets with the addition of water.

To promote and sustain the growth of SWNT carpets, the Iijima group advanced an approach to use $H_2O$ as a protective agent against amorphous carbon coated [1-2]. The water-assisted CVD growth (also referred to as “super growth”) revealed that the activity and lifetime of the catalysts are dramatically enhanced by the introduction of a small, well-defined amount of water into the growth chapter resulting in the rapid growth of highly dense, vertically aligned SWNT carpets of high purity with heights up to 2.5 mm after 10 min. Zhang et al. also reported a molecular oxygen-assisted growth of ultra-high-yield of SWNT carpets with heights up to 10 $\mu$m after 10 min. by plasma-enhanced CVD [3]. These results emphasize that oxidants are capable of increasing the activity and lifetime of the catalyst for growth of carpets. Water-assisted growth has the highest recorded catalyst activity reported for nanotubes, an estimated 84%, and is continuing to be optimized [4]. Because of these results, we investigated the role of an oxidant ($H_2O$) in water-assisted CVD to determine the mechanism behind the high efficiency of this process.
Methods

Thermal annealing studies were performed in the CVD chamber used for the growth of SWNT carpets at Rice. A detailed description of the CVD chamber and reaction conditions for SWNT carpets is given elsewhere [5]. The substrate consists of boron doped silicon (100) wafers with 10 nm Al₂O₃ deposited by e-beam evaporation supporting a 0.5-nm Fe film deposited by e-beam evaporation. The furnace was preheated to 750 °C, and the substrates were rapidly inserted into the furnace and annealed in both H₂ and H₂/H₂O at 1.5 Torr for 30 sec and 5 min. The respective flow rates were 400 sccm H₂ and 2 sccm H₂O. Prior to carrying out thermal annealing of the substrates in H₂, the incoming gas lines were resistively heated for 60 min at a background pressure of 1x10⁻⁶ Torr to ensure the removal of any water. After thermal annealing, the samples were rapidly cooled.

Discussion

The transformation of the catalyst films to nanoparticles during thermal annealing and their ripening thereafter are critical factors during nanotube growth. In order to understand the role of water during super growth, we studied the morphological restructuring of the Fe catalyst film under typical CVD annealing conditions (with H₂ pretreatment) and under super growth conditions (with H₂/H₂O treatment) at 750 °C, without the growth step, i.e., without introducing a carbon source. The AFM topography images (Fig. 11.1) of the Fe₂O₃ nanoparticles formed on the substrate after thermal annealing for 30 s, reveal that the nanoparticles formed on the substrate upon thermal treatment in H₂/H₂O ambient are significantly smaller in size than those formed in H₂ ambient. In fact, for samples thermally annealed in H₂/H₂O, it was difficult to resolve some of the smaller nanoparticles due to the limited resolution of the AFM. AFM
analysis revealed that the mean feature heights of the nanoparticles formed from the Fe films thermally treated in H₂ and H₂/H₂O are 3.5 and 2.6 nm, respectively (Fig. 11.2).

Figure 11.1. AFM images of catalyst nanoparticles formed on the substrate after thermal annealing in (a) H₂ and (b) H₂/H₂O for 30 sec.
Figure 11.2. Particle size distributions of catalyst nanoparticles found after thermal annealing in \( \text{H}_2 \) and \( \text{H}_2/\text{H}_2\text{O} \).

To confirm AFM result, plan-view TEM image were taken after the backside hand-polished and dimpled down and then ion-milled (Fig. 11.3). The TEM images confirm the results seen by AFM in that they reveal a significant difference in the ripening behavior of the catalysts under \( \text{H}_2 \) and \( \text{H}_2/\text{H}_2\text{O} \). The mean diameters of the nanoparticles formed by catalysts annealed in \( \text{H}_2 \) after 30 sec and 5 min were 10.1 nm and 10.5 nm while those annealed in \( \text{H}_2/\text{H}_2\text{O} \) were 6.18 nm and 6.8 nm respectively.
Figure 11.3. Plane-view TEM images of Fe$_2$O$_3$ nanoparticles formed on the substrate after annealing in H$_2$ for (a) 30 sec. and (b) 5 min. and in H$_2$/H$_2$O for (c) 30 sec. and (d) 5 min. (courtesy of Seung Min Kim)
The dependence of SWNT carpet height on the presence of water in the CVD chamber is shown by Figure 11.3(a). Using water-assisted growth conditions, highly dense SWNT carpets of high quality were grown; a representative FESEM image of a typical SWNT carpet grown using 0.5% C$_2$H$_2$ with H$_2$O is shown in (Fig. 11.3(b)). In the presence of H$_2$O, the carpet height increased linearly with growth time between 15 and 120 min. implying a long catalyst lifetime, whereas in the absence of H$_2$O, the carpet height remained roughly constant, suggesting the termination of growth occurs before 15 min. Repeated experiments under water-assisted growth conditions revealed that the carpet height continues to increase linearly even up to six hours.
Figure 11.3. (a) Plot of the SWNT carpet height as a function of growth time for reactions with H$_2$O and with no oxidant. (b) FESEM image of SWNT carpet grown using 0.5% C$_2$H$_2$ with H$_2$O. (courtesy of Cary Pint)
Summary

It is apparent from the TEM and SEM results that the presence of H₂O in the reaction chamber inhibits the ripening of the catalyst preserving more catalyst nanoparticles that have diameters less than 6 nm. Since 6-nm Fe₂O₃ nanoparticles are reduced to Fe nanoparticles in the range of 3-4 nm which have been observed to produce SWNT carpets. On the basis of these results, we propose that the addition of water in super growth is a means of inhibiting Ostwald ripening through the ability of the oxygen and hydroxyl species to reduce diffusion rates of catalyst atoms, and thus delay the termination of growth. We hypothesize that this termination could take place when metal catalyst atoms desorb from catalyst particles nucleating nanotubes and diffuse across the substrate. Larger particles are energetically favored over smaller particles due to the lower fractional surface energy and so larger particles grow while smaller particles shrink. Ultimately too much catalyst is lost and the nanotubes cease to grow. For carpet growth, each terminated nanotube imparts a mechanical drag force on an adjacent growing nanotube due to van der Waals forces which may cause the carpet to collectively cease to grow when enough nanotubes terminate growth. Water vapor or hydroxyl groups impede diffusion by temporarily complexing with the catalyst atoms. This reduces the ripening rate extending the life of the catalyst and resulting in taller carpets.

In summary, AFM and TEM results support the model that H₂O leads to increased carpet growth by inhibiting Ostwald ripening behavior of the catalyst. The results of our work do not allow us to rule out any of the mechanisms proposed so far to explain supergrowth, but do add another dimension to the understanding of the termination of carpet growth which may lead to improved growth, yield, and purity of carbon nanotube carpet synthesis.


Chapter 12: Summary

In this thesis we presented our work to understand the growth of carbon nanotubes in an effort to solve two of the largest questions in nanotube synthesis today – how to gain chirality control in the growth of single walled carbon nanotube, and why carpet growth terminates. In Part I, we summarized the basic premise of seeded growth for chirality control and the work we have done to explore the feasibility of this process. We explained how we formed a seed first by attaching a premade metal catalyst particle to the ends of tubes using a functional linker, then by removing the linker through controlled reductive docking.

In Part II, we summarized the snag and drag model for the scale up of seeded growth and showed implementations of “snag” and “drag” components. We nebulized SWNTs, and highlighted the importance of this discovery in the respiratory toxicity studies of carbon nanotubes. We showed that these nebulized nanotubes can be electrostatically collected on a carbon fiber to form self-assembled SWNT-carbon fiber structures. We next moved to the “drag” component by showing that nanotubes nucleated in growth gasses can be grown into long aligned fibers between two biased grids and the current used to monitor growth.

In Part III, we proposed Ostwald ripening as a mechanism for SWNT growth termination on a surface. We showed that iron films evolve into larger and larger nanoparticles when exposed to hydrogen. We showed that elevating the temperature appears to increase this result. Finally, we showed data supporting Ostwald ripening as an explanation for increase yield and length observed by water assisted growth. Together, this work suggests that Ostwald ripening of the catalyst particles may play a major role in the termination of carpet growth.