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APPLICATIONS AND PRODUCTION OF CARBON NANOTUBES

by

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ABSTRACT

Properties and Production of Carbon Nanotubes

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Carbon nanotubes, a recently discovered form of carbon fiber with structural perfection similar to that of a fullerene molecule, have interesting electronic, chemical and mechanical properties due to their size and structure. Nanotubes have great potential as a bulk material for strong, lightweight composite materials, and as individual nanoscale tools or devices. Initial work on applications with individual multiwalled nanotubes as field emission sources and scanning force microscopy tips is described. The nanotubes display intriguing field emission behavior interpreted as the nanotube unraveling under the influence of the electric field. The unraveling process is believed to result in facile field emission from linear atomic carbon chains at the end of the nanotube. Such atomic wires represent an excellent field emitter. The work on multiwalled nanotube SFM tips was equally encouraging. The high aspect ratio of the nanotube allows it to image deep trenches inaccessible to commercially available Si pyramidal tips, and it reduces the interaction with the ambient water layer on the sample which perturbs image quality. The most remarkable advantage of nanotube SFM tips is a result of their mechanical properties. It was found that the nanotubes will remain rigid during normal imaging, but conveniently buckle to the side if circumstances arise which create large forces known to
damage the tip and sample. This feature makes the tip more durable than Si tips, and is especially important for soft biological samples.

In these two applications, as well as others, and in the measurements of novel nanotube properties, high quality, small diameter (0.5 to 2 nm) diameter single-walled nanotubes are most interesting. Such material can be produced slowly and in small amounts by catalytic arc vaporization and catalytic laser vaporization of graphite. It is well known that nanotubes can be mass produced by catalytic chemical vapor deposition (CCVD), but the product consists only of large, defective multiwalled nanotubes. It has been found that the standard CCVD technique can be made to exclusively produce small single-walled nanotubes by lowering the concentration of reactants. It is shown that this change in product morphology is a result of a change in the rate limiting step of the CCVD reaction. Nanotube nucleation and growth termination are also studied for this CCVD system. Prospects for mass production of single-walled nanotubes by this modified CCVD technique are considered.
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1. Introduction

Carbon can form a variety of structures with remarkable properties due to its potential bond configurations. It can form \( sp \), \( sp^2 \), or \( sp^3 \) hybridized bonds which allow one, two, or three dimensional structures. Some allotropes of pure carbon that demonstrate these bonds are shown in Figure 1. Diamond, a crystalline form of the \( sp^3 \) configuration, has the highest thermal conductivity, the highest melting point, and the highest atomic density of any solid. It is also the hardest material in terms of deformations. Graphite, which consists of stacked sheets of trigonally bonded \( sp^2 \) carbon, has highly anisotropic electrical properties, and is the stiffest material in terms of in-plane elastic modulus [1]. The fullerenes, a new stable allotrope of pure carbon, were discovered in R. E. Smalley’s laboratory at Rice University in 1985 [2]. The fullerenes are carbon cages consisting of twenty to hundreds of atoms. The bonding structure of the cage walls most closely resembles a single sheet of \( sp^2 \) graphite (a single sheet is referred to as graphene) with pentagons incorporated in the hexagonal structure to create curvature. It was soon realized that many stable nanostructures could be conceived by starting with graphene sheets and incorporating pentagons and heptagons for curvature [3].

In 1991, Iijima discovered carbon nanotubes in material deposited on the cathode of a carbon arc discharge apparatus optimized for fullerene production [4]. From transmission electron microscopy (TEM) images and electron diffraction, he determined that the nanotubes consisted of graphene sheets rolled into coaxial cylinders of diameter ranging from 4 to 30 nm. The ends were closed with hemispherical, polygonal, or cone
Figure 1. Some allotropes of carbon: A. diamond, B. graphite, C. buckminsterfullerene, and D. a (10,10) nanotube.
shaped caps. Although similar structures were already known to carbon fiber researchers, [5], Iijima’s report was the first to connect carbon nanotubes to the fullerene family of molecules and nanostructures. This generated great interest in the production of nanotubes, both in calculations and measurements of novel nanotube properties, as well as in demonstrations of nanotube applications.

1.1 Nanotube Structure

A graphene sheet can be rolled into a cylinder in an infinite numbers of ways leading to nanotubes of various diameter and helicity. The set of all possible nanotube structures can be described by two positive integers, usually written \((n,m)\). These numbers describe the separation of two carbon atoms in a graphene lattice in terms of the lattice unit vectors. To form an \((n,m)\) nanotube, flat graphene is rolled into a cylinder so that the \((n,m)\) atoms overlap. The cylinder’s long axis is perpendicular to the line between the \((n,m)\) atoms (Figure 2). Nanotubes in which \(n=m\) are called “armchair” nanotubes because the hexagons at their open edge are arranged in the structural armchair isomer. Nanotubes in which \(m=0\) and \(n\) is any allowed value are called “zigzag” nanotubes due to their edge structure. Both armchair and zigzag nanotubes have zero helicity. All other sets of \((n,m)\) that do not fall into these categories form nanotubes with some non-zero helicity.

Nanotubes that consist of a single sheet of graphene rolled into a cylinder are called single-walled nanotubes. Multiwalled nanotubes consist of several single-walled nanotubes arranged coaxially, the wall-wall spacing being similar to the interplanar spacing of graphene sheets in a graphite crystal. Single-walled nanotubes are often
Figure 2. Two unit vectors, n1 and n2, of the graphene lattice define the positions in a graphene sheet that will overlap to form an \((nxn1, mxn2)\) nanotube.
aligned along their lengths in groups called ropes. Multiwalled nanotubes are also found aligned in groups called bundles. Figure 3 shows TEM images of single-walled nanotubes, multiwalled nanotubes, ropes, and bundles.

The final structural property of a nanotube is its tip (Figure 4). Most production methods give multi- and single-walled nanotube tips that are closed in graphitic domes, cones, or faceted structures. Purification by oxidation of multiwalled nanotubes will preferentially etch the nanotube ends, leaving them open [6]. Some nanotubes appear to be endless and are believed to form perfect tori [7].

1.2 Nanotube Properties

The chemical bonding in the walls of a nanotube is essentially the same as in graphite, giving nanotubes a similar chemical resistance to graphite. Sigma bonds make up the hexagonal network of carbon atoms, while pi bonds are delocalized above and below each graphene sheet. Nanotubes oxidize fastest at their ends, leaving open nanotubes after purification. Oxidation also leaves the nanotube surface covered with carboxylic, carbonyl, and hydroxylic groups, which may be of use in decorating the nanotubes with specific functional groups [8,9].

Due to the large in-plane elastic modulus of graphite and strong \( sp^2 \) carbon bonds, carbon nanotubes are expected to be exceptionally stiff and have high axial strength. Experimental measurements of nanotube Young's moduli by AFM deflection techniques [10] and by TEM measurements of thermal vibrations [11] have given values of 1.3 TPa and 1.8 TPa, which are higher than any other known material. Another interesting mechanical property of nanotubes is that they buckle, as opposed to fracture, when bent
Figure 3. A single-walled nanotube (a), a multiwalled nanotube (b), a rope (c), and a bundle (d).
Figure 4. TEM images of closed multiwalled nanotubes (a), an open multiwalled nanotube (b), and an SFM image of an endless single-walled nanotube "crop circle" (d).
past their elastic limit. When the load is removed they return back to their original shape with no permanent damage. This behavior has been predicted [12] and observed [13,10] and indicates that nanotubes will have good energy absorbing properties.

The electronic band structure of single-walled nanotubes can be calculated by assuming the electronic structure of graphene, with periodic boundary conditions that represent the diameter an helicity of the nanotube. In this model, nanotubes in which \( n=m \) have a metallic electronic band structure. For nanotubes in which \( n-m = 3k \), where \( k \) is an integer, the band gap is zero, although the curvature of the graphene sheet induces a small gap. Nanotubes in neither of these categories have a moderate band gap [14].
2. Applications

Many applications for carbon nanotubes have been suggested and pursued. Some involve the use of nanotubes as a bulk material. Examples include composite materials [15], and large surface area electrodes [16]. Other applications require only a single nanotube to act as a nano-scale tool or sensor. These include nanotube field emitters [17], scanning probe microscopy tips [13], and molecular wires [18]. In this chapter I will discuss two applications that I, along with others, have pursued at Rice.

2.1 Experimental

2.1.1 Nanotube Mounting

To allow work on characterization and applications of individual nanotubes, it is necessary to manipulate them directly. For these studies, nanotubes are mounted to the ends of macroscopic electrodes. The first important insight is that while the arc-grown multiwalled nanotubes are only 50 nm diameter at most, they are up to 10's of microns in length. Therefore, if they scatter enough light to be detected, their filamentous shape can be resolved in an optical microscope. The best method for viewing nanotubes by optical microscopy is with dark field (DF) illumination. DF is a reflected-light technique in which white light is focussed at the sample by a parabolic mirror circumferential to the lens. Only light that scatters off of the sample enters the lens. This creates a dark background against which faint signals can be seen. An example of an image of arc grown multiwalled nanotubes imaged by DF microscopy is shown in Figure 5. Most of the filamentous structures seen here are actually bundles of multiwalled nanotubes. After studying many nanotube samples, it becomes clear that a qualitative difference can be
Figure 5. DF optical microscopy images of purified multiwalled nanotube material on the surface (a), and at a torn edge (b).
seen between bundles and individual multiwalled nanotubes. The bundles appear brighter, more crooked, and mottled, while individual nanotubes are very dim, straight, and evenly luminous.

If a macroscopic piece of oxidatively purified arc-grown nanotube material is gently touched to the edge of a piece of tape (Electron Microscopy Sciences #77816), the nanotubes will stick out in space. Manual micrometers (Newport SM25) and translation stages (Newport 462), with a resolution of 0.5 micron, are sufficient to bring a sharpened macroscopic electrode alongside the nanotube. The macroscopic electrode used depends on the application. For field emission studies, multiwalled nanotubes are attached to 8 micron diameter graphite fibers which are silver painted to stainless steel electrodes. Nanotubes can also be attached to electrochemically sharpened Pt wires [19] and to commercially available Si AFM tips [Digital Instruments, FESP].

Once the macroscopic electrode and nanotube are brought into contact, there must be some binder which holds them together so that the nanotube can be removed from the purified material and survive later manipulation. In the case of nanotubes mounted to graphite fibers, the van der Waals attraction between them is sufficient. This van der Waals "glue" holds the nanotubes quite well, even through violent gas bursts in electron microscope vacuum transfer chambers. The van der Waals attraction is only sufficient for binding nanotubes to graphite. For Pt wires and Si AFM tips, a small coating of acrylic adhesive is applied to the tip by dipping it in the sticky surface of tape. The nanotubes are also held quite well in this adhesive. Figure 6 shows optical microscope
Figure 6. The nanotube mounting process.
views of the mounting process to a Si AFM tip. An SEM image of a nanotube mounted
by only van der Waals forces to a carbon fiber is shown in Figure 7.

When viewed in an optical microscope under dark field illumination, single-
walled nanotube material created by the laser vaporization technique [20] does not look
like arc grown multiwalled material as shown in Figure 5. The single-walled nanotube
ropes are thinner than multiwalled bundles, and they are coiled on length scales shorter
than the optical resolution limit. The single-walled nanotube material appears grainy and
gray. If the material is prodded around the material edge, ropes will stick to the probe
and make themselves apparent by moving the material when the probe is moved, as
though an invisible strand connects them. By this technique, ropes of length up to 50
microns have been observed. Even with acrylic glue, the ropes never adhere strongly
enough to the probe to be pulled from the tangle of rope material. To mount a rope, it
must first be stuck to the probe with acrylic glue, then broken between the probe and
material by passing a current through it until it heats and breaks like a fuse due to
oxidation. The brief flash of light of the incandescent rope can be seen in the optical
microscope.

2.1.2 FiberX Apparatus

Multiwall nanotube field emission was measured in an apparatus called FiberX,
shown schematically in Figure 8. A mounted nanotube electrode is placed in a 3 cm x 4
cm x 6 cm vacuum chamber that has a sunken window on the front face and 2.75 inch
conflat flanges on the other faces. The nanotube is mounted to a 1-D translation
feedthrough so that the z-position of the nanotube can be adjusted inside the chamber.
Figure 7. An individual multiwalled nanotube and a bundle mounted to a carbon fiber.
Figure 8. FiberX apparatus.
The chamber is pumped by a 160 L/s turbopump (Balzers TPU 170) which produces a base pressure of $4 \times 10^{-7}$ Torr. The nanotube electrode is a few millimeters across from a counterelectrode that collects the field emission current. A computer controlled negative bias, through a 100X amplifier (Trek 601A), can be placed on the nanotube to produce a large field at its tip. A picoammeter (Kiethley 147), capable of reading 0.1 pA, reads the emission current between the counterelectrode and ground. A collimated argon-ion laser beam (Coherent Innova 70) passes through a 10 cm FL focusing lens, then through a window on the side of the chamber and is focused to a 5 micron diameter spot near the nanotube tip. The focusing lens is mounted on an X-Y-Z translation stage (Newport 461), with electrostrictive actuators (Newport ESA-C), which allows the laser beam spot to be translated onto the tip, shaft, or completely off of the nanotube. The sunken window allows a small enough working distance so that a microscope with a high NA objective images the glowing nanotube tip. This image is projected onto a CCD array (Princeton Instruments TEA/CCD-512TKB/1) that has high quantum efficiency in the near IR. Finally, a gas addition system allows gases to be admitted into the chamber at a minimum pressure of $10^{-4}$ Torr.

2.1.3 MicroFiberX Apparatus

MicroFiberX, shown schematically in Figure 9, is similar to FiberX. The chamber is much smaller, only a 1.33” conflat cube (Huntington). It is pumped by a small 2 L/s ion pump (Varian) directly attached to the chamber, eliminating vibrations from a turbo-pumped vacuum system. The chamber sits on an inverted microscope (Zeiss Axiovert 100A), whose high NA objective lens (Olympus LCPlanFl 40X/0.6) is used to both
Figure 9. MicroFiberX
image the incandescent signal and to focus the laser beam (Uniphase 4301-020) to a 1 micron diameter spot. The objective lens is corrected for imaging through the 2mm thick vacuum window. Finally, a spectrometer (Acton SpectraPro 150) between the microscope and CCD array allows the incandescent signals to be spectrally analyzed from 400nm to 1100nm in order to measure the nanotube tip temperature.

2.2 Nanotube Field Emitters

Electron emission from a metal surface occurs when electrons in the bulk of the metal pass the surface potential barrier and escape to the vacuum. This process was described by Murphy and Good [21] in terms of the free electron theory of metals. The expression for current density \( J \) as a function of electric field \( F \), temperature \( T \), work function \( \phi \) and fermi energy \( W \) is quite complicated. For the limiting case of low fields and high temperatures, some electrons gain enough thermal energy to cross over the barrier classically. This process, called thermionic emission, obeys the Schottky formula:

\[
J = \frac{emk_B^2}{2\pi^2\hbar^2} T^2 \exp \left[-\frac{W - \sqrt{e^3 F}}{k_B T} \right]
\]

(1)

For the limiting case of high fields and low temperature, electrons can tunnel through the barrier. This process is called field emission and is described by the Fowler Nordheim equation:
\[ J = AF^2 \exp\left(-\frac{B\phi^2}{F}\right) \]  

(2)

For intermediate regions of temperature and field, analytic solutions for the electron current can be derived, but they are quite complicated. It is true in general, however, that the current will increase with higher temperatures and higher fields.

Electron optics, such as those used in electron microscopy, benefit from a bright, coherent, monoenergetic electron beam. Field emission produces a more monoenergetic beam than thermionic emission since the field-emitted electrons are produced from a smaller number of states than thermionic electrons. A current area of interest in field emission sources is field emission from tips that terminate in a single atom, such as those created with tungsten [22]. Electrons emitted from these tips would benefit electron optics, but the single atom tips made so far are not stable, making them unsuitable for commercial instruments. Nanotubes have the potential to serve as excellent field emitters. Their high aspect ratio allows large fields to be created at the tip at relatively low biases, and they have a stable, well-defined atomic structure. With the potential for emission from a small number of electronic states, nanotubes could be stable, monoenergetic electron sources.

2.2.1 Multiwalled Nanotubes

Studies of field emission from multiwalled carbon nanotubes mounted as described in section 2.1 have been performed. The state of the nanotube tip, whether it is
opened or closed, can be controlled with FiberX. We find that the nanotube tips are easily opened by heating them to \(-1500^\circ\text{C}\) in a 10mT oxygen atmosphere [6]. Alternatively, heating them to their sublimation temperature in high vacuum is expected to close the nanotube tips. The temperature of the tip is estimated from the intensity of the incandescent image produced by the CCD array. The state of the tip after such opening and closing procedures can not be directly confirmed by TEM imaging because thermal vibrations of the long nanotubes cause the image of their tips to be blurred. However, we believe these conditions do open and close nanotubes as described based on evidence from nanotube opening and closing experiments on bulk amounts of nanotubes imaged when supported on TEM grids, where the tip structure can be easily confirmed [6].

Field emission measurements for a typical nanotube are shown in Figure 10 at \(-75\text{V}\) bias for both the closed (A) and open (B) tip configurations. The data show the emission behavior as the tip was heated and cooled by exposing and shuttering the focused laser beam positioned at the nanotube tip. At the laser-exposed temperature of approximately \(1500^\circ\text{C}\), the closed tip emits 35 pA, while in the open tip configuration it emits 8 nA, which is more than a 100-fold increase. Assuming there are no chemisorbed H or O atoms surviving on the nanotube surface at this high temperature, the 100-fold enhancement upon tube opening must be due to the atomic-scale roughness of the exposed graphene sheet edges of the open tip as compared to the smooth hemifullerene surface of the dome-closed tip.
Figure 10. Open (A) and closed (B) tip multiwalled nanotube field emission at room temperature (solid line) and 1500 C (open circles), and the open room temperature emission on a faster time scale (C).
When the laser is shuttered and the tip drops to room temperature, the closed tip emission became smaller than our detection limit of 0.1 pA. The most striking aspect of Figure 10, however, is that when the laser is shuttered, the open nanotube emission does not decrease, as one would expect. Instead, it rapidly increases by a factor of 100 to a level of 0.4 to 0.8 μA, more than 1 million times greater emission than observed in Figure 10A for the dome-closed nanotube at room temperature.

Figure 10C, which shows an expanded time scale of a two-second period of the open nanotube emission data, reveals that the emission current in this mode switches rapidly between fixed levels. With our measurement electronics, these excursions are found to be faster than 0.25 milliseconds, our smallest time resolution, and we expect they are due to individual atomic-scale events. The frequency of these excursions was found to be roughly proportional to the background pressure in the $10^{-7}$ to $10^{6}$ Torr range, indicating that they are due to modification of the emitting structure by ion bombardment or chemisorption of the background gas. Note that many of these excursions change the net emission current by a factor of 5 to 10, indicating that at times nearly the entire current is being emitted from a single structure.

Lowering the magnitude of the bias voltage while the open nanotube is in this high field emission state reveals that the emission onset is now achieved at only −41V, less than half the −93V emission onset voltage measured for this same nanotube when the tip is closed. This low onset, and the dramatic increase in emission current seen in Figure 10B, must be due to the formation of either an especially sharp and exposed structure extending far off the tip of the opened nanotube, or arise from some site with an
especially low work function. In either case, the special site must be one that is readily destroyed by laser heating.

One conceivable explanation is that the dangling bonds on the exposed edges of the open tip are susceptible to reactions with the residual gases in the vacuum system, resulting in chemisorbed species that are dramatically better field emitters than the exposed C atoms. Exposing to the laser then heats the nanotube to 1500°C and desorbs these species, resulting in a lower field emission even though the temperature is much higher. However, we find that intentionally increasing the level of any of the known background gases (H₂O, H₂, O₂, CO, and small hydrocarbons) actually quenches the field emission. Furthermore, the rate of rise of the emission current when the laser is shuttered seems to be a property of each individual tip and does not correlate with the background gas pressure. Finally, the influence of adsorbed background gas atoms to a field-emitting tip is typically to raise the work function and lower the emission. For these reasons we are confident that whatever the special emitting structure is, it is not produced by chemisorption.

Another possible explanation for the emission increase is that the field at the surface of the emitting structure increased. Although the bias is held constant, this could occur if the emitting structure changes its geometry to become sharper. If the growth of a sharp feature on the nanotube is responsible, it must be made entirely of carbon, it must be destroyed by laser heating, and its emission must be deactivated by chemisorption reactions with the background gas.
Increasing the magnitude of the bias voltage on the open nanotube while in the high field emission state saturates the emission. For a typical open nanotube at \(-100\text{V}\) to \(-110\text{V}\) bias, the field emission ranges from 0.5 to 1.5 \(\mu\text{A}\). Under these conditions, we detect a very faint incandescence at the tip of the nanotube with the CCD camera. At slightly higher bias voltage, the nanotubes are typically found to shrink back by a process that is highly episodic. One particularly striking event is displayed in Figure 11, where successive panels show the integrated signal for successive 30 second intervals while the nanotube is held at \(-107\text{V}\). In Figure 11B and C, the nanotube incandesces dimly at the tip. However, during the 30 second exposure in Figure 11D, an extremely bright even occurs that lights up the side of the nanotube for 8 micron along its length. Figures 11E and 11F, reveal that this presumably destructive event must only have occurred for some of the layers because the tip is still in its original position, incandescing at the same dim level as in Figure 11B and C. This selective burn-back of the outer layer of a nanotube is an unusual but highly revealing event. As detailed below, we believe that it can only be explained by the unconstrained unraveling of a carbon chain from the outer layer of the nanotube. More typically, open nanotubes biased substantially above \(-110\text{V}\) and field emitting more than 2 \(\mu\text{A}\) suffer catastrophic burn-back events that are not restricted to a single layer. These produce a single bright streak in the CCD camera as they evaporate back to the point of attachment.

We are convinced that there is only one viable explanation for the field emission behavior described above. The structures responsible for the data of Figure 10B and Figure 11 are individual linear carbon chains – \(C_n\) atomic wires – that have pulled out
Figure 11. The incandescent glow from a multiwalled nanotube field emitter, including an unravelling event in (D).
from the open edges of the graphene sheets of the nanotube and are held taut under the influence of the electric field. Inasmuch as the first atom in the chain at the point of attachment is bonded to the delocalized π-orbitals of the graphene sheet, this all-carbon atomic wire is both physically and electrically well coupled to the macroscopic world in a reliable way. The conduction band of these wires is derived from the overlap of the cylindrically symmetric 2p-π-atomic orbitals on each successive $sp$-hybridized carbon atom. Although such one-dimensional atomic wires are susceptible to Peierls-like distortions opening up a small band gap, the bond length alteration for the pure Cn chain is calculated to be very small ($<2\%$) [23]. This shows that the dominant electronic structure is closer to the cumulenic form ($\cdots=C=C=C=\cdot$), than to the bond-alternate polyyne ($\cdots=C=C=C=\cdot$). Transport of electrons injected from the negatively charged nanotube down to the tip of the chain is therefore expected to be quite facile. According to local density functional calculations of a C$_{10}$ chain in an applied uniform electric field, the delocalized, cylindrically symmetrical π-bonding along the chain produces nearly metallic screening. In a uniform 2 V/A field, the concentration at the last atom on the tip of the chain produces fields up to 10 V/A [24]. The result is that high current field emission is obtained at low voltage in a room-temperature environment from what is effectively an atomic wire.

Remarkable as this atomic wire hypothesis may at first seem, it is actually the most straightforward explanation given that the emitting structure must be some arrangement of carbon evolved from the open edges of graphene sheets. Many other alternatives have
been considered in detail. The best of these is a section of one of the layers of the nanotube which has rearranged under the influence of the electric field into a roughly triangular section extending above the rest of the open tip. However, because the surface of the tip is already covered with atomically sharp edges of the various layers, this special field emitting structure would have to extend far out to explain the enhanced field emission. Electrostatic modeling of the field at the top of such a structure shows that it would have to extend out from the end of the open multiwalled nanotube by more than 2 to 3 nm (20\% of the tip diameter) to begin to explain the observed enhancement. This process would require successive, independent rearrangements of hundreds of atoms as the structure is built under the influence of the applied field, at a cost of many additional dangling bonds. We can find no plausible mechanism for the sudden assembly of such a structure at room temperature such as is required by the data of Figure 10B, nor for its sudden disappearance when the laser heating is resumed. Neither is there a mechanism apparent whereby all of the atomically sharp emission sites near the top of such a graphene structure can be deactivated by a single chemisorption event: as is required by the data of Figure 10C.

Figure 12 addresses the question of how and why C\textsubscript{n} chains would be pullout out by the electric field in these experiments. When the electric field has become high enough to begin to pull at the most exposed C atom (1) with sufficient force to break C-C bonds, there are three possible bonds to break. The direction of the applied field favors breaking the (2)-(3) bond. Note that only when the chain is extended by breaking this bond is the total dangling bond count kept constant. This occurs because atom (2) can
Figure 12. Schematic of the unraveling process. For simplicity, only a double-walled nanotube is shown. When the electric field has become high enough to begin to pull at the most exposed C atom (1) with sufficient force to break C-C bonds, there are three possible bonds to break. The direction of the applied field favors breaking the (2)-(3) bond. Note that only when the chain is extended by breaking this bond is the total dangling bond count kept constant. This occurs because atom (2) can compensate the loss of its bond to (3) by concertedly increasing the bond order of its attachment to (4). The net effect is to increase the carbon chain length by two toms without any decrease in the total bond order of the entire structure. Any other choice increases the dangling bond count by at least one. Further pulling by the electric field on the chain repeats the process, effectively unraveling the carbon chain from the open edge of the graphene sheet. Note, however, that when the unraveling reached a site that is "spot welded", such as (7) in this schematic, there is no way to continue the unraveling process without increasing the overall dangling bond count.
compensate the loss of its bond to (3) byconcertedly increasing the bond order of its attachment to (4). The net effect is to increase the carbon chain length by two atoms without any decrease in the total bond order of the entire structure. Any other choice increases the dangling bond count by at least one.

The cohesive energy of carbon in a \( C_n \) chain is estimated at 6.1 eV per atom [25], whereas that of an infinite graphene sheet, or large diameter nanotube, is 7.3 eV per atom [26]. Therefore, although there is no net change in the formal bond count, there is a cost of \( \sim 1.2 \) eV per atom to pull out a \( C_n \) chain from the open tip of a nanotube. However, any other structure will cost more. Estimates of the cohesive energy of graphite flakes [26] show that the cost to the overall cohesive energy due to the dangling bonds on the periphery is 1.5 eV per atom. All alternatives to the \( C_n \) chain require an increase by more than \( 2n \) in the number of these energetically costly edge atoms in order to produce a field-emitting structure of the same height.

This expected ease of unraveling a linear carbon chain then brings up the question of why it does not continue indefinitely, destroying the nanotube completely when it is in a higher electric field. In fact, we believe that this is exactly what happened to produce the catastrophic burn-back events discussed above for biases greater than \( \sim 110 \) V in magnitude. In the special case of Figure 11D, we believe that the incandescent flash that illuminated the side of the nanotube was caused by the outermost layer unraveling down the side of the nanotube to its point of attachment at the bundle. The bright incandescence was caused by resistive heating of the unraveling carbon chain as the emission current from the tip was 1 to 2 \( \mu \)A. The dim incandescence seen at the tip of the
nanotube in the earlier and succeeding panels is, we assume, due to a few carbon chains also heated to incandescence by the emission current, but somehow held up in their unraveling process.

As shown schematically in Figure 12a, we believe it is the presence of C atoms bridging between the layers of the multiwalled nanotubes that ordinarily keeps this unraveling process in check. The simplest possible bridge is a single C atom like that labeled atom 8 in Figure 12a. Such structure will serve as a barrier to further unraveling because it forces an increase in the dangling bond count. These layer-to-layer spot welds have been implicated in other research on multiwalled nanotubes from this group [27] and in recent calculations [28]. If this is the correct mechanism, the unraveling of the outermost layer will be unique. Once this layer has etched back behind the inner layers, bridging spot welds are no longer possible, and there is nothing to stop the unraveling. We know of no other way of explaining the data of Figure 11D.

The sudden destruction of these field emitting Cₙ atomic wires when exposed to the laser is readily understood as thermally induced evaporation of C₃ and other small carbon radicals from the tip of the chain until this chain is so short that the electric field at the tip is no longer sufficient to produce enhanced emission. We expect that there is a very steep temperature dependence of the effective resistance of the carbon chain, with nearly ballistic transport when the chain is cool, but frequent scattering and consequent chain heating and further increase resistance once the vibrations of the chain become excited.
Further evidence has emerged to support the unraveling hypothesis since the original report in 1995. Ab initio calculations of nanotubes in strong electric fields support the unraveling hypothesis [28]. Other simulations by Yakobson [29] of the destruction of a nanotube under axial strain shows that nanotubes tend to come apart by unraveling into carbon chains. Also, we have collaborated with a group at Delft University to measure the energy spectrum of electrons field emitted from multiwalled nanotubes. Although they do not have a focused laser beam to open the multiwalled nanotube tips in oxygen, they were able to achieve the open state by sputtering. Once in the open state, according to the I-V characteristics, the emission spectrum changed from broad to a few discrete peaks, which is typical behavior for single atom field emitters [30].

2.2.2 Single Wall Nanotube Field Emission

Field emission measurements were also made for single-walled nanotube ropes produced by laser vaporization of a graphite/Co/Ni target. The ropes are mounted to an electrochemically etched platinum probe as described in section 2.1. A typical plot of emission versus bias is shown in Figure 13. When trying to heat the invisible ropes with the focused laser beam, incandescence was never observed. We attribute this to the smaller rope diameter and lower mass density compared to multiwalled nanotubes. Also, at times when we can infer the position of an invisible rope by visible attached particles, we see that the beam perturbs the position of the rope, making it difficult to center the beam at the rope tip. Due to these technical problems, field emission was only measured for ropes which were not heated at the tip by the laser beam.
Figure 13. I-V curve from a field emitting single-walled nanotube rope.
The single wall field emission, plotted in Figure 13, was measured with MicroFiberX so that the incandescent spectrum could be analyzed. A faint incandescent glow was seen at the tip of the rope from Figure 13 at an emission level of 4.5 μA. With the spectrometer grating in place, the incandescence was captured for 100 seconds. A 100 second background with no incandescence was subtracted. The data was corrected for the microscope-spectrometer-CCD spectral response function. The data fits well to a 987K blackbody curve, confirming that the observed glow is incandescence, and that the single-walled nanotube rope tips are heated when field emitting at high current levels. The emission of this same rope was increased to 14 μA, and −215V. In trying to go beyond this point, the rope evaporated back, presumably having reached the maximum temperature it could withstand at that field. The single-walled nanotubes in the rope may have unraveled similar to multiwalled nanotubes, but with no interlayer atoms to control the unraveling, it was catastrophic.

2.3 Nanotube Scanning Force Microscopy Tips

The inventions of the scanning tunneling microscope (STM) in 1985, and the scanning force microscope (SFM) in 1986 have established the value of a physical connection between macroscopic devices and nanometer-scale objects for probing, manipulating, and fabricating on the nanometer scale. While good progress has been made in controlling the probe position to sub-Angstrom accuracy, and in designing sensitive detection schemes to monitor the tip-sample interaction for SFM, less has been accomplished in designing the probe itself. Ideally the probe tip should be at least as precisely defined as the object under investigation, and should maintain its integrity after
repeated use. The best tips currently used for scanning probe microscopy do sometimes achieve sub-nanometer resolution, but they seldom survive rough imaging conditions where the tip can "crash" into the sample. Most scanning force microscopy is performed with silicon or silicon nitride tips which do not have a well defined atomic configuration at the tip-sample interface. Nanotubes were attached to conventional SFM tips as described in section 2.1 to see if they could improve the current state of SFM tip technology.

2.3.1 Standard SFM

Scanning force microscopy, and related scanning force techniques, all make use of a similar detection scheme that accommodates three modes of operation. The basic configuration is shown in Figure 14. The sample is mounted on a piezo tube scanner capable of scanning a large area in X-Y (typically 100 x 100 microns) and moving in Z over several microns with high resolution. Above the sample, the tip is at the end of a cantilever, typically made of Si or Si₃N₄, which is 10's of microns long and about 1 micron thick. A laser beam reflects off of off the back of this cantilever and onto a split photodiode. When the cantilever deflects due to interaction of the tip with the sample, this registers as a change in the relative values of the voltages on the photodiodes. In most SFM techniques, a feedback loop adjusts the z height of the sample to hold a constant tip-sample interaction by keeping the deflection signal constant.

2.3.2 Contact Mode

The three modes of SFM are contact, noncontact, and tapping. In contact mode, the sample is raised until the cantilever is deflected so that the tip is applying a constant
Figure 14. The basic AFM setup (NOT to scale).
force to the sample, which is known if the deflection and spring constant of the cantilever are known. The sample begins to scan in X and Y. As the tip travels over surface features that are higher or lower than the original position, the Z piezo moves up or down to keep the cantilever deflection, and therefore the applied force, constant. A plot of the Z piezo height versus X-Y position produces an image of the topography of the surface. The image is actually a combination of the surface height at each point, and the local elastic features. Contact mode is only good for hard, flat samples, since it causes large compressional and lateral forces to the sample. Tips are quickly dulled in contact mode.

2.3.3 Noncontact mode

In noncontact mode, the tip oscillates near its resonant frequency just above the sample. If the tip trajectory is represented by a forced, damped, linear harmonic oscillator in which the cantilever provides the restoring force, damping parameter, and driving force, its equation of motion will be:

\[ m\ddot{z}(t) + b\dot{z}(t) + k_c z(t) = F_0 \cos(\omega t) \]

(3)

where b is the damping parameter, \( k_c \) is the restoring force due to the cantilever, m is the effective mass of the tip, and \( F_0 \) is the driving force which is applied through a vibrating piezo element in the cantilever holder. This equation of motion will result in a frequency response with an amplitude resonance peak at the following frequency:
\[ \omega_R = \sqrt{\frac{k_c}{m}} - \left( \frac{b^2}{2m^2} \right) \]

which is just the resonance frequency lowered by the damping term. As the tip approaches the surface it will feel the attractive van der Waals interaction with the surface. This interaction, which increases in magnitude as the tip approaches the surface, will act as another position dependent force term in the equation of motion, which modifies the amplitude resonance frequency:

\[ \omega_{rc} = \sqrt{\left( \frac{k_c - k_{vdw}}{m} \right) - \left( \frac{b^2}{2m^2} \right)} \]

The tip scans just above the sample surface set at a constant vibration frequency just below the amplitude resonance on the steep part of the frequency response curve, as indicated in Figure 15. As the tip scans over high or low features, it enters different parts of the van der Waals potential, causing the amplitude resonance to shift. Since the driving frequency is on the side of the resonance curve, a shift in the curve position causes a shift in the oscillator amplitude. The microscope monitors the tip amplitude and holds it constant by adjusting the Z height. The resulting plot of Z height versus XY position creates a topological image of the surface as in contact mode. The advantage of non-contact mode is that very small forces are applied to the sample, causing less damage to soft samples. The disadvantage is that it requires the tip to vibrate at very small amplitudes at low, 2 to 3 nm heights above the surface. Under these conditions, the tip is easily trapped in the ambient water layer when imaging in air.
Figure 12. Noncontact mode. The van der Waals forces between the tip and shift the amplitude resonance curve, causing a change in amplitude at a set driving frequency.
2.3.4 Tapping Mode

Tapping mode, also called intermittent contact mode, is similar to noncontact mode in that the tip oscillates above the sample, and the driving frequency is set just below the amplitude resonance. However, in tapping mode, the tip oscillates with much larger amplitude, 10's of nanometers, and higher energy. It strikes the surface on each cycle of oscillation, breaking though the ambient water layer if one exists. The mechanism by which the amplitude changes as the tip scans over features is not as straightforward as in noncontact mode. In the model we will use, the equation of motion must be broken into two parts: a) one for the tip above the sample, and b) another for the tip in contact with the sample (see Figure 16). The first is simply the equation for a forced, damped, linear harmonic oscillator:

\[
\ddot{z}(t) + \frac{\omega_c^2}{Q_c} \dot{z}(t) + \omega_c^2 (z(t) - z_L) = a_o \omega_c^2 \cos(\omega t)
\]

(6)

This time the equation of motion is written in terms of the resonance frequency of the cantilever, \(\omega_c\), and its quality factor \(Q_c\), rather than the mass, spring constant, and damping parameter. \(z_L\) is the rest height of the tip above the surface which is at \(z=0\). \(a_o\) is the forced vibration amplitude of the back of the cantilever. The second equation represents the mass of the tip and surface oscillating under the force of the cantilever and elastic surface forces.
Figure 16. In Tapping mode, two equations of motion are needed to describe the free tip (left) and the tip in contact with the surface (right).
\[ \ddot{z}(t) + \left( \frac{\omega_s}{Q_s} + \frac{\omega_s^2}{Q_s} \right) \dot{z}(t) + \omega_s^2 (z(t) - z_l) + \omega_s^2 z(t) = a_c \omega_s^2 \cos(\omega t) \]

(7)

Where \( \omega_s \) and \( Q_s \) are the resonant frequency and quality factor of the surface spring and tip mass system, since the surface is assumed to have negligible mass compared to the tip. Realistic values were entered into these equations and the trajectory of the tip was solved numerically using equation (6) when \( z(t) > 0 \), and equation (7) when \( z(t) < 0 \). The distance the tip travels into the surface per cycle in the steady state solution tells how much force the tip applies to the surface when tapping under these conditions [31]. Tapping mode generally produces forces in the \( 10^{-9} \) to \( 10^{-8} \) Newton range.

Nanotubes were mounted to commercial Si cantilevered tips by the techniques described in section 2.1. Typically, a 1-4 micron bundle is mounted that ends in a single multiwalled nanotube. When such a tip is first used, it may need to be modified before it produces good images. A convenient diagnostic of the nanotube tip structure is the Force Calibration mode. In this mode the X-Y raster scanning is disabled. The tip oscillates at the driving frequency, and the sample translates up and down at about 1 Hz, coming into contact with the tip for part of the cycle. If the amplitude and deflection are plotted versus sample position, the result for a typical tip is shown in Figure 17a. As the sample approaches, but the tip and sample are not in contact (region a), the tip has the full amplitude. As the tip starts to tap the surface, we see the amplitude drop to zero (region b), then recover as the sample moves closer (region c). As the sample approaches even closer, beyond region c shown in Figure 17a, the amplitude data varies wildly as the
Figure 17. The amplitude in ForceCal mode for a nanotube tapping the surface (top). Section A corresponds to the tip above the sample, the tip is tapping the sample at section B, and is in constant contact at C. The frequency response at each stage (bottom) shows that simulations that include the buckling term (b) represent the data (a) well.
bundle crashes into the surface. Ultimately, the bundle is completely pushed to the side and the Si tip contacts the surface, bringing the amplitude completely to zero. By measuring the length of these sections, the length of the single multiwalled nanotube and the bundle can be measured. Typically, the individual nanotube at the tip needs to be less than 500 nm to produce good images. If it is too long, we find that it can be shortened by applying 5V between it and the sample while just above the surface in Force Calibration mode. As the bias is raised, a short section will be etched off of the tip.

Perhaps the most amazing aspect of the nanotube tips is that the above Force Calibration procedure does not usually damage the tip. Most nanotube tips can go through this process hundreds of times and they almost always return to their original state. This is an important advantage of nanotubes, especially when imaging deep, tortuous samples. Images of a 0.5 μm wide by 1 μm deep trench taken by a nanotube tip and conventional pyramid tip illustrate the advantage of a high aspect ratio tip for imaging steep structures (Figure 18). Special tips are commercially available with high aspect ratio structures grown on a Si tip or etched by FIB, but these are often brittle and easily broken off during imaging. The nanotube tips offer a high aspect ratio tip, but it cannot be easily broken off. If the tip is crashed due to suddenly hitting the side wall of a trench, for instance, the nanotube will bend to the side and recover.

In addition to the Force Cal data, we studied the frequency response function while the nanotube tip tapped the surface. The result is shown in Figure 17b. When the nanotube tip was above the surface, the response function displayed the typical shape.
Figure 18. Silicon trenches imaged by a pyramidal SFM tip (a), and a nanotube SFM tip (b).
However, the response function became highly asymmetric when the tip was tapping the surface. The response function recovers in region c.

The Force Cal and response function data supplied an opportunity to understand how the nanotube responded to the tapping force during imaging. We attempted to simulate these data sets numerically with solutions to equations (6) and (7). For a Force Cal simulation of 17a, we would plot the trajectory with some realistic parameters, and some constant rest tip height $Z_L$. The steady state amplitude gave the amplitude at that $Z_L$. $Z_L$ was then varied and the steady state amplitude measured again, ultimately generating a plot of amplitude versus $Z_L$. The response function curve in 19b were simulated by setting an appropriate $Z_L$ and then measuring steady state amplitudes for various driving frequencies. The simulations were run on MatLab software and used a fourth order Runge-Kutta method to numerically calculate the trajectories.

The elastic properties of the nanotube were included in equations (6) and (7) by assuming the surface was very hard, and using the parameters $\omega_s$ and $Q_s$ to describe the nanotube elasticity. Again, the effective mass of the nanotube in the equations of motion is negligible compared to the tip mass. We assumed models in which the nanotube only compressed, which resulted in a spring constant much stiffer than the cantilever, but this gave neither the drop to zero of the amplitude in Force Cal, nor the asymmetric frequency response. We also tried assuming that the nanotube was deflecting laterally, which resulted in a spring constant lower than that of the cantilever, but this did not reproduce the measured Force Calibration or frequency response either. Many values of the spring constant and quality factor were tried, but none reproduced the measurements.
Finally, we considered the nanotube as an elastic column under a compressional force applied along its long axis. Such a column will show no deflection (only a slight compression) up to its Euler buckling force, beyond which it will undergo large lateral displacements as it buckles. The Euler buckling force is:

\[ F_E = \frac{\pi^3 Y r^4}{4 L^2} \]  

(8)

Where \( Y \) is the nanotube Young’s modulus, \( r \) is the nanotube radius and \( L \) is the length. For a nanotube tip of 250 nm length and 5 nm diameter, assuming the Young’s modulus to be \( \approx 1 \) Tpa, the Euler buckling force is \( \approx 5 \) nN. This means that if you apply up to 5 nN along the nanotube’s axis, no deformation will occur except a slight axial compression, so the nanotube tip is very stiff. Beyond 5 nN the nanotube will buckle to the side, allowing large displacements for a small increase in force, so at this point the nanotube becomes very soft. An approximation to this nonlinear term was entered into the numerical simulations of the equations of motion. The results, also shown if Figure 19, agreed well with experiment. The simulated Force Calibration curve dropped the amplitude to zero, and the response function of the tapping tip was asymmetrical.

This buckling behavior of the nanotube tip explains why it could so readily survive complete crashes into the surface. The individual nanotube at the end of the bundle buckled to the side, and then the bundle did as well. All tubes regained their original positions when the tip was retracted. This recovery from the buckled state has since been observed for individual nanotubes by SFM techniques [10]. SFM studies of
samples that can be damaged by large forces, such as biological samples, may benefit from the nanotube tip buckling. It insures that a force much greater than \( F_{\text{Euler}} \) will not be applied to the sample.

One of the principal limits in SFM imaging in air has been that at normal humidity the surface is covered with a layer of water, and the capillary adhesion forces produced when the tip makes contact are typically 10-100nN [32]. As a result, one must use high-force-constant cantilevers oscillating with substantial amplitude to ensure that the tip can break through the water layer on each tap. Owing to the small diameter of the nanotube, we find the capillary adhesion force of multiwalled nanotube tips is generally reduced to <5nN and often as low as 0.05 nN, permitting tapping mode imaging with cantilevers having force constants as small as 0.01N/m at a peak-to-peak amplitude of 10nm.

We were also successful in attaching a single-walled nanotube ropes to Si pyramids. We found that the single-walled nanotube ropes behaved in much the same way as the multiwalled nanotubes. As with the multiwall tip, we found that it was possible to adjust the length of the rope by applying a bias between the tip and surface in Force Calibration mode. However, to realize the full promise single-walled nanotubes hold as probes, a more precise method will be needed: one that will guarantee that just an individual single-walled nanotube of the desired length extends out from rope.
3. Nanotube Production

There are now several experimental routes to the synthesis of carbon nanotubes. Each has advantages and disadvantages regarding structural perfection, quantity of nanotubes produced, and levels of impurities.

3.1 Carbon arc

Soon after Iijima’s discovery, Ebbesen and Ajayan optimized the conditions for synthesis of multiwalled nanotubes by arc vaporization of graphite [33]. In a typical experiment, 9mm graphite electrodes were arc evaporated approximately 1 mm apart at 20V and 100A in an atmosphere of 500 Torr He. The evaporated material formed a deposit on the cathode with a hard gray shell surrounding an inner black material that consisted almost entirely of multiwalled nanotubes and nanoparticles. Wang et al found that running with larger electrodes to produce more material resulted in a gray core, similar to the outer shell that contains no nanotubes [34]. We believed that this defective area was due to tube-tube coalescence as a result of high temperatures at the center of the deposit. An arc apparatus was constructed in our group that used 12.5 mm graphite electrodes, but they were short and held by copper mounts that were designed for maximum water cooling. The increased cooling resulted in very even arcing conditions and high quality 12.5mm deposits with no gray core [35]. The multiwalled nanotubes and bundles shown in Figures 3 and 4 are examples of arc-grown nanotubes.

3.2 Catalytic Carbon Arc

In 1993, Iijima and Ichihashi [36] and separately Bethune, et al. [37] found that single-walled nanotubes could be formed by arc vaporization if a metal catalyst was co-
vaporized with the graphite rod. While the arc conditions were similar, Iijima used iron as the catalyst and a methane and argon gas mixture, while Bethune used a cobalt catalyst and the standard helium atmosphere. Instead of a cathodic deposit, single-walled nanotubes were found in web like material covering the inside surfaces of the reactor. In each case, the diameter distribution of these nanotubes was much narrower than multiwalled nanotubes, centered at 1.2 nm. The catalytic arc technique made single walled nanotubes that were much more interesting for study because they were not as varied in structure as arc grown multiwall tubes, and they resembled the smaller nanotubes that were the subject of many interesting calculations. Unfortunately, they grew in very low yield by this technique and were covered with amorphous carbon, making them difficulty to study.

3.3 Laser Vaporization

An important breakthrough in nanotube research in 1996 was the discovery in our laboratory by Thess et al of a technique for producing high quality, high yield single walled nanotubes by laser ablation of a Ni/Co doped graphite target [20]. The nanotubes were aligned along their length in trigonal lattices consisting of 100-500 nanotubes. The nanotubes were highly monodisperse in diameter around 1.38 nm. X-ray and electron nano-diffraction indicated that approximately 40% of the tubes in the ropes had the structure of a (10,10) nanotube, predicted to be metallic. While this technique does produce very pure nanotube samples at up to 70% nanotube yield, it is expensive to set up, experimentally difficult, and produces material slowly. A scaled up version of the
original apparatus using a 4” oven and 30 Hz lasers can produce 1 gram of raw material per hour, but only 50% of which is nanotubes [38].

Recently, Journet, et al. drastically improved the catalytic arc technique by running with a catalyst of 1 at % Y and 4.2 at % Ni in the graphite electrode[39]. The inside of the chamber was covered with a web-like material that consisted of high yield (approximately 80%) single-walled nanotubes. The morphology of these nanotubes is very similar to those produced by laser vaporization. Their diameter distribution is very narrow around 1.4 nm, and they form aligned ropes. This technique allows the production of grams of this material in just minutes, and it is cheaper and not as complicated as the laser vaporization technique.

3.4 Catalytic Chemical Vapor Deposition

The above techniques for nanotube production were given in chronological order. Another technique, which predates even the discovery of the fullerenes, is catalytic chemical vapor deposition (CCVD) growth of nanotubes which is carried out by flowing carbon containing gases over supported metal particles [40]. Most early reports of CCVD growth featured highly irregular carbon fibers several hundreds of nanometers in diameter. It is clear in some cases, however, that the smallest fibers with diameter 10-50nm had the same morphology as what are today called carbon nanotubes - graphene sheets rolled into coaxial cylinders with a hollow core. CCVD has been refined to exclusively produce 10-20 nm diameter multiwall carbon nanotubes [41]. CCVD multiwalled nanotubes typically appear more defective by TEM observation than those nanotubes produced by arc or laser vaporization techniques. This can be seen in the lack
of straightness, and deviations from parallelism of the graphene sheets that make up the walls. Figure 19 illustrates the differences between CCVD and arc grown multiwalled nanotubes.

3.5 Limitations

Early measurements of the properties of individual nanotubes were performed almost exclusively on arc grown multiwalled nanotubes, since CCVD tubes appeared highly defective and catalytic arc grown tubes were in too low yield to be useful. Electronic transport studies gave varying results dependent from nanotube to nanotube, and seemingly dependent on the details of their production. Although the properties are expected to vary with the nanotube structure, it was determined that defects played a major role in defining these properties [42].

Laser vaporization material provided much more interesting results. It allowed measurement of electronic properties that showed delocalization of conduction electrons on a length scale up to 140 nm, as is expected for metallic tubes [18]. Recently, STM images and STS analysis of the same individual single-walled nanotube has allowed initial confirmation of the structurally dependent properties [43,44]. The Y/Ni catalytic arc technique makes material which is expected to be of similar high quality.

Nanotube applications are expected to benefit from high quality single-walled nanotube material as well. In the area of nanotube field emission, most work has focussed on multiwalled nanotubes. Although this has allowed high currents and low biases, and shown interesting unraveling effects, it has not yet produced atomically well defined and stable field emitters. Single atom W field emission tips are widely studied
Figure 19. A CCVD multiwalled nanotube (top) has a more irregular structure than nanotubes produced by arc evaporation (bottom).
since they produce bright electron beams. Unfortunately, they are very difficult to produce, and not stable. A single-walled nanotube field emitter would give an atomically well-defined tip that is stable and should have good emission characteristics.

Multiwalled nanotubes have been shown to make excellent SPM tips with respect to aspect ratio and soft imaging. Single-walled nanotube tips would carry these advantages, as well as an unprecedented SFM resolution of approximately 1 nm. With an atomically well-defined tip, rational image deconvolution could be performed, as well as chemical derivitization of these tips for chemically sensitive imaging [45].

Both the studies of properties and applications of nanotubes, which until recently have been performed with multiwalled nanotubes, will be greatly advanced when high quality single-walled nanotube material becomes widely available. A scaled up version of the laser vaporization apparatus that produced high quality single-walled nanotube ropes can produce only about 1 gram per hour of raw nanotube material and is quite elaborate and expensive. The Y/Ni catalytic arc technique can produce 1 gram in minutes, but only produces a few grams per run. Then the chamber must be opened, material collected, electrodes replaced etc. Neither of these techniques can be easily scaled up to match the production levels at which CCVD multiwalled nanotubes are produced. Clearly, a method of producing high quality single-walled nanotubes by CCVD would make them more widely available and greatly accelerate research and development efforts.
3.6 Single-Walled Nanotubes by CCVD

To my knowledge, there are two reports of single-walled nanotubes prepared by CCVD. Peigney et al. reported a mixture of single- and multiwalled nanotubes resulting from decomposition of CH₄ at 1050ºC over an alumina-supported Fe catalyst [46]. They do not, however, report the relative amounts of single and multiwalled nanotubes, and the images shown do not indicate that single-walled nanotubes dominate the reaction products. Dai et al. reported the growth of single-wall and a small amount of double-wall nanotubes by the disproportionation of CO at 1 atmosphere pressure over alumina supported Mo particles at 1200ºC [47]. The nanotubes had diameters ranging from 1-5 nm and were 100 nm to microns in length. These nanotubes grew in unmeasureably low yield and appeared by transmission electron microscopy (TEM) observation to be more defective than single-walled nanotubes formed by the laser vaporization or arc techniques. Neither of these techniques produces enough material to alleviate the limitations discussed in the previous section.
4. Carbon Polymerization Resuscitation

Laser-vaporization and catalytic arc generation produce small nanotubes with a narrow diameter distribution because nucleation occurs as the carbon and metals condense from the atomic vapor. CCVD growth is performed on supported catalyst particles with a diameter distribution dependent on the catalyst preparation, which leads to a wider nanotube size distribution. We believe that it should be possible to use the monodisperse nanometer structure of the laser vaporization material to create a supported catalyst that would allow the growth of monodisperse single-walled nanotubes by CCVD. Specifically, we envision the following process: First, cut single walled nanotubes produced by laser vaporization material into open ended, 100 nm lengths. Second, attach catalyst particles to the ends of these pieces. Third, get the catalyst particles in intimate, chemical contact with the nanotubes required for growth. Fourth, apply CCVD growth conditions to so that the cut nanotube pieces continue their growth. If the growth proceeds slowly enough, each carbon atom will anneal to its most energetically favored position, which would be a continuation of the original nanotube structure, be it an armchair, zig-zag, or helical nanotube. This technique, which we call “Carbon Polymerization Resuscitation”, for obvious reasons, would allow CCVD growth of high quality single-walled nanotube material, but would have another potentially important advantage. If sorting techniques were developed which could separate nanotubes by diameter, helicity, or both, these sorted nanotubes could be used as seeds to produce structurally specific nanotubes by CCVD. Such a potentially important capability encouraged us to pursue the process described above.
4.1 Single-Walled Nanotube Cleaning and Cutting.

Raw single walled nanotube material produced by laser vaporization contains a substantial fraction of impurities in the form of fullerenes, amorphous carbon, and metal catalyst, see figure 20a. A purification procedure was devised, described in detail elsewhere [9], which involves refluxing in nitric acid followed by cross flow filtration. This produces high purity nanotube material, shown in figure 20b. Nanotube ends are rarely seen in these long tangles of single-walled nanotube ropes.

To create the short nanotube pieces we have found that sonication in an oxidizing acid is an efficient method for cutting this purified nanotube material. We believe that this method is effective because the collapse of cavitation bubbles in ultrasonication are known to produce microscopic regions of exceptionally high temperatures and pressures, leading to localized sonochemistry that etches away sections of ropes. Subsequent acid attack then cuts the tube open completely and slowly etches it along its length. Different acids used in this process have distinct effects. Sonication in the very strongly oxidizing mixture of H₂SO₄/H₂O₂ (4:1, 98% and 70%, respectively) appears to slice through the entire rope., resulting in thick rope pieces having roughly the original rope diameter. The less oxidizing mixture H₂SO₄/HNO₃ (3:1, 98% and 70% respectively) results in predominantly highly thinned rope pieces as well as substantial individual cut tubes. We attribute these differences to the known intercalation and exfoliation behavior of the latter mixture with graphite [48].
Figure 20. Raw single-walled nanotube material produced by laser vaporization of a graphite/Ni/Co target (top), and the same material after purification (bottom).
The cut nanotube pieces are then treated to further oxidizing treatments without sonication for further cleaning. Finally, they are washed on a filter with dilute NaOH and water to neutralize the acids. The cut, purified nanotubes do not suspend well in water. They do form stable colloidal suspensions with the assistance of Triton-X100 surfactant. These suspensions are spun onto HOPG substrates, and the substrates washed to remove excess Triton-X100. Heating the substrate to 1000°C in 50 mT H₂ serves to further clean the nanotubes and HOPG surface, although it also gives the tubes mobility causing them to clump and reduces the number of ends available for growth. AFM of such an HOPG substrate shown in Figure 21 reveals that it is now covered with short nanotube pieces, most being several hundred nanometers long and only a few nanometers high. A significant number of the cut nanotubes are only approximately 1 nm high in the AFM image, indicating they may be individual single-walled nanotubes.

4.2 Catalyst Particle Deposition

Small particles are attached to the ends by first evaporating a thin, sub-monolayer coating of the catalyst metal onto the surface. To achieve such low coverages, a metal wire evaporator was constructed, which is shown in Figure 22. A wire, long compared to the sample dimensions, of radius r, is positioned a distance d from the sample. When the wire is heated to some known temperature, the evaporation rate of material from its surface in gm/cm²-sec can be found in tables. This mass flux of metal from the surface, \( R_s \), can then used to calculate the mass flux some distance from the surface:

\[
R_d = \frac{2r}{d} R_s
\]
Figure 21. Cut single-walled nanotubes and ropes on HOPG imaged by SFM.
Figure 22. Metal wire evaporator (vacuum system not shown).
Where $R_d$ is the mass flux at a distance $d$ from the wire of radius $r$. The evaporator is built on a 6-way, 2.75” conflat cross mounted directly over a 170 L/s turbopump (Balzers TPU 170). The sample is mounted to a blank at one end of the conflat cross, while the heated wire, mounted to another end, runs through the center, parallel to the substrate. The wire is connected to electrical feedthroughs so that it may be resistively heated. Another end of the tee has a window for a direct view of the hot wire so that its temperature may be measured by an optical pyrometer (Microtherm Micro Optical Pyrometer). Another end of the conflat tee holds a one dimensional motion feedthrough that allows a shield to move into place between the hot wire and sample so that the wire temperature may be measured without exposing the sample to the evaporated metal. The final two ends are used to attach to the turbopump and hold an ionization gauge to measure the background pressure. Typical deposition conditions are .01 monolayers per second of Ni at a wire temperature of 1315°C, a wire radius of 25 um, and a wire to sample separation of 17mm. This thin wire technique is preferred over traditional evaporation techniques because its simple geometry allows a small, controlled, and easily calculated amount of metal to be deposited, eliminating the need to measure the deposition rate.

Once the deposition is complete, the samples are heated to 500°C in a low pressure H$_2$ environment (typically 10’s of millitorr) to reduce the metal and give it mobility to form particles as described above. This works quite well. Images of the same area of a sample of cut nanotubes on HOPG before and after catalyst particle deposition and reduction are shown in Figure 23. The specific parameters for this sample were:
Figure 23. Catalyst particles assembled on the nanotubes.
cleaning at 1000°C, 50 mT H₂ for 30 minutes, deposition of 0.05 monolayers of Ni, and reduction at 500°C, 25 mT H₂ for 30 minutes. Particles are all seen to go to the step edges or nanotube ends. Along cut rope pieces, the particles are often found along the sides, which is expected since individual nanotubes can end along the sides of a rope. Evidence for this can be seen in Figure 24 where a particle on a rope is located at the point where the rope becomes thinner. Also, particles are only found at the ends, rather than on the sides, of thin cut nanotube pieces that are suspected to be individual. The observation that the metal only sticks to nanotube ends suggests that the sidewalls of the nanotubes remain structurally intact after cutting and purification.

4.3 Particle Docking

Once the particles are deposited at the catalyst ends, they must be brought into chemical contact with the metal particles equivalent to that of nanotube growing under CCVD conditions. This is achieved by heating the substrate in a hydrogen environment. Carbon from the nanotube ends will dissolve in the particle and be converted to methane and other hydrocarbons at the catalyst particle surface. This etching reaction will shorten the nanotube length. Pre- and post-etching images of certain nanotubes from the sample in Figure 23 are shown in Figure 25. The etching conditions were: 20 mT H₂ at 800°C for 30 minutes. Although this reaction is carried out at low pressure H₂, the amount of H₂ striking the catalyst particle is not limiting the etching reaction rate. Treating the H₂ as an ideal gas, and assuming a 6 nm particle diameter, 6x10⁶ H₂ strike it per second. If the efficiency of conversion to methane is near 100%, the particle would etch a 1.4 nm single-walled nanotube at 30 microns per second, much faster than what is observed.
Figure 24. A metal particle sits where the rope appears thinner.
Figure 25. In each image, the left shows a nanotube before etching conditions and the right shows the same nanotube after etching.
This reaction is most likely limited by the formation of hydrocarbons on the particle surface. Although the chemical contact appropriate for nanotube growth is most likely disrupted when the system is exposed to air for SFM imaging, this etching step can be repeated just before growth attempts.

4.4 Growth

Once the particles are deposited and an etching reaction is carried out, the samples are exposed to a mixture of ethylene and hydrogen at a reaction quotient which favors carbon deposition (to the left of equilibrium for the reaction $C_2H_4 \rightarrow C + H_2$). As in CCVD nanotube growth, ethylene molecules are expected to dissociate on the particle surface, leaving their carbon to dissolve in the catalyst particle and precipitate in the nanotube structure. When such conditions were applied, nanotube growth was very rarely observed. In most cases, the nanotube lengths were unchanged, or shorter due to the etching step, and the particles were larger. For example, a sample with nanotubes and 0.05 monolayers Ni were reduced and imaged. They were then reduced again at 800 °C, 3 mT H$_2$, for 30 min, then exposed to growth conditions of 200 mT H$_2$ plus 500mT C$_2$H$_4$ for 60 minutes. Images before and after the growth experiment show the nanotube lengths unchanged (Figure 26) and the catalyst particles appear taller in AFM. In very rare cases where new nanotubes were observed by AFM after growth conditions (Figure 26, highlighted), it was never clear whether the nanotubes were a continuation of growth of a previous nanotube, or nucleation of a new nanotube from one of the particles. The lack of growth cannot be explained by slow arrival of ethylene. The ethylene flux to the
Figure 26. Before (top) and after (bottom) growth conditions.
particle at this pressure would give microns per second of growth if nearly all ethylene that strikes the particle dissociates and has its carbon atoms add to the nanotube.

The lack of growth and particle heightening after growth conditions lead us to believe that the particles were becoming encapsulated with carbon as opposed to growing nanotubes. We believed this was a result of the particles being too large. For example, a 5 nm particle attached to a 1 nm nanotube, encapsulation of the particle rather than nanotube growth, would be an energetically favored configuration due to the lower curvature (Figure 27). Such energetic arguments, which will be pursued in detail in the next section, indicate that the particles at the nanotube ends need to be about the same diameter as the nanotube itself for nanotube growth to be lower in energy than overcoating. We began to pursue such small catalyst particles by evaporating smaller amounts of Ni and Fe on the HOPG substrate. One problem was that such small particles at a nanotube end are not distinguishable from the nanotube by AFM, so we had to assume they were forming at the ends as the larger particles did even though we could not see them. Etching conditions known to shorten the nanotubes with larger particles were attempted with these small particles, but no etching was observed. One possibility is that the metal deposition technique will simply not produce particles of the right size at the nanotube ends due to nucleation kinetics, or that such small particles evaporate. Further studies with small particles have not yet been pursued.

Future CPR experiments will benefit from improved cutting and exfoliating of the single-walled nanotube material to produce more individual cut nanotubes, as opposed to cut rope pieces. Also, the first steps towards a rational method of chemically attaching
Figure 27. Ideal growth conditions in which the catalyst particle is about in size to the nanotube (top) lead to further growth. If the particle is much larger (bottom), encapsulation of the particle is energetically favorable.
nano-scale metal particles to the nanotube ends has been accomplished by manipulating
the oxide groups left at the nanotube ends after cutting [9]. Similar techniques may allow
the catalyst particles of a controlled size to be attached in liquid suspension.

It was not clear why the experiments with larger particles, up to 10 nm, did not at
least grow multiwalled nanotubes under the CCVD conditions as they are known to do in
typical CCVD nanotube growth. We began to suspect that there was a fundamental
problem with nanotube growth at low pressure that we had not considered. To test this
suspicion, the supported catalyst system reported in Hyperion’s international patent [49]
was made so it could be exposed to low pressure CCVD conditions to find if nanotubes
would grow. Interestingly, this catalyst system, known to produce multiwalled nanotubes
in a 2:1 atmosphere of ethylene and hydrogen by Hyperion’s standard CCVD technique,
produced single-walled nanotubes when exposed to low pressure ethylene/hydrogen
CCVD conditions. This observation is the subject of the next section.
5. Supply Limited CCVD Production

In this section we describe a new method of producing single-walled nanotubes by a variant of the well known CCVD technique. The resulting nanotube material appears to be of high quality by TEM observation and has a diameter distribution somewhat larger than laser vaporization or Y/Ni arc-grown nanotubes. The technique does not produce the extremely high yields and quantities of nanotubes as standard multiwall CCVD, but it is on par with the quantities produced by laser vaporization and Y/Ni catalytic arc. Apart from being a potential production method, this work provides new insights in nanotube growth by CCVD.

5.1 Previous Studies

Here, we will give a brief review of what is known about the formation of nanotubes by CCVD. Also, we will discuss the relevance of the nanometer size of the catalyst particles and how it affects models for growth.

5.1.1 CCVD Nanotube Nucleation and Growth Models

There are numerous reports regarding the formation of nano-scale carbon filaments by the CCVD technique [40]. Carbon filaments can be coiled, branched, or straight with diameters ranging from 5 – 100 nm. The graphitic planes of the walls can vary from parallel to perpendicular with respect to the fiber axis. The fibers can be hollow, have a core of amorphous carbon surrounded by graphitized walls, or have no inner structure at all. The term "carbon nanotube" is usually reserved for hollow filaments with well graphitized walls arranged parallel to the nanotube axis. While a wide variety of filament structures have been reported, each experiment usually produces
a small subset of structures, indicating that the resulting filament structure is highly
dependent on the catalyst and synthesis conditions. The wide variety of conditions and
resulting structures has lead to various models of how filaments nucleate and grow [40].

Although debate continues over the details of CCVD filament growth, some
general conclusions can be drawn that apply to all growth experiments. Controlled
Atmosphere Electron Microscopy (CAEM) allows high resolution imaging of catalyst
particles as they grow filaments under growth conditions. Early CAEM studies by Baker,
et al. [50] demonstrated that the filament grows via a metal catalyst particle at its end on
which carbon containing gases decompose. The carbon dissolves into the particle bulk
and precipitates in a filamentous structure. It was found that the filament diameter was
always similar to that of the particle, and that termination of the growth reaction occurs
by carbon over-coating the particle.

Figure 28 shows the catalytic growth process schematically. It can be roughly
broken into four states:

\[
\begin{align*}
[C_g] & \xleftrightarrow{k_1, k_{-1}} [C_f] \xrightarrow{k_2} [C_b] \xleftrightarrow{k_3, k_{-3}} [C_n]
\end{align*}
\]

(10)

[C\(_g\)] represents the concentration of carbon in the gas phase, which is proportional to the
pressure of feedstock hydrocarbon in the reactor. [C\(_f\)] is the concentration of carbon
atoms dissolved in the front of the catalyst particle. The rate constants \(k_1\) describes the
forward rate at which hydrocarbons strike the particle surface, dissociate, and dissolve
into the particle. \(k_2\) describes the reverse reaction in which dissolved carbon atoms come
to the surface of the particle, react with hydrogen, and leave the particle as a
hydrocarbon.
Figure 28. Growth mechanism deduced from Controlled Atmosphere Electron Microscopy studies: Carbon in the gas phase [Cg] dissociates to carbon in the front of the catalyst particle [Cf], which diffuses to the back of the particle [Cb] and precipitates in the nanotube [Cn].
Carbon transport through the particle, from \([C_\pi]\) to the back of the particle \([C_\delta]\), occurs by diffusion. The rate of carbon which flows from the front to back is represented by the rate constant \(k_3\) and is proportional to the diffusivity of carbon in the particle (well known for carbon in iron \([51]\)), and on the carbon concentration gradient across the particle.

Finally, the carbon can exist in the nanotube state at a constant concentration \([C_\alpha]\). The rate at which carbon transfers from the particle to the nanotube and from the nanotube to the particle are described by the rate constants \(k_4\) and \(k_5\) respectively.

CAEM allowed Baker et al. to measure the growth rate of individual filaments as a function of temperature over catalytic particles of several different metals. For each metal catalyst, the growth followed an Arrhenius temperature dependence. The measured activation energy corresponded to the activation energy of the diffusivity of carbon in that metal. This implies that diffusion of carbon through the particle is the rate limiting step for typically reported CCVD conditions which produce filaments including multiwalled nanotubes.

5.1.2 Catalyst Particles

The phase of the catalyst particle responsible for filament growth has been the subject of some controversy. Electron diffraction of iron particles after reaction with hydrocarbons and CO to produce filaments indicated that the particles consisted of iron carbides, such as cementite. Others studies found that using iron carbide as a starting material produced no filaments, suggesting that the catalyst particles are not composed of the metal carbide during filament growth, but perhaps formation of the carbide is
responsible for growth termination [40]. The close match between the activation energy for the growth rate and for carbon diffusion in the pure metal of the catalyst indicates that the catalyst particles consist of the pure metal during growth rather than carbide.

The small size of the catalyst particles gives them different properties from the bulk metal due to the large fraction of surface atoms which have a different free energy than atoms in the bulk. Relevant particle properties that can be affected include the melting point, evaporation rate, structure and lattice constant (for a review, see [52]). The size range of particles present in the Fe/Mo catalyst covers the range where these effects become important. Using the structureless packing model, the large 10 nm particles have about 40,000 atoms, 10% of which are surface atoms. These particles typically have bulk properties. The 2 nm particles, responsible for most single-walled nanotube growth, have about 350 atoms, with 57% being surface atoms. This is the size regime where surface effects become important. Although the bulk values used in calculations below may be incorrect due to these size effects, the qualitative effects should be similar in every case.

5.2 Experimental setup

5.2.1 CCVD Reactor

The experimental setup is shown schematically in Figure 29. All experiments are carried out in a one inch diameter quartz tube furnace. H₂ and C₂H₄ are admitted upstream of the quartz tube by 10 sccm mass flow controllers (MFCs) with 0.1% precision. Argon is admitted by a 1000 sccm, 0.1 % precision MFC. All three mass flow
Figure 29. The CCVD reactor.
controllers are run by a 4-channel MFC control unit which holds the flow at an adjustable setpoint.

5.2.2 Catalyst Preparation

The catalyst consists of particles of an Fe/Mo alloy supported on fumed alumina. It is prepared almost exactly as that which Hyperion Catalysis International uses to produce multiwalled nanotubes. The method is described in their international patent [41]. A mixture of 8 grams of fumed alumina and 28.5 mL of methanol is stirred to a thick paste in a round bottom flask. A solution consisting of 7.83 g ferric nitrate nonahydrate, 0.40 g bis(acetylacetonato)dioxomolybdenum(VI), and 30 mL methanol are added to the paste. The mixture is stirred for 1 hour to form a thick liquid, then rotovapped for several hours until it forms a moist solid. The solid is dried in a tube furnace at 100°C pumped to 20 mT by a LN2 trapped mechanical pump. This hard, dry solid is ground to a fine powder with a mortar and pestle, then passed through a 400 mesh sieve (38 micron opening). The resulting burnt orange powder is very light and fluffy, similar to chalk dust. It consists of 10’s micron size agglomerates of alumina and oxidized metal catalyst particles. These large micron scale objects will be referred to as “catalyst agglomerates”, while the nanometer scale individual metal particles responsible for nanotube growth will be referred to as “catalyst particles”.

The fumed alumina has a high surface area, specified at 150 m²/gram, which keeps the metal salt solutions from forming large micron size crystallites upon drying. An LN2 trap on the heating and vacuum drying system collects most of the nitrates and organic components from the metal salt solutions. The resulting solid is rust colored,
presumably consisting of oxidized metal particles. Reduction of the powdered catalyst in H₂ at 800°C results in a ~15% mass loss, due to further removal of organics, nitrates, and oxides. Based on the range of sizes of carbon nanotubes produced by this catalyst under various conditions, it is believed that the catalyst has a wide distribution of catalyst particle sizes ranging from 0.5 nm to 10’s of nm.

5.2.3 Reaction Conditions

Most nanotube growth reactions follow the same basic procedure, varying only the reaction temperature and time. Approximately 15 mg of 90:9:1 alumina:Fe:Mo catalyst is poured into the a ceramic boat, approximately 20mm long, 4 mm wide, and 4 mm deep. The empty boat is weighed, m₀, and then the boat containing the catalyst is weighed, m₀c. The boat is placed in the quartz tube at the center of the oven. The system is sealed and a flow of 1000 sccm argon + 0.33 sccm H₂ + 0.66 sccm C₂H₄ is established. This flows for a few minutes to purge the system. The ethylene supply valve is closed and the MFC turned off to avoid pressurizing the MFC to supply valve dead space. The system is allowed to flow argon and H₂ only for a few minutes to purge the C₂H₄ in the reactor. The oven set point temperature is raised to 800°C. The catalyst is allowed to reduce for 30 minutes after the oven reaches 800°C.

After this reduction step, the H₂ supply valve is shut and the H₂ MFC turned off. The temperature is then ramped to the desired reaction temperature. Once this temperature is established, the H₂ and C₂H₄ MFCs are switched back on and the supply valves open. The MFCs are still set at 0.33 sccm H₂ and 0.66 sccm C₂H₄. The reaction is allowed to proceed for the desired time, after which the ethylene and hydrogen supply
valves are closed and the MFC switched off. The oven set point is set at 0°C and the oven cools under argon. To make the cooling occur quickly so as to avoid further reactions, the furnace is partially opened.

5.2.4 Mass measurements

Once the oven temperature is below 80°C, we shut the argon supply valve, switch off the argon MFC, and remove the catalyst sample from the furnace. The sample, which now contains the catalyst, nanotubes, and any other solid reaction products, is weighed. The result defined as $m_{\text{bcr}}$. The boat is also re-weighed without the catalyst, called $m_{b2}$. Subtracting the boat weights gives the initial catalyst mass, and the catalyst plus product mass:

$$m_c = m_{bc} - m_{b1}$$

$$m_{cr} = m_{bcr} - m_{b2}.$$ 

These values can be used to find the product mass:

$$m_t = m_{cr} - m_c.$$

The mass $m_t$ actually corresponds to the mass of all sold reaction products, but since only nanotubes and catalyst particles are seen by TEM, nanotubes are assumed to dominate the product mass. The nanotube mass, $m_n$, defined in this way can be negative. The explanation is simply that the catalyst mass is actually smaller than $m_c$ after the initial heating in H2 due to reduction, loss of nitrates, and organics. If mt is plotted versus reaction time, the mass growth is linear, and this lowering of mc is equal to the negative
y-intercept. This mass loss is approximately 14% of the initial catalyst mass, can the be added to \( m_t \) to get the true value.

5.2.5 Imaging Techniques

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to observe nanotube structure and morphology. Insulating samples, such as the alumina and metal oxide catalyst, typically have to be coated with a thin layer of metal for electron microscopy imaging to avoid sample charging which can perturb the electron beam. In the nanotube covered catalyst samples, the nanotubes are typically dense and conductive enough to avoid this problem. Samples of the nanotube coated catalyst can be imaged in SEM as grown. For TEM observation, the nanotubes-catalyst material is dispersed in methanol by brief sonication. This suspension is then drop-dried on a TEM grid.

While the SEM images represent the morphology of the material as grown, the TEM images do not due to the sonication step. For some experiments, we wish to see the undisturbed morphology of the material in TEM. To achieve this, the catalyst powder is shaken in a vial with quartz wool. The quartz wool fibers are coated with small catalyst agglomerates and take on an even burnt orange appearance. However, the catalyst coating is thin enough that no catalyst agglomerates are observable to the eye. This quartz wool then undergoes the same growth conditions as the boat contained catalyst described above. The quartz fibers can be imaged in the TEM, and the nanotubes can be seen as grown on the catalyst agglomerates.
A side view of a single-walled nanotube rope makes the diameters of the individual nanotubes impossible to determine since many nanotubes are seen on top of each other. Sometimes, a bundle curves into the image plane in such a way that the nanotube cross sections can be measured, so the diameters can be measured easily (Figure 30).

5.3 Multiwall Nanotubes

To confirm that the catalyst had been prepared correctly, Hyperion’s multiwalled nanotube growth conditions were closely repeated to be sure they produced similar yield and morphology of reaction products. 46.6 mg of catalyst were put in a ceramic boat in a quartz tube outside the hot zone of the furnace. 20 sccm C$_2$H$_4$ and 10 sccm H$_2$ flowed while the oven heated to 650°C. Once at temperature, the boat was pushed into the hot zone with a vacuum sealed push rod. The reaction continued for 30 minutes, at which point the furnace was allowed to cool to room temperature. There was a huge volume increase, approximately 30x, and the material was black. The yield, in this case defined as mass of deposited carbon divided by input catalyst metal mass, was 79.3. Hyperion reported a value of 126, but their conditions were better optimized in that they spread their catalyst over quartz wool and had flow rates of 200 sccm C$_2$H$_4$ and 100 sccm H$_2$. TEM images of this material showed the expected multiwalled nanotubes (Figure 31). The similar yield and morphology to Hyperion’s report indicate that the catalyst was properly prepared.
Figure 30. TEM imaging of single-walled nanotube ropes usually shows their sides (lower eye), but occasionally the rope is seen through its cross section (upper eye), which allows easy measurements of diameter.
Figure 31. CCVD multiwall nanotubes grown with 20 sccm C2H4 and 10 sccm H2 over Fe/Mo catalyst particles.
5.4 Initial Single-Wall Nanotube Production

Since we were getting very little nanotube growth at low pressure reactants in the CPR experiments, we decided to try growth at low pressure and on the standard CCVD catalyst, such as that described in Hyperion’s international patent. The first experiments were performed at a low absolute pressure, which was achieved by turbopumping the system through a throttle valve. By adjusting the throttle valve and mass flow of gas into the system, the pressures of reactants could be controlled up to several Torr with 1 mT precision. A reaction of 72.4 mg of 90:9:1 alumina:Fe:Mo catalyst at 650°C in 333 mT H₂ and 666 mT C₂H₄ for 30 minutes was carried out. The catalyst turned black, but there was no measurable mass increase beyond the experimental error of the mass measurements. This material was imaged by TEM and single-walled nanotubes were found to be the dominant reaction product.

After this initial experiment, the conditions varied and we found that single-walled nanotubes could be grown at 700 and 800°C as well, with the low ethylene pressure keeping the amorphous overcoating at an acceptably low level. The experiments were time consuming and tedious in that the system had to be pumped out and the pressure and flow conditions carefully set for each run. We soon found that similar results could be obtained by simply flowing a low mass flow rate of C₂H₄ and H₂ in a high mass flow rate of argon, creating a low partial pressure of reactants. The standard conditions we chose were to flow 0.66 sccm C₂H₄, 0.33 sccm H₂, and 1000 sccm argon simultaneously, which corresponds to 0.5 Torr C₂H₄, 0.25 Torr H₂, and an atmosphere
(760 Torr) of argon. The procedure was eventually standardized to the one described in section 5.2.3 above.

The catalyst turns from orange (metal oxide) to gray (metal) when reduced. After the growth reaction, the catalyst is black due to the nanotubes on its surface. Also, the catalyst, which is initially powdery, becomes more consistent and tends to keep the shape of the boat when manipulated. There is no visibly detectable volume increase. TEM images of the material show alumina, overcoated catalytic particles, and single and some double wall nanotubes. Typical nanotube diameters are 0.5 to 3 nm. Most of the nanotubes are arranged in well-aligned bundles that extend microns in length like those of Figure 3c. By growing the nanotubes on catalyst supported on quartz wool fibers, as discussed in section 2.3, the material can be imaged in SEM and TEM without disrupting its morphology as grown. It is clear that the nanotubes bundles grow from the surface of the micron scale catalyst agglomerates and cover them in a thick mat (Figure 32).

5.5 Supply-Limited Growth Hypothesis

The key discovery here is that a CCVD system known to produce multiwalled nanotubes can be made to produce single-walled nanotubes by lowering the reactant concentration. Such a surprising observation offers a unique opportunity to understand the formation of nanotubes in CCVD. We propose that the low concentration of gas phase reactants changes the rate limiting step from diffusion of carbon through the metal particles to the nanotube, R_D, to supply of carbon to the metal particles from the gas, R_S. This change in the rate-limiting step causes nanotube nucleation and growth at a lower concentration of carbon in the metal than for standard multiwall nanotube CCVD
Figure 32. Single-walled nanotube ropes cover catalyst agglomerates on a quartz fiber.
conditions. The low carbon concentration allows nucleation and growth of the lowest energy structures possible. Energetic calculations indicate that the lowest energetic structures are single-walled nanotubes from the small particles, and encapsulation of the larger particles. The next several sections will present evidence for these hypotheses.

5.6 Mass Growth Rate

By running experiments at various reaction times, we studied the nanotube growth rate as a function of temperature. Plots of the mass gained as a function of time for 700°C and 800°C are shown in Figure 33. Since single-walled nanotubes are practically the only form of carbon visible by TEM imaging, it is assumed that the reaction product mass is made up entirely of single-walled nanotubes. Note that the mass increase is linear in time and independent of temperature. Fits to both the 700°C and 800°C data indicates a mass growth rate of 32 and 39 ug/min respectively. Several lines of evidence described below indicate that growth at low reactant concentration is limited by the rate of supply of ethylene, $R_s$, to the catalyst.

5.6.1 Top-Down Behavior

We find that during the constant growth rate regime of Figure 33, the catalyst formed nanotubes from the top surface of the powder down to the bottom. At early times, the top layer of catalyst was black (covered with nanotubes), while most of the powder was still gray, indicating that it had not yet reacted. As the reaction time increased, more catalyst powder was black relative to gray. When the reaction time reached the point at which the curve deviated from the constant growth rate (the last point in each curve of Figure 33), the catalyst was completely black. This behavior indicates
Figure 33. Mass growth rate at 700°C and 800°C. The fits correspond to 32 µg/min at 700°C and 39 µg/min at 800°C.
that at the beginning of the growth reaction, all of the ethylene that hit the top surface of the catalyst agglomerates reacted, not reaching the unexposed catalyst agglomerates underneath. Therefore, all of the catalytic particles did not nucleate at once, grow together at the same time, and terminate as one might first expect. For example, at 800°C, we saw that the growth increased at 39 µg/min until the yield reached ~15%, at which point it terminated. During these experiments, the top surface layer of catalyst agglomerates nucleated nanotubes, grew to 15% yield, then terminated. The ethylene was then free to diffuse down to the unexposed catalyst agglomerates underneath these terminated nanotubes so that this lower layer could grow. This pattern continued until all of the catalyst agglomerates have reacted. Such a “top down” reaction behavior, illustrated in Figure 34, indicates in itself that the reaction is supply limited. Also, this shows that ethylene diffusion between the micron scale catalyst agglomerates is rapid since the constant growth rate does not slow down for reaction with the bottom layer of catalyst compared to the top layer.

5.6.2 Temperature Dependence

Figure 33 shows a weak temperature dependence of the total growth rate of carbon nanotubes. The growth rate would have approximately doubled between 700°C and 800°C if carbon diffusion through that catalyst particle were rate limiting and one assumed the activation energy for carbon diffusion in iron [40]. The weak temperature dependence of the growth rate indicates that carbon diffusion is no longer the rate limiting step of the reaction. It also tends to rule out the transfer of carbon between the growing nanotube end and the particle since that would likely have had an Arrhenius
Figure 34. Illustration of the "top-down" reaction.
temperature dependence as well. The temperature dependence of $R_s$ could be approximated as that of the flux rate of molecules to a surface: $T^{-0.5}$. The actual temperature dependence will be more complicated due to turbulence and convection, but the observed weak temperature dependence is consistent with the assumption that $R_s$ is the rate-limiting step. The flaw in this argument is the assumption that the microscopic growth rate of the individual nanotubes is proportional to the measured bulk growth rate. This is not necessarily true. It is conceivable that the microscopic individual nanotube growth could be limited by carbon diffusion but still exhibit an altered temperature dependence in the bulk growth rate due to temperature dependence of the nucleation efficiency. That twice as many nanotubes would be growing at $700^\circ$C opposed to $800^\circ$C to cause the same weak temperature dependence in the bulk growth rate would be highly coincidental.

5.6.3 Mass Flow

The magnitude of the measured growth rate also supports $R_s$ as the rate-limiting step. An ethylene flow rate of 0.66 sccm corresponds to a flow of 660 ug/min. The observed growth rate of 35 ug/min only accounts for 5% of the available mass. A truly supply limited reaction should use 100% of the available reactants. That the conversion of carbon mass in the gas flow to product mass is not 100% is to be expected since not all of the ethylene will strike the catalyst. To estimate the total expected conversion rate of ethylene to nanotubes, consider the following model. The mass flow rate of argon at 1000 sccm through a 2.2 cm diameter quartz tube sets the flow velocity at 4.4 cm/sec. The catalyst powder is in the bottom of a boat that is 4.0 cm long, so the residence time
of the ethylene over the catalyst is 0.91 seconds assuming laminar flow. If the
diffusivity, D, of ethylene in argon at 800°C and one atmosphere medium is known, the
average distance each ethylene molecule will travel due to random thermal motion is

$$\langle x \rangle = 2 \sqrt{\frac{Dt}{\pi}}$$

(11)
in time t. Assuming it executes such motion along the cross section of the quartz tube as
it travels over the catalyst, it will diffuse through a path of about 1 cm during its
residence time over the catalyst. Now, again assuming laminar flow over the catalyst,
this means that half of the gas within 1 cm of the catalyst when it reaches the front of the
catalyst will strike the catalyst before it flows past. Therefore, the percent of the total gas
that strikes the catalyst can be calculated by a ratio of the cross sectional area of this 1 cm
distance from the catalyst divided by the total cross sectional area of the quartz tube. The
result is that about 5% of the ethylene strikes the catalyst. The exact agreement with the
measured value is coincidental, especially considering that the actual flow is turbulent
and quite different from this ideal, so an order of magnitude correspondence is all that is
expected. The 5% conversion is therefore quite consistent with the notion that all
ethylene which strikes the catalyst is converted to nanotubes.

5.7 Supply/Diffusion Limit determines carbon concentration

5.7.1 Qualitative Expectations

We will now consider what affect the transition from diffusion limited growth to
supply limited growth will have on the catalyst particles as they nucleate and grow
carbon nanostructures. A qualitative effect in terms of the model of section 4.1.1 is not
difficult to envision. Under carbon diffusion limited conditions, carbon will be added to
the particle faster than it can be transferred to the growing structure. One would expect
this to lead to supersaturation of the front face of the particle with carbon. Under supply-
limited conditions, carbon is added slowly compared to how fast it can move throughout
the particle and react with the nanotube. One would expect this to result in a lower
concentration of carbon in the particle. In fact, if the supply is considered very slow, one
would expect the particle to come into equilibrium with the nanotube and assume a
carbon concentration equal to the solubility of the nanotube in the metal catalyst particle.

5.7.2 Mathematical Model

By estimating the rate laws and rate constants described in section 4.1.1. these
qualitative effects can be verified by simulations. In the following description, concepts
that apply to bulk materials are used, and it is unclear whether they are relevant for small
nanometer size particles. Keep in mind, however, that 2 nm particles that grow single
walled nanotubes and larger 10 to 20 nm particles that overcoat are relevant to the
calculations. Bulk concepts should be acceptable for these large particles. For the small
ones, although the quantitative values may be incorrect, the effects must be similar.
Ethylene must decompose on the small particle surface, travel through the particle and
precipitate in the growing nanotube. The rate laws we assume for the reaction of
equation (10) are:
\[
\frac{d[C_g]}{dt} = 0 \quad (12a)
\]

\[
\frac{d[C_f]}{dt} = k_i[C_x] - k_3([C_f] - [C_b]) \quad (12b)
\]

\[
\frac{d[C_b]}{dt} = k_3([C_f] - [C_b]) - (k_3 - k_4)[C_b] \quad (12c)
\]

\[
\frac{d[C_n]}{dt} = 0 \quad (12d)
\]

In equation (12a) the carbon concentration in the gas phase is taken to be constant since it is being replenished by the gas flow. The value of \([C_g]\), in carbons/m^3, can be calculated from the ideal gas law:

\[
[C_g] = \frac{2N_A P}{RT}
\]

(13)

where P is the pressure, T is the temperature, R is the ideal gas constant 8.314 J/mol-K, and \(N_A\) is Avogadro’s number. The factor of 2 is included to account for the two carbons per ethylene molecule.

The addition of carbon to the front of the particle, \([C_f]\), is a simple first order reaction since the rate is proportional to the concentration of carbon in the gas phase.
The rate constant can be found by first considering the surface collision density of an ideal gas according to the kinetic theory of gases:

\[ Z = \frac{P}{\sqrt{2\pi m k T}} \]  

(14)

where \( m \) is the mass of the molecule and \( k \) is Boltzmann’s constant. To find the rate at which the concentration of carbon increases in the particle due to this term, multiply \( Z \) by the particle area to find how many carbons strike it, and divide by the volume to convert to a concentration. After canceling some terms:

\[ R_s = \frac{3P}{2r \sqrt{2\pi m k T}} \]  

(15)

Again, there is a factor of 2 for the two carbons per ethylene. Substitution of the expression for the pressure in (13) gives the rate in terms of the concentration, which reveals the rate constant \( k_1 \):

\[ k_1 = \frac{3R}{4r N_A} \sqrt{\frac{T}{2\pi m k}} \]  

(16)

We ignore the rate, \( k_2 \), of carbon leaving the particle as a gas phase hydrocarbon. In terms of equilibrium, the 2:1 ethylene to hydrogen ratio puts the system far to the left of the ethylene to graphite reaction, so the forward rate of ethylene dissociation is expected to dominate.
Next, we consider the carbon diffusion rate. Fick's first law of diffusion states that the flux of material across an imaginary plane in some medium is equal to the concentration gradient of the material at that plane times the diffusivity of material in the medium. In the current case, we approximate the gradient as the difference between the concentration of the front and back of the particle, divided by the particle diameter. We therefore expect the flux of material, in kg/m^2-sec, across the center to be:

\[ N = D \frac{\left( [C_f] - [C_b] \right)}{d} \]  

(17)

where D is the diffusivity of carbon in iron [51]. In order to find a reaction rate, the flux must be multiplied by the cross sectional area of the particle to get the absolute amount of material, and divide by (half of) the volume of the particle to find the effect on the concentration.

\[ R = \frac{3D}{4r^2} \left( [C_f] - [C_b] \right) \]  

(18)

Again, we have a reaction rate in terms of a concentration, or in this case a concentration difference. Therefore, the rate constant is:

\[ k_3 = \frac{3D}{4r^2} \]  

(19)

Finally, the reaction between the growing nanotube and the metal particle must be considered. Carbon in the nanotube, \([C_n]\), is in a solid state as opposed to a solid solution or gas, so its concentration is constant. The forward and reverse rates of carbon dissolution will therefore only depend on the concentration of carbon in the back of the
metal particle, \([\text{Cb}]\). If no carbon addition from the gas occurs, and the metal particle is in contact with the nanotube, an equilibrium carbon concentration in the particle will be reached. This concentration is the solubility of a nanotube in the metal particle. It depends on the chemical potential of the carbon in a nanotube and that of carbon dissolved in the metal. This solubility can be approximately assumed to be the solubility of graphite in iron. This quantity has been measured as a function of temperature. It is on the order of 0.01 weight % at the temperatures of interest \([53]\). This corresponds to the equilibrium concentration at the back of the particle \([\text{Cb}] = [\text{Ceq}]\).

We will only consider the net reaction rate of dissolution, \(R_n\), with a reaction constant \(k_{4-5}\) that corresponds to the difference between the forward and reverse reaction rates. If the concentration in the back of the particle is greater than \([\text{Ceq}]\), the net reaction rate will be positive, or towards the nanotube product. If the concentration is less \([\text{Ceq}]\), the net reaction rate will be negative, or toward the dissolved carbon state. Based on this reasoning, we choose the model rate law to be:

\[
R_n = k_{4-5}(\text{Ceq} - \text{Cb})
\]  

Although this rate law may not be exactly correct, it will give the right steady state solution in that it will drive the concentration of carbon in the back of the particle towards equilibrium with the nanotube. Since we know that this rate is faster than diffusion from Baker's work, and therefore faster than the supply rate in the current experiments. the back of the particle in the model is expected to be near equilibrium with the nanotube. Therefore, the use of this rate law is justified, as long as \(k_{4-5}\) is given a value faster than the diffusion and supply rate constants.
Before solving the differential equations 12b and 12c to find the carbon concentrations, one of the rate constants must be modified. The concentration of carbon in the gas phase, \([C_g]\), and the rate at which these carbons strike the particle, \(Z\), were simply determined from the kinetic theory of gases and the partial pressure of ethylene. If ethylene molecules simply bounced off of the catalyst particles, this model would be accurate. We have observed, however, that each ethylene molecule that strikes the particles is dissociated and does not re-enter the gas phase. For each catalyst particle, ethylene is lost in this way and similarly by all of the nearby catalyst particles. The result is a reduced ethylene concentration \([C_g]\) in the vicinity of the catalyst particles, and therefore a smaller arrival rate, \(Z\). This reduction can be included in the calculation by simply multiplying the ethylene pressure by some fractional term \(f\). This term can be approximated from the experimental data by calculating an observed flux of ethylene to the catalyst from the growth rate data, and dividing by the flux of ethylene that would be expected from a perfectly mixed gas.

\[
f = \frac{\text{flux}_{\text{obs}}}{\text{flux}_{\text{ideal}}}
\]  
(21)

The observed flux is calculated from the measured growth rate of 35 \(\mu g/min\), which corresponds to 1.46 \(\mu\)moles/min of carbon over the catalyst 3mm wide by 35 mm long giving a flux of:

\[
\text{flux}_{\text{obs}} = 0.00023 \text{ mmol/m}^2 \text{ sec}
\]  
(23)
According to the formula for the arrival rate, $Z$, of an ideal gas, the calculated flux of ethylene would be:

$$ \text{flux}_{\text{ideal}} = 3.5 \frac{\text{molecules}}{\text{m}^2 \text{sec}} $$

(24)

So a correction factor of

$$ f = 7 \times 10^{-5} $$

(25)

is needed to reduce the pressure to give a carbon flux to the catalyst that corresponds to the measured mass growth rate.

The two differential equations (12b) and (12c) determine the carbon concentrations in the front and back of the particle. Acceptable values for the rate constants have been determined above. There is an analytic solution to the equations, but it is quite complicated and was found with Mathematica software. With the solutions to the equations, the carbon concentration in the front and back of the particle can be plotted versus time for various experimental conditions. First, consider 2 nm and 10 nm diameter particles under low pressure CCVD conditions at 750°C. The diffusion rate constant is on the order of $10^6$ to $10^8$ sec$^{-1}$, so we set the dissolution rate constant, $k_{d,5}$, to $10^{12}$ sec$^{-1}$ to make it much faster. The carbon concentrations for the front and back of the particle are plotted in Figure 35. Both the front and back concentrations approach the equilibrium concentration, $C_{eq}$, which was set to be the solubility of graphite in iron at that temperature. The concentration at the back reaches equilibrium much faster due to the fast dissolution reaction with the nanotube, while the particle front must get carbon more slowly by diffusion from the back and from the gas phase. As carbon is slowly
Figure 28. The carbon concentrations, as a function of time, at the front (solid) and back (dashed) of the catalyst particles. The equilibrium solubility is $0.07 \text{ C/nm}^3$. At low pressure, the particle is near its equilibrium solubility of carbon. At one atmosphere of ethylene, the front of the particle is supersaturated.

a. 2 nm particle, 0.5 T ethylene

b. 10 nm particle, 0.5 T ethylene

c. 10 nm particle, 760T ethylene
added to the front, a small gradient is set up so that carbons diffuse to the back and are added to the nanotube. For this test, the model confirms our prediction that under supply limited conditions, the carbon concentration in the particles is the equilibrium solubility.

Next, the concentration is studied for typical diffusion limited conditions: a temperature of 650°C, 1 atmosphere of ethylene, and 2 nm and 10 nm diameter particles. The diffusivity and \( C_{eq} \) are adjusted for the lower temperature. The concentrations of the front and back of the particle versus time are also plotted in Figure 35. The back reaches equilibrium again due to the fast reaction between the nanotube and particle. The front face reaches a concentration higher than \( C_{eq} \), which indicates that carbon is supersaturated in the particles at the front face. The simulations support the hypothesis that diffusion limited growth results in supersaturation of the front of the catalyst particle with carbon.

From these results, it follows that under supply-limited conditions the equilibrium carbon concentration and slow growth rate allow the carbon time to anneal to its most energetically favored structure. In contrast, a diffusion limited particle will grow a structure under a steady state supersaturated carbon concentration. This will lead to quicker growth and less time to anneal. The model predicts this trend in that the steady state difference \([C_f] - [C_b]\), and hence the growth rate, increases with pressure.

5.8 Energetic Considerations

Without yet considering the details of nanotube nucleation from the catalyst particles, we will assume consider which carbon structure formed by a catalyst particle represents the energetic minimum. The only structures observed in the product of a
growth reaction are single-wall nanotubes and encapsulated particles, ignoring the double-walled nanotubes for the moment. Other structures, such as flat sheets precipitating from the particle are assumed high in energy due to the large fraction of edge atoms with dangling bonds. The energies of the nanotubes and capsules are estimated by formulas for the energy increase of a curved graphene sheet above the energy of flat graphene. The single-walled nanotube will be treated as graphene rolled into a cylinder of diameter equal to the catalyst particle. The capsule will be treated as a large fullerene of diameter equal to the catalyst particle.

One expects the single-walled nanotube always to be lower in energy per carbon atom than a spherical capsule of the same diameter since the nanotube has curvature in only one dimension as opposed to two. However, the van der Waals interaction between the graphene capsule and the metal particle will lower the energy per atom of the capsule. Therefore, encapsulation is energetically favorable for larger particles, while the single-wall nanotube structure is still lower in energy for small particles.

From ab initio calculations of nanotubes and large fullerenes, simple expressions for the energetic cost of such structures compared with a graphene sheet can be written. The energy of each structure can be plotted versus particle size to see which structure is energetically favored for a given size. For graphene capsules, Adams, et al. found that the following empirical formula for the energy in terms of the planarity of an n-atom fullerene agrees well with quantum molecular dynamics calculations [54]:

\[ E(n) = 0.6976 \left( \frac{60}{n} \right) - 0.2593 \left( \frac{60}{n} \right)^2 \text{ eV/atom} \]  (26)
Note that this expression does not account for the van der Waals attraction between the cap and the metal particle. The magnitude of this effect can be estimated from the work of L’nyanoy, who determined the energy of the graphite-ferrite interface by studying the formation rate of graphite on super-cooled solutions of carbon in ferrite [55]. Comparing this with the surface energy for the basal plane of graphite gives an approximate value of 18-36 meV/atom for the reduction in energy of a graphite surface that surrounds an iron particle. We thus subtract 27 meV/atom from equation (21) to account for the metal interaction.

For the energy per atom of a nanotube compared to graphene, Sawada and Hamada [56] found the following empirical expression for the energy increase due to rolling up an graphene sheet:

$$E(n) = \frac{0.0141}{r^2} + \frac{0.000157}{r^4} \text{ eV/atom} \quad (27)$$

where the radius $r$ is in nanometers. Since we are only concerned with the energy of adding carbon to the walls, the nanotube ends are ignored. When equations (26) and (27) are plotted versus particle size (Figure 36), we see an agreement with qualitative expectations described above. In fact, the nanotube energy is lower in a diameter range similar to the single-walled nanotube diameters we find in our experiments. This implies that under supply limited conditions, when the growing structure reaches its energetic minimum, the small (0.5 to 3 nm) catalyst particles produce single-walled nanotubes, while the larger particles encapsulate, exactly as observed.
Figure 36. Energy per carbon atom above that of a graphene sheet for a single-walled nanotube (dashed) and a capsule (solid) versus diameter. Note that the nanotube is lower in energy for sizes up to about 3 nm while the capsule is favored for larger sized.
5.9 Further tests of the SL CCVD hypothesis

The previous evidence described in the last 3 sections suggests that the supply-limited growth hypothesis is correct. To further test the hypothesis, we have run reactions under two sets of conditions that we expect to once again be diffusion limited. Even at the low, 0.5 Torr ethylene concentration, these should produce multiwalled nanotubes according to the hypothesis. First, since the diffusion constant drops by an Arrhenius dependence on temperature, a low enough reaction temperature will ultimately slow the diffusion of carbon through the particle enough that it falls below the supply rate and becomes the rate-limiting step. A reaction was carried out at 600°C with the Fe/Mo catalyst under the low pressure 0.5 Torr ethylene conditions described in section 5.2.3. The mass growth rate fell below the supply limited mass growth rate, as expected if the reaction once again became diffusion limited, and multiwalled nanotubes were formed.

Second, a nickel catalyst was used in the standard supply-limited reaction conditions at 800°C. The carbon diffusion coefficient in Ni is known to be several orders of magnitude lower than in Fe, which will lead to a slower diffusion rate, $R_D$, which may made $R_D$ rate limiting and create multiwalled nanotubes. Using Ni, the mass growth rate was lower than the supply limited growth rate of Figure 33 (indicating a diffusion limited reaction), and the product consisted of multiwalled nanotubes. These experiments further confirm the supply-limited single-walled nanotube growth hypothesis.

In summary of sections 5.3 to 5.8, we have shown experimental evidence which demonstrates that the rate limiting step of the catalytic nanotube formation reaction changes from diffusion of carbon through the catalyst particle to the supply of reactant to
the catalyst particle surface upon switching from 1 atmosphere to low pressure reactant conditions. We have also shown calculations which indicate that growth under supply-limited conditions occurs at the equilibrium solubility of graphite in the catalyst particle, as opposed to supersaturated conditions as in diffusion limited growth. Finally, we showed that the structures which are expected grow when there is time to anneal to the lowest energy structure, as would be expected at the equilibrium solubility, are the same as those observed: small 0.5 to 3 nm diameter nanotubes and larger encapsulated particles.

5.10 Early Growth Stages

A great advantage of nanotube growth from supported catalytic particles as opposed to laser vaporization or arc generation is that the nucleation, growth, and termination mechanisms can be studied with more control over the growth process. The product mass versus time curves described above are an example. Another possibility is to grow nanotubes for very short times, then suddenly stop the reaction and image the product. This allows one to see the early stages of tube growth and rope formation. With the catalyst supported on quartz wool fibers, reduction conditions were carried out in 1000 sccm argon, 0.33 sccm H₂, 800°C, for 10 minutes. Next, growth conditions were carried out for only 1 minute. Images of the unperturbed catalyst agglomerates shows the nanotubes in an early growth stage, radiating outwards (Figure 37). Higher magnification images of these structures indicate that they are individual single-walled nanotubes. This reveals that the ropes form when individually nucleated nanotubes collide as they grow and align due to van der Waals forces.
Figure 37. Single-walled nanotubes radiating from catalyst agglomerates as the result of a short growth experiment.
The individual single-wall nanotubes in Figure 37 are too long to image their ends due to thermal vibrations, but shorter nanotubes can be found whose end structure can be determined. Imaging can be quite difficult because the insulating catalyst material is not well coated with nanotubes for the short growth samples. When imaging a short nanotube at high magnification to determine its end structure, it often disappears, probably due to charging of the catalyst powder. Still, we have time to see that the ends are all closed without particles at their tips, but we usually don’t have time to record an image. Occasionally we see an end with a particle attached, which confirms that these single-walled nanotubes grow in this CCVD system as they are known to grow in others: by a catalytic particle of similar diameter to the nanotube. A typical closed end and one of the ends with a particle attached are displayed in Figure 38.

Such observations of the early stages of nanotube growth can be used to deduce a nucleation mechanism. Since most ends we see are closed, and we know that all nanotubes must have a particle at least one end, we conclude that most of the nanotubes nucleate from small particles which remain in the alumina support while the closed nanotube grows outward.

With this model of the growing nanotube, the nucleation can be understood by considering the growth process in reverse (Figure 39). If the nanotube is closed at one end, and has a particle at the other, reversing the growth will eventually lead to a particle with a hemispherical carbon cap. We believe hemispherical graphene caps form on all of the particles and grow along the surface, since they represent a lower energy structure for the carbon than being dissolved in metal. Once the cap has grown to cover half of the
Figure 38. A single-walled nanotube with catalyst particle attached (right), and the more typical closed nanotube end growing from the catalyst surface.
Figure 39. The yarmulke mechanism can be deduced by extrapolating back in time from the observed structures.
particle, it can either continue along the surface, encapsulating the particle, or it can nucleate a nanotube. Assuming it forms the lowest energy structure, the cap will nucleate a nanotube on small particles and encapsulate large particles, as described in section 5.8. This cap nucleation mechanism has been described previously and is known as the yarmulke mechanism [47].

5.11 Double Wall Nanotubes

In section 5.3, we noted that the single-walled nanotube material we produce has some amount of double wall nanotubes. These should not be thought of as part of the class of large, 10nm to 20nm multiwalled nanotubes produced under diffusion limited growth conditions. These double wall nanotubes are grown under supply limited conditions, and are similar in diameter to the single-walled nanotubes. Growth reactions were carried out at 700°C, 775°C, 800°C, and 850°C. Between 50 and 100 nanotubes cross sections were observed for each sample and the number of single-walled and double-walled nanotubes were counted for each. The relative number of double wall nanotubes compared to single wall increases with increasing temperature, as shown in Figure 40. A rope cross section showing some double wall nanotubes is in Figure 41. Like the higher rate of termination, the relative number of double-walled nanotubes to single-walled nanotubes increases as the reaction temperature increases. The mechanism responsible for double-walled nanotubes will be discussed with the termination mechanisms.
Figure 40. The relative number of double-walled nanotubes as a function of temperature.
Figure 41. Cross sectional TEM image of some double-walled nanotubes.
5.12 Termination Data

The plots of product mass as a function of time at 700°C and 800°C in section 5.6 only show the portion where the growth rate is constant. In this regime, we have argued that the growth is supply limited, so the mass growth rate is independent on the amount of catalyst being exposed, as long as the catalyst powder has about the same geometry in the boat so that it is exposed to a similar amount of gas. Therefore, to see the constant growth rate, a plot of product mass as a function of time is appropriate. At both temperatures, the growth will ultimately deviate from this constant rate. In this latter growth regime, the amount of material produced is now limited by the amount of catalyst used in the experiment. Since this amount varies from experiment to experiment, we plot the yield as a function of time. The yield is defined as the nanotube mass divided by the input catalyst mass.

The yield as a function of time at 800°C is plotted in Figure 42. For the constant growth regime, a line is given based on the growth rate measurement described in section 5.5 and assuming a 15mg input mass. At 800°C, the growth suddenly stops after 50 minutes at a yield of 15%. As described in section 5.6.1, each catalyst agglomerate grew nanotubes to this percent yield, then terminated so that those agglomerates underneath them could be exposed to ethylene for nanotube growth. The termination mechanism at 800°C will be discussed later.

The yield data for 700°C, shown in Figure 43, indicates that the termination mechanism is fundamentally different. The growth is constant up to 30% after 130 minutes. Beyond this point, it does not suddenly stop. The growth rate assumes a
Figure 42. Yield as a function of time after the growth rate has deviated from constant growth at 800 C.
Figure 43. Yield as a function of time after deviation from constant growth at 700 C.
sublinear dependence on time. We believe that diffusion of ethylene through the mat of nanotubes covering the catalyst agglomerates is responsible in this case. This effect can be easily modeled to check the time dependence and the magnitude of the growth rate. Assume the catalyst is made up of spherical, 38 micron diameter catalyst agglomerates (equal to the spacing of the sieve), whose surfaces are covered with catalyst particles. Nanotubes grow from each particle creating the nanotube mat. Further assume that every ethylene that reaches the catalyst agglomerate surface adds two carbon atoms to the nanotube mat. The process is shown in Figure 44, where a planar geometry is assumed since nanotube mats are typically less than 1 micron thick while the agglomerate diameter is tens of microns. According to Fick’s first law of diffusion, the flux, \( N_z \), at some point along the z-axis will be:

\[
N_z = -D_{\text{eff}} \frac{d[C_g]}{dz}
\]

(28)

Where \( D_{\text{eff}} \) is the diffusivity of ethylene in the nanotube mat, and \([C_g]\) is the ethylene concentration in the gas phase inside the mat. Under steady state conditions, assume a linear drop of \([C_g]\) from the ambient gas level outside the mat, \([C_{g0}]\), to zero at the agglomerate surface, so that the concentration gradient is simply the ambient concentration divided by the thickness \( d \), simplifying the flux to

\[
N_z = -D_{\text{eff}} \frac{[C_{g}]_o}{d(t)}
\]

(29)
Figure 44. Once the nanotubes grow a thick mat over the catalyst, ethylene must diffuse through this mat in order to react with the catalyst.
If \( N \) is the flux of mass to the catalyst, the mat thickness will increase as:

\[
d'(t) = \frac{N(t)}{\rho_B}
\]

Equating (24) and (25) for \( N(t) \) and solving for the thickness gives:

\[
d(t) = \sqrt{\frac{D_{\text{eff}}[C_s]}{\rho_s}t}
\]

This model predicts that the thickness, and therefore the mass, will increase as the square root of time. A fit to the ethylene diffusion limited portion of the 700\(^\circ\)C yield curve (Figure 45) is in good agreement having a \( t^{0.5} \) dependence.

Apart from predicting the time dependence, the absolute growth rate can be calculated. We approximate the nanotube mat as 10 nm diameter ropes running along the vertices of a cubic lattice with a 20 nm lattice constant. The diffusion coefficient for a gas through a porous medium in which the pore size is smaller than the mean free path of the gas is:

\[
D_{\text{eff}} = \frac{\varepsilon D_K}{\tau}
\]

where \( D_K \) is the Knudsen diffusion coefficient, \( \varepsilon \) is the porosity and \( \tau \) is the tortuosity.

Assuming each 10 nm diameter rope consists of fifteen 2 nm diameter single-walled nanotubes, the elemental rope density is 0.91 g/cm\(^3\). The bulk density, which includes
Figure 45. 700C termination data with a fit that indicates a $t^{0.49}$ dependence
the spaces between the ropes, is 0.54 g/cm$^3$. The porosity is 1 minus the ratio of the bulk density to the elemental density, or 0.41 in this case. The tortuosity is related to the length of the path that a molecule must follow to get from one point to another. It is between one and ten for typical porous systems. The Knudsen diffusion coefficient is given by:

$$D_K = \frac{2r}{3} \sqrt[3]{\frac{8RT}{\pi M_g}}$$

(33)

where $r$ is the pore radius, 7.5 nm for the mat under consideration. Combining these terms gives a diffusion constant:

$$D_{eff} = 1.76 \times 10^{-2} \frac{cm^2}{sec}$$

(34)

Using this diffusion coefficient, and the concentration of ethylene at 0.5 Torr in (26), the thickness growth rate is:

$$d(t) = 8 \times 10^{-5} \sqrt{t} \frac{cm}{\sqrt{sec}}$$

(35)

To find the mass yield that this would produce, the surface area per gram of the catalyst must be known since the nanotube mass only grows on the surface of the catalyst agglomerates. Since all of the catalyst material passed through a No 400 sieve, assume all catalyst agglomerates are spheres of 38 microns diameter. Using this model catalyst, the mass of each agglomerate can be calculated as well as the amount of nanotube
material that grows on the surface. These masses can then be divided to find the yield as a function of time for the catalyst. The result is:

\[ yield(t) = 0.14t^{0.5} \]  

(36)

where \( t \) is in minutes. The fit to the yield of the diffusion limited data of Figure 45 has the following form:

\[ yield(t) = 0.011t^{0.5} \]  

(37)

As mentioned previously, the power of the time exponent matches well, but the pre-factor of the measured data is lower than that predicted by a factor of 13. However, many of the parameters chosen for the model were rough estimates that would affect this value, such as the pore structure and the catalyst agglomerate size. Also, we did not insert a value for tortuosity, which would lower the yield prefactor for the model of equation (31).

The termination has been studied at several temperatures and the data is displayed in Figure 46. Although the data are not complete enough to fit constant growth and ethylene diffusion limited curves, it is clear that at temperatures of 800\(^\degree\)C and above, some termination mechanism limits growth to 15\% or less. At 700\(^\degree\)C, the growth only slows after its departure from the constant growth regime and displays diffusion limited behavior. At intermediate temperatures, an intermediate behavior is observed which indicates that the termination mechanism in effect at 800\(^\degree\)C becomes more prevalent with increasing temperature.
Figure 46. The nanotube yield versus reaction time at several reaction temperatures.
These studies reveal important aspects of growth termination. The most important being that, for at least this system, there is no fundamental termination mechanism that limits the catalytic growth of nanotubes for certain temperatures. At 700°C, they can be grown to unlimited lengths, in principal. Experiments towards the bulk production of nanotubes by this iron-ethylene system should be carried out at this temperature. For other catalysts, such as nickel, cobalt, or alloys, similar termination behavior may exist.

5.13 Termination Mechanisms.

Nanotube growth appears to be unlimited at 700°C while some termination mechanism occurs at higher temperatures. One possible mechanism is the transformation of the metal particle to some catalytically inactive phase, such as a metal carbide. This phase may be inactive due to slow diffusion of carbon through the particle or a lack of the ability to dissociate hydrocarbons on its surface. This mechanism could explain the termination in the current experiments, but unfortunately it is difficult to confirm. Since the particles responsible for growth are buried in the alumina catalyst under the nanotube mat, they are not readily available for electron diffraction studies to determine their crystal structure. Even if they were accessible by somehow removing the nanotubes and alumina, their post-growth structure may not reveal the relevant phase that terminated the growth reaction. In order to truly determine that an inactive particle phase is responsible for growth termination, the crystal structure would have to be determined at growth conditions by CAEM. The inaccessibility of the particles precludes this for the current catalyst system.
Another possibility is detachment of the growing nanotube from the catalyst particle. Again, this is difficult to confirm since the nanotube-particle interface sites are buried under the nanotubes. The mechanism here is that the catalyst particle grows a closed nanotube tip and rolls to the side of the nanotube. This process has been observed to occur for multiwalled nanotubes when heated in vacuum with iron particles at their tips [57]. However, under growth conditions it seems that after detachment the particle should nucleate a new nanotube, allowing growth to continue, unless the particles grow too large during the experiment due to mobility of metal on the alumina surface.

We have also considered evaporation of the catalyst particles as the termination mechanism. Simply applying the bulk evaporation rate for the reaction temperatures indicate that the particles should not significantly evaporate on the time scale of the reduction and growth experiments. The actual evaporation rate may be higher, however, due to the nano-scale size of the particles. To test the evaporation hypothesis, we ran an experiment with a reduction period at 800°C for 10.5 hours, and then growth at 800°C for 35 minutes. If the particles are evaporating to cause termination in about 1 hour for typical growth conditions at 800°C, this 10 hour reduction at 800°C should evaporate the particles resulting in no nanotube growth. We still observed nanotube growth, at the typical rate determined from the curve of Figure 34, so we do not believe that the particles are evaporating. Particle growth due to mobility of metal on the alumina could cause the particles to grow as the reaction takes place, eventually becoming large enough to encapsulate. However, the 10 hour reduction experiment refutes this hypothesis as well.
A commonly accepted termination mechanism in CCVD filament growth is encapsulation of the exposed surface of the catalyst particle, shielding it from further hydrocarbon dissociation. This has been directly confirmed by CAEM for some CCVD systems [58]. Termination by overcoating for the current experiments would occur in a fashion similar to the nucleation described in section 5.10. Once a nanotube has been nucleated, extra yarmulkes could still form, although one might expect the rate to be lower than for a bare particle since carbon atoms can now add to the low energy nanotube structure. If, however, an extra yarmulke did form on the face of the particle that faces the reactant gas, it could grow, encapsulate the particle, and terminate the growth reaction. This "extra yarmulke" mechanism can also explain the growth of double-walled nanotubes. If an extra yarmulke forms on the region of the particle surface inside the growing nanotube, it could grow and lift off, creating a double wall nanotube. These processes are illustrated in Figure 47.

The temperature dependence of the termination and relative amount of double-walled nanotubes supports the extra yarmulke hypothesis. In section 5.7, we proposed that under supply limited growth conditions, the catalyst particle has a carbon concentration equal to the nanotube solubility in that particle. Consider the reaction:

\[ C_{\text{nanotube}} \leftrightarrow C_{\text{metal}} \]

The solubility, which is the equilibrium concentration, is determined by the difference in free energy of carbon in the product states and reactant states. Since the entropy for carbon dissolved in metal is larger than carbon in a nanotube, an increase in temperature will cause a greater reduction in the \( C_{\text{metal}} \) free energy. This will increase its equilibrium
new yarmulke on front face...

...leads to termination by encapsulation

new yarmulke on rear face...

...leads to a double-walled nanotube

Figure 47. Extra yarmulke termination mechanism.
concentration with increasing temperature. It seems reasonable to assume that higher concentrations of carbon will result in more frequent formation of new yarmulkes, explaining the more frequent termination and double wall nanotube formation at higher temperature.

Unfortunately, although evaporation, particle growth, and detachment were refuted by experimental observations, we cannot definitely determine whether an inactive phase of the catalyst particle or encapsulation of the catalyst particle is responsible for termination at high temperatures. We consider the encapsulation argument to be strongest, since it is known to occur for multiwalled CCVD filaments, and it also explains the observation of double-walled nanotubes, and the temperature dependence of both the amount of double-walled nanotubes and the rate of termination.
6. Bulk Production

As discussed in section 3, catalytic laser vaporization and catalytic arc generation of nanotubes produce high quality material, but are limited to gram amounts. Traditional CCVD techniques can produce kilogram quantities, but the material is not as attractive due to its defects and large nanotube diameter. Now that single-walled nanotubes of apparent high quality can be produced by CCVD, it would seem that they could be produced in bulk and readily available.

It is clear that current experiments are far from this goal. The highest yield yet attained was by reaction of 0.5 Torr ethylene at 700°C (where there is no fundamental termination mechanism) for about 10 hours, which produced only 7.3 mg of single-walled nanotube material from 14.1 mg of catalyst. 104 mg of the same catalyst produces 1,243 mg of multiwalled material in 30 minutes when reaction occurs at 500°C ethylene. There are three reasons for the slower production of single-walled nanotubes.

The first is simply a direct result of the low ethylene concentration required to form single-walled nanotubes as opposed to multiwalled nanotubes. The flow rate of ethylene is typically 100 times lower in supply-limited single-walled nanotube production experiments than in standard multiwalled growth, so there is a factor of 100 times less carbon available for growth. This is really just a limit on the rate of mass production, and not the yield since all of the gas could be made to react with a small amount of catalyst to produce high yield nanotubes. Unfortunately, this limitation is fundamentally tied to the supply-limited growth method.
Second, the single walled nanotube yield (mass of nanotubes divided by catalyst mass) is partially limited by the number of small ~2 nm particles in the particle size distribution. Assuming that all 0.5 to 3 nm particles form a nanotube at least one micron in length, the total nanotube mass will be about 100 times the mass of these particles. In a typical experiment, a catalyst with 1.5 mg of metal produces 3 mg of nanotube material, leaving the amount of metal active in nanotube growth to be only .03 mg. Therefore only 2% of the metal is in the form of small particles which forms single-walled nanotubes. This is an upper limit on the amount of active metal since each particles produces a nanotube which is likely greater than 1 micron. Such a small amount of active metal is not surprising since the catalyst was most likely optimized by Hyperion for 10-20nm particles for multiwalled nanotube production. This limitation to bulk production could likely be improved by optimizing the catalyst for smaller particles, possibly by varying the Fe/Mo ratio.

Finally, the problem of ethylene diffusion through the nanotubes to the growing catalyst particles is worse for single-walled nanotubes. The ropes curl on a tighter radius than multiwalled nanotubes, creating a smaller effective pore size for the ethylene to diffuse through. The ropes are able to curl more tightly because their single-walled nanotube components are not as stiff as multiwalled nanotubes due to their smaller diameter. Although rope diameters are similar to multiwalled nanotube diameters, individual nanotubes within a rope are able to slide against one another, so the ropes do not become proportionately stiffer with their number of nanotubes. Hyperion also
observes the ethylene diffusion problem for multiwalled nanotube growth, but not at such low yields.

The ethylene diffusion problem can be solved for supply limited growth. We showed in section 5.12 that the growth is limited by diffusion of ethylene through the nanotube mat growing on the catalyst agglomerate, which holds the catalyst particles on its surface. For supply-limited growth to occur, only the flux of ethylene to the catalyst agglomerate surface must be kept slow. Therefore, as the nanotube mat grows, the ethylene concentration outside of the mat can be increased to hold the flux of ethylene to the catalyst agglomerate surface constant. This would at least allow the nanotube production to proceed at a constant, albeit slow, rate. Assuming that the carbon concentration increases linearly with the ethylene mass flow rate \( F_{eth} \), equation (26) can be written as:

\[
m(t) = \sqrt{KF_{eth}t}
\]

(38)

Where \( k \) is some constant set by the diffusion constant, mat density, and catalyst surface. Section 5.12 demonstrated that some of these parameters are not well known, but in the current case we can use the measured yield data to find \( k \). Using 0.66 sccm for \( F_{eth} \) and equating equation (38) with the measured form for the 700°C termination data (37), gives a value for \( k \). If the value of the flow rate, \( F_{eth} \), in equation (38), increases in time as:

\[
F_{eth}(t) = At
\]

(39)
the mass growth rate would be a constant value, whose magnitude depends on the constant $A$. To be sure the growth remains at supply limited conditions, we will set $A$ such that the supply limited growth rate occurs of 32 ug/min at 700°C. This value is found by simply equating the first derivative of (38) with 32 ug/min, to find $A=0.13$ sccm/min.

To test this method of defeating the ethylene diffusion limit, we put a typical ~15 mg of catalyst in the reactor, reduced at 800°C, 0.33 sccm $H_2$ and 1000 sccm argon, for 30 minutes. We then went to the standard growth conditions: 0.33 sccm $H_2$, 0.66 sccm $C_2H_4$, 1000 sccm argon, 700°C for 165 minutes. According to Figure 43, all of the catalyst has been exposed and the growth becomes ethylene diffusion limited at 154 minutes, so we will need to plot the new data point 11 minutes earlier on the graph to make up for the late start. After the initial growth, we began to raise the ethylene flow rate according to (35), we also raised the $H_2$ flow rate to maintain a 2:1 $C_2H_4$: $H_2$ ratio. We continued to increase the flow for 40 minutes, then stopped the ethylene and hydrogen flow and cooled under argon. The result, plotted in Figure 48, shows that the new data point follows the original growth curve as opposed to the ethylene diffusion curve. The ethylene diffusion limit can apparently be avoided in this way. Ultimately, increasing the ethylene concentration will result in an unacceptable level of pyrolytic carbon coating the nanotubes. If one assumes that up to 100 Torr of ethylene is acceptable at 700°C, the constant growth would produce up to 30 mg of material from 14 mg of catalyst, just over 200%
Figure 48. Product mass when the ethylene concentration is increased to counteract the effect of ethylene diffusion through the mat of nanotubes covering the catalyst surface.
Now, considering that the ethylene diffusion limit has been solved, we will consider the potential mass production rate of the supply limited CCVD technique. Currently, we produce 32 ug per minute at 700°C. This corresponds to only 5% of the total ethylene flow forming nanotubes. Presumably, if we spread the catalyst over a larger area, this could be increased to 100%, so a factor of 20 increase in the growth rate at 700°C gives 640 ug/min. If the same reactant concentration and flow velocity were set up in a 4 inch tube furnace, another factor of 16 increase in the growth rate would give 10.2 mg/min. Therefore, with a 4 inch furnace, a gram of material could be produced in just under 100 minutes, which is within an order of magnitude of laser vaporization and catalytic arc production.

The purity, in this case defined as the nanotube mass over total mass of nanotubes and impurities, is typically between 50-80% for arc and laser vaporization. For supply limited CCVD, the purity could be controlled by the amount of input catalyst used. It could range from negligibly small to as high as 70% if the ethylene concentration increases to counteract slow ethylene diffusion.

Overall, the supply-limited CCVD technique is similar to or worse than laser vaporization and arc generation in terms of mass production rate and purity. It has advantages over these techniques in that the impurity is metal and alumina particles that may be easier to remove than the amorphous carbon which can result from laser vaporization and arc generation. Also, it is a much simpler technique, requiring only mixtures of metal oxides and salts to produce the catalyst, and a tube furnace and gas handling equipment to grow the nanotubes. Finally, this production technique gives
rough control over the number of walls in the nanotubes. Figure 40 shows that the relative number of double wall to single-walled nanotubes varies from 30% to 70% with reaction temperature. Experimental studies of the effects of inter-wall interactions on nanotube properties, such as vibrational modes measured by Raman spectroscopy, could use this material with a known fraction of double walled nanotubes.
7. Conclusions

Carbon nanotubes show great promise as tools and building blocks for the increasingly small devices to be built in the future. Before they can be use as such, their production must be optimized and their properties better understood. Although CCVD produces multiwalled nanotubes of low quality compared to laser vaporization or carbon arc techniques, it is the best method for the bulk production of nanotubes. We have demonstrated that by carrying out the CCVD reaction with very dilute reactants so that the rate-limiting step is the supply of carbon, high quality single-walled nanotubes can be produced by the CCVD technique. We have also shown that at some temperatures the growth is only limited only by the diffusion of gaseous feedstock to the catalyst particles. Further progress to overcome the feedstock diffusion limitation and push the growth rate higher, while still being supply limited, may allow efficient bulk production of high quality single-walled nanotube by this method.
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