TOWARDS LARGE SCALE PRODUCTION AND SEPARATION OF CARBON NANOTUBES

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ABSTRACT

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Since their discovery, carbon nanotubes (CNTs) have boosted the research and applications of nanotechnology; however, many applications of CNTs are inaccessible because they depend upon large-scale CNT production and separations. Type, chirality and diameter control of CNTs determine many of their physical properties, and such control is still not accessible. This thesis studies the fundamentals for scalable selective reactions of HiPCo CNTs as well as the early phase of routes to an inexpensive approach for large-scale CNT production.

In the growth part, this thesis covers a complete wet-chemistry process of catalyst and catalyst support deposition for growth of vertically aligned (VA) CNTs. A wet-chemistry preparation process has significant importance for CNT synthesis through chemical vapor deposition (CVD). CVD is by far, the most suitable and inexpensive process for large-scale CNT production when compared to other common processes such as laser ablation and arc discharge. However, its potential has been limited by low-yielding and difficult preparation processes of catalyst and its support, therefore its competitiveness has been reduced. The wet-chemistry process takes advantage of current nanoparticle technology to deposit the catalyst and the catalyst support as a thin film of nanoparticles, making the protocol simple compared to electron beam evaporation and sputtering processes. In the CNT selective reactions part, this thesis studies UV irradiation of individually dispersed HiPCo CNTs that generates auto-selective reactions
in the liquid phase with good control over their diameter and chirality. This technique is ideal for large-scale and continuous-process of separations of CNTs by diameter and type.

Additionally, an innovative simple catalyst deposition through abrasion is demonstrated. Simple friction between the catalyst and the substrates deposit a high enough density of metal catalyst particles for successful CNT growth. This simple approach has potential for metal catalyst deposition to grow vertical array CNTs on large surface substrates as well as to develop nano- and micro-patterns of catalyst and CNT growth. The CNTs produced from abraded catalyst have similar qualities to CNTs synthesized from evaporated catalyst.
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Chapter 1

Introduction

Carbon Nanotubes, background and historical review:

The discovery of carbon nanotubes (CNTs) is attributed to the Japanese researcher Sumio Iijima who in 1991\(^1\) published his experimental observations of double and multi wall carbon nanotubes (MWCNTs) by transmission electron microscopy (TEM), Figure 1. Two years later, Iijima and Bethune both reported the existence of single walled carbon nanotubes (SWCNTs).\(^2\),\(^3\) Although these publications initiated large efforts within the scientific community to conduct CNT research, there is evidence that CNTs existed 10000 years ago\(^4\) and their applications were already being exploited as early as the 17\(^{th}\) century.\(^5\)

![Figure 1. CNTs tubular structures. a, b, c) revealed by transmission electron microscopy micrographs reported by Iijima.\(^1\) b) Computer generated triple wall CNT.\(^6\)](image-url)
TEM evidence shows that the famous Damascus Steel, which has been the focus of metallurgists for thousands of years, had multiwall CNTs on its composition. Although other researchers have observed MWCNTs before Ijima, (Radushkevich & Lukyanovich in 1952, Bacon et al. in 1960, and Endo et al. in 1976, and Tibetts in 1984), it is evident that the discovery of fullerenes by R. E. Smalley, R. Curl and H. Kroto in 1985 gave the necessary impetus for further work in carbon nanostructures and had an impact on Ijima’s 1991 report. Since then, the CNT has remained an icon of nanotechnology and its applications.

Early theoretical reports highlighted the physical properties of CNTs and proposed their use in a diverse set of applications. Scientists such as Smalley, Ijima and Endo recognized the potential of CNTs early on, thus they have directed efforts towards its large scale synthesis. Smalley and his group had achieved gram production of SWCNTs as early as 1996 using laser ablation synthesis and gram to Kg with HiPCo in 1999. More importantly, Smalley proposed new human priorities for the next century and illustrated how CNTs could become a key component for providing solution to the major problems of society, such as energy. HiPCo, a technique for SWCNT synthesis patented by Smalley, was perhaps the only large production technique ten years ago and since then it has been distributed worldwide. This has enhanced the understanding of SWCNTs physical and optical properties. It is not a surprise that more than 60% of the world’s scientific literature on CNTs has some relation or make reference to HiPCo. Additionally, HipCo SWCNT’s are likely the most well characterized and best understood form of CNTs to this day.
**CNT Structure, Classification and Nomenclature:**

CNTs are commonly described as a single sheet of graphene rolled upon itself along a specific angle to form a seamless cylinder. The angle at which the graphene sheet is rolled is known as the chiral angle (θ) and determines the physical properties of CNTs. A single sheet of graphene is shown in Figure 2 where the vertices represent sp² hybridized carbon atoms that are bonded to each other in a honey-comb lattice structure. The vectors Ch and T are the lattice vectors and define the unit cell in a plane. Ch is the vector that defines the circumference on the surface of the tube connecting two equivalent carbon atoms, \( Ch = n \hat{a}_1 + m \hat{a}_2 \), where \( \hat{a}_1 \) and \( \hat{a}_2 \) are the two basic vectors of graphene and n and m are integer numbers. Integers n and m are called indexes and they are correlated to the chiral angle θ through the equation: \( \theta = \tan^{-1} \left[ \frac{\sqrt{3}(n/(2m+m))}{2} \right] \).

**Chirality:** Chiral angle determines the electronic properties of the SWCNT: armchair (n = m, \( \theta = 30^\circ \)), zig-zag (n > 0, m = 0 and \( \theta = 0^\circ \)) and chiral (0 < |m| < n and 0 < \( \theta < 30^\circ \)). Armchair CNTs are metallic with zero band gap. Zig-zag and chiral tubes can be quasi-metals with a finite band gap if \( (n-m)/3 = I \) (I being an integer and m ≠ n) or semiconductor in all other cases. The band gap for the quasi-metallic and semiconductor nanotubes scales approximately with the inverse of the tube diameter, giving each nanotube a unique behaviour. This means, each chirality of carbon nanotubes represents a unique carbon nanotube family with a unique density of states (DOS) arising from its symmetries. This factor is more relevant to the electrical properties of the carbon nanotubes, which vary strongly according to the band gap therefore their chirality: two thirds of chiralities are semiconducting, one third are metallic or quasi-metallic.
Figure 2. Schematic representation of rolling graphene sheet to obtain SWCNTs with different chiralities. Blue shade determines only zig-zag ($\theta = 0^\circ$) while red shade determines armchairs tubes ($\theta = 30^\circ$) and all chiral all angles in $0 < \theta < 30^\circ$. 
Figure 3. Calculated density of states of individual armchair SWCNTs reveals that Fermi energy is located at 0 eV and the Van Hove singularities that occur as mirror-image spikes at both sides of 0 eV.

Density of States:

The density of states (DOS) of SWCNTs were theoretically predicted as early as 1992\textsuperscript{15} however it was not universally validated until ~5 years later\textsuperscript{16} and experimentally supported almost at the same time.\textsuperscript{17, 18} Each type, metallic, quasi-metallic and semiconductor SWCNTs, exhibit different density of states (DOS) near the Fermi level. It is known that the density of states is constant at the Fermi level and develops cumulative spikes around the Fermi level known as van Hove singularities.\textsuperscript{19} True metallic SWCNTs (armchair) with equal chiral-indexes (n = m) and zero band gap allow conduction under
infinitesimal potential gradients with their Fermi energy located at 0 eV, Figure 3. Although quasi-metallic SWCNTs have no bandgap, a very small bandgap is introduced by the curvature effects of the cylindrical structure. SWCNTs (14,5) and (22,19) have band gaps of 0.03 eV and 0.002 eV respectively. quasi-metallic SWCNTs act essentially as conductors at room temperature due to their meV bandgaps that are overcome by thermal broadening. Their DOS near the Fermi level is the same as for armchair metallic. Semiconducting SWCNTs, on the other hand, have a finite bandgap at the Fermi level between the spikes of the first van Hove singularities. The average size of this bandgap gets smaller with increasing nanotube diameter, for example ~2 nm diameter SWCNT has 0.5 eV band gap while a 1.1 nm tube has a 1.9 eV band gap.

**SWCNT:** Single-walled carbon nanotube; it is probably the simplest form of CNT made from a single graphene sheet, also the most studied CNT in the world.

**MWCNT:** Multi-walled carbon nanotube; a nanometer tube made of several concentric layers of graphene sheet. The multiple layers are spaced uniformly as graphene layers and the number of walls can vary from 2 to several tens.

**VA-CNT:** Vertical array of carbon nanotubes also know as arrays, forests and carpets. Unlike the typical CNTs synthesized in a gas phase with a random orientation and length, VA-CNTs are perfectly aligned NTs, they have the same length and they are typically attached to a substrate.

**CNTs Physical Properties:**

Shortly after Ijima's report\(^1,2\) many extraordinary physical and chemical properties of CNTs were reported. It has been suggested that the intrinsic properties of
CNTs have not been matched by any other material available in nature, therefore several technological applications have been proposed across scientific disciplines. For this discussion the most important properties are the mechanical, electrical, optical and thermal properties.

Besides the unique CNT properties and the promising advantages of its applications, currently there are few reported uses and products. Because CNTs are materials synthesized through precise atomic manipulation and arrangement, their size is at the lowest dimension limits of nanoscience, therefore their application involves individual characterization and handling of the nanoscale objects. The diversity in diameter, chirality, length, electronic band gap of CNTs in the as-synthesized mixture has limited the progress and applications. Additionally, some application require macroscale control of length and alignments, the as synthesized CNTs are typically mats of random orientation and length. The VA-CNT growth is the central topic of this thesis because CNTs produced has interesting advantages such as alignment, size control and almost catalyst free.

An important factor in the advance of CNT research is the analytical characterization of their physical properties. Raman, fluorescence, UV spectroscopy, TEM, atomic force microscopy (AFM), scanning tunneling microscopy (STM), scanning electron microscopy (SEM) and many other characterization techniques have been adopted for specific purposes. Raman is one the richest information sources for CNTs since it provides diameter characterization known as radial breathing modes (RBM), tangential vibration known as G modes, quality of the sp² conformation know as D band and G’ which has been assumed as indicator of the metallicity, although this peak’s
origin is still under investigation. Figure 4a illustrates the RBM and the SWCNT population as a function of their diameter and excitation energy. Fluorescence provides great detail about the semiconductor CNT distribution, Figure 4b, although its ability to provide full distribution of the semiconductors is limited to the excitation sources available, which is also a limitation of the Raman. UV spectroscopy was a key instrument to determine the electronic transitions of the individual CNTs in the mixture, especially after individual dispersion of CNTs in solvents. All microscopy techniques such as AFM, TEM, SEM, STM are extremely relevant as in many other nanotechnology fields, although each has advantages and disadvantages over the others.

**Figure 4.** CNT optical characterization techniques, a) Kataura Plot and three different excitation source wavelengths. b) typical CNT photoluminescence spectra.

**Electrical Properties:** Perhaps the most important properties of CNTs are the intrinsic ballistic current conduction of the metallics over relatively long distances and the extraordinary mobility of semiconducting CNTs. The ballistic conductivity of the metallics is due to the one dimensional characteristic of the SWCNTs and the ability to
localize electrons on its surface. Although these measurements have been performed on micron length individual SWCNTs, ideally it is expected to keep these properties in macroscopic samples such as ropes or fibers. A SWCNT-based device has resistance due to contacts rather than dissipation within the CNT itself,\textsuperscript{32} therefore electricity transport conductors could be replaced by CNT fibers that would transport electricity with no loss of electrons due to heating. Although this assumes a perfect metallic and continuous CNT, in reality today the continuous and selected metallic CNT growth has been limited to mixtures and a couple centimeters of CNTs. Another source of energy dissipations are intrinsic defects due to $sp^3/sp^2$ carbon atoms surface arrangement that are considered as scattering points and contribute to the resistivity increase.\textsuperscript{33}

**Mechanical Properties:** Given the analogy to graphite, the remarkable mechanical strength and toughness of CNTs was expected since CNT discovery. As the research progresses in the field, more theoretical and experimental results have been reported.\textsuperscript{34,35} Perhaps the most comprehensive studies were reported by Yu et al.\textsuperscript{36} where different diameters MWCNTs were studied and tensile strength and Young's modulus were determined. For the outermost wall the tensile strength was 11-63 GPa and Young's modulus were determined to be in 270-950 GPa. Although these reported values are still lower than the theoretical limits, they are already higher than other known carbon fibers.\textsuperscript{36}

**Thermal Properties:** Impressive theoretical thermal properties of CNTs, as high as 6600 W/mK, have been reported.\textsuperscript{37} Although experimental measurements of SWCNT thermal conductivities are almost $\frac{1}{2}$ of the theoretical values,\textsuperscript{38} other calculations have suggested that thermal conductivity depends from the temperature, radius as well as
chirality of the CNT. Experimental thermal conductivity of aligned CNT fibers have been measured, 220 W/mK, along the CNT alignment. However the assembled fiber has different lengths, diameters of CNTs and multiple junctions which might act as thermal propagation barriers. Additionally, thermal conductivity improvements of epoxy/and polypropylene/CNT composites have been reported, where as low as 1% addition of CNTs has increased the thermal conductivity of an epoxy in order of magnitude.

**Optical Properties:** Optical characterization of the CNTs is a valuable tool for determining many properties of CNTs. CNT absorbance covers a large range of absorptivities from the UV to far IR regions and is a direct measurement of the electronic structure of the CNTs. A typical well dispersed CNT solution has a defined set of unique peaks known as Van-Hove singularities which are very useful in determining changes in the electronic structure of the CNTs. Furthermore, other optical techniques such photoemission and Raman can help to determine the diameter, band gap and type. Based on these optical properties, many applications were attempted such as optoelectronic, photonic, and photo-electrochemical devices; photo-synthesizers and thin films for photovoltaics. The intrinsic band-gap of semiconductor CNTs could be used to generate and detect light. A promising field of optoelectronics has been exploring CNTs for diverse applications such as light emitting diodes (LED) and waveguides.

**CNT synthesis:**

Many different CNT synthesis methods have been developed over the years. The most common ones are: carbon arc discharge, laser vaporization or laser ablation, chemical vapor deposition and flame synthesis although there are many other variations and combination from these. Many of these growth techniques have been
developed to suit some specific requirement of applications, such as plasma enhanced (PE) CVD which has been proposed for applications on electronics, or applications where CNTs need to be grown directly on the devices. Another application-driven growth is CNT on fluidized bed reactors for large scale MWCNT growth. Standard catalytic CVD has proven very effective, well controlled and perhaps it is the most promising as large scale CNT growth process. CVD combined with the atomic hydrogen generator hot filament has been shown to be a reliable and well-controlled technique for VA-CNTs.

In the growth process, a CNT needs a metal catalyst as a nucleation site to initiate its growth. During growth the metal catalyst nanoparticle can remain attached to the surface; a modality known as base-growth, or it can travel at the tip of the tube, known as tip-growth, Figure 5. This principle seems true for all catalyst supported growth processes regardless of whether the CNT grows from Fe, Co, Ni with high known carbon solubility. A carbon feedstock gas is supplied and most likely decomposed on/in the surface of the catalyst particle and precipitated in a well arranged hexagonal lattice structure that continuously grows a nanotube. The mechanism remains under debate. There are several parameters that need further understanding such as whether the carbon atoms addition onto the CNT lattice occurs as mono-, bi-, tri-atomic molecules? is the catalyst particle liquid, semiliquid or solid? If solid what is their crystalline phase? What is the function of the Al₂O₃? Although there is large scientific data supporting the metallic active state of the catalyst, there are reports that support that the active catalyst is metal oxide or metal carbide.
Figure 5. Illustration of the growth types: base- (root-) growth compared to tip-growth.\textsuperscript{59}

A critical component of the CNT growth is the catalyst nanoparticle; the correlation between the catalyst nanoparticle and the CNT diameter has been studied extensively.\textsuperscript{66} Regardless of the origin of the catalyst nanoparticle, either liquid phase-premade and introduced into the reactor on substrates or in-situ generation through sintering, researchers have still observed particles at the tip of the CNTs. Besides particle size, composition of the catalyst has been investigated, although the most efficient are metals with high carbon solubility, researchers have already been successful growing CNTs from metal particles with low or no carbon solubility.\textsuperscript{67, 68}

In case of base-CNT growth, the substrate has become relevant. It not only determines successful growth of CNTs, but also the quality of the tubes. A large variety of surfaces have been studied by the scientific community: alumina,\textsuperscript{55, 56} quartz,\textsuperscript{69} MgO,\textsuperscript{70} stainless steel,\textsuperscript{71} and aluminum foil,\textsuperscript{72} etc., however, of all these substrates, alumina has become the preferred catalyst support. Apparently catalyst substrates are determinant for keeping the catalyst particle active, and avoiding sintering, which drives
large particle formation and makes the catalyst inactive.\textsuperscript{73} Among other reasons why the CNT growth stops is the metal catalyst diffusion into the catalyst support,\textsuperscript{74} however this topic needs further understanding.

**CNT separations:**

Significant effort on separations have been focused on SWCNTs mainly looking at type separations of metalics or semiconductors from the synthesized mixture, although separation by length and number of walls has also been reported. Many potential applications of SWCNTs as components on nano-related devices such as sensors, microelectronics, transparent conductors, energy storage and optoelectronics, require CNTs separated from their peers in order to truly exploit the individual physical properties of individual CNTs.\textsuperscript{61,75}

As-produced CNTs have a large variety of diameters and chiralities. Perhaps the most well characterized SWCNT are the HiPCo produced tubes, which comprise 50-70 different diameters and chiralities\textsuperscript{13}, and depending on their chiral angle they can behave as semiconductors, semi-metallics or metalics.\textsuperscript{76} SWCNTs produced using the HiPco process contain approximately one-third metalics and two-thirds semiconductors.\textsuperscript{44} This diversity of tubes and the extreme difficulty of separating them by type has prevented many applications from being further developed and has hindered research progress in the field.

There are several SWCNT type- and diameter-selective separations attempts reported in the literature.\textsuperscript{77-84} Most of them have made significant improvements or enrichments based on preferential reactions with either semiconducting or metallic SWCNTs but only few have came close to fully separation. The majority of attempts are
simple enrichments and their separation attempts showed mixed success. Most enrichment techniques require additional chemical reagents that not only degrade the dispersion quality of the SWCNTs but also require additional treatments to separate the reagents from the nanotubes after reaction. Examples include physisorption and chemisorption processes such as those that use octadecylamine (ODA); those that use electron transfer reactions such as ozone, nitronium ions, and diazonium salts; and others based on thermal and HCl oxidations. Bromine and Fe complexes have shown selective complexion with metallic SWCNTs.

Non-chemical selective processes such as dielectrophoresis and photon irradiations have shown promising selectivities, although the scalability of these techniques is still under study. Selective photo-oxidation using high-power-density lasers has been reported where a specific wavelength enhances the resonance of selected SWCNTs, generating chiral-selective reactions. Laser photon-induced selective reaction of metallic SWCNTs with Triton X-100 has also been reported, light assisted oxidations with H₂O₂ exhibit a dependence on the SWCNT diameter and band gap and photochemically generated singlet oxygen reacted selectively with metallic SWCNTs. In the solid phase, UV photons induce oxidation of MWCNTs and SWCNTs and longer UV wavelengths were used to crosslink SWCNTs, leading to improvements in mechanical strength and conductivity. Theoretical studies that support and explain photon-induced oxidation have been reported. Also, a recent publication has used a high power Xe lamp (500 W) to selectively destroy the metallic and small diameter SWCNTs in the solid phase.

Perhaps the most successful separation techniques achieved have been published
during the last three years, which seem the continuous effort on this field since their first reported results: density gradient ultracentrifuge\textsuperscript{106, 107} and DNA roping.\textsuperscript{108, 109} Density gradient ultracentrifuge separation became popular due to its ability so separate small fractions of CNTs by type, chirality and even number of walls based on their fractionation on a layered density gradient solvent upon long hours of centrifugation. Although this technique is time consuming and the volume of separated CNTs is very small, start-up companies have started selling individual SWCNTs at incredibly expensive prices.

Recently a follow-up article has been published with perhaps easier separation technique, although the pricing might be still exorbitant. This approach uses specifically engineered DNA sequences that selectively bind to unique chiral angle CNTs.\textsuperscript{109}

Both successful separation methods discussed above have a couple of basics in common: the individual dispersion of the tubes and the media that allows the tubes to be isolated. The methods use density and mass of the tube as identification properties in one case while the other uses the physi-chemical binding affinity of the tube. Chapter 5 and 6 deal exclusively with selective reaction approaches ideal for separations. Chapter 5 details a novel way of tuning complexation of CNTs to Fe ions and hydroxides. Chapter 6 discusses another novel technique that depends on SWCNTs individual optical properties. Both chapters provide important evidence of the selectivity although the separations need further experimental studies.

**CNT Applications:**

CNT applications cover an extended range of technologies. In the early days of CNTs, an author compared possible applications of CNTs to fullerenes,\textsuperscript{110} he concluded
that CNT application would cover a entire book while fullerene applications will fit in a single sheet. Despite the numerous extraordinary individual CNT properties, CNTs applications are still very limited and the most relevant properties are not being exploited in commercial products. Most of the delays are due to the current inability to produce large scale well controlled diameter and chirality CNTs. In spite of the unappealing circumstances, scientists around the world have managed building and testing devices and prototypes in a very large scope of fields.

**Micro- and nano-electronics:** Novel technological devices have been reported: radio receivers and demodulators,\textsuperscript{111, 112} nano-speakers,\textsuperscript{113} field emitters,\textsuperscript{114, 115} capacitors,\textsuperscript{116, 117} sensors,\textsuperscript{118, 119} field effect transistors (FET),\textsuperscript{120, 121} ultrafast electronics,\textsuperscript{122, 123} highly sensitive chemical and biological sensors,\textsuperscript{118, 124} nonvolatile random-access memories,\textsuperscript{125} rotational bearings and motors,\textsuperscript{126} and electromechanical oscillators.\textsuperscript{127}

**Materials:** In the field of materials, significant improvements have been developed for CNT addition to polymer matrixes through surface functionalization of the CNTs. The perfect sp\textsuperscript{2} lattice CNT surface is extremely hydrophobic and the van der Waals binding energy between CNTs in parallel bundles is \(~500\) eV/\(\mu\)m.\textsuperscript{43} As a consequence, CNTs individual coatings for successful dispersion has been critical in this field. As-grown CNTs are bundled and entangled. In order to exfoliate and disperse CNTs in solution, many surfactants, SDS, SDBS, Pluronic, Triton-X, CTAB have been used. Between the organic solvents, 1,2-dichlorobenzene, chloroform, \(N,N\)-dimethylformamide (DMF) and \(N\)-methylpyrrolidone (NMP) are considered good solvents/dispersants, between wrapping polymers, poly(methyl methacrylate) (PMMA),
polypyrrole (PPy), polyaniline, and poly(p-phenylene benzobisoxalone) have shown uniform coating of CNT surface.

Between CNT addition into several polymers and composites, extremely encouraging reports on enhanced tensile modulus, tensile strength, torsional modulus, toughness, glass transition temperature, thermal conductivity and compressive strength have been reported. Additionally, CNTs have been utilized to enhance properties of resins for specific field processes in the polymer industry such as thermosetting and thermoplastic resins, H2O soluble and conjugated polymers. Furthermore, CNT applications have been expanded to reinforce ceramics and metal matrices. Currently there are few polymers composites available on the market. These include AURUM™ CNT Grade, from Mitsui Chemical INC and FIBRIL nanotube based master batch from Hyperion.

**Sensors:** Since its first demonstration, CNT applications as sensors have been extended to several fields, including environmental, medical and military just to mention few. Environmental applications have focused mainly on gas detection, such as NH3, NO2, CO, CO2, H2, CH4, SO2, H2S, O2. Since CNTs are a perfect surface arrangement of carbon atoms on a tubular structure, its conductivity depends almost entirely on the surface atoms, therefore any small change such as physical adsorption will change the local chemical environment and its conductivity along the tube. The conductivity measurements have been done using single and network of CNT-FET devices and the sensor sensitivity and selectivity to gases has improved using partial coating of the CNTs.
CNT applications as biomolecular sensor have been extended significantly, picomolar detection sensitivities have been reported.\textsuperscript{137} Detection of proteins,\textsuperscript{138} such as streptavidin and HupR,\textsuperscript{139} carbohydrates,\textsuperscript{140} DNA,\textsuperscript{141, 142} glucose\textsuperscript{143, 144} was possible. Also, CNT based sensors have future in military application for detection of explosives and chemical warfare agents (CWA).\textsuperscript{129, 145, 146} Detection of nitrotoluene, 2,4-dinitrotoluene (DNT), cyclotrimethylenetetranitramine, commonly known as RDX, and ethylene glycol dinitrate (EGDN), components found in military grade explosives, have been reported.\textsuperscript{119, 129, 145} Common CWAs such as dimethyl methylphosphonate (DMMP)\textsuperscript{119} for sarin, diisopropyl methylphosphonate (DIMP) for soman and thionyl chloride (SOCl$_2$) for nerve agent precursors were successfully detected.\textsuperscript{129, 145, 147}

**Energy:** CNTs are promising components for the development of electrical energy storage systems. Regardless of the source from which energy is harvested, (solar, wind, hydro, thermal, nuclear), the energy needs to be stored and transported. Sustainable energy supply sources and storage systems are at the forefront of today's research all over the world and CNTs have attracted high attention for use in storage.\textsuperscript{148} Due to the unique electrochemical stability, large surface area and conductivity,\textsuperscript{149} CNTs have been found as a promising electrode in supercapacitors\textsuperscript{150} and electrochemical double layer capacitors.\textsuperscript{151} Also, intensive investigation of hydrogen storage on CNTs has been performed since the first publication on hydrogen uptake of SWCNTs by Dillon et al.\textsuperscript{152} Different weight percent uptakes have been reported since then\textsuperscript{153-155} and the most promising results were achieved on metal doped CNTs.\textsuperscript{156}

**Others:**

Exotic CNT applications have been reported and there are still many others in
progress at the lab bench. Just to mention few of these applications: molecular filters,\textsuperscript{157}, \textsuperscript{158} speakers,\textsuperscript{113} and TEM grids.\textsuperscript{159} Although some of these applications are state-of-the-art assemblies with very small likelihood of mass production, there are other application where large scale of CNT are required, such as the case of fiber-composites, films, coatings, additives, etc. Many of these applications have triggered the search for low cost and large scale CNT production processes and applications that were hard to believe ten years ago\textsuperscript{110} might become a reality.

References:


Chapter 2

Dendrimer assisted Fe nanoparticle self-assembly monolayer for vertical array of large diameter carbon nanotubes growth

Introduction:

Many prospective carbon nanotube (CNT) applications demand large scale synthesis methods, however CNT mass production is still an inefficient and expensive process. Chemical vapor deposition (CVD) to make the vertical array (VA) – CNTs has several advantages compared to other methods: alignment, control over the length and reduced catalyst content. In addition, CVD is a promising possibility for an inexpensive large scale CNT production process as well as providing more accurate control over the synthesis parameters. Although CVD has many advantages, the synthesis protocol required for catalyst and catalyst support deposition, typically high vacuum processing, has hindered its progress compared to other techniques.

It is very likely that inexpensive and large scale CNT production would be viable through a liquid phase catalyst deposition. This approach invokes the catalyst synthesis in the liquid phase, where it is possible to have better control over the diameter of catalyst particles, followed by a careful and controlled assembly of these particles as a two dimensional monolayer of particles on a catalyst support surface. A similar, but less controlled and non-chemical catalyst assembly approach has been reported by Nishino et al. as well as Gunishima et al. where apparently a simple spin coating was able to deposit two dimensional layers of catalyst that supported VA-CNT growth.
This chapter focuses on synthesis of VA-CNT from premade Fe nanoparticles that were assembled as a monolayer through a chemical bonding of the particle to the Al₂O₃ surfaces. The particle assembly takes place through a carboxylic acid terminated dendrimer, 5th generation, to the substrates as well as to the catalyst nanoparticles; Figure 1 illustrates the catalyst particle assembly and VA-CNT growth. The CNTs grown with this approach have physical characteristics similar to carbon nanotubes synthesized using electron beam evaporated catalyst.

Figure 1. Dendrimer assisted Monolayer self assembly of Fe nanoparticles on Al₂O₃ substrates, vertical array of carbon nanotubes grown from monolayers of Fe nanoparticles.

Most previous research on characterization and applications has been focused on small diameter CNTs; perhaps the most well studied so far is HipCo CNTs. However, large diameter (LD) -CNTs have interesting electrical and optical properties. Optical applications in the IR range of the spectrum are possible because the E₁₁ transitions are directly related to the CNT diameter. LD-CNT are excellent IR absorbants. Furthermore, it has been reported in the literature that CNTs sidewalls would be able to retain their
curvature only up to a certain diameter; LD tubes would collapse and have a more ribbon like geometry.\textsuperscript{4}

**Experimental:**

Carboxylic acid terminated poly(amido amine) dendrimers ([NH$_2$(CH$_2$)$_2$NH$_2$]: (G=4.5); dendri PAMAM(NHCH$_2$CH$_2$COONa)$_{128}$) (MW = 26252), which will be referred as CO$_2$H-PAMAM throughout the manuscript, methanol and hexanes were purchased from Sigma-Aldrich and they were used as received. The dendrimer monolayer was deposited at 60 °C from a methanol solution ( ~674 µM) followed by the Fe nanoparticle complexation at 50 °C in hexanes. The reaction times for the dendrimer monolayer formation and Fe particle complexation were 30 min each, followed by methanol rinse and wash after each reaction. Because methanol at 60 °C tends to evaporate readily, it is necessary to have an optical method to determine the concentration of the solution after the reaction and make methanol additions to bring it back to the original concentration. The optical concentration curve is shown in Figure 2. After each washing, the substrates were dried with a N$_2$ flow and calcined at 375 °C under air before placing them in the CNT growth reactor. CNT growth takes place at 750 °C for 15 min using C$_2$H$_2$ as the carbon source; H$_2$ and H$_2$O were provided in a manner similar to the supergrowth technique.\textsuperscript{5, 6} The catalyst was reduced to metallic Fe through 30 s atomic hydrogen exposure, which is generated by a hot W filament. The growth process has been detailed elsewhere.\textsuperscript{6, 7}
Figure 2. Calibration curve to determine CO$_2$H-PAMAM concentrations. (a) Original UV-Vis absorption of CO$_2$H-PAMAM at different concentrations. (b) Calibration curve extracted from UV absorption at 287 nm.

During the experiments two different sources of Fe nanoparticles were used: 4.3 nm particles synthesized by the Dr. Barron’s Group and 8.8 and 15 nm particles synthesized by the Dr. Colvin’s group. The different particles were made using slightly different synthesis methods, mainly regarding the Fe precursor. The 4.3 nm Fe nanoparticles were synthesized using a modified Sun method$^8$ whereby Fe(III) acetylacetonate were reduced by excess 1,2-hexadecanediol in the presence of oleic acid and oleyl amine that assemble as ligands on the particle surfaces. The reactants were added together at room temperature using benzyl ether as the solvent, and brought to reflux under a blanket of N$_2$ for a period of 45 min. The particles were then precipitated using excess ethanol and repetitive centrifugation at 4000 rpm for 5 min. The precipitated particles were solubilized in hexanes with oleic acid and characterized.

The 8.8 and 15 nm Fe nanoparticles were synthesized from FeO(OH) as a
precursor following the published method. Typically, using a three necked flask, a mixture of 0.178 g of FeO(OH) fine powder (2.00 mmol), 2.26 g of oleic acid (8.00 mmol) and 5.00 g of 1-octadecene was heated under stirring to 320 °C and kept at that temperature for 30 min. These particles were precipitated using ethanol and then redispersed in hexanes.

**Results and Discussion:**

Much attention has been devoted to dendrimer applications, as a building block for thin films, monolayers and multilayers, drug delivery vehicles, heterogeneous catalysis, etc. In the field of CNTs, dendrimers have already been explored for catalyst growth, mostly to assist diameter control over the catalyst particles when synthesized in the liquid phase. Amana et. al, have used amine terminated dendrimers as templates to promote size control over the catalyst particles and large diameter multiwall CNT growth. To assist diameter control over the catalyst particles, other dendrimer-like molecules have been used. Artificial Ferritin and metal-complexed surfactants are examples of this approach. A common characteristic of these approaches is simple physisorption of the catalyst on the substrate. Typically, with dipping in or spin coating on substrates, it is possible to collect enough particles on a surface to act as CNT nucleation sites, however without proper substrate and dendrimer selection, this process can be difficult to reproduce.

The efficiency of carboxylic acid complex formation with aluminas was reported previously by several researchers. Particularly Boehmite was extensively studied and it was demonstrated that oxygen in the carboxylic acid binds to Al due to a precise
surface arrangement of Al atoms with respect to CO$_2$H. In a similar manner, CO$_2$H makes a stable ligand with Fe.

Typically, most of the Fe nanoparticles synthesized in the liquid phase are dispersed in solvents such as hexane using oleic acid.\textsuperscript{8,9,26} The carboxylic groups (CO$_2$H) from oleic acid bind to the iron particle surface, making a hydrophobic shell around the nanoparticle. This ligand formation seems very stable; Fe nanoparticles dispersed with this technique can remain in solution for months. Obviously, without the oleic acid ligand it is not possible to disperse Fe nanoparticles in hexanes. Based on these arguments, a molecule with many CO$_2$H groups such as CO$_2$H-PAMAM dendrimer would be ideal for assembling or adhering Fe nanoparticles to an Al$_2$O$_3$ surface in SAM fashion.

**Dendrimer Monolayer Film Development:**

A dendrimer interacts with an alumina surface, through many active CO$_2$H sites that are in contact with the Al$_2$O$_3$, thereby forming strong ligands and building-up a monolayer. Although many active sites of the dendrimer are already complexed with the alumina due to the large number (128) of CO$_2$H termini, a dendrimer has many ligands that are free, normal to the surface and not interacting with the alumina surface. Through this process, it is expected that chemical bond formation of the monolayer dendrimer on alumina is a self saturating reaction. Once particles cover the entire surface, there are no more chemical forces driving more particles to the surface. The AFM images in Figure 3 illustrate the homogeneity and continuity of the monolayer.
Figure 3. CO$_2$H-PAMAM dendrimer assembly on an electron beam evaporated Al$_2$O$_3$ surface showing homogeneous cover over substrates. (a) Complete surface coverage of the substrate and, (b) closer view which reveals the surface morphology.

Prior studies have shown that at a specific pH it is possible to build a multilayer of dendrimers, one monolayer at a time.\textsuperscript{11} Furthermore Tomita et al.\textsuperscript{11} were able to determine the pH range at which multilayer formation was not possible; he had observed that at pH 7 and above multilayer dendrimers disintegrated. The fact that we can observe a thin layer of iron nanoparticles and CNT growth leaves no doubt about the dendrimer assisted particle monolayer formation. This methodology is schematically illustrated in Figure 4.
Catalyst Nanoparticle Monolayer Selfassembly:

Particle monolayer film preparation has been studied extensively. Perhaps the most well-established and studied is that of Au nanoparticles using the common approach involving thiol-surface ligand formation. SAMs of the particles have been proposed for several applications including plasmonic systems, surface enhanced Raman, and sensors. Most of the methods that have been developed for nanoparticle SAMs are controlled by capillary forces, surface tension, density and viscosity of the solvent. In many of physic-adsorption methods, film formation is subjected to solvent drying effects.
rather than chemical bonding, although VA-CNT growth has already been reported from Fe nanoparticles deposited with simple spin coating. However, the reproducibility with this approach when applied to larger surfaces is difficult. From our experience, catalyst nanoparticle self-assembly through physisorption is mainly affected by the solvent and the surface, and it is difficult to control as particles tend to aggregate randomly upon drying.

Figure 3. Different surface coverage and morphologies of VA-CNT observed from physisorbed catalyst particles. The images are a few from a collection of several attempts to assemble catalyst particle layers on Al₂O₃ substrates by drop drying and spin coating.
Bi-layer and multi-layer catalyst particles are detrimental for diameter controlled CNT growth as they will enhance particle sintering, which directly affects the diameter correlation and the CNTs surface coverage. Figure 5 illustrates a few samples from a variety of morphologies of CNT arrays grown from physisorbed catalyst particles, which reveal the CNT surface irregularity. The catalyst particles were spin-coated, dipped and drop-dried; in all cases dissimilar morphologies were observed.

**Monolayer Film Characterization:**

![AFM image of dendrimer-assisted Fe catalyst nanoparticle monolayer film](image)

**Figure 6.** AFM image of dendrimer-assisted Fe catalyst nanoparticle monolayer film (a) and XPS spectra of the Fe nanoparticle monolayer film compared to 1 and 4 nm thick electron beam evaporated Fe catalyst (b).

The main advantage of using carboxylic terminated PAMAN is the homogeneity and complete coverage of catalyst nanoparticles that guarantees the growth of VA-CNTs. The AFM image in Figure 6a reveals a fully covered substrate that resulted from dendrimer-assisted deposition of 4.3 nm catalyst nanoparticles SAM. Besides the quality
of CNT growth, ellipsometry measurements and quantitative XPS spectra (Figure 6b) provide important evidence about the thickness of the catalyst layer. Ellipsometry measurements provide supporting evidence of monolayer formation, although the thickness of the film (22 nm) is larger than the particle size. This apparent discrepancy could be explained by: first, the lack of availability of an accurate refractive index for nanoparticles compared to bulk Fe₃O₄; second, the size distribution of the Fe nanoparticles used in the experiments is wide (4.3 nm average diameter measured for 381 nanoparticles, with a minimum and maximum particle size of 2.0 and 11.5 nm respectively). A narrower particle distribution should provide better correlation of thickness measurements between the particle size and the thin film. Figure 7 illustrates AFM (a) and TEM (b) images of the catalyst particles used for VA-CNT synthesis.

Figure 7. AFM (a) and TEM (b) of Fe nanoparticles used for building the monolayers of catalyst and growth of the VA-CNTs.

In XPS spectroscopy, it is commonly accepted that core electrons from a 10 nm deep layer film are not able to reach the detector; thus no signal can be observed. In our
experiments, we have compared two different electron beam evaporated Fe films (1 and 4 nm) to the 4.3 nm iron catalyst nanoparticle SAM film. All these samples have a 10 nm Al₂O₃ layer underlying the Fe film, thus the Al signal intensity in XPS is a reasonable comparison parameter for comparing the thickness of Fe layers over Al₂O₃. A typical 1 nm evaporated Fe gives a similar Al signal intensity as our SAM of Fe nanoparticle film, unlike a 4 nm evaporated Fe film which has less than 1/4 of the Al signal intensity than our SAM Fe particle film. Since Al₂O₃ is an underlayer film to the Fe catalyst SAM film, and if we assume that there is more than one complete layer of Fe nanoparticles, we should expect a similar low Al XPS peak intensity for our Fe - SAM as for the 4 nm evaporated Fe. The fact that the Al XPS intensity from the nanoparticle SAM is at least four times more than the 4 nm evaporated film, suggests that there are voids for the Al core electrons to travel through the Fe nanoparticles SAM to the detector. Furthermore, the XPS signal intensity for the Fe nanoparticle SAM has a similar oxide profile but lower intensity than 4 and 1 nm evaporated Fe. The higher spots shown on the AFM image (Figure 7a) over the nanoparticle SAM surface are most likely extra particles that were not washed away with the ethanol washing or particles that do not fit perfectly in the SAM film.

**CNT Growth and Characterization, SEM, TEM:**

Successful VA-CNTs grown from premade nanoparticles have been reported, however larger CNT diameters were observed using small diameter particles.³ This is probably an indication of sintering of particles when more than one particle layer is present. It is likely that a monolayer arrangement of particles on the surface is absolutely necessary to achieve a reliable correlation between particle and CNT diameters. In
another similar approach, Nishino et al.\textsuperscript{2} have tried to optimize the catalyst nanoparticle layers in order to successfully grow VA-CNTs rather than focusing on monolayer assembly.

The CNTs grown from 4.3 nm of Fe catalyst nanoparticles (Figure 8a, 8b) are quite similar in length to typical evaporated catalyst samples. The VA-CNTs are free standing with a typical height of \textasciitilde 25 \textmu m (Figure 8c) and cover the entire surface of the substrate (Figure 8d). Unlike CNTs grown from spin coating or drop drying Fe nanoparticles, where we often have observed patches and changes in surface morphology of VA-CNTs, dendrimer-assisted growth is quite similar to CNTs grown from evaporated catalyst and covers the entire surface. The CNTs grown from premade Fe nanoparticles have typical diameters of 4 and 5 nm (Figure 9a), mostly with 2 walls although 3 and 4 walls have also been observed. Further studies with this technique are highly recommended to better define a quantitative correlation between particle diameter and CNT diameter.
Figure 8. SEM images of VA-CNTs grown from dendrimer assisted Fe nanoparticle monolayers. (a) 3D top view, (b) higher magnification of the 3D top view, (c) side view that illustrates the height of the CNT array and (d) top view that illustrates the continuity and morphology of the VA-CNT top surface.

The Raman spectra taken on solid samples with 514, 633 and 785 nm excitation wavelength reveal that CNTs are similar to CNTs grown from electron beam evaporated catalyst (Figure 9b) with similar RBM peaks. D/G ratios are low and their length is in the same range. An important contribution of this technique is to open a route to diameter
controlled production of CNTs; we think it will be possible to determine CNT diameter based on the ability to control the particle size.

![TEM images and Raman spectra of CNTs](image)

**Figure 9.** TEM images (a) and Raman spectra (b) of CNTs grown from dendrimer assisted Fe particle monolayer films.

**SAM Films with Large Diameter Catalyst Nanoparticles:**

**CNTs from 8.8 nm Nanoparticles:**

Further experiments with a narrower diameter distribution of catalyst particles provided by the Dr. V. Colvin’s Lab, 8.8 nm and 15.4 nm, were performed. Figure 10a and 10b show AFM images of the SAM films prepared with 8.8 nm nanoparticles. Once again it is possible to observe a densely packed film and complete coverage of the substrate. Unlike 4.3 nm Fe catalyst nanoparticles, the 8.8 nm catalyst nanoparticle did not grow well-aligned CNTs under the same growth conditions unless the nanoparticle SAM was calcined under air at 375 °C for 20 h.
Figure 10. AFM images of dendrimer assisted assembly of 8.8 nm Fe nanoparticles in SAMs by height (a) and amplitude (b).

The VA-CNTs grown from the 8.8 nm catalyst particles were characterized with SEM, TEM and Raman spectroscopies. Figure 11a shows a top view of the CNT arrays while Figure 11b shows the typical height which is quite similar to tubes grown from an evaporated catalyst. Figure 12a shows the diameter of a typical CNT grown from the 8.8 nm nanoparticles, where the CNTs are similar to the particle size. Raman spectroscopy (Figure 12b) reveals higher D/G ratios compared to CNT grown from evaporated catalysts.
Figure 11. SEM images of VA-CNTs grown from dendrimer assisted 8.8 nm Fe nanoparticle SAMs; (a) top view that illustrates the surface morphology and homogeneity and (b) height of the grown VA-CNT.

Figure 12. TEM images of CNTs grown from dendrimer assisted 8.8 nm Fe nanoparticle SAMs; typical diameter measurements (a) and Raman spectroscopy taken on solid state samples with 514, 633 and 785 nm excitations.
CNTs from 15 nm Catalyst Nanoparticles:

PAMAM-CO₂H assisted SAM of 15.4 nm Fe nanoparticles have more empty spaces on their surfaces (Figure 13a, 13 b), suggesting that it will be more difficult to assemble larger particles with this approach under the same conditions as the 4.3 and 8.8 nm nanoparticles. The lower particle coverage also impacts the VA-CNT growth. Typically, CNTs must be dense enough to support themselves as a vertical array; if the concentration of tubes is low, the alignment is poor, resulting in shorter tubes.

**Figure 13.** AFM images of dendrimer-assisted 15.4 nm Fe nanoparticle SAMs (a) by height and (b) amplitude.

SEM images Figure 14a and 14b reveal the poor growth of CNTs, top view and side view respectively. In fact, they barely support themselves to form an array. This is expected due to the lower catalyst particle concentration in the SAM film; however, we have observed that 15.4 nm nanoparticles are less active to nucleation. Although we have mostly observed double and triple wall CNTs, we have also observed multiwall CNTs.
TEM images show CNTs in ribbon-like structures with 19.4 nm widths; most likely these are CNTs that have collapsed on the surface and therefore they no longer have tubular structure. Assuming that this ribbon-like structure is a collapsed CNT, the original diameter before collapsing should be ~13 nm. This CNT diameter has reasonable correlation if grown from a 15 nm diameter catalyst particle. Figure 15b shows the Raman spectroscopy of the CNTs grown from 15.4 nm catalyst particle SAMs.

Figure 14. SEM images of dendrimer assisted 15.4 nm Fe nanoparticle SAM; (a) top view that illustrates the surface morphology and homogeneity and (b) height of the VA-CNT grown from 15.4 nm Fe nanoparticles.
Figure 15. TEM images of CNTs grown from dendrimer assisted 15.4 nm Fe nanoparticle SAMs; typical diameter measurements (a) and Raman spectroscopy taken on solid state CNT arrays at 514, 633 and 785 nm excitations.

Conclusion:

In summary, monolayer films of Fe nanoparticles on Al₂O₃ surface were assembled. This process is a promising approach for making self-saturated monolayer films of catalyst particles for CNT growth. The approach is an important contribution towards diameter-controlled large scale CNT production. Because the catalyst SAM process relies on surface chemistry, reliable growth of VA-CNTs over large areas is likely. Also, we have successfully grown large diameter VA-CNTS from pre-made catalyst nanoparticles with a correlation between the diameter of the particles and the CNTs.
Experimental Contribution:

My contributions to the experimental work in this chapter are all the data collected and characterizations provided. The ~4 nm Fe nanoparticles were synthesized by Alvin Orbraek (Barron Lab); the 8.8 and 15.4 nm Fe nanoparticles were synthesized by Dr. Fen Li and Ezekial Fisher, respectively, both from the Colvin Lab.

References:


Chapter 3

Alumoxane Substrates for Large Scale Production of Vertically Aligned Carbon Nanotubes

Introduction:

Many CNT applications require large scale CNT production methods. Among traditional CNT synthesis methods, chemical vapor deposition (CVD) has emerged as the most promising with regard to large-scale, low-cost CNT production, simplicity of parameter control, and suitability for large area (wafer-scale) and irregular substrates. In addition, CVD has several advantages compared to most plasma-related growth techniques, such as the absence of uncontrollable radicals and ions. Scale-up of CNT production, while maintaining simplicity in the growth process, has been a common goal of recent research efforts.

As simple as the CVD method might be, its potential for CNT mass production has been hindered by difficulties related to catalyst and catalyst support deposition. Besides the traditional evaporation methods, there are several catalyst deposition procedures reported in the literature; Nanoparticle spin coating, dip coating, sol-gel, and layer-by-layer metal deposition, among others, have been used to successfully produce CNTs. Vertical arrays of CNTs have several advantages over CNTs produced with others techniques. Although catalyst deposition methods have been explored extensively, successful VA-CNT growth still requires thin films of evaporated or sputtered catalyst supports, typically Al₂O₃. Evaporation and sputtering are time consuming and require vacuum procedures that impose limitations for large scale catalyst
support deposition. Several researchers have overcome this difficulty by using different supporting substrates for CNT growth. Among these are zeolites, metal oxides, sapphire, quartz and aluminum foil. However, most of these techniques have not generated large quantities of CNT yet and the quality of the tubes has been compromised. Other researchers have tried to overcome the catalyst support deposition problems by using multi-component catalyst materials (incorporating Fe, Co and Ni), and bulk materials to assist the growth process. Although there have been major efforts applied toward achieving these goals, there are important questions that need to be addressed: What is the function of the catalyst support? Is it only an insulator? Does the support contribute to the catalyst life, CNT length and diameter?

Although this chapter does not answer all of these questions, it provides valuable evidence that Al$_2$O$_3$ is an active component of CNT growth, regardless of how it is deposited. It also depicts a complete wet process of VA-CNT production that starts with nanoparticles of catalyst and catalyst support in the liquid phase. This approach is intended to overcome the difficulties and limitations of evaporation processes for large scale catalyst and catalyst-support deposition. Pre-made Fe nanoparticles were used as catalysts on top of a thin film catalyst-support made of alumoxane (aluminum oxide hydroxide) nanoparticles. The thin film of alumoxane deposition is produced through a simple spin coating of alumoxanes on SiO$_2$ wafers or dipping the wafers directly in the alumoxanes solution, (Scheme 1). This technique is simple, cost-effective and ideal for large-scale production of VA-CNT growth. The procedure has the potential to convert the catalyst-support deposition process into a simple process, therefore lifting the limitation that the evaporation of the catalyst and its support have on CNT production by CVD.
Alumina particles as substrates have been used in the past for CNT growth with very limited quality and yield of CNTs.\textsuperscript{12, 13} Other synthesized Al hydroxide substrates were also used as catalyst support for CNT growth,\textsuperscript{14-16} however in none of these cases were VA-CNTs produced.

\textbf{Scheme 1.} The alumoxane solutions are ultracentrifuged at 29K rpm for 12 h to obtain a narrow nanoparticle size distribution. The supernatant with alumoxane nanoparticles was spin-coated onto SiO\textsubscript{2} wafers to make a catalyst support film where Fe was deposited by evaporation and as pre-made particles. On the right side of the scheme, CTNs grown from electron beam evaporated Fe (top-right) and premade Fe nanoparticles (bottom-right) are shown.
Experimental Section:

Alumoxane solutions were prepared using boehmite particles (Catapal) from Sasol, according to a procedure described by Callender et al.\textsuperscript{17} Boehmite (20 g) was slowly added, with stirring, to a mixture of acetic acid (51 mL, 667 mol) in water (200 mL). After stirring for 10 min, the slurry was decanted and centrifuged at 4400 rpm for 1 h. The supernatant was collected and then volatiles were removed under vacuum at 90 °C. The residual solid was then redissolved in water. This solution is called A-Alumoxanes (A-A) in this manuscript. To prepare MEEA-Alumoxanes solution, (20 g) of Catapal and [(methoxyethoxy)ethoxy]acetic acid (102 mL, 668 mmol) were refluxed in water (400 mL) for 72 h. The reaction mixture was centrifuged at 4400 rpm for 1 h. The decanted supernatant is called MEEA-Alumoxanes (MEEA-A) in this thesis.

Different concentrations of MEEA-A solution were spin coated onto clean SiO\textsubscript{2}. The ideal concentration for film preparation of 0.015 mg/L was determined by spin coating a range of dilutions of MEEA-A and measuring the efficacy of VA-CNT growth from evaporated catalyst. By spin coating at 4000 rpm, we were able to consistently produce films which were active toward VA-CNT growth. MEEA-A coated substrates were dried before evaporating Fe on them. The substrates were placed in the oven at 150 °C under continous N\textsubscript{2} flow for 60 min immediately after spin coating. For the evaporated catalyst, 0.5 and 1 nm of Fe deposition was performed at 10\textsuperscript{-6} Torr in an electron beam evaporator. Both A-A and MEEA-A contain particles that are several tens of nanometers in size; therefore, both solutions were centrifuged at 29,000 rpm in a swing bucket ultracentrifuge for up to 12 h. The progress toward obtaining samples with ever smaller particle size was monitored using tapping mode AFM (Nanoscope).
The pre-made catalyst nanoparticles were synthesized using a modified Sun method, whereby Fe(III) acetylacetonate is reduced by excess 1,2-hexadecanediol in the presence of oleic acid and oleyl amine that form as ligands on the particle surfaces. Unless otherwise noted, all chemicals were purchased from Sigma-Aldrich and used as received. The reactants were added together at room temperature using benzyl ether as solvent, and brought to reflux under inert atmosphere for a period of 45 min. The particles were then precipitated using excess ethanol and centrifuged at 4000 rpm for 5 min. The precipitated particles became soluble in hexanes in the presence of oleic acid. The total concentration of Fe nanoparticles was determined with inductively coupled plasmon-atomic emission spectroscopy (ICP-AES); the Fe concentration was found to be 40,000 ppm once the particles were synthesized and made soluble in approximately 15 mL of hexanes. The solution was then diluted in an iterative process to obtain maximal growth results by the further addition of hexanes. Once the optimal concentration was found for SWNT growth, ICP-AES was carried out to determine the particle concentration. Initially 100 µL of the maximal solution was digested in 500 µL of a 25% solution of hydrochloric acid with heating to digest the organic ligands; this was carried out twice. Then the metal particles were digested in concentrated nitric acid overnight and then diluted in nanopure water to carry out the ICP-AES. The sizes of the particles were found to be 4.3 nm as determined by small angle X-ray scattering using a Rigaku SmartLab instrument. The successful nanoparticle concentration that was deposited in order to growth VA-CNTs were drop dried using 40-50 µL of a 0.128 mg/L suspension of Fe. Assuming a 4 nm particle to contain 1,300 Fe atoms, the particle concentration was calculated to be ~5.38 x10^{23} nanoparticle/L.
CNT growth occurs in a hot filament CVD reactor whose characteristics are detailed elsewhere. In short, the evaporated films are reduced using atomic hydrogen for 30 s and in all cases CNTs were grown for 15 min at 750 °C. In the case of the pre-made Fe nanoparticles, they were reduced with 60 s exposure to N₂H₄ vapor at 600 °C at 10 mTorr.

Results and Discussion:

Several aluminum hydroxides as catalyst supports for CNT synthesis have been tested and reported in the past.\textsuperscript{14, 15} It has been reported that commercially available Al(OH)₃ resulted in more effective substrates for CNT growth although the quality of CNTs was not determined and no VA-CNT production was achieved.\textsuperscript{15} Al₂O₃ as catalyst support has been used mainly to prevent catalyst particle sintering, reducing the mobility of the catalyst particle, in contrast to SiO₂. However, recently the catalytic activity of the Al₂O₃ has been revised and questioned and it has been considered as an active component for CNT growth in CVD reactors.\textsuperscript{23} Researchers have compared CNT growth on γ-Al₂O₃ to amorphous Al₂O₃ substrates and have arrived at some interesting conclusions: γ-Al₂O₃ gives more efficient growth than amorphous\textsuperscript{16} and γ-Al₂O₃ is more sensitive to Fe catalyst changes.\textsuperscript{23} Although these results have improved the understanding about the effect of the support on the catalyst, further investigations are still required.

A crucial component of CNT growth by CVD is the catalyst support, typically evaporated or sputtered Al₂O₃ thin films that support active metal catalyst such as Fe, Co, Ni, etc. Metal evaporation of films has several limitations: geometry of the substrate limits the evaporation primarily to the side directly facing the evaporation source, maximum pressures of 10⁻⁵ Torr are required, and makes the entire process time-
These limitations have a significant impact on the development of VA-CNTs grown through a CVD process. A reliable liquid phase method for catalyst and catalyst-support deposition is a significant advance towards CNT mass production. In our studies, although parallel processes were carried out for each alumoxane solution, the most promising results were obtained with MEEA-A; the results and characterization data presented here are focused on MEEA-A.

**MEEA-A Thin Film Preparation:**

Alumoxanes are nanoscale particles that are exfoliated from boehmite. These nanoparticles are dispersed in H$_2$O through aluminum complexation by carboxylic acid ligands.$^{17}$ Several varieties of carboxylic acids have been used to disperse alumoxanes in solution. Barron and coworkers have explored MEEA-A applications in the past and have documented the surface area, porosity and shrinkage of the films as a function of alumoxanes fractional composition$^{19, 20}$ as well as other physical properties such as hardness, refractive index and dielectric constants.$^{17}$ They were able to develop and produce micron-thick substrates that would be suitable for micro electromechanical systems. Therefore, coating of large surface substrates with alumoxanes is not new and smooth surfaces are not required, as a result ultra-centrifuging was not explored in the past. For our experiments, we have selected acetic and MEEA ligands for our alumoxane studies based on the alumoxane stability in these solvents and better dispersibility in solution. Vogelson et al. have already reported that A-A and MEEA-A solutions showed robustness to changes in pH and no aggregation was observed at pH ~6.$^{21}$
Figure 1. AFM images from A-alumoxanes that were extracted as supernatant-aliquots at different times during ultra-centrifugation (1, 3 and 12 h). The aliquots were spin-coated onto SiO₂. After 12 h of ultra-centrifuge the particles can barely be detected by the AFM tip due to their small size and the formation of a continuous thin layer film.

As-prepared alumoxanes have a broad distribution particles sizes. We began the process of alumoxane thin film deposition by removing larger particles from solution by ultracentrifugation. The AFM images in Figure 1 are A-A nanoparticles that were extracted as aliquots at 1, 3 and 12 h during ultra-centrifugation and spin coated on SiO₂ substrates. As evidenced by AFM images, Figure 1 - 12 h, most of the large particles are gone; in fact, AFM is no longer able to resolve the individual particles. Instead it appears that no particles remain after ultra-centrifugation. Although only the AFM images for A-A are provided in Fig. 1, the large particle removal from MEEA-A by ultra-centrifugation is quite similar to the A-A decant. The remaining nanoparticle decants had a narrower and smaller size distribution and the particle sizes were not able to determine by AFM in a film like prepared sample after spin-coating. In fact subsequent dilutions of the MEEA-A decant was determinant to image individual MEEA-A nanoparticles where only less than 4 nm heights were observed. Smaller sized alumoxane particles guarantee smoother...
surface films so the roughness of as-prepared films are very similar to evaporated or sputtered Al₂O₃. On a film-like structure, the alumoxane nanoparticles appear to be densely packed in the film with a typical RMS surface roughness that varies from ~0.2 to ~0.7 nm, which is similar to evaporated Al₂O₃ catalyst support. The thickness of the film was determined using an ellipsometer; two different films were prepared by similar procedures, and measurements of 10 random spots on each film were taken. An average of 10.3 ± 2.05 nm was obtained for the first film and an average of 8.8 ± 1.02 nm was obtained for the second film. A 632 nm laser at a 70° fixed angle with 1.7 refractive index (Nf1) and Ns 385 as setting parameters were used to measure the thickness of the alumoxane film.

Figure 2. TEM images of a) MEEA-Alumoxane and b) A-Alumoxane individual particles after 12 h ultracentrifugation. The particles were drop dried on a 10 nm carbon thin film TEM grid from H₂O decants extracted after 12 h. The darker spots on a) are particle aggregate dry-outs while the small rod-like particles distributed all over the surface are the alumoxanes. The A-A particles in b) are larger and more obvious to
Despite using the same boehmite (Catapal) and similar acids to disperse alumoxanes in solution, we have observed that alumoxane particles dispersed in each solvent have significant differences in their shapes and sizes. Alumoxanes functionalized with MEEA exhibit more rod-like structures (Fig. 2a), while those in acetic acid look have flake-like structures (Fig. 2b). For reasons we can not yet explain, films spin-coated...
from A-A were not as uniform as the MEEA-A films, therefore VA-CNTs growth on A-A have non-homogenous surface morphology with different heights being obtained and further improvement in film preparation is required.

**CNT Growth and Characterization:**

MEEA-Alumoxane film preparation was optimized through a change in particle concentration. After a series of dilutions, 0.015 g/mL of alumoxanes was found to be the best for film preparation through spin-coating at 4000 rpm. 200 μL of solution with 0.015 g/mL concentration of alumoxanes was able to uniformly coat a ~4 cm² of SiO₂ surface. The most important evidence of the complete coverage is the uniform VA-CNTs grown after 0.5 nm thick Fe catalyst evaporation as seen in Figs. 3a, 3b, 3c and 3e. Conversely, the same volume of 0.005 and 0.025 g/mL solutions spin coated on SiO₂ at the same rpm have grown CNTs with a non-uniform surface morphology, more like islands of forest with different heights (Figs. 4a, 4b, 5a and 5b). In both cases we have observed fully covered surfaces; however, the uniformity was always affected at this concentration. Although we were able to grow VA-CNTs in all cases, when the solution was more dilute than 0.005 g/mL or more concentrated than 0.025 g/mL, the heights were uneven and patches of CNTs taller than others were observed. We have also observed that small areas of the thin films made with 0.025 g/mL solutions of MEEA-A can become as thick as ~500 nm. These thicker films were lifted off from the substrate during the growth process. It is interesting that a small change in a single parameter, concentration, significantly affects the homogeneity of the films, considering that film preparation from a colloidal nanoparticle solution has a complex contribution of many parameters such as capillary effects, electrostatic charges, density and viscosity of the solvents. One possible
explanation is that the density of MEEA is 1.161 g/mL compared to acetic acid 1.049 g/mL and the resulting MEEA-A solution appears more viscous than that of A-A, so most likely the capillary forces are more important and predominant in the film making process. By increasing the concentration of the particles in solution, we have improved the film characteristics until the capillary forces are overcome and no longer determine the position of the particles, resulting in particle aggregation. The alumoxane concentration of the optimized solution concentration was determined by TGA. A volume of 0.1 mL MEEA-A was dried in the oven at 100 °C, then the sample was heated to 800 °C under Ar. The total remaining mass was 1.5 mg; therefore, the alumoxane concentration was 0.015 g/mL.

Figure 4. SEM images of VA-CNTs grown from films prepared with 0.005 g/mL concentration of MEEA-A. a) Visualize the surface morphology of the VA-CNTs while b) shows a closer view of the VA-CNTs.
Figure 5. SEM images of VA-CNTs grown from films prepared with 0.025 g/mL concentration of MEEA-A. a) Shown is a higher magnification of the VA-CNTs and b) visualizes the patch-like dry out of the alumoxanes and the CNTs grown with that morphology.

As is shown in Figs. 3b, c and d the quality of CNTs as shown by SEM are quite similar to that of CNTs grown in our lab on evaporated Al₂O₃ substrates. The height of the VA-CNT are ~15 µm (Fig. 3c) for a 15 min growth time which is slightly shorter than CNTs grown on single crystal alumina (M cut) ~18 µm, and much shorter than on evaporated Al₂O₃, which yield ~40 µm CNTs. The reason for this is still under investigation. To investigate the importance of the alumoxane film for CNT growth, we have performed a control experiment whereby a clean SiO₂ substrate with no alumoxane film and another with a MEEA-A film, were placed in the evaporation chamber to deposit Fe catalyst at the same time. Both substrates were placed in the CVD reactor for a 15 min growth period. As expected, the clean SiO₂ substrate grew CNTs only along surface while the MEEA-A substrate produced a perfect carpet of VA-CNTs.

MEEA-A as well as A-A are hygroscopic solutions, so after alumoxane film
deposition on substrates, solvent from the film was evaporated in a moisture-free environment. Immediately after spin coating, the sample was carried to a N₂ purged oven at 150 °C and the solvent was allowed to evaporate for 60 min. This is an important post-film-forming step in order to guarantee surface planarity of the film. In cases where drying was not done immediately after film preparation, we have observed that within a few minutes, a uniform film loses its surface uniformity and creates droplet-like agglomerates or aggregates that distort the planarity of the substrate.

Figure 6. TEM images of CNTs grown using MEEA-Alumoxanes as substrates and evaporated catalyst using a) a larger scale and b) a closer view.

TEM images of VA-CNTs grown on alumoxane substrates from evaporated catalyst have shown a variety of diameters and walls so far (Figs. 6a and 6b). Typically 3-7 nm diameter CNTs and CNTs with double and triple walls were observed. The quality of the TEM images becomes reduced due to the alumoxane particles present on the TEM grid. After 5 min of VA-CNTs bath sonication in ethanol, a drop of the solution was transferred to the TEM grid and dried at 100 °C in air; therefore, the alumoxane particles
were transferred to the TEM grid together with CNTs. Raman spectroscopy reveals the
presence of smaller diameter single wall CNTs (Fig. 7a). Laser sources with 514, 633 and
785 nm wavelengths detect radial breathing modes (RBMs) below 300 cm$^{-1}$ that is typical
of CNTs with diameters 2.5 to 0.7 nm, and common for VA-CNTs grown on evaporated
Al$_2$O$_3$. The D/G ratio, which is an indication of quality that is based on the relative ratio
of sp$^2$ hybridized C atoms from a perfect graphitic matrix compared to sp$^3$ C atoms
arising from defects in the nanotube surface, is low. This ratio has been estimated as 18%
for 514 nm and is relatively higher compared to CNTs grown from evaporated
catalyst/catalyst-support substrates. Given the MEEA-A films porosity, it is expected that
Fe catalyst would have higher mobility and perhaps diffuse into the alumoxane film.
CNTs grown from the diffused catalyst would disrupt the perfect alignment, and perhaps
contribute to stress generation during growth which would lead to relatively higher D
bands. The MEEA-A films characterized by XPS supports the aluminum coating,
although its spectroscopic signal intensity is ~3 times smaller than that of evaporated
Al$_2$O$_3$. The XPS signal intensity of alumoxane was multiplied by 3.15 before
normalization in Figure 7b. Considering that MEEA-Alumoxane is a film made
completely from nanoparticles, it is expected to have higher porosity than evaporated
Al$_2$O$_3$; therefore lower intensity signal for similar thickness seems reasonable. This is
supported by the ellipsometry measurements of the film, where we have observed similar
thickness to evaporated Al$_2$O$_3$. 

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Besides catalyst-support deposition by a liquid phase method, a complete wet CNT production process by CVD requires a liquid premade catalyst deposition as well. It is idealized that a monolayer of closely packed Fe particles would grow a perfectly aligned CNT array. We have used two approaches to build monolayer of particles: spin coating and drop drying. Spin coating appears to be a less reliable approach than drop drying, as evidenced by frequent accumulation of particle patches. The patch sizes and shapes changed as a function of the rpm and particle concentration utilized; however, through drop-drying of a 40-50 μL of particle solution, we were able to make semi-monolayers of particles which support VA-CNT growth, Fig. 8a. This topic needs further improvement and understanding, and the findings will be reported separately. Using premade Fe nanoparticles should suppress catalyst diffusion into the alumoxane thin film. The Raman characterization of the VA-CNTs grown from 4.3 nm Fe nanoparticles reveal slightly smaller D-bands than CNTs grown from metal evaporated catalyst on alumoxane,
Fig. 8b. This is reasonable because premade nanoparticles have a fixed size already therefore less ability to diffuse and penetrate into the porous alumoxane thin film. Furthermore, OH-rich aluminum surfaces have been claimed to be more effective substrates for CNT growth, perhaps due to better catalyst-particle interaction during metal deposition.\textsuperscript{13} We believe alumoxanes would be ideal substrates for retarding Ostwald ripening of catalyst due to its OH richness as well. If true, this would be excellent supporting evidence for the theory reported by Amana et al.\textsuperscript{24} and would become a great candidate to extend catalyst life during the CNT growth process.

**Figure 8.** VA-CNT grown from 4.3 nm premade Fe nanoparticles, a) SEM image and b) Raman Spectra at 514, 633 and 785 nm excitation wavelengths.

An additional factor for scaling up CVD through complete liquid process consists in finding a homogenous catalyst particle reduction technique different from the hot filament currently used in our Lab; this has been addressed by Pint et al.,\textsuperscript{22} where N\textsubscript{2}H\textsubscript{4} vapor exposure was used for metal oxide catalyst reduction at temperatures above 200 °C. N\textsubscript{2}H\textsubscript{4} reduction has several advantages compared with our current hot filament generating atomic hydrogen. First, it avoids complications of the dimension and geometries of
filament required in order to evenly reduce the particles on surfaces, especially for large surface area supports; second, the particle reduction process can be done at lower temperatures. Growth has been observed for $N_2H_2$ reduction temperatures as low as 400 °C. The hot filament generates atomic hydrogen but the efficacy of reduction is limited to areas that are facing the filament. Alternatively, $N_2H_4$ reduction is more robust and the probability of hidden or unreacted areas is much smaller. Therefore our liquid phase approach to metal catalyst/catalyst support deposition combined with $N_2H_4$ vapor reduction removes these limitations and converts CVD to a more promising large-scale production system. Basically a CVD reactor with three sequential compartments could be used in a continuous process: A catalyst support drying chamber where alumoxane films will dry out at 150 °C under inert gas, followed by a catalyst reduction chamber where Fe particles will be exposed to $N_2H_4$ at ~600 °C and then finally, the substrate passes to a CNT growth chamber.

**Conclusions:**

A procedure for large scale carbon nanotube (CNT) production has been developed through liquid phase deposition of aluminum oxide hydroxides (Alumoxanes) and Fe nanoparticles as catalyst supports and catalyst respectively. Through a simple spin coating of alumoxanes (boehmite) nanoparticles, cm$^2$ uniform thin films surfaces were developed and used as catalyst support followed by catalyst deposition. Typical evaporated Fe and liquid phase premade Fe nanoparticles, that were drop died onto the alumoxane catalyst support, grow vertical arrays (VA) of CNTs successfully. The quality of CNTs grown from electron beam evaporated Fe on alumoxane films are similar in quality and length to CNTs grown on standard evaporated alumina substrates. Through
simple changes in alumoxane nanoparticle concentration we were able to deposit homogenous thin films of Al₂O₃ that have comparable smoothness to evaporated Al₂O₃ and yield CNTs with similar characteristics. Additionally, premade catalyst particles that were deposited on alumoxanes films combined with premade catalyst particle reduction using N₂H₄ lifts completely the barriers of the CVD process to become a competitive large scale CNT production method. We envision large scale CVD reactors with three sequential compartments: solvent drying under inert gas environment, catalyst reduction using N₂H₄ at the right temperature, and CNT growth compartment with C₂H₂/H₂O/H₂.

**Experimental Contribution:**

My contribution to the experimental work in this chapter are all the data collected and characterizations provided. Alumoxane solutions were prepared by Christopher E. Hamilton and Fe nanoparticles were synthesized by Alvin Orbraek.

**References:**


Chapter 4

Abrasion as a Catalyst Deposition Technique for Carbon Nanotube Growth

Introduction:

Scale-up of CNT production, while maintaining simplicity in the growth process, has been a common goal of many researchers and research efforts. The search for a cost-effective production process has motivated investigation into alternative catalyst deposition methods,\textsuperscript{1-4} multi-component catalyst materials (besides Fe, Co and Ni),\textsuperscript{5, 6} and new substrates and catalyst supports to aid and assist the growth process.\textsuperscript{7, 8}

One crucial aspect of CVD-grown CNTs is the requirement for external deposition of catalyst on a solid oxide surface prior to growth. There have been a wealth of studies documenting unique catalyst deposition techniques such as metal evaporation,\textsuperscript{9} roll-to-roll metal and oxide support evaporation,\textsuperscript{4} sputtering,\textsuperscript{10} nanoparticle spin-coating,\textsuperscript{1} dip-coating,\textsuperscript{2} sol-gel,\textsuperscript{3} and layer by layer metal-deposition,\textsuperscript{11} among others. All of these approaches support CNT growth, although some are more effective than others. In addition to catalyst deposition techniques, several studies have focused on different supporting substrates for CNT growth. The use of quartz and glass instead of Si is quite common, and recent studies have emphasized that growth can be achieved on bulk metals, including stainless steel (SS) foils, where additional metal catalyst is not required.\textsuperscript{12-14} Recently, CNT growth has been reported from grinding hardened steel balls with graphite, with mechanical milling followed by thermal annealing at 1400 °C.\textsuperscript{15} In that study, milling times as long as 200 h were used to produce CNTs. In addition, Yuan et al. have recently reported CNT growth on quartz where the catalyst was deposited via scratching\textsuperscript{16} in a manner similar to our studies. Another approach towards continuous
CNT production involves the use of aluminum foil as the catalyst supporting surface, although this route still requires Fe catalyst deposition to achieve CNT growth. To date, the water-assisted supergrowth process utilizing an alumina catalyst support remains the most efficient process for high yield, high-quality CNT growth in a dense, aligned structure.

This chapter studies abrasion as a simple, cost-effective deposition technique of catalyst that supports high density CNT growth and nanoscale patterning. Mechanical friction applied between a metal surface and the growth substrate abrades enough catalyst onto an oxide supporting layer to result in the growth of dense vertically-aligned CNT forests (VA-CNTs) with a reasonably high quality compared to other processes for CNT synthesis. In addition, we demonstrate that this simple abrasion process can be used to fabricate micro- and nano-scale patterns of VA-CNTs. The result of our studies confirms that a simple mechanical abrasion is a new route toward catalyst deposition from easily-obtained bulk materials, with the capability to improve cost-effectiveness of currently developing CNT applications.

**Experimental:**

The catalyst deposition technique relies on simple mechanical friction generated between a solid metal catalyst source and a 10 - 100 nm thick film of Al₂O₃ deposited on a SiO₂ substrate. A number of different catalyst sources were used, including magnetic Fe, cast Fe, carbon steel, 99.98% pure Fe from Alfa Aesar and stainless steel (SS) series 300 (SS-302, SS-316) and 400 (SS-416, and SS-420). The catalyst sources involved have many different shapes and forms such as discs, blades, bars, granules and wool fibers. By rubbing any Fe metal object against a Al₂O₃/SiO₂ substrate, catalytic Fe particles are
transferred to the growth substrate, as shown in Figure 1. The pressure applied during the abrasion resulted in the deposition of a light to heavy coating of Fe particles on the substrate, depending on the conditions. At low pressures, CNTs were observed on the surface only as randomly oriented CNTs grown parallel to the substrates (mats) or sparsely grown domains. However, when greater pressure was applied, a higher concentration of catalyst particles was deposited on the growth substrate, resulting in the formation of a vertical array of CNTs.

**Figure 1.** Scheme that describes catalyst deposition through abrasion. Any object with Fe metal content abrades catalyst in the form of particles that can be used as nucleation sites for CNT growth.

CVD growth experiments were carried out in a hot filament chemical vapor deposition (HF-CVD) apparatus, which has been described elsewhere.\textsuperscript{4, 21, 22} In order to chemically reduce the deposited metal and produce an active catalyst, a brief exposure to atomic hydrogen produced via a hot tungsten filament preceded the growth process after rapid insertion of the abraded substrate into a hot furnace. A total flow rate of ~400 standard cubic cm per min (sccm) of H\textsubscript{2}, 2 sccm H\textsubscript{2}O, and 2 sccm C\textsubscript{2}H\textsubscript{2} at a total pressure of 1.4 Torr was maintained in the 1 inch tube furnace while the abraded substrate was
introduced and CNTs were grown. The temperature was maintained at 750 °C for the duration of the process, conditions that have been found to yield the highest quality growth in water-assisted conditions.²²

Alumina coated substrates, with 100 nm thick Al₂O₃ deposited through atomic layer deposition (ALD) onto a clean SiO₂ wafer, were provided by Sundew Technologies LLC. 10 nm thick Al₂O₃ was prepared by electron beam evaporation of alumina at typical pressures of 10⁻⁶ Torr.

**Results and discussion:**

**Dense Forest and micro-patterns of VA-CNTs:**

Stainless steel has been previously and simultaneously used both as the catalyst source and the substrate¹²-¹⁴, ²³, ²⁴ for CNT growth. Other processes require additional Fe to be deposited on the SS substrates²⁵-²⁷ in order to achieve CNT growth. The results here indicate that all the Fe-containing alloys abraded on Al₂O₃ grow CNTs, once deposited on a proper supporting substrate, although some Fe-containing sources appear more efficient than others. Figure 2a shows VA-CNTs grown on Al₂O₃ substrates as a dense forest while Figure 2b shows micron-wide patterns of CNTs where SS-420 was abraded through single stripes made by a sharp scalpel. As shown in Fig. 2b, patterns of dense, aligned CNTs can be easily obtained in this technique with a feature resolution determined by the size of the object used for abrasion.
Figure 2. SEM images of (a) a top-down view of a dense CNT forest and (b) a top-down view of micro-scale patterned CNTs, both formed from abrasion of Fe (SS-420) catalyst through abrasion on Al₂O₃ substrates. Inset images show higher resolution images of (a) the CNT alignment in the dense array, and (b) a single line formed from abrasion. Scale bars in inset images are 20 μm.

We also note that some Fe sources abrade more easily than others. The SS-420 hardness on the Hardness Brinell scale (HB) is higher than that of SS-316, however abrasion occurs more easily with SS-420. This is probably related to the machinability, of SS-420 compared to SS-316; SS-316 machinability rates are lower and cause higher tool wear than SS-420. SS has many potential active components for CNT growth, including Fe and Ni, both of which are known catalysts for CNT growth. However, the SS-400 series (SS-416 and SS-420), has no Ni in the SS matrix, but still results in the growth of VA-CNTs. This suggests that Ni is not a required component in the growth process, and allows us to focus on Fe as the likely dominant component of CNT growth. Table 1 summarizes the composition of the different Fe sources used in our experiments. In addition, Cr and C content appear to have some effect on the abrasion process. The
presence of Cr presumably results in surface hardness enhancement of SS that affects the Fe transfer through abrasion. The presence of carbon in the SS also increases hardness and might accelerate the nucleation and growth of CNTs.

Table 1. Elemental composition of several Fe sources used as catalyst.

<table>
<thead>
<tr>
<th>Fe sources</th>
<th>Fe %</th>
<th>C %</th>
<th>Cr %</th>
<th>Ni %</th>
<th>Mo %</th>
<th>Si %</th>
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<tr>
<td>Fe granules</td>
<td>99.98</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cast Fe</td>
<td>96.9 - 93.0</td>
<td>2.1 - 4</td>
<td></td>
<td>1 - 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C steel</td>
<td>98</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SS-304</td>
<td>72.96</td>
<td>0.04</td>
<td>18.3</td>
<td>8.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SS-316</td>
<td>69.26</td>
<td>0.04</td>
<td>17</td>
<td>11</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>SS-420</td>
<td>87.47</td>
<td>0.03</td>
<td>12.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CNT Characterization, TEM, Raman and XPS:

In order to study the properties of the CNT arrays grown from abraded catalyst, data from Raman spectroscopy (laser excitation at 514, 633 and 785 nm) was collected and is shown in Figure 3a. In all spectra, the D/G ratio remains small, indicative of the low-defect CNT growth that is characteristic of the water-assisted CVD process. The low D/G ratios are comparable to those VA-CNTs grown from e-beam evaporated catalyst sources. Raman spectra of CNTs in the solid state and CNTs dispersed in H₂O using sodium dodecyl benzene sulfonate (SDBS) surfactant show no significant D/G ratio difference. The radial breathing modes (RBM) in Fig. 3a indicate the presence of CNTs with walls less than ~ 2 nm in diameter, which can be due to the inner walls of multi-walled carbon nanotubes (MWCNTs), or small diameter single-walled carbon nanotubes.
Figure 3b shows an atomic force microscope (AFM) image of particles deposited in a single stripe abrasion with a SS scalpel. A large particle size distribution was found, including many particles larger than 10 nm. The diameter range of VA-CNTs grown from these particles suggests that it may not be necessary to have small diameter (< 10 nm) particles present in order to sustain uniform nucleation and growth of VA-CNTs.

Figure 3. (a) Raman spectra from a typical dense forest of VA-CNTs grown from Fe catalyst (surgical scalpel SS-420) deposited through abrasion on an Al2O3 supporting surface. (b) AFM image of single stripes drawn with a surgical scalpel (SS-420) on an Al2O3 substrate before CNT growth, revealing the particles that form during abrasion and support VA-CNT growth. The image is 20 um on a side while the inset is 1 um on a side collected from the area in square (not to scale).

Transmission electron microscope (TEM) images (Figure 4a) obtained after dispersing the CNTs through 15 min of bath sonication in ethanol and deposition on lacy carbon TEM grids suggest the presence of a variety of CNT species, including SWCNTs,
double-walled CNTs and MWCNTs. When dispersed in SDBS with 6h of bath sonication, the CNTs display fluorescence, albeit weak, with excitation at 660 nm, indicating the presence of small amounts of 0.7-1.3 nm diameter semiconducting SWCNT species.\textsuperscript{31}

\textbf{Figure 4.} TEM images of CNTs from a typical dense forest of VA-CNTs grown from abrasion deposited catalyst (surgical scalpel SS-420) on an Al\textsubscript{2}O\textsubscript{3} film. The CNTs were removed by sonication and dispersed in ethanol and applied to a lacy carbon grid for imaging (a), inset image scale bar is 200 nm. Fe content comparison by XPS spectra between catalyst deposited through abrasion and e-beam evaporation on Al\textsubscript{2}O\textsubscript{3} substrates (as prepared).

Comparison of XPS spectra of the catalysts deposited by abrasion and e-beam evaporation provides further support for the presence Fe on abraded substrates. XPS analysis indicates that Fe deposited through abrasion has features similar to a 1 nm Fe layer deposited by e-beam evaporation (Figure 4b), the later being the most common catalyst layer used in VA-CNT growth.\textsuperscript{4,32,33}
Figure 5. SEM images of a surgical scalpel (SS-420) before and after use as a catalyst source to abrade Fe on Al$_2$O$_3$ substrates. a) before abrasion, b) after abrasion

In addition, SEM images of a surgical scalpel (SS 420) used as a catalyst source before and after metal abrasion reveals the removal of some material from the initial scalpel, Figure 5. To demonstrate that this approach is applicable to larger areas, the scalpel was used to abrade a rotating substrate (~1500 or 3000 rpm), quickly generating circular patterns of catalyst on ~1 cm diameter substrates in an open environment, as shown in Figure 6a. Furthermore, exposure to water-assisted growth conditions resulted in VA-CNT growth with circular patterns as shown in Figure 6b.
Figure 6. SEM images of (a) abraded Fe (SS-420 surgical scalpel) deposited on a spinning Al₂O₃ substrate. Scale bar in the inset image are 25 μm. (b) SEM images of CNT grown from catalyst deposited through abrasion on a spinning Al₂O₃ substrate.

Nanopatterns of Catalyst:

An interesting similarity to catalyst abrasion is a common drawing pencil which abrades graphite particles onto paper as shown in Figure 7a. The composition of the pencil lead determines its hardness, which determines the mass of graphite abraded on the paper in a single pass. A pencil with higher hardness number will abrade very small amounts of graphite that can be hardly seen, however, a pencil lead with lower hardness will deposit a significant mass of graphite at even light pressures. The similarity with catalyst abrasion lies on our current ability to make nano-rods of Fe that could be used as drawing tools with catalyst for nanometer-sized patterns of CNTs.
Figure 7. Similarities of graphite abrasion from a common pencil to Fe catalyst deposition by abrasion on substrates. (a) A pencil on its early days of applications compared to actual pencils used today that illustrates the similarity to the current sharpest iron tools available for nano-scale patterns. (b) Different amounts of graphite deposited with current available pencils that are based on their pencil-lead harness.

In addition to using abrasion geared toward large-scale production of VA-CNTs or forming microscale patterns of VA-CNTs, the use of abrasion for the formation of nanoscale patterns has been explored. A 12 nm layer of Fe was e-beam deposited onto a conventional silicon AFM tip. Using contact mode AFM, catalyst patterns were drawn. Figure 8 is a patterned catalyst stripe having a length of ~ 5 μm on ALD-deposited alumina substrates. Prior to deposition of the Fe, the AFM tip diameter was ~20 nm; after Fe deposition the diameter should be twice 12 nm plus 20 nm, approximately 44 nm. As a result the resolution of the Fe pattern obtained is limited by the size of the tip, similar to the process described in Figure 2. To demonstrate this, Fe was deposited using 2, 5 and 10 AFM scans, as shown in Figure 8a (10 scans). Following catalyst deposition, the
catalyst stripe was exposed to water-assisted CVD growth conditions, which resulted in the growth of a significant number of CNTs, as shown in Figure 8b. The height of the deposited catalyst was typically found to be greater than 1 nm, although some larger particles at the edges of the pattern were observed, as expected, the amount of catalyst deposited decreased with the number of scans. It should be noted that this catalyst deposition process can be just as easily carried out with a used AFM tip, decreasing the cost of the nano-patterning, although a standard contact mode AFM tip should be used. The radius of curvature of the contact mode AFM tip might be larger than tapping mode one, which would affect the width of the patterns, however they are typically stronger and robust.

![Figure 8](image)

**Figure 8.** (a) AFM image of catalyst patterns drawn from abrasion using an AFM tip coated with a thin layer of evaporated Fe metal. (b) CNTs grown from a nano-patterned catalyst drawn with the Fe-coated AFM tip.

There are additional advantages to the abrasion catalyst deposition method. It is generally accepted that catalyst particle size determines the diameter of the CNT.\textsuperscript{19, 34}
As is evident from the AFM images of particles deposited through abrasion (Figure 9a), the majority of deposited particles are much larger than that expected to grow CNTs of diameters and quality shown in Figures 2-4. In conventional VA-CNT growth substrates, the catalyst film thickness is generally the factor which determines the size of islands that nucleate CNTs. Among others, Wei et al. has reported that an optimum catalyst thickness is required to successfully grow VA-CNT. The fact that dense, uniform CNT growth is observed on a full 1 cm\(^2\) substrate is interesting in the framework of understanding CNT growth from nanoscale particles. From the AFM images of Figure 9a, it is evident that these larger Fe particles exposed at 750 °C for 60 s in CNT growth gas mixture results in the formation of smaller semispherical particles as shown in Figure 9b. It is generally observed that nanoparticles larger than a typical CNT diameter have smoother and flatter surfaces initially (Figure 9a), and changes in the early stage of CNT growth, as they are exposed to reduction conditions at 750 °C. At this temperature under reduction conditions, dome-like structures emerge with feature sizes generally corresponding to the range of CNT diameters observed (Figure 9b). This indicates that these “nano-dome” features are the precursors for nucleation and subsequent CNT growth.
Figure 9. AFM images of abraded Fe on Al₂O₃: (a) before and (b) after heating to 750 °C for 60 s in a typical CNT growth environment (C₂H₂/H₂/H₂O). After heating, the surface of the abraded catalyst particles has developed into a “nano-dome” surface morphology that supports CNT nucleation and growth.

Figure 10. SEM images of SS-316 before (a) and after (b) exposing to C at 750°C for 15 min. There was observed plenty of C precipitate however no VA-CNT growth was observed.
Several mechanisms for CNT growth have been proposed in the literature; however the process is not fully understood. The most accepted mechanisms are bulk carbon diffusion and precipitation, surface migration, and carbide formation. In a similar manner to particle size changes reported by Park et al., Zhou et al. and Gao et al., we have observed a large number of nm-sized particles forming on SS substrates when exposed at 750 °C for 15 min under C₂H₂, H₂ and H₂O flow. Similar experiments performed by exposing clean SS-316 shims (Figure 10a) to our typical CNT growth condition, reveals significant change on the bulk SS surface. The substrate undergoes a complete surface morphology change and as a result of crack development and sintering of particles (Figure 10b), only fibrillar carbon precipitates were observed with no VA-CNTs. This is evidence of C diffusion into the substrate, but since diffusion is continuous throughout the bulk Fe metal, the concentration of C is not high enough to promote CNT nucleation. This observation suggests that C diffusion followed by saturation and precipitation are important steps for CNT growth. A SS-420 scalpel that had been previously heat-treated in a growth environment was used for catalyst abrasion on a new Al₂O₃ substrate. This C rich SS was quite easily abraded onto Al₂O₃ substrates and promoted good CNT growth with denser and longer CNTs than a typical SS abraded catalyst. This observation is similar to results reported by Liu et al., where sputtered cast Fe gave better growth than pure Fe, suggesting that pre-absorbed C in the catalyst promotes faster CNT nucleation.

Growing CNTs on metallic substrates or conductive substrates is essential for the development of CNT-based applications such as field emitters and other electronic devices, where good electrical contact between the CNTs and the metallic contacts is
needed. Although there has been a reasonable level of success achieved along these lines, there still remains significant room for improvement of CNT properties, and simple catalyst deposition techniques that result in high yield and scalable growth of high quality CNTs are needed.

**Route to Large Scale Catalyst Deposition:**

Although abrasion is a simple and effective technique for catalyst deposition, the application of manual force to generate abrasion leads to difficulty in reproducing specific conditions of the abrasion process. To study this process quantitatively, a controlled mechanical device was developed to enhance reproducibility in consecutive experiments. This was achieved with the use of a vortex agitator having a fixed substrate on the bottom surface held via double-sided adhesive tape. The substrate was covered with ~10 g of a Fe source (granules, SS-420 powder or SS-420 balls) and agitated for different periods of time, resulting in a more controlled abrasion of the Fe onto the substrate. This setup allowed control of variable parameters time, speed, and power intensity of the vortex, which provides better control of the pressure and abrasion forces between the particles and substrate. Initial studies indicate a more homogenous distribution of catalyst transferred over the entire substrate. Formation of island-like patches of transferred catalyst have been observed (Figure 11a) that supports the nucleation and growth of dense CNTs (Figure 11b). This process can be used for uniform, large-area coating of catalyst layers that support dense CNT growth. Future work may lead to control of parameters that result in the most uniform and reproducible deposition of catalyst with uniform size. Thus, abrasion deposition of catalyst could be an effective route toward nanoscale and microscale patterning of catalyst, research-scale
uniform catalyst deposition for CNT array growth, as well as large scale and controllable catalyst deposition for dense CNT growth over large areas.

![Figure 11](image.png)

**Figure 11.** Larger surface coverage, catalyst deposition through abrasion using 100 mesh SS particles in a vortex agitator. (a) As-deposited catalyst, inset image scale bar is 2 μm. (b) CNTs grown from Fe deposited through a vortex system abrasion, inset image scale bar is 10 μm.

It is not clear whether the abrasion process results in a catalyst that is strongly or weakly adhered to the substrate. To better determine this, the catalyst-abraded substrate was washed with ethanol and the rinse was dried on a different, clean Al₂O₃ substrate. Both the abraded and the rinse-exposed substrates were then exposed to the CNT growth conditions and both exhibited CNT growth. In the first case, the substrate on which abrasion was carried out grew patches of CNTs, indicating that the abraded metal was firmly attached to the Al₂O₃ surface. However, the growth observed on the second substrate (from the dried ethanol rinse) typically occurred from small flakes of alumina containing abraded metal that had lodged on the surface and grew micro-fibrillar, dense
CNTs as shown in Figure 12. It should be noted that this growth process was similar to “flying carpet” growth, with some of the catalyst-coated flakes growing away from the substrate (Figure 12a) or growing CNT fibrils from the substrate (Figure 12b) based upon the orientation of the catalyst on the flake with respect to the supporting surface.

Figure 12. SEM images of CNT grown from surgical scalpel (SS-420) – Al₂O₃ flakes that had been transferred through rinsing to a second substrate before CNT growth. (a) VA-CNTs with an Al₂O₃ flake attached on the base of the array, and (b) a rope of CNTs without an Al₂O₃ flake or support.

**CNT Growth on Bulk Al₂O₃:**

In addition to catalyst deposition, dense aligned CNT growth by CVD also requires the presence of a thin oxide layer (Al₂O₃) to support the metal catalyst. In the processes described thus far, an e-beam deposited Al₂O₃ layer was used to support the abraded catalyst. Al₂O₃ is very well known abrasive, therefore, it is no surprise that abraded Fe particles could be used as catalyst for CNT growth. However, in order to ease the catalyst deposition, it would be significantly better if we do not depend on evaporated Al₂O₃ substrates for the CNT growth process. The options are to abrade an Al layer onto
the SiO₂ wafer and convert to Al₂O₃ or to use bulk alumina substrates. As a first experiment, we have focused on the abrasion of Al on a SiO₂ wafer, followed by Fe abrasion. Although Al abrasion can be simply achieved, the planarity and smoothness of the surface that required for uniform abrasion of Fe is lost. As a result, CNT growth on these substrates no longer produced a continuous dense forest over the whole surface.

The direct abrasion of catalyst onto bulk Al₂O₃ surfaces to support the growth of dense CNTs has been investigated as well. In general, it was observed that this process does promote the growth of dense CNTs but is complicated by the enhanced surface roughness of Al₂O₃ discs and other inexpensive forms of Al₂O₃. The root mean square (RMS) roughness of a typical polycrystalline, unpolished, bulk alumina substrate is on the order of microns, while the RMS roughness of a typical ALD deposited Al₂O₃ layer is less than 0.25 nm. The low RMS roughness appears to be important for the abrasion process to yield catalyst layers that will support the growth of uniform, dense CNT arrays. In order to study the abrasion process on bulk Al₂O₃ materials, we used single crystals of Al₂O₃ that were epitaxially polished. This leads to smooth surfaces that allow the abrasion of Fe similar to that observed for the e-beam or ALD deposited Al₂O₃ layers. Fe abraded onto the single crystal substrates grow uniform, dense, aligned carbon nanotubes over the entire abraded surface, except for one. For the different A-, C-, M-, and R- crystals cuts, only the C-cut exhibited poor growth. Analysis of the RBMs of the resulting CNTs shows a variety of SWCNT diameters, but only slight differences between growth on the different crystal cuts. However, distinct differences arise when comparing the D and G bands (Figure 13a), as the D/G ratio appears smaller for CNTs
grown on A, M and R cuts. Interestingly, the D/G ratio is consistently large for the growth that occurs from the C-cut Al₂O₃ that demonstrated poor growth (Figure 13b).

![Raman spectra](image)

**Figure 13.** Raman spectra (633 nm) of CNT grown from abraded Fe (surgical scalpel SS-420) on A, C, M, and R single crystal cuts of Al₂O₃ substrates. (a) Spectra showing both the RBM region and D and G bands for CNTs grown on the different cuts, and (b) D/G ratios for all cuts at the three different laser excitation energies utilized.

Since the RMS surface roughness of all four surfaces are not substantially different, there may be a fundamental difference in the efficiency of a catalyst supported on a C-cut Al₂O₃ surface compared to the other faces, even though there is no obvious reason why the catalyst deposition process should be different on the various surfaces. Nonetheless, catalyst deposition for uniform and high-quality CNT growth can be achieved on smooth bulk Al₂O₃ surfaces, which further illuminates the capability and utility of the abrasion process for catalyst deposition.
Conclusions:

Mechanical abrasion of stainless steel (SS) surfaces is demonstrated as an effective technique for the deposition of catalyst to support growth of high density layers of carbon nanotubes (CNTs) in water-assisted catalytic chemical vapor deposition. In all cases of Fe-containing materials abraded on Al₂O₃ substrates, CNT growth is observed; the 400 series of SS appears to deposit catalyst most efficiently. We demonstrate that this simple abrasion technique enables both micro- and nano-scale accuracy in catalyst patterning as well as large area catalyst deposition for uniform, dense CNT growth. Raman spectroscopy characterization indicates high quality CNTs grown by this method, comparable to CNT growth from traditional ultra-thin evaporated catalyst layers. This technique provides an inexpensive and simple route for addition of catalyst for Fe-based surface growth of CNTs. The microscopic morphology of the film is important as well as the nucleation behavior of the framework of large particle (nano-dome) formation. Finally, growth results for abrasion catalyst deposition on single crystal cuts of Al₂O₃ suggest that A, M, and R faces are better than the C-cut for catalyst abrasion to support dense CNT.

Experimental Contribution:

My contributions to the experimental work in this chapter are all the data collected and characterizations provided.

References


Chapter 5

Selective Redox Chemistry with Metallic Single-Wall Carbon Nanotubes

Introduction:

This chapter studies a selective reduction-like electron transfer reactions of individualized SWCNT suspended in sodium dodecylbenzene sulfonate (SDBS) "decants"\(^1\textsuperscript{-3}\) with iron-based species in solution. Low-valent iron (iron metal and iron(II) hydroxide) species produced by three different routes were found to reduce small diameter semiconducting SWCNTs as well as all metallic SWCNTs. Centrifugation of the resulting SWCNT-iron complexes yielded precipitates enriched in metallic SWCNTs and supernatants consisting primarily of larger-diameter semiconducting SWCNTs. The selectivity of complexation was determined spectroscopically and the results are consistent with the range of oxidation potentials of metallic SWCNTs found by Okasaki, et al.\(^4\) as well as diameter selective oxidation of semiconducting SWCNTs by organic acceptors reported by O’Connell.\(^5\) These novel redox-selective SWCNT reactions have been practiced at the microgram scale. This simple process appears to be readily scaleable, and limited only by the availability of high quality SWCNT decants.

Simple metal complexation that leads to SWCNT separations in the liquid phase has advantages that are easily adaptable to large scale compared to other separation or enrichment techniques. Separation by length, type, and diameter techniques have been reported previously, including size-exclusion chromatography,\(^6,\)\(^7\) charge-exchange complex precipitation\(^8\) gel-electrophoresis,\(^9\) ion-exchange liquid chromatography,\(^10\) dispersion-centrifugation,\(^11\) density-gradient ultracentrifugation,\(^12\) dielectrophoresis,\(^13\textsuperscript{-18}\)
current-induced selective breakdown, covalent functionalization, selective adsorption, ion exchange chromatography, electrophoresis, and antenna chemistry. Electron transfer processes between various species and SWCNT resulting in either p- or n-doping have been extensively reported as well, in particular, FeCl₃ has been employed previously as p-type dopant for SWCNTs in the solid state and as an oxidizer for large diameter semiconducting SWCNT in solution.

Materials and Methods:

SWCNT for these experiments was HiPco (Rice University Carbon Nanotechnology Laboratory) batch number 145.1 and all decants were prepared using DI water at 18 MΩ from a Barnstead Nanopure reverse osmosis system (Dubuque, IA). Reagents employed were used without further treatment unless noted; these include iron(III) chloride 98.1%, iron(II) chloride 99.5%, iron granules 99.98% (1-2 mm) purchased from Alfa-Aesar. Iron powder (99%, 100 mesh) and sodium hydroxide (0.1N) were purchased from Fisher Scientific (Fair Lawn, NJ) and SDBS – technical grade was purchased from Sigma-Aldrich (St. Louis, MO). While some solutions were degassed with ultra high purity nitrogen gas (99.999%) from Matheson Tri-Gas for 60 min prior to reactions, no significant differences in the results were observed between those and non-degassed samples. Unless otherwise noted, reactions were performed in either Pyrex glassware or soda-lime scintillation vials without flame drying or any other treatment.

Decants were produced from raw SWCNTs and 1% SDBS dispersed in 200 mL of DI water using high shear mixing for 1 hour (Dremel Multipro Mod. 275, South Pasadena CA). The dispersion was sonicated using a cup horn sonicator (Cole Parmer...
CPX-600, Vernon Hills IL) for 10 min. After sonication, the sample was centrifuged (Sorvall 100SE Discovery ultracentrifuge with Surespin 630 swing-bucket rotor, Japan) at 129,000 G for 4 h.\textsuperscript{1}

Near IR fluorescence spectra were obtained with a Nanospectralizer system NS1 (Applied NanoFluorescence, LLC, Houston TX) fitted with quartz four-window cuvettes (Starna Cells, Inc.). The UV-visible spectra collected with the Nanospectralizer were compared with UV-visible spectra recorded using a Shimadzu UV-3101PC Model, using quartz cuvettes from Starna and no difference was observed in the range of analysis.

AFM Images were recorded with a NanoScope IIIa - Digital Instruments (Veeco Metrology Group, Santa Barbara CA) in tapping mode. Cantilevers were 1-10 Ohm-cm Phosphorus (n) doped Si (MPP-11100-140 from Veeco)

**Results and Discussion:**

During the course of prior research,\textsuperscript{15} we observed transient fluorescence quenching of small diameter (those with $E_{11}$ emission below about 1100 nm) semiconducting SWCNT suspended in SDBS when exposed to freshly cleaned surfaces of mild steel components. Fluorescence quenching of *large* diameter semiconducting SWCNT by oxidizing species is by now well known,\textsuperscript{3,5,26} but such an inverted quenching selectivity is unknown in the SWCNT redox literature, and has only been observed upon covalent functionalization of SWCNT decants using diazonium salts.\textsuperscript{20,31} Stainless steel surfaces generated no such effect, so we inferred that some corrosion induced iron species was responsible for this anomalous result and sought to identify it.
We thus systematically examined the effect of Fe$^{2+}$ and Fe$^{3+}$, as well as Fe metal as the source of ions, on the fluorescence of SWCNTs species suspended in SDBS decants. We found that Fe$^{2+}$ and Fe$^{3+}$ species, both supplied as the chlorides, generally suppress fluorescence of the SWCNT decants (Figure 1). However Fe$^{2+}$ solution quenches non-selectively (Figures 1a and 1b) while Fe$^{3+}$ selectively quenches the fluorescence of the larger diameter semiconducting nanotubes, specifically those with emissions at wavelengths greater than about 1050 nm (Figures 1c and 1d). The mechanism appears to be a selective quenching of the large semiconductor SWCNTs by an oxidative electron transfer reaction from the nanotube to Fe$^{3+}$, an inorganic version of the redox process previously demonstrated by O’Connell using organic charge transfer reagents. The range of fluorescence quenched is consistent with the known oxidation potential of Fe$^{3+}$ (eq 1).

$$\text{Fe}^{3+} + e^- = \text{Fe}^{2+} @ +0.771 \text{ V vs. NHE} \ (1)$$

Both the general fluorescence suppression and quenching by both Fe$^{3+}$ and Fe$^{2+}$ were reversible upon increasing the pH to 10 with sodium hydroxide. These results demonstrate that oxidation by the higher-valent Fe$^{2+}$ or Fe$^{3+}$ ions from chlorides cannot generate the originally observed selective quenching of fluorescence of small diameter semiconductor nanotubes.
Figure 1. NIFR at 785 nm excitation wavelength for Fe$^{2+}$ and Fe$^{3+}$ at different ratios (inset legend) of Fe salt atoms (0 in reference) to carbon atoms present in SWCNT/SDBS solution identified by colors. a) and b) correspond to plots after treatment with various concentrations of Fe$^{2+}$ on a common scale (as collected), and normalized, respectively; c) and d) correspond to plots after treatment with various concentrations of Fe$^{3+}$ on a common scale (as collected), and normalized, respectively.
We further examined potential SWCNT reductive processes by passing SWCNT/SDBS decants over a packed bed of freshly cleaned iron particles and powder and by generating reduced iron colloids in-situ. The first approach indeed produced a solution with diminished fluorescence of small semiconducting SWCNTs (Figure 2a). We also observed in the UV-Visible absorption spectra from these reactions significantly reduced peaks attributed to metallic SWCNTs (Figure 2b) suggesting that electron transfer from iron species to metallic and small diameter SWCNT occurred. As observed in Figure 2a, the fluorescence of the small diameter SWCNT did return after increasing the pH. From the absorption spectra, we estimate that more than 85% of the original metallic SWCNT absorption was depleted. The reduction processes generating these observations could be driven by either Fe\(^0\) (eq 2) or Fe\(^{2+}\)(OH)\(_2\) (eq 3).

\[
\text{Fe}^{2+} + e^- = \text{Fe}^0 @ -0.447V \text{ vs. NHE (2)}
\]

\[
\text{Fe}^{3+}(\text{OH})_3 + e^- = \text{Fe}^{2+}(\text{OH})_2 + \text{OH}^- @ -0.56V \text{ vs. NHE (3)}
\]

**Figure 2.** a) Fluorescence change of SWCNTs due to Fe reduction of SWCNTs/SDBS solution. The reference is the starting SWCNT/SDBS solution. A vial with 10 mL
SWCNTs/SDBS solution was packed with Fe (steel wool) and left for 12 h. (a) The sample collected (red line) had a pH ~7, the pH was increased to 11 (green line) by adding NaOH (0.1 N). b) UV-Vis absorption of SWCNTs in the supernatant before and after treating the SWCNT solution with Fe.

In parallel experiments, iron colloids were generated by adding FeCl₃ (~50 mg) into the SWCNT/SDBS decant (5 mL, 4 mg/L). This generated a dark flocculate that quickly precipitated. The supernatant was removed from this solution and added to another unreacted aliquot of SWCNT/SDBS decant with a SWCNT concentration of 4 mg/L and centrifuged. The resulting supernatant solution appeared to be enriched in large-diameter semiconducting SWCNT, as evidenced by reduced fluorescence for smaller tubes as well as decreased UV-Vis absorption in the metallic region between 500 and 600 nm, similar to the results from iron powders above. After increasing the pH of the solution to 7-8 with NaOH (0.1 N), the solution was further centrifuged at 129,000 G for 2 h and Raman spectra were obtained from the precipitated pellet using 514 nm excitation. The resulting spectra displayed a large increase in the G⁻ to G⁺ ratio (Figure 3a) as a result of significant increase of the asymmetric Breit-Wigner-Fano peak at 1500 cm⁻¹ thereby indicating a high degree of enrichment of the metallic SWCNTs in the pellet compared to the original solution. Further evidence is supplied by the Raman spectrum taken from the pellet at 633 nm excitation (Figure 3b) which shows that the radial breathing mode peaks below 230 cm⁻¹ had increased significantly, indicating that metallic SWCNT [(13,4), (9,9) and (12,6)] concentration had been enriched. Scheme 1 summarizes the selective SWCNT redox equations proposed based on our observations.
Scheme 1. Proposed selective redox equations of metallic (m) and semiconducting (s) SWCNTs.

\[
\begin{align*}
\text{Fe}^{2+} + \text{m-SWNT} + \text{s-SWNT} & \rightarrow \text{Fe}_x - \text{m-SWNT}^{\oplus} + \text{s-SWNT} \\
\text{Fe}^{3+} + \text{m-SWNT} + \text{s-SWNT} & \rightarrow \text{m-SWNT} + \text{Fe}_x - \text{s-SWNT}^{\oplus}
\end{align*}
\]

Figure 3. SWCNT/SDBS and Fe\(^{2+}\) solution reactions: a) 514 nm and b) 633 nm excitation wavelength Raman spectra on the precipitate compared to the SWCNT/SDBS reference solution (before treating with Fe\(^{2+}\)).

Further experiments using Fe\(^{2+}\) generated in an electrolytic cell at pH ~10 confirms these results. At pH 8 or higher, the Fe\(^{2+}/Fe^{3+}\) concentration ratio (as hydroxides) is greatly enhanced,\(^{32}\) creating a favorable condition for metallic SWCNT reduction by Fe\(^{2+}(OH)_2\), thereby avoiding oxidation of large diameter semiconductor SWCNTs. UV-visible absorbance spectra from the SWCNT decant solutions after electrolytic processing showed significant depletion of metallic peaks below 630 nm. In
addition, the fluorescence of large diameter semiconductors remained almost unchanged from the starting solution, indicating that only metallic and smaller semiconducting SWCNTs form iron complexes under these conditions. AFM images taken of these samples show that a fraction of the tubes are coated with agglomerated sizeable rounded particles on them (Figure 4a), while others are quite long and without any visible coating or particulate matter on their surfaces (Figure 4b). The height of these coated tubes are ~1.7 nm and above while the long clean tubes are typically ~0.8 nm. It is possible that the long, pristine tubes are the semiconductors responsible for NIR fluorescence, while the agglomerated tubes are the metallic complexes whose UV-Visible absorption was bleached.
Figure 4. Both tapping mode AFM images were obtained from SWCNTs that had been treated with electrolytically generated Fe$^{2+}$(OH)$_2$ and spin-coated from 1% SDBS solution onto a silicon surface. a) Fe coated SWCNTs, 1.74 nm and b) clean SWCNTs without any visible coating, 0.81 nm.
Figure 5. Fluorescence of SWCNTs using 785 nm excitation wavelength that illustrates a combination of effects that Fe at different oxidation states can generate. The black dotted line is the fluorescence of individual SWCNTs used as a reference, the blue line is the reduction process from reaction with Fe(OH)$_2$ and the purple line is the oxidized SWCNTs by Fe$^{3+}$.

A combination of reduction and oxidation of SWCNTs are shown in Figure 5. Fluorescence and intensities of small diameter SWCNTs disappear when treated with Fe(OH)$_2$ contrary to SWCNTs treated with Fe$^{3+}$ where the fluorescence of large diameter SWCNTs was quenched. This is a unique way of tuning and driving complexation and coating of SWCNTs by using a single metal with different oxidation states. In fact, this
might be relevant to generate reactions that depend on the SWCNT band-gap and diameter besides of the type.

**Metal coated CNT nanostructures:**

Additional experiments performed using electrochemically generated Fe\(^{2+}\) let us generate uniform and tapered coatings on SWCNTs. Typical experimental conditions require Fe and graphite sheets as electrodes and 3 to 4 Volts of DC potential. The initial current is typically \(\sim 10\) ma although it changes to 30 ma during the course of \(\sim 10\) hrs. The initial pH was set at 10.94 but it increased to 11.42 over the same period of time. Ideally we expect that Fe\(^{2+}\) will reduce the metallic SWCNTs and coat their surface uniformly while leaving the semiconductors uncoated. The AFM image in Figure 6 illustrates the full coating of SWCNTs which is supported by the height measurements. Tapered SWCNT structures are shown in Figure 7 with height measurements changing along the SWCNT. The thinnest part of the CNT is 0.7 nm which is in the range of uncoated Hipco while the thickest part is more than double the widest HipCo CNT diameter. Furthermore, the uncoated SWCNTs have more uniform height measurements and they are in the range of typical individual SWCNT, Figure 8.
Figure 6. Fully coated SWCNT with height measurements 2.57, 1.98 and 1.71 nm by AFM which is higher than any HipCo tubes used in our experiments (the units in the top figures are nm)
Figure 7. Partially coated tapered-SWCNT compared to the fully coated SWCNT, red measurement 2.92 nm. Height measurements on the tapered CNT are: 3.74 nm the thickest, 2.81 nm the middle part and 0.7 nm the thinnest part.
Figure 8. Thinner SWCNT with height measurements 1.36, 1.23 and 0.97 that fall in the typical height range of uncoated HipCo SWCNTs.

It is important to mention that uniformly coated and tapered SWCNTs might have interesting properties, especially if the tubes are coated with metals such as Fe that can be ferromagnetic, paramagnetic and diamagnetic if synthesized under proper conditions.
More studies and characterizations of the coaxial coating on SWCNTs are necessary and would probably reveal interesting physical properties.

**Redox Potentials of Metallic SWCNTs:**

The results, supported by UV-Vis, Raman and NIR fluorescence spectra, demonstrate an efficient route towards selective reaction with semiconducting and metallic SWCNTs using a simple redox process. Based on the data, the key step involves reduction of metallic SWCNTs by low-valent transition metal complexes. There are some literature reports where redox potential of metallic SWCNTs have already been determined theoretically\(^{33,34}\) and experimentally.\(^{4,33,35,36}\) Kim et al.\(^{23}\) also have determined that large diameter metallic SWCNTs are readily reduced while the small diameter are more resistant to reduction, however in his report the SWCNT reduction depends mostly on the diameter rather than type. Additionally, his studies were done on heavily acid doped SWCNTs where carboxylic acid groups on the SWCNT ends and surface are required for a successful dispersion in dimethyl formamide (DMF). Paolucci et al.\(^{36}\) have also determined the redox potential of SWCNT dispersed in organic solvents with assistance of alkali metals. These reports, while important and useful, may not be directly applicable in interpreting the present results, due to significant SWCNT modification by functionalization, doping and/or solvent effects. There are other reports where SWCNT complexes have shown reduction-like reaction, Doyle et al.\(^{31}\) and Duque et al.\(^{26}\) We assume that oxidation and reduction processes for semiconducting SWCNTs in solution are fundamentally the same as those established for inorganic semiconductors in electrolytes, based on photocatalysis research as reviewed, for example, by Nozik.\(^{37}\) Specifically, we expect that semiconducting SWCNTs accept electrons at their
conduction band minimum (CBM) and donate electrons from their valence band maximum (VBM), as indicated in Figure 5. Thus, we can locate the CBM of the small diameter semiconducting SWCNT that react with Fe$^{2+}$(OH)$_2$ in the range between -0.08 and -0.56 V vs. the normal hydrogen electrode (NHE). This is consistent with prior results based on spectroscopic bleaching of semiconducting SWCNT decants in SDS (sodium dodecylsulfate) reported by Strano$^3$ and O’Connell.$^5$ This conclusion is also consistent with the work of Okazaki,$^4$ who determined Fermi levels for both metallic and semiconducting SWCNTs in an elegant spectroelectrochemical study based on the variation of intensity of Raman scattering peaks from individual SWCNT radial breathing modes (RBMs) as a function of bias potential. Since RBM frequencies ($v_{rbm}$) are uniquely related$^{38}$ to nanotube diameter ($d_t$) by Eq 4,

$$v_{rbm} = \frac{A}{d_t} + B \quad (4)$$

(where $A = 223.5 \text{ cm}^{-1}$ and $B = 12.5 \text{ cm}^{-1}$), and the bandgap florescence wavelength ($\lambda_{11}$) of semiconducting SWNTs varies to first order inversely with diameter$^{39}$ where $\lambda_{11} = 1167d_t$ (both in nm), we can obtain simple relationships for the Fermi levels (and thus redox potentials) of SWNTs as a function of their fluorescence frequency and diameter. Combining Okazaki’s equations,$^4$ (Eqs 5 and 6):

$$V_{f(\text{met})} = 1.15 + 0.022 \cdot v_{rbm} \quad (5)$$

$$V_{f(\text{semi})} = 1.59 + 0.012 \cdot v_{rbm} \quad (6)$$
(V_{f(semi)}, V_{f(met)}) in V below vacuum; ν_{rbm} in cm⁻¹) with the above relationships, we obtain Eqs 7 and 8 for the electrochemical potentials of metallic (U_{met}) and semiconducting (U_{semi}) SWNTs in anionic decants as a function of fluorescence frequency or diameter (Eqs 7 and 8, respectively).

\begin{align*}
V_{f(met)} &= 1.15 + 0.022 \times (12.5 + 223.5 / d_t) \quad (7) \\
V_{f(semi)} &= 1.59 + 0.012 \times (12.5 + 223.5 \times 1167 / \lambda_{11}) \quad (8)
\end{align*}

**Figure 9.** Proposed reduction potential scheme for semiconductor SWCNTs related to their fluorescence wavelength and diameter under 785 nm excitation wavelength.
Fluorescence spectra are shown in the upper part of the diagram, where the black dotted line represents the SWCNTs reference, the blue solid line represents SWCNTs undergoing reduction, and the purple dashed line represents SWCNTs undergoing oxidation. The horizontal blue line (at -0.560 V on the right axis) indicates the redox potential of the reducing agent and the horizontal purple line (at 0.771 V on the right axis) corresponds to the redox potential of the oxidizing agent, shown with their corresponding formulae on the diagram. The black ($V_{f_{\text{met}}}$) metallics and red ($V_{f_{\text{semi}}}$) semiconductors solid curves are the Fermi levels (left axis) of the SWCNTs based on equations derived by Okasaki.\(^4\) VBM and CBM are the black dashed lines above and below the semiconductor Fermi level. The thick white arrows indicate the movement of electrons.

We show this graphically in Figure 9, where we take 0 V on the NHE electrochemical scale to correspond to a Fermi level 4.5 V below vacuum.\(^3\)\(^7\) The redox levels for key processes and resulting SWCNT fluorescence spectra are shown to illustrate the redox chemistry in this system. We note that the curves drawn for semiconducting SWCNTs are very similar to those reported by O'Connell, et al.\(^5\) in their study of SWCNT fluorescence quenching by organic acceptors. The curvature in our lines arises from the $1/d_t$ and $1/\lambda_{11}$ terms in eqs 7 and 8, respectively. The curve for metallic SWCNTs in particular is an extrapolation of a relationship generated from nanotubes with a diameter of about 1.5 nm while our HiPco SWCNT average is about 1.1 nm in diameter. Thus, the indicated potentials for small metallic SWCNTs much below 6 V vs. NHE are probably unrealistic, since oxidative reactions with water or surfactant would likely occur. However, this presentation of SWCNT redox levels demonstrates
that a reductive process must drive the selective reaction of low valent iron with metallic SWCNTs.

This model could be also give mechanistic insight into other metallic SWCNT-selective reactions previously reported in the literature.8, 20-22 For instance, preferential functionalization of metallic SWCNTs by diazonium species is by now well known.20, 21 Diazonium (cationic), diazo anhydride (neutral) and diazotate (anionic) species exist in equilibrium under the reaction conditions.20 From the redox perspective, metallic selectivity would be expected of the anionic diazotate, which is electron rich and should readily react with metallic SWCNTs that have a high oxidation potential in SDBS decants. Indeed, the diazo equilibrium is shifted strongly towards the anion under the alkaline conditions, supporting this redox view of the diazonium functionalization mechanism.40 Another preferential reaction that illustrates this fact is the Br\(^-\) ions complexation with SWCNTs.22 It has been shown that Br\(^-\) complexes selectively with metallic SWCNTs, which is what we would expect from a typical electron rich molecule according to our model. We can use this model to predict that reducing agents slightly weaker than Fe(OH)\(_2\) should interact exclusively with metallic SWCNT in anionic surfactant decants.

While the valence levels indicated in Figure 9 for semiconductors are supported by data from the NIRF quenching studies reported here and previously,5 the levels indicated for metallics should be considered approximate until further studies with well-characterized reactants can spectroscopically show differential effects for metallic SWCNTs of various diameters. The SWCNT redox potentials (both here and previously) were obtained in aqueous SDS or SDBS; assumptions that the indicated potentials
directly translate into neutral or cationic surfactants may not be valid and should be verified separately. It is noteworthy that Fermi levels determined via Raman for SWCNTs adsorbed on a gold surface translate well to redox levels for SWCNTs suspended in anionic surfactants, especially when it is considered that these lines were extrapolated from data obtained from laser-oven SWCNTs, which are about 50% larger in diameter than the HiPco SWCNTs used in the present study.

Conclusions:

In summary, both reduction and oxidation reactions of SWCNT/SDBS decants with aqueous transition metal complexes have been characterized using Raman, NIR fluorescence and UV-Visible absorbance spectroscopies. The Fe$^{3+}$ ion is shown to be a strong oxidizer that selectively quenches the fluorescence of large diameter semiconducting SWCNTs. Fe$^{2+}$ ions (from chlorides) tend to quench fluorescence of all semiconducting species without any diameter selectivity. SWCNT-selective reactions have been demonstrated with iron and it is inferred that the active species are iron hydroxides generated in-situ. An expanded SWCNT redox model has been developed that includes the oxidation potentials of metallic SWCNTs in solution. Based on this model, we conclude that the metal-selective reactions reported here arise from a reductive mechanism, and that previous reports of metal-selective SWCNT reactions in similar environments could also be explained by reductive processes. The metallic SWCNT-selective chemistry reported here is simple and appears to be a promising basis for physically separating metallic and semiconducting SWCNTs.
Experimental Contribution:

My contribution to the experimental work in this chapter are all the data collected and characterizations provided.

References:


Chapter 6

Selective Photochemical Functionalization of Surfactant-Dispersed Single Wall Carbon Nanotubes in Water

Introduction:

Current synthesis methods of CNT can not provide material of uniform diameter, chirality, or electronic type yet. Separated CNTs are needed for many important studies and technological applications. There are many selective reactions in the literature, predominantly chemical. Among non-chemical selective processes such as dielectrophoresis\(^1,2\) and photon irradiations\(^3,4\) have shown promising selectivities, although the scalability of these techniques is still under study. Selective photo-oxidation using high-power-density lasers\(^3\) has been reported where a specific wavelength enhances the resonance of selected SWCNTs, generating chiral-selective reactions. Laser photon-induced selective reaction of metallic SWCNTs with Triton X-100 has also been reported,\(^4\) light assisted oxidations with H\(_2\)O\(_2\) exhibit a dependence on the SWCNT diameter and band gap\(^5,6\) and photochemically generated singlet oxygen reacted selectively with metallic SWCNTs.\(^7\) In the solid phase, UV photons induce oxidation of multi-wall carbon nanotubes (MWCNTs) and SWCNTs.\(^8,9\) Longer UV wavelengths were used to crosslink SWCNTs, leading to improvements in mechanical strength and conductivity.\(^10,11\) Theoretical studies that support and explain photon-induced oxidation have been reported.\(^12\) Also, a recent publication has used a high power Xe lamp (500 W) to selectively destroy the metallic and small diameter SWCNTs in the solid phase.\(^13\)
This chapter studies and reports a selective and progressive covalent photo-hydroxylation of nearly all detectable semiconducting and eventually some small diameter metallic SWCNTs using 254 nm UV light. The resulting functionalized SWCNTs have increased oxygen content, as determined by X-ray photoelectron spectroscopy (XPS), apparently in the form of hydroxyl (-OH) moieties, and further determined by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. Our results show high selectivity for semiconducting SWCNTs and small diameter metallic tubes, with little or no functionalization of the large diameter metallic SWCNTs. This suggests that the pristine metallic and functionalized semiconducting SWCNTs could be physically separated in a simple manner. The reaction appears to be scalable.

**Experimental:**

Using a standard protocol reported in the literature, HiPco SWCNTs were dispersed in several surfactants: sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (SDBS), Triton X-400, Pluronic F-108 (BASF 30085465), or Na cholate. Typical UV experiments were performed using a pen-ray 4.4 mW low pressure Hg lamp from UVP (Upland, CA). The SWCNTs/surfactant solution was degassed in a 100 mL home-made glass photochemical reactor that had an inlet and outlet for the N₂ sweeping gas on top. The solution inside of the reactor was degassed with N₂ flow with stirring and heating at 80 °C for 60 min. After degassing the SWCNT/surfactant solution, fluorescence and absorption spectra were collected to ensure the quality of the solution and compare with later spectra of the treated solution. All the surfactants were purchased from Sigma-Aldrich and were used without further purification.
The degassing reactor, Scheme 1 (32 mm ID and 180 mm tall Pyrex glass), was equipped with a quartz test tube (10 mm ID) that protruded into the SWCNT solution. The 254 nm Hg lamp was placed inside the quartz finger in a coaxial-type configuration ensuring that the light-emitting part of the lamp was covered by the solution. The SWCNT/surfactant solution, typically 20 mg/L SWCNTs in 1% SDS was subjected to UV irradiation for various time periods. Samples were collected in quartz cuvettes during irradiation and the progress of the reaction was followed by near-infrared (NIR) fluorescence and visible (VIS) absorbance (Nanospectralyzer, model NS1, nanoFluorescence, Houston, TX, USA), and Raman spectroscopy (inVia microRaman Spectrometer, Renishaw, Gloucestershire, UK) in the liquid phase. ATR-FTIR (Nexus 870 FTIR, Thermo Nicolet, Fitchburg, WI, USA) analysis and XPS (Quantera, Physical Electronics, Chahassen, MN, USA) were used for additional characterization. pH measurements were taken with a digital pH/mV/Temperature Meter, model IQ150 equipped with a PH30-GS probe from IQ Scientific Instruments (Carlsbad, CA). pH meter calibration was performed periodically using Buffers at pH 4, 7 and 10 purchased also from same manufacturer. AFM images were taken with a Nanoscope IIIa (Veeco Instruments, Plainview, NY, USA).
Results and Discussion:

Photo-hydroxylation reactions were set up by first degassing the SWCNT/surfactant dispersion. In order to determine the consistency of the reaction in different surfactants, screening reactions were performed using all the surfactants above, however for reasons discussed later, only the results with SWCNT/SDS are reported here. The degassing method is similar to that reported by Dukovic et al.\textsuperscript{15} who detailed a simple method to desorb O\textsubscript{2}, CO\textsubscript{2} and endoperoxide from the solution and the surface of
SWCNTs. Solutions degassed in this manner remain fluorescent in acidic conditions (pH 3) demonstrating that the vast majority of the O₂ has been removed from the solution. Several years ago it was suggested that direct protonation of SWCNTs at low pH was the cause of fluorescence quenching and absorption bleaching.¹⁴,¹⁶ That assumption was confirmed and further detailed by Dukovic et. al., who found that O₂ is necessary for absorption bleaching and fluorescence quenching by H⁺.¹⁵

Degassing the SWCNT/surfactant solution increases its fluorescence intensity, as was observed by Dukovic et al.¹⁵ Even though the temperature used here for degassing is 18 °C less than that used by Dukovic, a similar fluorescence recovery was observed when these nanotube solutions were degassed at low pH. An acidified sample with almost no fluorescence at pH 3.2 fully recovers its original (pH 6.5) fluorescence intensity as the solution was heated to 80 °C for 60 min under nitrogen purge. The 80 °C temperature was determined by heating the SWCNT/SDS solution at different temperatures and registering the stability of the micelle by changes in SWCNT fluorescence. At temperatures higher than 80 °C the fluorescence intensity of the SWCNTs started decaying, possibly due to micelle disturbance and bundle formation.¹⁷ For a typical SWCNT/SDS decant, the fluorescence intensity and pH (8.5 - 9.5) after degassing were higher than those of the original near-neutral (pH 6.5) solution exposed to air.

**Selectivity Characterization:**

The selectivity of the photo-hydroxylation reactions was monitored in the solution phase by near IR fluorescence (Fig. 1a) and Raman spectroscopy (Fig. 1b). After 4 min of UV irradiation the fluorescence intensity of (8,3), (6,5), (7,5) and (10,2) semiconducting tubes was quenched almost completely while the fluorescence of larger diameter
SWCNTs remained, becoming more intense in some cases (Fig. 1a). Typically, it took almost 30 min of irradiation to quench all fluorescence of SWCNTs, as observed when excited at either 785 nm or 660 nm. The Raman spectra obtained from liquid samples at different irradiation times are strong evidence of covalent functionalization of the SWCNT surface. As observed in Fig. 1b, the radial breathing mode (RBM) intensities of semiconducting SWCNTs that resonate at 633 nm decreased as the reaction progressed with no effect on the bands <200 cm$^{-1}$. In order to avoid characterization and interpretation errors of the Raman spectra, all the Raman data were collected from samples in the liquid phase. Previous studies in our laboratories have advised about interpretation errors due to changes in morphology of the samples on analysis by Raman in the solid state.$^{18}$ Also it can be observed that the D-band increases with time, suggesting covalent bond formation on the surface of the affected tubes.$^{19}$ The D-band increase accompanied by ordered fluorescence decay, led by the small-diameter SWCNT, as the reaction progresses is strong evidence that selective photo-reaction has occurred. It has been demonstrated that covalent functionalization of the SWCNT surface destroys the electronic band structure.$^{19, 20}$ Therefore, those nanotubes that were functionalized will no longer be resonance enhanced.$^{21, 22}$ The fact that after 30 min of UV irradiation the RBM of the metallic SWCNTs has not changed while all the semiconductor SWCNTs were nearly gone is particularly notable.
Figure 1. Effect of 254 nm UV irradiation on SWCNTs solution at different time intervals: a) Fluorescence at 785 nm excitation wavelength during the 15 min UV irradiation. All fluorescence was quenched after 30 min irradiation (not shown). b) 633 nm Raman spectra on liquid samples collected during the irradiation process.

The reaction bleaches the E\textsubscript{11} semiconductor (900 to 1600 nm) and E\textsubscript{22} semiconductor (550 to 900 nm) electronic transitions of the SWCNTs in the absorption spectra after different periods of UV irradiation (Fig. 2a). As expected, covalent bond formation on the SWCNT surface broadens the van-Hove singularities in general (Fig. 2a). The spectroscopic evidence collected suggests that the photoreaction is driven by SWCNT absorption of UV light; if this assumption is correct, the fluorescence quenching should be independent of the surfactants used, the pH of the reaction mixture as well as the temperature. In fact, that is what has been observed. The UV irradiation reactions on SWCNTs dispersed in different ionic and nonionic surfactants (SDS, Na Cholate, Pluronic F-108 and Triton X-400) proceeded in a similar fashion. However, even after 5 h of irradiation, no reaction was detected by spectroscopic means in SDBS. This is evidently due to strong absorption by SDBS at wavelengths below 275 nm, while the
other studied surfactants are transparent at 254 nm (Fig. 2b). SDS is clearly the surfactant of choice due to its minimal absorption in the region of interest and the efficacy with which it forms SWCNT decants.

**Figure 2.** Absorption spectra of: a) SWCNT/SDS after different periods of UV irradiation that shows the progress of the photo-hydroxylation versus time and b) UV-absorbance of different surfactants that shows SDBS as the only surfactant that strongly absorbs 254 nm UV light.

**Functional Group Identification:**

XPS (Figure 3) and ATR-FTIR (Figure 4) results show that the oxygen content of the photo-functionalized SWCNTs increases substantially, and that this oxygen is present in the form of hydroxyl groups. The oxygen content increase on the SWCNT surface is striking because the solution is low in O₂ before irradiation and the only sources of additional oxygen are SDS and H₂O. The XPS spectra were collected from samples before and after irradiation and were prepared in a similar manner: spin-coating then drying the samples in the oven for 60 min prior to XPS analysis in order to remove H₂O from the spin-coated sample. Four separate samples from different reactions show higher
oxygen content after UV irradiation, with increases from 20 to 40%. The IR spectrum in Figure 4 shows a significant broadening of the peak at 3400 cm⁻¹ which is indicative of OH content, and three peaks at 1153, 1131 and 1115 cm⁻¹ in the region where C-O stretches are expected for a tertiary alcohol.

Based on the abundance of oxygen on the functionalized material, it is likely that H₂O is directly involved in the reaction. Note that the energy provided by 254 nm photons, 112.3 kcal/mol, is barely sufficient to homolytically dissociate the O-H bonds of H₂O molecules (110 kcal/mol²). Since water is essentially transparent at this wavelength, the SWCNTs themselves are the only good absorbers available. It is interesting to note that crashing SWCNTs out of UV irradiated solutions requires twice as much acetone as non-irradiated solutions. Furthermore, irradiation in D₂O requires more time to achieve similar fluorescence quenching than irradiations in H₂O. These observations are consistent with the idea that the reaction involves water and results in hydroxylated SWCNTs.

Figure 3. XPS spectra of SWCNT/SDS: a) Increase in the O₂ content after UV irradiation, b) Atomic concentration of C, O, S and Na before and after UV irradiation.
Figure 4. ATR-FTIR spectroscopy of SWCNT/SDS before and after UV irradiation: a) full spectrum and b) IR fingerprint region.

The overall process is termed a photo-hydroxylation because the SWCNT photolysis product is hydroxylated. In this type- and diameter-selective reaction, the term ‘photooxidation’ would imply that the reaction step that drives selectivity extracts electrons from the SWCNT. Oxidative processes involving organic acceptors at high oxidation potentials have been convincingly shown to react preferentially with the large diameter (or small band gap) SWCNTs first, then progressively attack the smaller diameter SWCNTs. Studies in our laboratory show similar trends for inorganic oxidizing species, and demonstrate that reducing agents preferentially attack small diameter (large bandgap) semiconducting SWCNT. This results in an inverted order of fluorescence quenching compared to oxidizers. It is quite clear from Fig. 1a that the small diameter tubes are quenched first, indicating that the key selective reaction behaves like a reductive process. However the initial step of this reaction is the production of a SWCNT excited state, and electron transfer from the SWCNT may be a reaction of a highly excited state with a very short lifetime that is dependent on the band gap of the.
particular SWCNT. Until the reaction mechanism involved in this reaction is determined, we will describe the process as a photo-hydroxylation so as not to connote any particular mechanism.

**Nanostructure Formation upon Irradiation:**

AFM images, taken on spin coated (3.5 K rpm) SWCNT samples on mica before (Fig. 5a) and after (Figs. 5b-5d) UV irradiation show significant differences. Samples after UV irradiation exhibit unusual aggregations completely different from the side-by-side aggregation normally seen in SWCNT bundling. Fig. 5b is a typical image collected after UV irradiation where aggregations of tens of tubes have shapes that are distinct from the common side-by-side bundling. Other aggregations, Figs. 5c and 5d, that are more drastically different from the common ropes were also observed and may have come, in part, from the spinning solvent-based evaporation forces or they were ropes before UV irradiation and as a result of the photoreaction they have accumulated more tubes on their surface. These images are a representative summary of hundreds collected during these studies. Overall, this effect is consistent with photo-hydroxylation of the SWCNT. SDS surfactant molecules would be unlikely to form a micelle monolayer on the polar functionalized SWCNT surface. Indeed, a densely hydroxylated surface would be expected to enable aggregation, as observed, via inter-tube hydrogen bonding.
Figure 5. AFM images of SWCNTs spin coated on mica: a) a typical image before UV irradiation, b) a typical image after UV irradiation, c) and d) additional images observed after UV irradiation.
Further Diameter Selectivities:

Longer periods of irradiation (up to 100 min) were performed to further test and confirm the selectivity of the technique. As is observed in Fig. 6, normalized Raman spectra of the liquid phase from samples after 100 min irradiation provide important highlights. The 514 nm Raman spectra (Fig. 6a) show mostly metallic SWCNTs. In fact, it is observed that the RBMs of small diameter metallic ones also disappear, however the D/G\(^+\) band ratio is much smaller compared to ratios observed at 633 nm. Additionally, 633 nm Raman spectra (Fig. 6b) support the statement that after 100 min the RBMs of metallic SWCNTs remain (only RBM peak observed at 633 nm), even when all the Raman features observed at 785 nm (Fig. 6c) were gone. More surprisingly, the semiconductor SWCNTs that resonate at 785 nm lose all their Raman features after 100 min UV irradiation. The D/G\(^+\) ratios calculated from Fig. 6 spectra (after baseline correction) are shown in Table 1. The results demonstrate that large diameter metallic SWCNTs have not reacted since they still resonate at 633 nm, and are therefore nearly unreactive in this overall photo-hydroxylation process.
Figure 6. Raman spectra of SWCNT/SDS solutions before and after 30 and 100 min UV irradiations. a) 514 nm excitation shows relatively lower D to G ratios compared to b) 633 nm excitation. c) Excitation at 785 nm preferentially shows semiconductor SWCNTs. The spectra after 100 min of irradiation shows no RBMs nor G+ peaks, indicating that all the semiconductor SWCNTs were heavily functionalized.

Table 1: D/G+ ratios after 30 and 100 min UV Irradiation

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<th>514 nm</th>
<th>633 nm</th>
<th>785 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>2%</td>
<td>3%</td>
<td>NA</td>
</tr>
<tr>
<td>30 min</td>
<td>31%</td>
<td>63%</td>
<td>80%</td>
</tr>
<tr>
<td>100 min</td>
<td>46%</td>
<td>100%</td>
<td>NA</td>
</tr>
</tbody>
</table>

Reaction Mechanism Insights:

Prior work with 254 nm UV irradiation of SWCNTs was reported to have caused photodesorption of O₂ from the SWCNT surface in the liquid\textsuperscript{16} and solid/gas phases\textsuperscript{26}.
while Parekh et al. used this wavelength to effect SWCNT photo-hydroxylation in the solid phase. The discrepancy between whether the SWCNTs will be degassed or photo-oxidized may arise from the different photon irradiance, also called intensities and fluence, of the UV sources used in each case. It is likely that lower total photon flux leads only to photodesorption of O₂ from the SWCNT surface, while higher intensities cause the photo-hydroxylation reported here. The apparatus used in our experiments ensures that most of the emitted photons from the Hg lamp impinge the SWCNT solution. The theoretical report by Grujicic et al. serves as the basis for an understanding of O₂ adsorption on the SWCNT surface. The calculations indicate that 7-5-5-7 and Stone-Wales defects on the SWCNTs have a higher likelihood of adsorption than the defect-free surface. However Grujicic’s results were based on an O₂ environment in contrast to the present experiments where most of the oxygen was removed from solution. Surprisingly, Grujicic et al. found that there is no significant difference in the interaction of O₂ with different types and chiralities of SWCNTs. His calculations were supported by experimental evidence reported by Savage et al.

Although the mechanism of this photo-reaction is not yet understood, there is no doubt about radical generation during the irradiation process. This assumption is supported by experimental evidence when irradiations were performed in air- or oxygen-saturated rather than degassed solutions. O₂ is a well-known radical scavenger, so in the presence of O₂ from air, the reaction rate should be suppressed, as it nearly completely was, by capture or scavenging of radical reactive intermediates. It was found that CO₂ saturated solutions proceeded at essentially the same rate as degassed solutions. Additional supporting evidence of radical generation is provided by ESR data of
SWCNT/SDS solutions (Figure 7) where ESR was able to detect an increase of the radical content with the irradiation times. In fact, an initial signal that could hardly be discerned had increased almost 200 times for a sample irradiated for 45 min.

![ESR spectra of SWCNT/SDS solutions under UV irradiation](image)

**Figure 7.** ESR spectra of SWCNT/SDS solutions under UV irradiation. Radical generation evidence at different UV irradiation times.

A potential candidate for the reactive intermediate generated upon UV irradiation is the hydroxyl radical, which has been implicated in some previous reports. It was reported, for instance, that SWCNT oxidation in H$_2$O$_2$ was enhanced using 488 and 515 nm laser light, leading to selective elimination (burn out) of specific SWCNTs to generate CO and CO$_2$. A decrease of certain RBM peaks was provided as evidence for the selective reaction, although H$_2$O$_2$ dissociation at 488 and 515 nm is unlikely because H$_2$O$_2$ does not absorb light at either of these wavelengths. The same authors in a later work proposed light assisted oxidation of SWCNTs in H$_2$O$_2$ and it was suggested that weak fluorescence emission of SWCNTs at the near-IR wavelength where H$_2$O$_2$ absorbs
is the origin of H$_2$O$_2$ dissociation. The dissociation of H$_2$O$_2$ generates OH radicals that oxidize the SWCNT surface. The authors did not mention the possibility of SWCNT excited states being formed as a result of the irradiation wavelength employed in any of these mechanisms. We also performed a comparison experiment, irradiating SWCNTs in H$_2$O$_2$ at 254 nm. Upon initial addition of H$_2$O$_2$, SWCNT fluorescence is partially quenched, with preferential suppression of large-diameter SWCNT emission. UV irradiation of H$_2$O$_2$/SWCNT/SDS solutions (1.5%, 7.5% and 15% H$_2$O$_2$ in volume) demonstrated that the reaction proceeds in a manner similar to the reaction without H$_2$O$_2$, although the quenching appeared to be slower as the H$_2$O$_2$ concentration increased. After 30 min of UV irradiation, the fluorescence of many SWCNTs was still intense. When H$_2$O$_2$ was degassed prior to addition to the degassed SWCNT/SDS solution, higher fluorescence quenching was observed for the same periods of UV irradiation.

Overall, these results indicate that the reaction is initiated by the SWCNT photon absorption, leading to the generation of an excited state which thereafter activates small molecules, likely water, in their close surroundings. Semiconducting SWCNTs would be good candidates for the specific sensitizers initiating the process. While a broad range of excited state lifetimes are reported in the literature, metallic tubes are consistently found to have two or three orders of magnitude shorter lifetimes (femtosecond range) than semiconducting species (picosecond range).$^{30-33}$ This physical property gives the semiconducting tubes enough time to react with the molecules in their surroundings and produce selective reactions, while metallic SWCNT should be essentially unreactive toward photo-hydroxylation. Reactive intermediate molecules generated in the vicinity of semiconducting SWCNTs would presumably have a finite lifetime of their own, and
would have to diffuse to metallic SWCNTs to react. To our knowledge, this is the first non-contaminating selective reaction in the liquid phase that uses an intrinsic property of the tubes and can be scalable; current experiments use 100 mL solutions. Current efforts are focused on physical separation of the functionalized semiconducting tubes to establish a reliable separation method, as well as efforts to elucidate the reaction mechanism.

**Kinetics of the reaction:**

![Graphs showing fluorescence decay of SWCNTs/SDS solution under UV irradiation as a function of time.](image)

**Figure 8.** Fluorescence decay of SWCNTs/SDS solution under UV irradiation as a function of time. a) Smallest diameter SWCNT (0.757 nm) emission observed at 785 nm excitation. Its decay shows a single, obvious-minimum at ~17 min although there appears to be a small jump around 5 min. A slightly larger SWCNT (0.884 nm) (b) shows two minima and the second minimum appears to be at the same time as the small diameter 0.757 nm.
Studies of the photoreaction of the CNTs as a function of time reveal two different minima in fluorescence quenching. The minimum at ~6 min is almost not visible for the smallest diameter SWCNT, however, this minimum becomes increasingly obvious as the diameter increase. In fact, the width of the minima at ~6 min increases and takes the shape of a valley for the largest diameter SWCNT. Also, the fluorescence decay seems linear until the first minimum is reached. Afterwards, nearly all of the SWCNTs regain fluorescence as the time of irradiation increases. We need to mention that additional fluorescent species that emit a broad fluorescence at ~1040 nm are generated as the irradiation time increases. In fact, this new fluorescence emission becomes dominant after 30 min of UV irradiation. This new emission also increases with time; therefore, the initial emission of this broad fluorescence might contribute to the fluorescence recovery of the SWCNTs after they have reached the first minimum. This needs to be addressed with smaller diameter nanotubes, perhaps from single chirality solutions of SWCNTs.

**Intensity Measurements, Actinometer:**

During our experiments, we have observed that the UV photon flux emitted from different sources might determine whether SWCNT photochemistry is produced or not. Different UV sources utilized in our experiments, a low pressure Hg lamp (from UVP, used for all of experiments provided in this chapter), a high pressure (HP) Hg lamp (from Newport) and other low pressure Hg lamps including a Rayonet photoreactor (from Southern New England UV Company), produce different results. The photoreaction is very efficient with a low pressure (4 mW) Hg lamp located at less than ~2 mm from the CNT solution; however no reaction was observed with a 350 W lamp located 60 cm away
from the sample, nor irradiation in the Rayonet, which had the lamp ~10 cm away from
the sample. We have taken measurements using power meters including a bolometer and
photodiode based power-meters and we have found different irradiance intensity
measurements in each case, mainly due to the geometry of irradiated surfaces. In order to
avoid any ambiguity in the UV irradiance intensities, we have used chemical actinometer
measurements. Potassium ferrioxalate (K₃Fe(C₂O₄)₃), Scheme 2, was synthesized for this
purpose which is a widely used complex for UV intensity measurements.³⁴ The
potassium ferrioxalate complex has three bidentate oxalate ions that are bound to Fe at
the center. Upon 254 nm UV light absorption, ferric iron (Fe³⁺) is reduced to ferrous iron
(Fe²⁺), however Fe²⁺ does not absorbs UV light (equation 1). Addition of 1,10-
phenanthroline makes a complex with Fe²⁺ which has a unique absorbance at the 510 nm
wavelength and provides good measurement accuracy.

Scheme 2. Potassium ferrioxalate (K₃Fe(C₂O₄)₃); the chemical actinometer reactant.

The following equation has been suggested as a mechanism for the (K₃Fe(C₂O₄)₃)
reaction under UV light irradiation.

\[
2[\text{Fe(C}_2\text{O}_4)]^{3-} \rightarrow 2\text{Fe(C}_2\text{O}_4) + 3[\text{C}_2\text{O}_4]^2+ + 2\text{CO}_2
\]

\text{eq. 1}
These experiments were performed in a dark environment under only a dim photographic light to avoid any errors due to ambient light. The technique is very sensitive to UV light; 30 sec of irradiation was long enough to observe significant reduction of Fe$^{3+}$. In order to determine a calibration curve (Figure 9a), FeSO$_4$ was dissolved in H$_2$SO$_4$ and upon addition of 1,10-phenanthroline, absorption spectra were collected at different concentrations. From this calibration curve we determine the extinction coefficient of Fe$^{2+}$-phenanthroline complex (Figure 9b). Table 2 and Figure 10 summarize the intensity ratios for each UV source utilized for our experiments. The fact that the pen lamp provides 241 times more photons than the 350 W HP Hg lamp explains why the reactions do not proceed forward using the HP Hg Lamp. In fact, these results demonstrate that UV photon collection is the determining factor and it mainly depends on the geometry of the reactor and distance between the lamp and the solution.

Figure 9. a) Calibration curve of Fe$^{2+}$-1,10-phenanthroline complex. b) Visible absorbance of the complex Fe$^{2+}$-1,10-phenanthroline formed as a result of the (K$_3$Fe(C$_2$O$_4$)$_3$) decomposition using different UV irradiation sources (30 s irradiation time).
As can be observed in Table 2, the ratio of photon collection efficiency of our setup, Scheme 1, is 241 times greater than a 350 W HP Hg lamp. Absorbance at 510 nm measures the degree of Fe\(^{3+}\) to Fe\(^{2+}\) conversion. V1 is the volume of irradiated sample for each UV source. Io measures the experimentally calculated photon flux for each UV source. The last column is a simple ratio between photon flux of our PL equipped photoreactor compared to the other UV sources.

**Table 2: Calculation of Lamp power measurements**

<table>
<thead>
<tr>
<th>UV source</th>
<th>Absorption @ V1 (mL) 510 nm</th>
<th>Io (q/s) (flux)</th>
<th>ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rayonet</td>
<td>2.07695</td>
<td>2.16E+16</td>
<td>13.298</td>
</tr>
<tr>
<td>350W HP Hg</td>
<td>0.11386</td>
<td>1.19E+15</td>
<td>242.568</td>
</tr>
<tr>
<td>PL - Cuvette</td>
<td>2.04584</td>
<td>2.13E+16</td>
<td>13.500</td>
</tr>
<tr>
<td>PL - Ph Reactor</td>
<td>1.29971</td>
<td>2.87E+17</td>
<td>1.000</td>
</tr>
</tbody>
</table>

**Figure 10.** Graphical bar that illustrates the flux intensities of the UV sources utilized in our experiments.
Conclusions:

Evidence has been provided for a photochemical reaction initiated and dependent on the SWCNT absorption, as well as the selectivity of the reaction towards semiconducting and small diameter SWCNTs. UV irradiation of SWCNTs individually dispersed in surfactants leads to diameter and type-selective photo-hydroxylation of the nanotubes. Photo-hydroxylation of first semiconductor and then small diameter metallic SWCNTs was confirmed after 254 nm UV irradiation in acidic, neutral and basic aqueous solutions at ambient and elevated temperatures. The selectivity of the reaction is supported by Raman and fluorescence spectroscopy as well as absorbance in the liquid phase. The increased oxygen content of the SWCNTs after UV irradiation, as detected by X-ray photoelectron spectroscopy, suggests that SWCNTs were oxidized by reaction with water. Attenuated total reflectance Fourier transform infrared analysis provides evidence of hydroxyl functional groups on their surface. This photochemical reaction is impeded by molecular oxygen and appears to involve a reactive intermediate generated in the vicinity of semiconducting SWCNTs. To our knowledge, this is the first non-contaminating selective reaction in the liquid phase that uses an intrinsic property of the tubes.

Experimental Contribution:

My contributions to the experimental work in this chapter are all the data collected and characterizations provided.
References:


