RICE UNIVERSITY

SWNTs in the Aqueous Phase

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

Doctor of Philosophy

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HOUSTON, TEXAS

December, 2002
ABSTRACT

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Fullerene nanotubes were suspended as individuals in aqueous sodium dodecylsulfate (SDS) by sonication and ultra centrifugation. Ultra centrifugation was found to remove bundles of nanotubes and metal catalyst particles, since they have a density greater than water. The supernatant contained individual fullerene nanotubes encapsulated by a SDS micelle. SWNTs suspended in an SDS micelle could be further stabilized by associating the nanotube with a polymer and removing the surfactant. Polymer-wrapped SWNTs could be used in various separation techniques. The absorption spectrum (190nm-1800nm) of these individual tubes was much better resolved when compared to all previous methods. These earlier methods of suspending nanotubes contained large numbers of bundles. The individualized semiconducting nanotubes were found to have structured fluorescence in the near-infrared. This fluorescence was not previously observed, because of quenching by metallic tubes in bundles.
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1. General properties of carbon

1.1. The element carbon

Carbon is the most versatile element in the periodic table, owing to the type, strength, and number of bonds it can form with many different elements. The diversity of bonds and their corresponding geometries enable the existence of structural isomers, geometric isomers and enantiomers found in large complex and diverse molecules and are the reason for the endless diversity of organic molecules.

Carbon, the first element in column IV, is considered a nonmetal while the next two elements, silicon (Si) and germanium (Ge), are metalloids and the last two elements, tin (Sn) and lead (Pb), are metals. Because these elements are in the same group as carbon, they should share similar properties. However, elements in column IV range from nonmetals to metalloids to metals, and as we shall see, carbon can act as all three types confirming carbon as the most versatile element.

Carbon’s properties are a direct consequence of the arrangement of electrons around the atom’s nucleus. The electrons of carbon occupy the 1s (2 electrons), 2s (2 electrons) and the 2p (2 electrons) atomic orbitals. Since, the 2p atomic orbital can hold up to six electrons carbon can make four bonds. However, valence electrons, those involved in chemical bonding, occupy both the 2s and 2p orbitals.

Covalent bonds are formed by promotion of one 2s electron to a 2p orbital and the orbitals hybridize in one of three ways. The first type of hybridization is when the 2s electron pairs with one of the 2p electrons, forming two sp^1 orbitals that are separated by an angle of 180° and are linear. sp^2 orbitals are the second type of hybridization. Hybridization of the 2s orbital with two of the 2p orbitals forms three sp^2 orbitals that are
separated by 120° and are trigonal planar. In the third hybridization type, sp³, one 2s electron hybridizes with the three 2p orbitals separated by 109.5° and yields the characteristically tetrahedral sp³ bond. In all three cases, the energy required to hybridize the atomic orbitals is given by the free energy of forming chemical bonds with other atoms.

Hybridization of the carbon atom orbitals determine the type and geometry of the bonds formed with other atoms. There are two types of bonds carbon can form: a sigma (σ) bond and a pi (π) bond. The sigma bond has a cylindrical symmetry made up of two electrons from overlapping orbitals of two atoms. The pi bond is made up of two electrons in dumbbell shaped orbitals that overlap. The resulting bonds of a sp¹ hybridized carbon atom are 2 σ bonds and 2 π bonds. Sp² hybridized carbon forms 3 σ bonds and 1 π bond. The sp³ hybridized carbon atom forms 4 σ bonds. These hybridized bonds and their associated geometry determine the properties of carbon allotropes.

1.2. Allotropes of carbon

Carbon in the solid phase can exist in three allotropic forms: graphite, diamond, and buckminsterfullerene (fig. 1). Diamond is a crystal made up of sp³ hybridized sigma bonded carbon atoms. In diamond, each carbon is bonded to four other carbon atoms in a tetrahedral arrangement. The crystalline network gives diamond its hardness (it is the hardest substance known) and excellent heat conduction properties (about 5 times better than copper) (7). The sp³ hybridized bonds account for its electrically insulating property and optical transparency. Graphite on the other hand, is soft, slippery, opaque and electrically conductive, due to the difference in the geometry of the chemical bonds. Graphite is made up of planar sheets of sp² hybridized carbon atoms bonded together in a
hexagonal network. In contrast to diamond, each carbon atom in a graphite sheet is bonded to only 3 other carbon atoms. Electrons can move freely from an unhybridized p orbital of one carbon atom to another in graphite forming an endless delocalized π bond network that gives rise to graphite's electrical conductivity. Buckminsterfullerenes, or fullerenes, are the third allotrope of carbon and consist of a family of molecules of varying shape and size. The fullerenes are spheroidal to cylindrical molecules with all of the carbons sp² hybridized. The tubular form of the fullerenes, nanotubes, will be the subject of this dissertation and a detailed description of their properties will be given in the next section.

Figure 1. The three allotropes of carbon (2).
2. Fullerenes to nanotubes (a brief history)

Fullerenes were discovered in 1985 by Rick Smalley and coworkers (3). C_{60} was the first fullerene to be discovered. C_{60}, or "bucky ball" is a soccer ball (icosahedral) shaped molecule with sixty carbon atoms bonded together in pentagons and hexagons. The carbon atoms are sp\(^2\) hybridized, but in contrast to graphite are not planar. The geometry of C_{60} strains the bonds of the sp\(^2\) hybridized carbon atoms, creating new properties for C_{60}. Graphite is a semimetal, whereas C_{60} is a semiconductor. In 1990, at a carbon-carbon composites workshop, Rick Smalley proposed the existence of a tubular fullerene (4). He envisioned a bucky tube that could be made by elongating a C_{60} molecule. Experimental evidence of the existence of carbon nanotubes came in 1991 when S. Iijima imaged multiwalled carbon nanotubes using a transmission electron microscope (5) and in 1993 S. Iijima discovered single walled nanotubes (6).
3. Carbon nanotubes

There are two general classifications of carbon nanotubes: multiwalled and single walled. Multiwalled nanotubes (MWNTs) are concentric layers of tubes ranging from a double walled nanotube to tens of walled nanotubes. Each MWNT is a random mixture of conducting and semiconducting concentric tubes. Each MWNT has the possibility of being unique in a sample, which makes bulk sample characterization a difficult task. Single walled carbon nanotubes (SWNTs) are the subject of this research and are described in detail below.

The structure of a carbon nanotube is similar to that of graphite and consists of a planar hexagonal lattice of carbon atoms rolled into a tube and capped on the ends with hemispherical fullerenes. Nanotubes are on the order of a nanometer in diameter and a typical nanotube’s length can be only a few nanometers up to a few microns, although theoretically they could be endless.

3.1. General properties of single walled carbon nanotubes

The geometric arrangement of atoms in carbon nanotube determines its properties, unique only to this third allotrope of carbon. The carbon atoms in a nanotube are sp² hybridized, but like C₆₀, the bonds are strained. The strain placed on the bonds is a direct consequence of the nanotube’s curvature. The curvature and hence bond strain is determined by the diameter of the tube. Typical single walled carbon nanotube (SWNT) diameters range from 0.7 nm to 1.8 nm. The diameter affects the electronic properties as well as the chemical reactivity of the nanotube. Smaller diameter tubes are more chemically reactive than larger diameter tubes. In addition to the strained bonds, the
orientation of the hexagons with respect to the tubes length can vary giving rise to new and unique properties.

3.2. Electronic properties of SWNTs

Before the electronic properties of a SWNT can be understood a basic description of electrical conduction must be given. For a solid material, conduction takes the form of an electric current (i.e. the flow of electric charge). The ability of a substance to conduct electricity can be classified into four categories: insulator, semiconductor, conductor/metal, and superconductor. An insulator cannot conduct electricity and a semiconductor can conduct electricity only when a certain voltage or energy level is reached and will carry more current with increasing temperature. A metal will conduct electricity at room temperature, but will carry less current with increasing temperature. Superconductors conduct electricity with no resistance below a certain critical temperature. Conduction properties of a material result from its number and arrangement of molecular orbitals.

SWNTs act as metals, semiconductors, or superconductors and this behavior can be described by molecular orbital theory (MOT). The hybridization of atomic orbitals was useful when describing the allotropes of carbon, but the molecule as a whole must be considered to describe its unique chemical and physical properties. This provides the basis for the description of metals and other types of solids. The most important point to consider from MOT is that for N atomic orbitals in a molecule, there will be N molecular orbitals (MOs). Two atoms will yield two molecular orbitals: one bonding and one antibonding. These orbitals will be separated by a specific energy value.
The ability of an electron to jump from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) requires a specific amount of energy. The system is said to be quantized when there are only discrete energies allowed for a given transition. One of the implications, for spectroscopy, of these quantized energy states is that only certain photon energies or frequencies are allowed to induce electrons to jump from lower energy levels to higher energy levels. The other implication, if the system is luminescent, is that only certain photon energies will be emitted when electrons fall from higher energy states to lower energy states, leading to analytical methods called absorption spectroscopy and emission spectroscopy. For carbon nanotubes, these two types of spectrometry are valuable characterization tools. Spectroscopy of electronic and vibrational transitions will be discussed in section 4.4.4.

To understand the role of molecular orbitals in determining the behavior of molecules such as carbon nanotubes or a bulk solid we must return to MOT and transition to solid state physics terminology. The separation between the available energy levels decreases with increasing molecular size. In the case of a nanotube, with a large number of atoms, the energy spacing between the molecular orbitals decreases to a continuum forming a band, due to all of the bonding and antibonding orbitals being in the same energy ranges (i.e. overlap). The valence band is made up of occupied molecular (bonding) orbitals which are analogous to the HOMO of the small molecule. The conduction band contains the unoccupied molecular (antibonding) orbitals that are analogous to the LUMO of a small molecule. The difference in energy between the valence band and the conduction band is called a bandgap ($E_g$). The energy level between the valence and conduction bands is the Fermi level ($E_F$) and for metals is defined as the
top of the available electron energy levels at absolute zero. The position of the Fermi level with the relation to the conduction band and the density of states (DOS) are factors in determining electrical properties.

In solid state terminology, a molecular orbital is called a state and the density of MOs in a band is called the density of states. The DOS for nanotube has singularities (spikes in the population) at certain energies for a given tube. The reason for this is that the electronic energy levels are packed more closely together at some energies than others as a result from overlap of molecular orbitals. The spikes in the DOS are called van Hove singularities and are analogous to the discrete available energies for an atom or small molecule. An electronic transition in an atom or small molecule is a jump from the HOMO to the LUMO. In a SWNT, an electronic transition is called a van Hove transition and occurs between the electrons occupying the valence van Hoves to the corresponding van Hove in the conduction band. Both semiconducting and metallic nanotubes have van Hoves, and these transitions can be probed spectroscopically.

Carbon nanotubes can act as metals or semiconductors depending on the diameter and the chirality of the tube as predicted by theory (7-10) and confirmed by experimental work (11, 12). For a semiconductor, the Fermi level is represented by the equation \( E_F = E_g / 2 \). Semiconducting nanotubes have a bandgap with zero DOS at \( E_F \) while metallic nanotubes have no bandgap (Figures 2a and 2b respectively). A metallic tube has some electrons occupying the energy levels above the Fermi level (i.e. in the conduction band) at room temperature.
Figure 2. Electronic DOS for two zigzag nanotubes a) DOS for a semiconducting SWNT, note the gap in the DOS near the Fermi level. b) DOS for a metallic SWNT, note that there is no gap in the DOS. The sharp spikes are the van Hove singularities (13).
The electronic properties of nanotubes will vary by diameter from the $\pi/\sigma$ bonding orbitals mixing and $\pi^*/\sigma^*$ anti-bonding orbitals mixing due to the curvature in the graphene sheet. SWNTs are considered one dimensional conductors because the diameter of the tube is smaller than the electronic planar wave and the path of conduction is along the tube axis (14). The orientation of the hexagon network (and hence MOs and bonds) with respect to the tube axis will also determine the electronic properties of the nanotube.

\[ (n,m) = (5,5) \]

\[ (n,m) = (9,0) \]

\[ (n,m) = (10,5) \]

Figure 3. Examples of the three general classifications of SWNTs. Top) armchair nanotube, middle) zigzag nanotube, bottom) chiral nanotube (13)
The possible orientations of hexagons in a nanotube result in a general classification system of three tube types, zigzag (achiral), chiral and armchair (Figure 3). Identification of a specific diameter, chirality and type of any given nanotube can be denoted by two integers \((n,m)\) on a hexagonal lattice. The hexagonal symmetry of the lattice can allow many equivalent cylinders to be defined. A graphene sheet (or hexagonal lattice) with boundaries separated by an angle of 30 degrees creates an area where all defined cylinders are unique. Figure 4 (13) shows the possible orientations of the hexagons and tube diameters and the coordinate system for classifying each type of tube. The chiral vector, \(C_h\), and hence the chiral angle determine the type of nanotube formed. \(C_h\) is defined by the equation \(C_h = n*a_1 + m*a_2 = (n,m)\) where \(a_1\) and \(a_2\) are unit basis vectors, and \(n\) and \(m\) are integers. For a chiral tube \(0 < |m| < n\), for an armchair nanotube \(n = m\), so \(C_h = (n,n)\) and a zigzag tube \(m = 0\) and \(n > 0\), then \(C_h = (n,0)\). The chiral angle for a given nanotube can be calculated by using the equation \(\sin \theta = ((\text{SQRT} 3)m)/(2(\text{SQRT}(n^2+m^2+nm)))\).
**Figure 4.** On the graph below a nanotube can be made by rolling the graphite sheet from the origin at (0,0) to the desired tube described by the chiral vector (J3).

The electronic behavior of the three SWNTs types can be generalized. All armchair tubes are metallic. One out of three zigzag and chiral tubes are semi-metals with a small bandgap (J4). All other tubes are semiconducting with a bandgap that scales approximately with the inverse of the tube radius. Bandgaps of 0.4 – 1 eV can be expected for SWNTs whose diameter range between 0.6 to 1.6nm (2).

The rule for predicting electronic behavior is depicted in Fig. blah where n minus m is divisible by 3 is a metal (n,m in red in Fig 4) and n minus m not divisible by 3 is a semiconductor (n,m in black in Fig 4). From theoretical predictions, a metallic nanotube will have electrical conductivity better than copper (J5).
3.3. Other physical Properties and applications of nanotubes

Nanotubes have other unique properties. Carbon nanotubes are the strongest material known and are 100x stronger than steel in tensile strength at only 1/6th the weight (16-18). Nanotubes are the most rigid molecule known and still exhibit a high degree of elasticity, which makes SWNTs and MWNTs prime candidates for structural materials such as fibers and composites. SWNTs are the best thermal conductors, even better than diamond (19-21). Nanotubes conduct heat along the axis of the tube and could be used to pipe heat away from a source. This heat conduction might play a crucial role in nanocircuits where heat could be a limiting factor.

Because of their dimensions and multitude of electronic properties, nanotubes are the best suited material for the development of molecular electronics. Carbon nanotubes might replace silicon as the material for computer chips and enable circuits to shrink to the dimensions of molecules. Many, if not all types of electronic components could be fashioned from nanotubes. The conductivity of individual carbon nanotubes has been measured (22) and a nanoscale transistor made from SWNTs has been demonstrated (23). Chemical sensors made from carbon nanotubes show the extreme sensitivity of a one dimensional conductor (24-28). Capacitors made from SWNTs have also been tested (29). Nanotubes have a low work function and have been used as field emitters in displays (30) and even as an x-ray source (31).

3.4. Synthesis and purification

Several methods of SWNT production have been discovered. Each method will be briefly described, as will the characteristics of the material synthesized. The quality of the material made by each method can be described in terms of percent yield of SWNTs and
the types of byproducts created, which are important when considering the cleaning processes needed to isolate or purify the nanotubes. Beyond the purification of SWNT material, one must consider that nanotubes are produced in a variety of lengths, diameters and chiralities. The different types of tubes have different properties; therefore separating the metals from the semiconductors is another goal that needs to be reached.

3.4.1. Laser ablation method

The first large scale (gram quantities) production of SWNTs was achieved in 1996 by the Smalley lab at Rice University (32). The laser ablation technique uses a 1.2 atomic % Cobalt/Nickel with 98.8 atomic % of graphite composite target that is placed in a 1200 C quartz tube furnace with an inert atmosphere and vaporized with a laser pulse. Nanometer sized metal catalyst particles are formed in the plume of vaporized graphite. The metal particles catalyze the growth of SWNTs in the plume, and byproducts are formed at the same time. The nanotubes and byproducts are collected on a cold finger down stream from the target. The yield varies from 20% to 80% of SWNTs by weight. The byproducts of this synthesis are graphitic and amorphous carbon, “bucky onions” (concentric fulleroid spheres) surrounding metal catalyst and small fullerenes (C60, C70…etc.). The diameter distribution of SWNTs made by this method is between 1.0 nm and 1.6 nm.

3.4.2. Carbon arc synthesis

The carbon arc method for synthesizing SWNTs and MWNTs can also produce gram quantities of material. The method is similar to the Kratschmer-Huffman method of generating fullerenes and the procedure to make carbon whiskers used by Roger Bacon 30 years ago (13). The arc synthesis uses a low voltage, ~12-25 volts, high amp, 50-120
amps, power supply (an arc welder can be used). An arc is produced across a 1 millimeter
gap between two graphite electrodes 5-20 mm in diameter. A flowing inert gas is used to
cool the reaction. Iijima produced the first MWNTs by this method (5). He found that
nanotubes are formed on the cathode along with soot and fullerenes. SWNTs can be
made by adding a transition metal catalyst to the anode. The yield is claimed to be around
20% weight of SWNTs and the other 80% is made up of fullerenes, amorphous carbon,
metal carbide, and polyhedral nanoparticles (13). The diameter distribution of SWNTs
made by this method is between 0.7 nm and 1.6 nm.

3.4.3. Catalytic Vapor Deposition

Catalytic vapor deposition (CVD) produces SWNT material in gram quantities
like the first two methods, but the nanotube material is obtained in higher yields. The
CVD process uses an inorganic substrate such as alumina, silica, and zeolites (33).
Patterned substrates can also be used to create ordered arrays of SWNTs (34). The
transition metal catalyst can be applied as nanoparticles to the porous substrate or coated
onto the substrate, which forms nanoparticles when placed in the oven at 600 C to 1100
C. The carbon source for the nanotube growth can be a wide variety of molecules.
Examples of carbon sources are benzene, methane, alcohols and carbon monoxide. The
metal nanoparticles catalyze the decomposition of the carbon feedstock molecules to
make SWNTs. The yields and the byproducts vary by the conditions used. Yields are
claimed to be between 70 to 90 % by weight. The byproducts of this reaction are metal
catalyst particles, amorphous carbon, MWNTs, graphitic carbon, catalyst particles
encapsulated with graphitic carbon layers, catalyst support, and metal carbide particles.
SWNT diameters made by this method are generally between 1.0 nm to 1.6 nm.
3.4.4. HiPco

One of the latest methods for producing SWNTs in gram to kilogram quantities is the HiPco (high pressure carbon monoxide) process (35, 36). This process is a variation of the CVD synthesis of SWNTs. Unlike CVD, the HiPco process does not use a substrate to hold catalyst particles. Instead the catalyst is formed in situ when Fe(CO)₅ and or Ni(CO)₄ is injected into the reactor along with a stream of carbon monoxide (CO) gas at 900 C – 1100 C and at a pressure of 30 atmospheres to 50 atmospheres. The reaction to make SWNTs is the disproportionation of CO by nanometer sized metal catalyst particles. Yields of SWNT material are claimed to be up to 97% atomic purity. The SWNTs made by this process have diameters between 0.7 and 1.1 nm. This method is a quantum leap forward for SWNT synthesis and is the material used for my dissertation work.

3.5. Cleaning and purification of raw nanotube material

Carbon nanotube material made by any of the methods described above will need to be purified to isolate the SWNTs. The byproducts to be removed are determined by the method used to make the tubes. The purification methods used for most molecules are chromatography, recrystallization, sublimation, filtration and centrifugation. These purification methods have been attempted (discussed in chpt.5), but with only limited success. Solubility is the key to purifying most molecules. SWNTs are not soluble in any known solvent at this time. Other methods were needed and have been developed.
3.5.1. Oxidation

Oxidation is the most widely used reaction to purify SWNTs. Oxidation can be performed in the liquid phase or in the gas phase (37, 38). A popular method of removing non-nanotube material is refluxing in an oxidizing acid solution (39). HNO₃ at 1-5 molar concentration will oxidize reactive carbon species to create CO₂ gas and can form salts with the transition metal catalyst rendering the metal soluble. The aqueous HNO₃/SWNT mixture is filtered after the reflux to retain the “cleaned” SWNT material and remove the metal salts. Gas phase oxidation can be used with raw nanotube material by passing air or oxygen, in a carrier gas such as argon, over a solid sample of nanotubes at elevated temperatures (>150 C). This method will burn away any reactive carbon and will oxidize the transition metal catalyst. The remaining material can then be washed with aqueous HCl to remove the metal.

The oxidation methods are somewhat effective at cleaning the nanotube material, but also can produce unwanted reactions with the SWNTs. Two possible reaction sites exist for the oxidation of SWNTs. The first one is the end of the nanotube and the other is the side of the nanotube. The end of the SWNT is more reactive than the side since a tube is capped by a hemisphere made up of heptagons and pentagons. The sp² bonds in the cap are more strained than the sides due to the geometrically induced curvature of the hemisphere, and thus requires less energy to break (40-42). The nanotube is left opened with carboxylic groups on the terminal carbons when attacked with oxidizers from the ends. This has been experimentally observed in Liu et al. (39) and was theoretically described in Mazzoni et al. (43).
As mentioned, the smaller the tube diameter, the more reactive it becomes from bond strain. Oxidation can damage tubes and is an important factor in the case of HiPco material; this will be discussed in the dissertation research section. The reactivity difference between metallic SWNTs and semiconducting SWNTs is also a factor. The metallic SWNTs are more reactive than the semiconductors, because of their lower work function. This difference in reactivity has been exploited by Collins et al. (44) to burn away the metallic tubes and leave only semiconductors.

In all purification methods the SWNTs remain in bundles along with some impurities that cannot be removed. In order to clean and purify nanotubes, a technique to disentangle the individual SWNTs and free the impurities must be found. The procedure should also use mild conditions that do not damage the sidewalls and change the properties of the nanotube. The usual purification processes stated at the beginning of this section will work if SWNTs can be suspended as individuals in some solvent and this is the topic of the next section.
4. Nanotubes in a liquid medium

4.1. Colloids – a brief introduction

The colloid state is a suspension of finely divided particles (0.5 nm to 5 μm in size \((45)\)) of a substance distributed homogeneously throughout a continuous medium, which does not settle out of the medium rapidly. Settling out is the reason for the upper size limit; for particles larger than the upper size limit, external forces such as gravity become more important than Brownian motion. The continuous medium can be a gas, liquid, or a solid. The work described here will be concerned with colloids in a liquid medium.

The difference between a colloidal suspension and a true solution has to do with the size of the solute. In a true solution the solute is usually a molecule with a size on the order of the solvent molecule (less than 0.5 nm). True solutions are usually stable indefinitely whereas colloids have varying degrees of stability. For example, charged colloidal particles form aggregates and precipitate out of the suspension when ions of opposite charge are added. Another contrast between colloids and true solutions is that colloidal particles exhibit the Tyndall effect, while true solutions do not \((45)\). This phenomenon occurs when light is scattered in all directions, revealing the path of a beam of light as it passes through a medium containing discontinuities. Examples of colloids include biological macromolecules (e.g. proteins and polysaccharides), clays, polymer-latex and silica nanoparticles. When dispersed in a solvent, carbon nanotubes demonstrate the characteristics of a colloidal suspension.

Colloidal solutions (sols) fall into two categories when relating their interaction with a liquid medium: lyophilic (solvent loving) or lyophobic (solvent hating). If water is
the dispersing medium, they are known as hydrophilic or hydrophobic colloids.

Hydrophobic colloids can be precipitated by small concentration of electrolytes or oppositely charged colloids.

In the case of lyophilic sols, the particles readily disperse in a solvent with mild mechanical agitation. The lyophobic sols, on the other hand, require vigorous mechanical agitation to disperse in a solvent, as they have no affinity for the dispersing medium and thus are not solvated. However, lyophobic colloids can be dispersed and stabilized by the adsorption of ions from the solvent. Lyophilic colloids are solvated, but can be charged as well. Their charge usually comes from an ionic functional group attached to the colloid.

The large surface area of a lyophobic colloid will preferentially adsorb ions when placed in a solvent. The absorbed charged particles repel each other and prevent the aggregation and precipitation of the lyophobe. The adsorbed ions on the surface of the particle attract oppositely charged ions, and form a charged double layer. The greater the absorbed charge, the more stable a lyophobic colloid will be. As will be discussed later, nanotubes preferentially adsorb ions.

4.1.1. Colloid solubilizing agents

Surface active agents, known as “surfactants”, are defined as compounds that reduce the surface tension of water when used in low concentrations. Chemically, surfactants can be amphiphilic molecules and/or polymeric molecules. An amphiphile is a molecule that is divided into two chemically different regions: one that is hydrophobic the other is hydrophilic. Detergents, the best known example of an amphiphile molecule, usually have a polar or ionic head group, which can interact with water in an
energetically favorable manner. The head group is attached to a non-polar aliphatic chain, an aromatic group, or mixture of both that will interact with a hydrophobic substance. At low concentrations, some amphiphilic molecules dissolve in water and form a true solution; other amphiphilic molecules tend to form a monolayer at the air-water interface such that the polar part interacts with the water and the non-polar part is held above the surface. If the concentration of amphiphile is raised and no room is available at the air/water interface, then the amphiphiles will agglomerate in the bulk of the solution forming micelles. Micelles begin to form when a critical concentration of amphiphiles is reached: the CMC (critical micelle concentration). Micelles of a surfactant at a given concentration and temperature contain roughly the same number of molecules (25 to 100). These micelles can increase the solubility of hydrophobic compounds and are responsible for the detergency of most surfactants. There are many variations on the basic amphiphile structure. Some surfactants are polymeric, behaving in a similar manner to soap molecules by adhering to the surface of a hydrophobic particle to give a hydrophilic coating.

The polymer surfactants can be roughly divided into two classes. The first type can be considered an amphipathic polymer. These polymers are usually block copolymers with two or more regions of differing chemical composition (hydrophilic regions and hydrophobic regions). The other type of polymer surfactant is not an amphipath, but rather a surface acting agent. This type of polymer can be heterogeneous or homogeneous in monomer composition. If the polymer is heterogeneous it can be a random mixture of differing monomers or a very specific sequence of monomers (i.e. a protein). Many of these types of polymers have a hydrophobic to semi-hydrophobic
backbone with hydrophilic side groups. These polymers can adsorb onto a colloid surface as a result of coulombic interactions, hydrogen bonding, dipole-dipole interactions, van der Waals interactions or some combination of these forces (fig 5 below).

<table>
<thead>
<tr>
<th>Type of interaction</th>
<th>Model</th>
<th>Example</th>
<th>Interaction energy dependence on distance</th>
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<tbody>
<tr>
<td>Charge – Charge</td>
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<tr>
<td>Longest range force</td>
<td><img src="image" alt="Model" /></td>
<td>Na + Cl -</td>
<td>1/r</td>
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<tr>
<td>Hydrogen bond</td>
<td><img src="image" alt="Model" /></td>
<td>&gt;N-H...O=C&lt;</td>
<td>Fixed bond length</td>
</tr>
<tr>
<td>Charge attraction + partial covalent bond</td>
<td><img src="image" alt="Model" /></td>
<td>-NH₃⁺ -O⁻H₂</td>
<td>1/r²</td>
</tr>
<tr>
<td>Charge – Dipole</td>
<td><img src="image" alt="Model" /></td>
<td>-O=C&lt;⁺ -O=C&lt;⁺</td>
<td>1/r²</td>
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<tr>
<td>Oriented dipole</td>
<td><img src="image" alt="Model" /></td>
<td>-NH₃⁺ -O⁻H₂</td>
<td>1/r²</td>
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<tr>
<td>Dipole – Dipole</td>
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<tr>
<td>Mutual orientation of dipoles</td>
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<td>1/r²</td>
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<tr>
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<td>-NH₃⁺ -O⁻H₂</td>
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<td>Dipole depends on polarizability of molecule</td>
<td><img src="image" alt="Model" /></td>
<td>-NH₃⁺ -O⁻H₂</td>
<td>1/r⁴</td>
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<td>Dipole induced – Dipole</td>
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<td>Dispersion</td>
<td><img src="image" alt="Model" /></td>
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<td>1/r⁶</td>
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<tr>
<td>Mutual synchronization of fluctuating charges</td>
<td><img src="image" alt="Model" /></td>
<td>+ - - +</td>
<td>1/r⁶</td>
</tr>
<tr>
<td>van der Waals</td>
<td><img src="image" alt="Model" /></td>
<td>SWNT</td>
<td>1/r¹²</td>
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<td>Occurs when outer electron orbitals overlap</td>
<td><img src="image" alt="Model" /></td>
<td>SWNT</td>
<td></td>
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The adsorbed linear polymers wrap around a particle to form a supramolecular complex. The wrapping starts with a loose polymer conformation. The polymer adsorbs with some segments attached to the surface and other segments extending out into the solution as loops and tails. With time, more parts of the polymer are adsorbed and the polymer adopts a flatter conformation (45). Colloids are stabilized by adsorbed polymer layers on their surfaces due to steric/entropic stabilization. As polymer wrapped colloidal particles approach one another, the polymer chains interact and lose some disorder giving rise to an entropically driven stabilizing effect. Other stabilizing effects such as charge-charge repulsion may also play a role in the case of a polyelectrolyte.

The free energy of a system determines if a surfactant works. Gibbs free energy ($\Delta G$) is defined as $\Delta G = \Delta H - T\Delta S$, where $\Delta H$ is the contribution of energy from heat, $T$ is the temperature, and $S$ is a measure of disorder. If a reaction or interaction gives off heat (exothermic) it is favorable (i.e. will occur spontaneously). The higher the disorder, the more favorable the reaction will be. Creating order requires an input of energy. For example, water forms hydrogen bonds with other water molecules, due to a partial negative charge on the electronegative oxygen and a partial positive charge on the hydrogen. The hydrogens on a water molecule are electrostatically attracted to oxygen on another water molecule, forming a large fleetingly stable network. The hydrogen bonding network is disrupted when a hydrophobic substance is introduced into water, because the non-polar molecule cannot form hydrogen bonds. Water must form a clathrate cage structure around the non-hydrogen bonding substance. The structure formed, similar to that of ice, requires water to become more ordered around the substance. This increased
order is energetically unfavorable and results in the aggregation of hydrophobic molecules.

The hydrophobic molecules try to form a minimum surface (a sphere) with water to minimize the energy spent in “ordering” the surface. Surfactant molecules that are part hydrophilic and part hydrophobic often arrange themselves into micelles, in which the hydrophobic tails of the amphiphile cluster together leaving the polar or ionic head groups to interact with the water. A hydrophobic substance can exist in an aqueous environment without being energetically unfavourable if it resides in the hydrophobic region of a micelle.

4.2. Mechanical dispersion

Dispersion of a colloid throughout a solution can be achieved by simple stirring in some cases, but for nanotubes stirring is not enough. Two methods of dispersion used with SWNTs for my research are introduced and briefly described below.

4.2.1. Homogenization

Mechanical shear, produced by a rapidly rotating impeller, is used to reduce to particles and disperse them throughout a fluid. Homogenization can be used to make an emulsion uniform in consistency, especially to render (milk) uniform in consistency by emulsifying the fat.

4.2.2. Sonication (ultrasonic irradiation)

Ultrasonic irradiation applied to water produces cavitation bubbles. At an ultrasonic frequency of 20 kHz, the liquid will undergo $2 \times 10^4$ compression and rarefaction cycles each second. Microscopic bubbles grow in size during the “rarefaction” half-cycle of the sound wave when these bubbles collapse, temperatures of approximately
3000-5000 K are generated in a jet that is ejected into the bulk solution (46). The violent sonication process can be used to finely disperse material throughout a solution. Additional products similar to those found in combustion systems are formed and water vapor in the bubble is dissociated into hydroxyl radical (OH) and hydrogen atom (H). Sonication is known to cut polymers and degrade a wide variety of molecules. Sonication can cut nanotubes (39) and induce defects (47) in SWNTs during prolonged exposure.

4.3. Nanotube colloids prior art

The fundamental problem preventing the practical use of single walled carbon nanotubes has been the inability to obtain a stable solution or suspension. SWNTs appear to be lyophobic and are not soluble in any solvent to date. However, SWNTs can be suspended in several organic solvents with vigorous mechanical agitation. Many solvents can wet a SWNT, but nanotubes prefer other nanotubes much more than any solvent. Nanotubes have an exceptionally strong van der Waals interaction (on the order of 0.5 eV/nm) and prefer to aggregate or rope rather than stay in suspension (32, 48). This roping tendency blocks all attempts to separate and study the individual SWNTs and their corresponding properties. Despite this problem, many attempts have been made to dissolve SWNTs in various solvents.

4.3.1. Organic solvents

Fullerenes are soluble in toluene, halogenated benzene, halogenated alkanes, and polar solvents such as dimethyl formamide (DMF) and N-methyl pyrrolidone (49).

Attempts at suspending nanotubes (a.k.a. fullerene tubes) in the same solvents that were found to dissolve the spherical fullerenes have been studied. SWNTs produced by the carbon arc and laser ablation methods (tube diameters larger than fullerenes) do not
dissolve in toluene or any other solvent. However, when sonication was used to disperse the nanotubes, several solvents were found to be useful, although only at SWNT concentrations between 10-100 mg/L (39, 50, 51).

The best organic solvents shown to suspend SWNTs are dimethyl formamide (DMF), N-methyl pyrrolidone (NMP), aromatic amines and mono, di, and tri-halogenated benzenes (39, 50, 51). Although HiPco material produces tubes with diameters in the range of buckyballs, no solvent was found to solublize the smaller diameter SWNTs and the results obtained by Bahr et al (51) were similar to previous studies. Organic suspensions of nanotubes are only meta-stable and are not homogenously dispersed as individuals (i.e. many tubes are present as small clusters).

The primary reason that nanotubes are even meta-stable in organic solvents is that they adsorb charged species when suspended in a solvent, as would be expected for a lyophobic colloid (52). When millimolar quantities of salt are added to the solution, the nanotubes flocculate. The salt screens the repulsion from the charges on the tubes and allows aggregation. This outcome further demonstrates the role of the adsorbed ions.

The stability of suspended SWNTs in an organic solvent can be improved. One established way is to add a counter ion (cation), such as triethylamine (TEA) to the negatively charged SWNT (53). Stability of carbon nanotubes in organic solvents can also be improved by wrapping the nanotubes with a polymer. For example, multiwalled carbon nanotubes (MWNTs) were wrapped by polymerizing phenylacetylene around the tubes in situ (54). Also, PMPV, [poly(m-phenylene-co-2,5-dioctoxy-p-phenylenevinylene)] which is similar in structure to poly(phenylacetylene), was used to encapsulate SWNTs in a helical polymeric structure that rendered the complex soluble in
a wide range of solvents (55). However, the nanotubes stabilized by these methods were not suspended as individuals.

4.3.2. Dissolved SWNTs?

Only two solvents known to date are claimed to disperse SWNTs without sonication: aromatic amines and concentrated H₂SO₄. In the former case, nanotubes were suspended in aromatic amines by refluxing and stirring (56). The authors report that the nanotubes react with the aromatic amines and are chemically modified or at least charged by the electron transfer of the amine group with the side of the tube. In the latter case, concentrated sulfuric acid was used to intercalate the nanotubes bundles and disperse the material in the liquid phase (57). The principle behind both of these techniques is charging the nanotube to render it soluble. It is unknown if either of these techniques truly renders the tubes soluble.

4.3.3. Chemically functionalized SWNTs

Covalent modification of the nanotubes is another method implemented to make the tubes soluble in water or organic solvents. Two possibilities exist for covalently functionalizing nanotubes. The first method functionalizes the ends of the carbon nanotube via oxidation. This is achieved by placing nanotube material into a solution containing oxidizing agents such as HNO₃ (39). The oxidation process leaves the ends of the carbon nanotubes open and terminating in carboxylic acid groups. The oxidized tubes can then be covalently attached to a molecule that will render the tubes soluble in some solvent (58-64).

The second method is the covalent functionalization of the sides of the carbon nanotube. Side wall modification requires highly reactive species such as fluorine or a
carbine (65-69). Covalent modifications of the sides of SWNTs have produced stable suspensions of individualized nanotubes. The assertion that the nanotubes are individuals comes from the analysis of AFM images of nanotubes from a solution (see section 6.1.2.1.). The sidewall functionalization renders the tube soluble, but destroys the desirable physical characteristics of SWNTs. The electronic structure of the nanotube is so altered that no information about the pristine SWNT can be obtained from spectroscopy. The conduction properties are altered with the change in chemical bonds. The nanotubes are less conductive and theoretically could become insulators. The incredible strength properties of the nanotube are also compromised.

4.3.4. Aqueous phase

In contrast to chemical modification, surfactants and polymers have been used to suspend SWNTs in water without disruption of electronic structure (39). Two of the surfactants used were Triton X-100 and sodium dodecyl sulfate (SDS). These sols were not found to be made of individual nanotubes in a micelle. SWNTs were solubilized in water by adsorbing linear polymers to the sides of the tubes (70). The polymers used were polyvinyl pyrrolidone (PVP; 40 kD and 360 kD), poly(1-vinyl pyrrolidone-co-vinyl acetate) (PVP/VAc; 50 kD, 1.3:1 PVP:VA), poly(1-vinyl pyrrolidone-co-acrylic acid) (PVP/AA; 96 kD; 25% by weight AA), poly(1-vinyl pyrrolidone-co-dimethylaminoethyl methacrylate) (PVP/dMAEMA; ca. 1 MD), poly(methyl methacrylate-co-ethyl acrylate) (PMMA/PEA; 101 kD, > 5% ethyl acrylate), poly(sodium 4-styrenesulfonate) (PSS; 70kD), poly(sodium styrene sulfonic acid-co-maleic acid) (PSS/MA; 20 kD; 3:1 SS:MA), dextran (428 kD), dextran sulfate (500 kD), bovine serum albumin (BSA), polyvinyl alcohol (PVA; 70-100 kD), polyethylene glycol (PEG; 100 kD, 1 MD, 5 MD, and 8 MD),
polyethylene imine (various molecular weights), polyvinyl sulfate (50 kD), and polyallyl amine (70 kD).

The wrapped tubes opened the door to aqueous phase manipulation techniques such as chromatography and electrophoresis. Examples of these techniques with PVP wrapped tubes are given below. While polymer wrapping was a giant step forward in SWNT liquid phase manipulation, it was plagued with one fatal problem: not all the nanotubes were suspended as individuals. This problem excluded the possibility of separating the tubes by their types, characterizing each type, and assigning a n,m value to each tube present in a sample.

So far there have been no ways to disperse single walled carbon nanotubes as individuals in any solvent without covalently modifying them and/or destroying their unique properties.
5. Separation of Macromolecules

In general, macromolecules and colloids can be separated by density, size, solubility, charge, and binding affinity for a given substrate. Several of the techniques used to separate biological macromolecules have been applied to SWNTs. A brief description of each technique and the prior art will be discussed. To maintain the focus of this dissertation, methods not used with SWNTs will not be discussed.

5.1. Column chromatography

Column chromatography encompasses many permutations of a basic theme: a cylindrical container packed with a solid material, such as micron to millimeter size inorganic grains or beads made from organic polymers. A carrier liquid phase containing the molecules to be separated is passed through the column. As the molecules pass through the column they interact with the surface of the packing material and can be separated in various ways.

5.2. Size exclusion (SEC)

Size exclusion chromatography separates macromolecules based on their molecular size using porous beads as the packing material in the column. The packing material can either be made of organic gels (cross-linked polysaccharide material) or inorganic material, such as controlled-pore glass. Macromolecules are placed on the column and eluted with a solvent of choice. Larger molecules elute before smaller molecules because larger molecules do not get trapped in the pores. The separation of the macromolecules is based upon entropy, the measure of disorder, and can be calculated from \( k^* \ln(\Omega) \) (\( k = \) Boltzman’s constant, \( \Omega = \) probability of macromolecule states). Larger
macromolecules have less of a probability of remaining in the pore, while smaller molecules have a higher probability of being in the pore.

SEC was performed on SWNTs using controlled pore glass (CPG) with an average pore size of 300 nm (71, 72). Both MWNTs and SWNTs were passed through a column and separated by length, but true separation by length was unsuccessful because the nanotubes were suspended in SDS at concentrations between 1 to 5 g per liter and, as evidenced by AFM images of the collected fractions, the majority of the tubes were not individuals. The authors claim to have separated the nanotubes material from the byproducts and catalyst material. Purification is unlikely when the nanotubes are present as bundles, as they will retain much of the impurities intermixed with the tubes. I have tried this method of purification and length separation and obtained similar results.

Another matrix used for column chromatography was potassium polyacrylate (73). This method assumes that the cavities in the polymer are big enough to entrap the nanoparticles, but are too small to entrap nanotubes and anything larger. This method has been tried, in my research group by Michael Strano, and was not found to work with HiPco material.

5.3. HPLC

High-pressure liquid chromatography separates the desired solute from the solvent by forcing the solution through a non-compressible resin. Liquids are forced through the column at pressures between 5,000 and 10,000 pounds per square inch. The sample is less likely to spread out in this process because diffusion has little time to occur. This process is also less time consuming than other column chromatography techniques, separating the solution in a matter of minutes rather than hours.
HPLC was used to purify nanotubes that were chemically functionalized by
attaching a long chain alkane to the end of the SWNT by an amide bond to yield:
SWNT-CONH(CH₂)₇CH₃ (74-76). The column was a gel permeation chromatography
(GPC) system and was found to remove impurities. After the SWNTs were passed
through the column and collected as a fraction, they were found to fluoresce in the visible
region, which indicates damage of the sidewall of the functionalized SWNT (77).

5.4. Differential Centrifugation

This technique separates macromolecules by their density or, when the molecules
are of equal density, by their size via mobility. The technique relies on a centrifugal field
created by spinning a sample around an axis that provides a force: \( F_c = m\omega^2r \), where \( F_c \) =
the centrifugal force, \( m \) = mass of the particle, \( \omega \) = angular velocity and \( r \) = distance from
the axis (78). This force is opposed by a buoyant force \( (F_b) \) and a frictional force \( (F_f) \). The
buoyant force is the force it takes to displace solvent when a particle moves through the
centrifugal field. The frictional force represents the drag on the particle as it passes
through the solvent. These two forces are respectively defined as: \( F_b = -m_o\omega^2r \) and \( F_f = -
f\nu \), where \( m_o \) = the mass of the displaced solution (78), \( f \) = frictional coefficient and \( \nu \) =
velocity of the particle. The particle will move at a constant velocity such that the total
force equals 0. Thus, \( F_c + F_b + F_f = 0 \), or \( m\omega^2r - m_o\omega^2r - f\nu = 0 \). More information about
the system can be obtained by substituting \( m\nu\rho_s = m_o \), where \( \nu \) = partial specific volume
of the particle and \( \rho_s \) = density of the solvent (78).

These equations describe some general phenomena: the more massive and denser
(i.e. the smaller its \( \nu \)) a particle, the faster it moves in a centrifugal field; the denser the
solution and the greater the frictional coefficient (factors such as viscosity, particle shape,
and etc. influence this parameter); the slower the particle will move. The particle velocity is 0 when the solution density is greater than the particle density. The greater the centrifugal force ($\omega^2 r$) is, the faster the particle sediments.

This separation method was used for the work described in the research chapter.

5.5. Gel electrophoresis

Electrophoresis is a technique used to separate and/or purify colloids - usually proteins and nucleic acids. When an electric field $E$ (where $E$ is the field strength in volts per meter) is applied to a solution, it exerts a force $EZe$ on molecules with charge $Ze$ (where $Z$ is a positive or negative integer and accounts for the net charge of the molecule and $e$ is the elementary unit of charge in coulombs). The charged species move toward the electrode of opposite charge. The frictional force $f\nu$, where $\nu$ is the velocity of the particle and $f$ is the frictional coefficient (which depends on the size and shape of the molecules), exerted on the particle by the medium resists the migration. A migration velocity for each molecule (also call the electrophoretic mobility) is determined by the ratio of these two forces and is the basis of separation.

The molecules are separated within a gel matrix based on their charge to size ratio. Most commonly, the gel is cast in the shape of a thin slab, with wells for loading the sample. The gel is immersed within an electrophoresis running buffer that provides ions to carry a current and to maintain the pH at a relatively constant value.

The gel is composed of either agarose or polyacrylamide, each of which has attributes suitable to particular tasks. The higher the concentration of the gel, the smaller the pores are. The gel can act as a filter if some of the particles are too large for the pores.
Optimal separation of a given size distribution of molecules can be obtained by adjusting the gel concentration. The type of gel used is a critical consideration.

Agarose is a polysaccharide extracted from seaweed and is used at concentrations of 0.5 to 2%. Agarose gels have a large range of separation, but relatively low resolving power. By varying the concentration of agarose, fragments of DNA from about 200 to 50,000 base pairs can be separated using standard electrophoretic techniques (78).

Polyacrylamide gels are made by cross-linking polymers of acrylamide with bis-acrylamide. The length of the polymer chains is dictated by the concentration of acrylamide monomer used, which is typically between 3.5 and 20%. Polyacrylamide gels have a rather small range of separation, but very high resolving power. For DNA, polyacrylamide is used for separating fragments of less than 500 base pairs. Under certain conditions, fragments of DNA differing in length by a single base pair can be resolved.

PVP wrapped nanotubes were separated by size using gel electrophoresis (70). 75 µL samples of PVP wrapped nanotubes in a 25 mM tris(hydroxymethyl)-aminomethane, 192mM glycine, and 1% sodium dodecyl sulfate buffer solution were placed in a 0.5% agarose gel and subjected to 100 volts for five hours (Figure 6). The migration distance was 18cm. The samples were then electro-eluted into wells spaced 5mm apart. The first fraction is the end of the black streak furthest from the origin and the higher numbered fractions are toward the origin in 5mm increments. The shorter tubes are found in the fractions furthest from the origin and increase in length towards the origin. Several fractions were placed onto aminated silicon chips as previously described (79), and were then imaged with an AFM (fig 7). The histogram of fractions 2, 4 and 7 can be seen in figure 8.
Figure 6. Agarose gel electrophoretic separation of SWNTs

Figure 7. AFM tapping mode images of fractions seven and two
Figure 8. Histogram of electrophoretically separated SWNTs. Fraction 2 had a mean length of 90.5 nm, fraction 4 had a mean length of 169.9 nm and fraction 7 had a mean length of 463.2 nm (70).
6. Nanotube characterization techniques

6.1. Microscopy

The size of a nanotube is on the order of one nanometer in diameter and the length can vary from a few nm to \(~1\ \mu\text{m}\). These dimensions determine the types of microscopy that can be used to characterize, or "see", nanotubes. Since the diameter is around \(~1\text{nm}\), optical microscopy is not useful, given that an optical microscope has a resolution limit on the order of hundreds of nanometers due to the wavelength of light. To visualize smaller objects several non-optical microscopes have been developed.

6.1.1. Electron Microscopes

6.1.1.1. TEM

The Transmission Electron Microscope (TEM) was the first type of electron microscope to be developed and is patterned exactly on the optical transmission microscope, except that a focused beam of electrons is used instead of light to "see through" the specimen. The TEM has lenses like the optical microscope; except the lenses are magnets instead of glass (fig 9). The resolution attainable for TEM images is many orders of magnitude better than that of a light microscope because the wavelength of electrons is much smaller than that of light. Thus, TEMs can reveal the finest details of structure - in some cases as small as individual atoms.
Figure 9. Comparison of transmission optical microscope to TEM (78)

The resolution capabilities of the TEM make it an excellent tool for imaging and analyzing nanotubes. S. Iijima used a TEM to discover nanotubes in 1991 (5). The TEM is still used routinely for analyzing SWNT samples and is useful for gathering morphological and topological data (fig 10). Some TEMs are equipped with detectors that can give elemental compositional information. For a nascent nanotube sample, the catalyst particles and byproducts can be imaged. The elements and compounds the sample is composed of and their relative ratios, can be determined in areas a few nanometers in diameter (if the TEM is so equipped).
Figure 10. TEM image of a bundle of SWNTs (32)

6.1.1.2. SEM

The scanning electron microscope (SEM) is analogous to an optical reflection microscope except that a focused beam of electrons is used instead of light to capture a reflected image of the specimen (fig 11). The SEM’s resolution ranges from a few millimeters to 1 nanometer (80), although a 50 nm resolution for nanotube samples is common (70). The large depth of field that a SEM has, allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. SEMs only require the sample to be conductive. The combination of high magnification, larger depth of focus, good resolution, and ease of sample observation makes the SEM an excellent tool for analyzing bulk nanotube samples.
Figure 11. Schematic of a SEM (78)

Figure 12 shows SWNTs as ropes and tangles in contrast to PVP wrapped SWNTs that have no signs of bundling (70). The difference in topography between these two samples is due to the difference in the side wall interactions. The bare SWNTs were filtered from an organic solvent and form ropes as they stick together via van der Waals forces. The PVP wrapped tubes do not come into van der Walls contact when filtered from an aqueous suspension. The PVP coats the tubes and disables the roping mechanism. The individual SWNTs have not been imaged with SEM, even though it is theoretically possible.
Figure 12. SEM images of SWNTs Top) buckey paper formed by filtering SWNTs from organic or surfactant suspension, consisting of large ropes, bottom) buckey paper formed by PVP wrapped SWNTs, note that the PVP tubes do not form large ropes owing to the difference in the sidewall interactions. Scale bars are 500 nm (70).

6.1.2. Scanning probe microscopy:

6.1.2.1. AFM

The atomic force microscope (AFM) was invented in 1986 by Binning, Quate and Gerber (81). Like other scanning probe microscopes, the AFM utilizes a sharp probe to scan over the surface of a sample. In the case of the AFM, the probe is a tip on the end of
a cantilever which bends in response to the force between the tip and the sample. The interaction force between the sample and the probe tip can be detected and recorded as the probe scans an area.

The first AFM used a scanning tunneling microscope (discussed next) at the end of the cantilever to detect the bending of the lever, however modern AFMs employ an optical detection technique. The optical detection method uses a laser beam focused on the end of the cantilever. As the cantilever flexes, the light from the laser is reflected onto a split photo-diode and bending can be detected (fig 13). By measuring the difference between the diodes’ signal, changes in surface height can be precisely measured.

AFM has been used to characterize the dispersion of SWNTs in various solvents. The solvent suspension of nanotubes can be placed on a suitable surface such as a silicon chip or a cleaved piece of mica. The solvent can then be removed by three methods: 1) spin coating the sample (39) 2) placing a drop of nanotubes on the surface to dry or 3) an aminated silicon chip can dip into a suspension of SWNTs, rinsed to remove unbound material and dried (method 3 was used for figure7) (79).

The AFM height measurement can help determine if the nanotubes were dispersed as individuals or small ropes. The nanotubes are about one nanometer high while ropes start at three nanometers. This method is not entirely accurate, since only a small number of tubes can be examined; nevertheless, this was the only available method until recently (82).
Figure 13 Schematic of an AFM (78)

The AFM has also been used for many other tasks for SWNTs: two examples are nanolithography (83) and strength measurements (84). Nanotubes have even been used as probes for AFM imaging (85).

6.1.2.2. STM

The scanning tunneling microscope (STM) was invented in 1986 by Binning, Rohrer, Gerber and Weibel (86, 87). STM is a type of scanning probe microscope based on the quantum mechanical phenomenon called tunneling, in which a high potential barrier does not eliminate the possibility of finding a particle in a region of high potential or even beyond a region of high potential (e.g. the sample surface). A very sharp conductive probe (or needle) is scanned over a conductive surface and a tunneling current is induced. Measurements can be made in by holding the voltage constant and measuring the change in electrical current, or the current can be held constant and the change in voltage needed to sustain the current is measured. The tunneling current decreases exponentially with
increasing tip to surface separation. It should be noted that the tip does not make contact with the sample surface and is the reason a high potential barrier exists.

To increase the probability of an electron tunneling through the potential barrier, a bias voltage is applied that raises the potential energy between the sample and the tip. By using a piezo-electric device to position the tip within a few angstroms of the sample, the electron wavefunctions in the tip and the sample overlap, leading to a tunneling current flow when a bias voltage is applied. The tunneling current is on the order of nano-amps, but can vary by orders of magnitude. In view of the fact that the current or signal is so small, it must be amplified and fed into the computer that will use a negative feedback loop to keep the current constant by adjusting the tip to sample distance (z-axis). The computer can collect the z-axis data and create an image plot of the surface. The image represents the electron density of the sample surface. This electron density plot can be interpreted as the arrangement of atoms on a conductive surface. Needless to say, the resolution of an STM is unsurpassed.

The STM can also be used in scanning tunneling spectroscopy mode. For this mode, the scan is disabled and the tip is moved to the desired position with the feedback loop closed to adjust the tip to sample distance. The system is allowed to stabilize and the feedback loop is turned off. A potential can then be applied to the system and the current (I) to voltage (V) relationship is measured. The spectroscopic data is then normalized for the measured current voltage curves with the equation \((\frac{dI}{dV}) / (I/V)\). The normalized data gives information about the local density of electronic states.

The STM has been used to image and verify the structure of SWNTs [(11, 88-92). The STM has also been used in scanning tunneling spectroscopy (STS) mode to
determine the density of states (DOS) for particular SWNTs (12, 14, 93-98). The STM is a powerful tool for characterizing SWNTs, but the STM can only characterize one nanotube at a time. A better method needed to be found, one that can be used on bulk SWNT material.

6.2. Spectroscopy

As described above, light is not useful for imaging individual SWNTs, but light can be a potent tool for characterizing individual SWNTs in a bulk sample. Spectroscopy refers to a wide variety of characterization techniques that detect and analyze absorbed or emitted electromagnetic radiation by a chemical species. These techniques are commonly used to determine atomic and molecular structure. Until recently (82), spectroscopy has been of little use in the characterization of bulk nanotubes.

6.2.1. UV-Vis-NIR

Absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption spectroscopy (UV-Vis) is usually applied to molecules or inorganic complexes in solution. Absorption measurements can be at a single wavelength or over an extended spectral range. The energy from the light excites the outer electrons of the molecule to higher allowed energy levels. The amount of energy required for this excitation is equal to the difference in energy values between the two electronic energy bands. This energy is quantized for all atomic, ionic, and molecular species in the sample as discussed in sect 3.2. Each atom, ion, or molecule has its own unique set of energy values required for promotion to the next available energy state. These energy values ($\Delta E_{\text{transition}}$) correspond to specific light frequencies ($\nu$) given by the equation $\Delta E_{\text{transition}} = h\nu$, where $h$ is Planck's
constant. For most molecules ultraviolet (UV), 190 nm to 400 nm, and visible (Vis), 400 nm to 800 nm, light are energetic enough to promote outer electrons to higher energy levels, but for nanotubes the useful wavelength range for electronic transitions extends down (in energy) into the near infrared (NIR), 800 nm to 2000 nm.

Some structural information about a molecule can be gained by UV-Vis spectroscopy. Different molecules absorb light at different wavelengths. An absorption spectrum will show a number of absorption features corresponding to functional groups within the molecule. For example, the absorption that is observed in the UV region for the carbonyl group in acetone is of the same wavelength as the absorption from the carbonyl group in methyl ethyl ketone. More often than not, the UV-Vis spectra have broad features that are of limited use for sample identification, but are very useful for quantitative measurements.

The concentration of an analyte in a solution can be calculated by measuring the absorbance at given wavelength and entering the obtained value into the Beer-Lambert Law (Beer’s Law) equation. An extinction coefficient (ε) can be determined by measuring the absorbance of standards at various concentrations. The absorbance values obtained (y-axis) from the corresponding standard at a particular concentration (x-axis) are plotted to generate a calibration line that has an intercept at the origin. The slope of the line is equal to the extinction coefficient (ε). Absorbance (A) is directly proportional to the path length (l) and the concentration (c) of the absorbing species. Beer's Law is

\[ A = ε/c. \]

Unlike most other molecules, the identification of SWNTs and structural information can be obtained from absorption spectroscopy. In the past UV-Vis has not
been very useful for nanotubes; one could only determine concentration and a general
diameter distribution for nanotubes. In order for absorption spectroscopy to be useful, the
SWNTs need to be suspended in a liquid medium as individuals.

6.2.2. Raman

As mentioned above, light can interact with molecules to induce transitions
between energy states. Most photons incident to a molecule are elastically scattered, a
process which is called Rayleigh scattering. In Rayleigh scattering, the emitted photon
has the same wavelength as the incident photon. Raman spectroscopy is the measurement
of the wavelength and intensity of the inelastically scattered light from molecules. The
Raman scattered light is shifted from the incident light to lower (Stokes) or higher (anti-
Stokes) energy wavelengths by the molecular vibrational energies. The Raman effect
comprises a very small fraction, about 1 in 10⁷, of the incident photons (99). To gather
the small amount of Raman information available, a sensitive detector and an intense
monochromatic light source such a laser are generally used.

For nanotubes and other molecules, the energy of the (Raman) scattered light is
less than the incident light for the Stokes line and the energy of the (Raman) scattered
light is more than the incident light for the anti-Stokes line. The Stokes shift is a result of
the absorbed incident light losing energy from non-radiative processes in the molecule.
The anti-Stokes shift occurs only for molecules that are vibrationally excited prior to
irradiation. Hence, the anti-Stokes lines are less intense than the Stokes lines in the
obtained spectrum. Much information can be obtained from the Stokes and anti-Stokes
shifts. The energy increase or decrease from the excitation is related to the vibrational
energy spacing in the ground electronic state of the molecule and therefore the
wavenumber of the Stokes and anti-Stokes lines are a direct measure of the vibrational energies of the molecule.

A SWNT has several non-radiative or vibrational modes that it uses to release the energy absorbed from the incident photon radiation. Quantum mechanics requires that only discrete frequencies and atomic displacements are allowed. These are known as the normal modes of vibration of the molecule. A nanotube with 2N atoms in a unit cell has 6N calculated vibrational modes. Only a few of these modes are used for routine Raman analysis of SWNT samples.

The mode useful in identifying a particular diameter and even the specific (n,m) SWNT is the radial breathing mode (RBM), which occurs between 100 cm\(^{-1}\) to 300 cm\(^{-1}\) shown in fig 14C). By changing laser frequencies, different tube types can be detected. This is due to an effect called resonance enhancement, which occurs when the laser frequency is coincident with the electronic transition energy of a specific SWNT. The electronic transition energy or van Hove singularity, in the absorption spectrum shows up as a local maximum in absorption. For this reason Raman spectroscopy for SWNTs complements both UV-Vis-NIR absorption spectroscopy and Fluorescence spectroscopy.

The tangential mode or “G-peak” that occurs around 1590 cm\(^{-1}\) does not have a frequency dependence on diameter, but it does show a frequency difference for the two electrical property classes, metallics and semiconductors. The G-peak at 1592 cm\(^{-1}\) shows up for semiconductor nanotubes and at 1577 cm\(^{-1}\) for metallic tubes (100). Metallic nanotubes have an additional peak, not present for semiconductors, that splits off from the G-peak called the Fano line at ca.1540 cm\(^{-1}\). These two peaks can be used to differentiate between tube types in a sample.
Another useful Raman mode shows up at ca. 1330 cm\(^{-1}\), but is not predicted by group theory (101). The presence indicates damage or disorder to the sidewall of nanotubes; hence this mode is called the “D-peak” or disorder peak (102). The curvature (i.e. diameter) of a nanotube affects the peak position.

6.2.3. Fluorescence

Absorption spectroscopy measures the amount of light absorbed at a given wavelength and complementary information from that absorbed light can be obtained from the processes a molecule uses to lose that energy. One way a molecule can lose the absorbed energy is through vibration where the energy is lost as heat (this is useful in Raman spectroscopy). Another method of energy loss is the emission of photons (luminescence). There are three types of luminescence: fluorescence, phosphorescence, and chemiluminescence. As will be described later in research chapter, SWNTs are found to fluoresce. So, I will give a brief description of fluorescence here and omit the other two types of luminescence, since they do not apply to nanotubes at this time.

Fluorescence is the emission of light (loss of energy) when an electronically (energetically) excited molecule returns to the ground state. Absorption of light by a molecule excites it from a vibrational level in the electronic ground state to one of the many vibrational levels in the electronic excited state. The light used to excite a molecule is higher in frequency than the light emitted by that molecule. The difference in energy can be accounted for by energy loss through non radiative processes such as molecular vibration. This excited state is usually the first excited singlet state, which means that the excited electron is spin paired with another electron in the ground state energy level from which it was excited (Pauli exclusion principle (99)). This means the electrons have
opposite spins, one up and one down. If the excited state has a spin change such that the electron in the excited state has the same spin as the electron it was paired with in the ground state, then the state is called a triplet. The triplet state (phosphorescence) has a much longer lifetime (seconds) than the singlet state (nanoseconds).

Studies of photoluminescence from single-walled and multi-walled nanotubes have been reported. Several of the reports claim luminescence in the visible region after the nanotubes were chemically sidewall functionalized or when a charge transfer between a chemical species and the sidewall occurred (56, 77, 103, 104). The photoemission in the visible region is unexpected for underivatized nanotubes. Nanotubes have their lowest energy electronic transition in the near infrared, so any photoemission should come from the NIR region when the excitation source is higher in energy. The emission from the nanotubes, mentioned above, is not very useful for determining the electronic structure and identity of pristine nanotubes.

One report on photoluminescence from MWNTs claims no chemical functionalization; the photoemission occurred as a broad hump from about 600 nm to 900 nm (105). The emission spectrum of the MWNTs was suspiciously similar to graphite. The MWNTs were suspended in a mixture of naphthalene/dimethylformamide. It is unknown if the MWNTs were suspended as individuals. Even if they were, spectroscopic data would be of little use for identifying the tube types present, given that each MWNT is composed of concentric nanotubes and no two MWNTs are necessarily the same. The tubes present in a MWNT can transfer energy to each other. If a metallic nanotube is present in the MWNT no photoemission should occur. The metallic nanotube has no bandgap (i.e. has a density of states between the valence and conduction bands). All
available energy will be transferred to the metallic tube and dissipated through vibrational modes. The cause and the source of the photoemission cannot be determined from the data given in Brennan et al.
7. Research Introduction

The goal of my research was to introduce pristine nanotubes into an aqueous medium as individuals and develop methods of stabilizing the SWNT suspension for prolonged periods. Water was chosen as the suspending medium for this study of carbon nanotubes because it is inexpensive, readily available, and nontoxic. Additionally, water provides access to the biological world and many established biological macromolecule separation techniques use water as a carrier solvent.

Several research groups have reported some progress in producing suspensions enriched with individually suspended SWNTs; however, most samples were dominated by small nanotube bundles (39). A procedure was needed that frees nanotubes from bundles, applies a hydrophilic stabilizing coating, and then removes aggregates and metal catalyst particles from the solution. A method was developed that used high shear mixing followed by vigorous sonication to enrich the solution with individual SWNTs. These individually suspended nanotubes were then isolated by ultracentrifugation and if needed, the tubes were wrapped with a polymer that rendered them water soluble and prevented aggregation.

Methods for stabilizing SWNTs in water were already available from my previous work of wrapping the tubes in a polymer (70), which was discussed in section 4.3.4. Isolation of each nanotube in a micelle or polymer wrap was crucial to the spectroscopic study of their properties. Besides isolation of the individual nanotubes, the environment surrounding the nanotubes was an important factor for the spectroscopic study. Ideally, SWNTs should be characterized in a vacuum: the least perturbing environment. Given that a vacuum environment was unobtainable, another goal of this research was to find a
suitable environment for the nanotubes to be spectroscopically analyzed. The polymers used to wrap the nanotubes were found to perturb the absorption spectrum, but amphiphile micelles with hydrocarbon interiors were found to provide an excellent environment for spectroscopy.

With the nanotubes suspended as individuals, more possibilities opened up, such as the separation of the tubes by type and developing methods of placing chemical handles on the tubes in water without functionalizing the SWNTs. The separation of nanotubes by length, by diameter, and by size is an additional goal of my work.

The polymorphisms of tube diameters, lengths, chiralities, and aggregation states in nanotubes samples produced by the various preparation methods have confounded all attempts to separate the nanotubes. Ropes and bundles of nanotubes readily form from solvent suspensions with a van der Waals binding energy of ca. 0.5 eV per nanometer of tube to tube contact \((9, 32, 106)\). This bundling perturbs the electronic structure of the tubes and obstructs all attempts to spectroscopically characterize the individual species of SWNTs, separate the tubes by size or type, or to chemically manipulate them as individual species.

7.1. Theory

The water suspended SWNTs were present as a mixture of individual nanotubes coated with a columnar micelle and as small bundles of tubes surrounded by surfactant. Differential centrifugation was found to remove the bundles of SWNTs and catalyst particles and leave just the individually suspended tubes. A rough calculation of the densities of these three species encased in a columnar micelle found that a single nanotube has a density of 1.0 g/L, a bundle of tubes has a density of ca. 1.2 g/L, and a
catalyst particle has a density of about 2-3 g/L. Thus, centrifugation will bring tube bundles and catalyst particles to the bottom of the centrifuge tube, leaving a supernatant enriched with individual nanotubes.

**Density calculation of a bare (n,m) nanotube** (all equations are from (13, 107)):

\[
\text{Diameter of SWNT} = d_t = |C_{\text{h}}| / \pi = (a \sqrt{3(n^2 + m^2 + nm)}) / \pi, \text{ where } a \text{ is the lattice constant equal to 0.144 nanometers} * \sqrt{3}
\]

Total radius of a nanotube \((n,m)\) with van der Waals distance \((R_{\text{SWNT}})\) is:

\[
R_{\text{SWNT}} = d_t / 2 + r_{\text{van der Waals}}, \text{ where } r_{\text{van der Waals}} = 0.175 \text{ nanometers}
\]

Cross sectional area = volume per unit cell length = \(\pi R_{\text{SWNT}}^2\)

Length of a unit cell for \((n,m)\) nanotube = length of translation vector \((T)\):

\[T = (\sqrt{3}) \times L / d_{R2}, \text{ where } L = |C_{\text{h}}| \text{ and } d_{R2} = d \text{ if } (n-m) \text{ is multiple of 3d or 3d if } (n-m) \text{ is not a multiple of 3d, where } d = \text{ the greatest common divisor of } n \text{ and } m\]

Total volume of a unit cell = \(V_{\text{SWNT}} = \text{(length of translation vector)} \times \pi R_{\text{SWNT}}^2\)

Calculate mass of a \((n,m)\) nanotube:

Calculate number of hexagons in a unit cell, \(N = (2(n^2 + m^2 + nm)) / d_R\)

Multiply this number by two, for there are 2 carbon atoms per hexagon in a unit cell.

Multiply this number by the molecular weight of a carbon atom in grams, which is

\[\text{Mass (carbon atom)} = 12.01 \text{ grams} / 6.02 * 10^{23}\]

Total mass per unit cell = \(M_{\text{SWNT}} = 2N \times 12.01 \text{ grams} / 6.02 * 10^{23}\)

Density of \((n,m)\) nanotube is:

\[\text{Density} = \text{mass} / \text{volume} = M_{\text{SWNT}} / V_{\text{SWNT}} \quad \text{Units should be in grams/cm}^3\]
Density calculation of a surfactant coated nanotube:

\[ \rho \approx 1.0 \]

Assumptions: Assume that the surfactant forms a solid cylindrical coating around the tube; assume that this coating is of uniform density \( D_{\text{surfactant}} \) and that that density is equal to the dry density of the surfactant; assume that the radial contribution made by the surfactant to the overall radius of the nanotube-surfactant complex is equal to the linear projection length of the surfactant molecule plus the van der Waals radius of the carbon on the starting closest to the tube.

\[ R_{\text{SWNT + surfactant}} = R_{\text{SWNT}} + r_{\text{van der Waals}} + R_{\text{surfactant}}, \text{ where } R_{\text{surfactant}} = 1.6 \text{ nanometers} \]

\[ V_{\text{SWNT + surfactant}} = \pi \cdot (R_{\text{SWNT + surfactant}}^2) \cdot T \]

and

\[ V_{\text{surfactant}} = \pi \cdot (R_{\text{SWNT + surfactant}}^2 - R_{\text{SWNT}}^2 - r_{\text{van der Waals}}^2) \cdot \text{length of } T \]

Total mass = mass of nanotube + mass of surfactant = \( M_{\text{SWNT}} + M_{\text{surfactant}} \)

\[ M_{\text{surfactant}} = D_{\text{surfactant}} \cdot V_{\text{surfactant}}, \text{ where } D_{\text{surfactant}} = 0.9 \text{ g/cm}^3 \]

Final density = total mass/ \( V_{\text{SWNT + surfactant}} \)
Surfactant adds both volume and mass to nanotube. The volume contribution outweighs the mass component resulting in an overall decrease in density.

**For a heptameric bundle** ($R_{\text{bundle}}$):

![Diagram of a heptameric bundle with a density $\rho \approx 1.2$](image)

The assumptions are the same as above for individual with surfactant. The only difference is that the radius will have three van der Waals radius contributions: two from the SWNT (two nanotubes next to each other radially) and one from the surfactant.

$$R_{\text{bundle}} = 3*R_{\text{SWNT}} + 3*r_{\text{van der Waals}} + R_{\text{surfactant}}$$

Then just use same procedure to back out volume and hence mass of surfactant.

$$V_{\text{surfactant}} = \pi * T * (R_{\text{bundle}}^2 - 3*R_{\text{SWNT}}^2 - 3*r_{\text{van der waals}}^2)$$

$$M_{\text{surfactant}} = V_{\text{surfactant}} * D_{\text{surfactant}}$$

$$D_{\text{bundle}} = (7*M_{\text{SWNT}} + M_{\text{surfactant}}) / (\pi*T*R_{\text{bundle}}^2)$$
7.2. Experimental

The work in this section consists of two steps: sample preparation and sample analysis. The sample preparation used involves a technique that suspends carbon nanotubes in water and then separates the individually suspended tubes from the bundles of tubes and catalyst particles. The sample analysis was performed by three spectroscopic techniques: UV-Vis-NIR absorption spectroscopy, fluorescence spectroscopy, and Raman spectroscopy. Each step is followed by a discussion of the results.

7.2.1. Procedure

40 mg to 100 mg Raw nanotube material produced via the HiPco (i.e. high pressure carbon monoxide) method (35) was dispersed in 200 milliliters (mL) of aqueous SDS (sodium dodecyl sulfate) or other suitable surfactant (1% by weight) by high shear
mixing (Polyscience X-520) for 2 hours. The resulting dispersion was then sonicated in a
cuphorn sonicator (Cole Palmer CPX-600) for 10 minutes at a power level of 540 W. The
measured temperature of the solution after sonication was 70\(^\circ\) C. After the sample cooled
to 40\(^\circ\) C, samples were centrifuged (Sorvall 100S Discovery Ultracentrifuge with
Surespin 630 swing bucket rotor) at 122,000 g for 4 hours. The top 80% of supernatant
was then carefully decanted, giving micelle-suspended nanotube solutions at typical
yields of 10%-20%.

The SDS/SWNT decants were found to be much more stable than prepared nanotube
samples before the centrifugation step and suspensions of nanotube bundles produced by
milder sonication (39). Samples containing 10 to 50 mg/L of nanotubes in 1% SDS can
be heated to 70\(^\circ\) C and cooled to 10\(^\circ\) C, addition of up to 40 % to 50% methanol, NaCl
concentrations up to 200 mM, and MgCl\(_2\) concentrations up to 10 mM for periods of
greater than 24 hours without flocculation.

7.2.2. Wrapping procedure

After obtaining the decant material, the nanotubes can be wrapped, if needed, in one
of the following polymers: a linear, biological, or conducting polymer (see examples in
table below).
<table>
<thead>
<tr>
<th>Biological Polymers</th>
<th>Molecular weight</th>
<th>Monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly α-D-Glucose</td>
<td>10 kD and 50 kD</td>
<td><img src="image1" alt="Monomer" /></td>
</tr>
<tr>
<td>Bovine Serum Albumin (BSA)</td>
<td>ca. 67 kD globular protein</td>
<td><img src="image2" alt="Monomer" /></td>
</tr>
<tr>
<td>Poly-L-histidine</td>
<td>Random mixture of molecular weights</td>
<td><img src="image3" alt="Monomer" /></td>
</tr>
<tr>
<td>ssDNA Poly dA potassium salt</td>
<td>Random mixture of molecular weights</td>
<td><img src="image4" alt="Monomer" /></td>
</tr>
<tr>
<td>ssDNA Poly dG potassium salt</td>
<td>Random mixture of molecular weights</td>
<td><img src="image5" alt="Monomer" /></td>
</tr>
<tr>
<td>ssDNA Poly dC potassium salt</td>
<td>Random mixture of molecular weights</td>
<td><img src="image6" alt="Monomer" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Linear polymer</th>
<th>Molecular weight</th>
<th>Monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVP</td>
<td>10 kD, 40kD and 360 kD</td>
<td><img src="image7" alt="Monomer" /></td>
</tr>
<tr>
<td>Poly Acrylic Acid</td>
<td>50 kD</td>
<td><img src="image8" alt="Monomer" /></td>
</tr>
<tr>
<td>Polypyrrole (PPy)</td>
<td>Random mixture of molecular weights</td>
<td><img src="image9" alt="Monomer" /></td>
</tr>
<tr>
<td>Polyaniline (PANi)</td>
<td>Random mixture of molecular weights</td>
<td><img src="image10" alt="Monomer" /></td>
</tr>
</tbody>
</table>
To wrap the SDS-suspended nanotubes in a linear polymer, such as PVP, the polymer was added at 1% of the volume weight of SDS/SWNTs decant and stirred for 24 hours. For biological or conducting polymers, the SDS-suspended SWNTs were dialyzed in H₂O with either 10:1 biological polymer to SWNT by weight or conducting polymer added at 0.1% by volume weight. Excess polymer was removed from all polymer-suspended solutions, by a tangential flow filtration system.

7.2.3. Sample analysis:

7.2.3.1. UV-Vis-NIR

The individualized SWNT surfactant suspensions were characterized by absorption spectroscopy. The UV-Vis-NIR (Ultra Violet-Visible-Near Infrared) absorption spectrum was taken from 1400 nm to 190 nm in H₂O and 1800 nm to 190 nm in D₂O. The van Hove singularities were much sharper and more resolved than before the centrifugation step (fig 14).
Figure 14. Comparison: before and after centrifugation The individualized SWNTs are much better defined. The tubes before centrifugation have features that are more red-shifted and so broadened that little structure can be discerned. We attribute this broadening to interactions between bundled tubes in side-by-side van der Waals contact (9).

Several surfactants were examined to find the best one for the spectroscopic characterization of nanotubes. Several surfactants were selected: sodium dodecyl sulfate (SDS), which is anionic; dodecyl tetra ammonium bromide (DTAB), which is a cationic; Sarkosyl, which is a zwitterionic surfactant; and Brij-23, which is a dodecyl chain attached to a polyethyleneoxide chain (23 units long). Absorption spectra for three of these surfactants are shown in figure 15. SDS gave the sharpest and most blue shifted spectrum of all surfactant systems, demonstrating that SDS provided the least perturbing environment for the nanotubes.
Figure 15. Comparison of surfactant suspended SWNTs in D$_2$O

As discussed in section 7.4.1, the UV-Vis-NIR absorption spectral features for nanotubes are electronic transitions. The semiconducting tubes have their first valence band to conduction band transition, at energies denoted $E_{11}$ in near IR region in the 800 – 1600 nm wavelength range. The second van Hove transition, with energy denoted $E_{22}$ for the semiconducting tubes falls in the 550 – 900 range, which overlaps some of the $E_{11}$ transitions. The lowest energy van Hove transitions of the metallic tubes are between 400 and 600 nm, that overlap some of the $E_{22}$ and $E_{33}$ semiconductor transitions. Thus, the absorption spectrum for a prepared decant sample is a linear combination of individual SWNT spectra. If the nanotubes are present as individuals inside of a nonperturbing micelle, then the deconvoluted spectrum should contain peaks from distinct electronic transitions from each nanotube species with a peak width on the order of $kT$ in the first van Hove region (i.e. the energy available at room temperature: $\sim 0.025$ eV or 200 cm$^{-1}$)
at full width at half maximum (FWHM), as was found to be the case with the SDS/SWNT decanted material.

The pH of the solution was found to have an effect on the absorption spectrum of SDS suspended tubes (see fig. 16), but had no effect on DTAB, Brij-23 or PVP suspended tubes until a very low pH of ca. 1 was reached (pH effect is discussed further in fluorescence section). The SDS micelle is negatively charged, so it attracts protons in low pH solutions creating an effectively lower local pH in the vicinity of the SWNT. The other surfactants do not electrostatically attract protons and thus do not show the same effect as SDS.

![Graph showing the effect of pH on SWNT absorption spectrum in SDS/D$_2$O](image)

**Figure 16. The effect of pH on the SWNT absorption spectrum in SDS/D$_2$O**

I$_2$ (Iodine), when added to an aqueous SWNT suspension shows a similar effect to SDS suspended tubes at low pH. I$_2$ interacts with tubes suspended in any surfactant or
polymer as it does not have an ionic dependence (see fig 17). I$_2$ is expected to oxidize tubes by removing electrons. The I$_2$ effect was reversed and the absorption spectrum restored after the addition of acrylamide, which forms covalent bonds with I$_2$. The pH effect appeared to be a reversible oxidation. Later, it was discovered that oxygen was needed to mediate the “protonation” of nanotubes. In the absence of oxygen, no pH effect was observed. O$_2$ and other small molecules were previously reported adsorbed on SWNTs and could be photodesorbed by UV light (82, 108-114).

Figure 17. The plot shows the effect of iodine on the nanotube absorption spectrum. The tubes were suspended in SDS, then PVP with I$_2$ was added (loss of first van Hoves). The spectrum is recovered upon addition of bis-acrylamide, but is red shifted form the PVP (discussed below).
Absorption spectroscopy was then used to analyze SWNT samples under various conditions: SWNTs heated in air at 150°C to oxidize metal catalyst particles and amorphous carbon (i.e. "cleaned tubes") were compared to raw material; the competitive absorption of PVP polymer was monitored for SDS suspended tubes; and the effect of HiPeo reaction pressure, 30 atmospheres compared to 50 atmospheres, on the diameter distribution of SWNTs.

The absorption spectrum of the oxidized sample shows drastically reduced absorption in the first van Hove transition region. The oxidation process used to purify SWNTs (37) as described in section 3.6.1. apparently alters the electronic structure of the nanotubes by either introducing sidewall defects or by chemically functionalizing the sidewall of the tube.

Figure 18. Comparison of the van Hoves from air oxidized material (high pressure run 86) and raw material (high pressure run 87) suspended in SDS/H₂O
SWNTs suspended in SDS can be wrapped with PVP (or other polymer) by simply adding the polymer to the solution. The absorption spectrum red shifts (see fig 19) upon the addition of PVP, indicating a local environment change for the nanotubes. The polymer side group is a polar analog of DMF and NMP (section 4.3.1.); these molecules are amides. SWNTs appear to favorably interact with nitrogen containing groups such as amides and amines (83).

Figure 19. The absorption spectrum shows that addition of PVP to the SDS micelles causes the peaks to red-shift and broaden, reflecting a more polarizable and inhomogeneous environment.

The effect of HiPco reaction pressure on nanotube diameter distribution was monitored with absorption spectroscopy (see fig. 20). The average nanotube diameter was observed to change with pressure. The same (n,m) nanotubes were present in both samples, albeit at different concentrations.
Figure 20. The absorption spectra of two reactor batches, made at CO pressures of 50 and 30 atmospheres. The van Hove peaks in these two spectra match exactly in wavelength, but differ substantially in relative intensity. This indicates that the peaks arise from specific \((n,m)\) tubes common to both samples; smaller diameter tubes are more abundant in the higher pressure sample.

7.2.3.2. Fluorescence

Nanotube samples were examined by fluorescence spectroscopy and were found to be luminescent. The luminescence lifetime was on the order of a nano second and the quantum yield was estimated as 0.1 \%, so it was classified as a radiative decay from a singlet state: fluorescence. The fluorescence spectrum matched the NIR absorption spectrum, where the direct bandgap semiconducting nanotubes have their first van Hove transition, \(E_{11}\). There is a slight red-shift in the emission spectrum by \(~ 45 \text{ cm}^{-1}\) \((82)\), only a fraction of \(kT\). Therefore, the emission must be from the semiconducting nanotubes and the small spectral shift implies just minor geometrical differences between
the ground and excited states. The peaks of the deconvoluted emission spectrum have widths of about 0.025 eV, similar to the deconvoluted absorption spectrum. This structured NIR fluorescence is in contrast to previous studies involving visible luminescence from nanotube samples (56, 77, 103-105).

**Figure 21.** A comparison of the emission spectrum of SWNTs in SDS micelles in D2O following pulsed laser excitation at 532 nm to the overlaid absorption spectrum of the same sample almost match exactly.

The highest frequency emission peak at ca. 875 nm (1.42 eV) in Figure 22, originates from the E_{11} van Hove transition of the smallest diameter SWNT present in the HiPco sample. TEM and Raman studies show the smallest diameter tubes in these HiPco samples to be on the order of a buckyball in diameter ~ 0.7 nm. The 1.42 eV emission feature is higher in energy than predicted from prior STM/STS studies (see section 6.1.2.2.).
Fluorescence was used to characterize aqueous phase SWNTs under various conditions: the variation of fluorescence intensity with changing pH and nanotube bundling was examined, the effect of polymer wrapping, and the electronic transition energies corresponding to a particular type of bandgap semiconducting nanotube.

The SDS suspended tubes’ fluorescence is reduced at pH < 7 and continues to decrease monotonically until it is quenched at pH 3. The fluorescence is restored at pH 7 and enhanced, but constant at a pH of 8 and above. The larger diameter semiconducting SWNTs have the highest sensitivity to acidic conditions. Thus the sensitivity of the nanotube to pH is dependent on bandgap, as the bandgap decreases the sensitivity increases. The metallic SWNTs, which have no bandgap, should show the greatest sensitivity to pH changes, but cannot be examined by emission spectroscopy.

The direct bandgap fluorescence intensity is either dramatically reduced or eliminated by aggregation of the individually suspended nanotubes. Similar to the absorption spectrum, the emission spectrum is sensitive to the pH of the SDS micellar suspension. The reason fluorescence is quenched by bundling of SWNTs is the presence of a metallic tube. The excited semiconducting SWNT will transfer its energy to the metallic tube, which has a continuum of DOS and can lose the energy through vibrational modes.

Nanotubes wrapped with linear polymers such as PVP, in water or dried from a water solution with excess polymer ~10 by volume weight to form a solid film, show fluorescence intensities comparable to SDS-suspended samples. The PVP wrapped SWNT emission spectrum nearly identical to the absorption spectrum and is red shifted a slightly broadened relative to the SDS/SWNT spectrum.
Emission spectroscopy offers a way to characterize the electronic transition energies corresponding to each type of bandgap semiconducting nanotube present in a sample. The van Hove transitions $E_{11}$ and $E_{22}$ are absorption maxima for a given tube; thus if light is used to excite a particular tube at $E_{22}$, emission will occur at that tube's $E_{11}$. Emission intensity at a specific wavelength can be monitored as the excitation light is scanned over the $E_{22}$ region in increments.

The excitation spectrum for the 875 nm $E_{11}$ emission peak of the smallest semiconducting tube present in the sample shows a $E_{22}$ peak at 581 nm (fig. 22). The ratio of $E_{22} / E_{11}$ value for this nanotube is 1.51; this is in stark contrast to the value of 2.0 predicted by tight binding theory (115). Other emission results show that the $E_{22} / E_{11}$ ratio varies, but averages to a value ca. 1.7.

![Figure 22. The fluorescence excitation spectrum of the 875 nm van Hove emission feature.](image)
7.2.3.4. Raman

The Raman spectrum of the SDS suspended individual SWNTs was examined and the disorder peak was nearly absent, which indicates that the sonication used to disperse the tubes does not substantially damage the sidewalls. The breathing modes indicate tube diameters between 0.7 and 1.1 nm (82). Fluorescence was observed with a 785 nm and a 1064 nm excitation source.

![Raman spectra graph](image)

**Figure 23.** Raman spectra of nanotubes with 785 nm excitation source: Black trace) Homogenized SWNT sample in 1% SDS/H2O – no fluorescence, Red line) Homogenized and sonicated SWNT sample in 1% SDS/H2O before centrifugation – fluorescence peaks observed from 1100 cm\(^{-1}\) to 3500 cm\(^{-1}\), Blue trace) SWNT in 1% SDS/H2O after centrifugation – fluorescence intensity increased

7.3. Conclusion

Nanotubes have finally suspended in a liquid medium as individuals, without altering the original structural properties of the tubes. This enabled the discovery of a new
property: fluorescence, which will be a great help to characterizing the true nature of SWNTs. The individually suspended nanotubes can now be separated by methods previously unavailable and can be wrapped by polymer absorption to stabilize the suspension and give functional groups to the sidewalls of the tubes without changing their desirable properties.
8. Bibliography

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