Controlling the Structure and Properties of Carbon Nanotubes

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1.0 Overview and Introduction

Carbon nanotubes are a hollow, cylindrical form of elemental carbon that was discovered by Sumio Iijima in 1991 [1]. These carbon tubes are typically one to several nanometers in diameter and tens of microns in length, although nanotubes as long as several centimeters have been synthesized.

Nanotubes are considered both the stiffest and strongest materials known to man, and have Young's moduli and tensile strengths that are orders of magnitude greater than high-performance metals. Electrically, they are capable of ballistic (scattering-free) transport of electrons at very high current densities, as well as highly-efficient electron emission. Carbon nanotubes also are stable at high temperatures and have very high thermal conductivities. These properties make carbon nanotubes well-suited for a wide range of applications.

Some of these applications now are beginning to reach commercial maturity, with carbon nanotubes being used as probe tips for atomic force microscopes and as field emitters for next-generation displays. Increased control over the structure of carbon nanotubes will be required, however, before advanced nanotube-based electronic devices can take full advantage of nanotubes' remarkable properties. This structural control, which may be achieved by developing novel synthesis or extraction processes capable of producing or isolating nanotubes with uniform electrical properties, could enable the development of sophisticated nanotube-enabled computers, memories, or sensing devices. This report reviews the progress that has been made toward developing these processes, and provides a summary of the methods currently available for controlling or influencing the structure and properties of carbon nanotubes.

2.0 Physical Structure of Carbon Nanotubes

The carbon atoms in nanotubes are arranged in long, hollow cylinders. Although it is not physically accurate, these cylinders can best be visualized by imagining a sheet of graphite that has been rolled into a tube. Depending on how tightly the sheet has been rolled, one can easily envision tubes of different diameters. These tubes can also exist in a nested concentric arrangement, with a series of ever-smaller tubes contained within a large outer shell. This ensemble of nanotubes is collectively known as a multi-walled nanotube (MWNT), while an isolated tube of only one carbon layer is known as a single-walled nanotube (SWNT). MWNTs that are composed of only two layers are known as double-walled nanotubes (DWNTs). Examples of both SWNTs and MWNTs are shown in Figure 1.
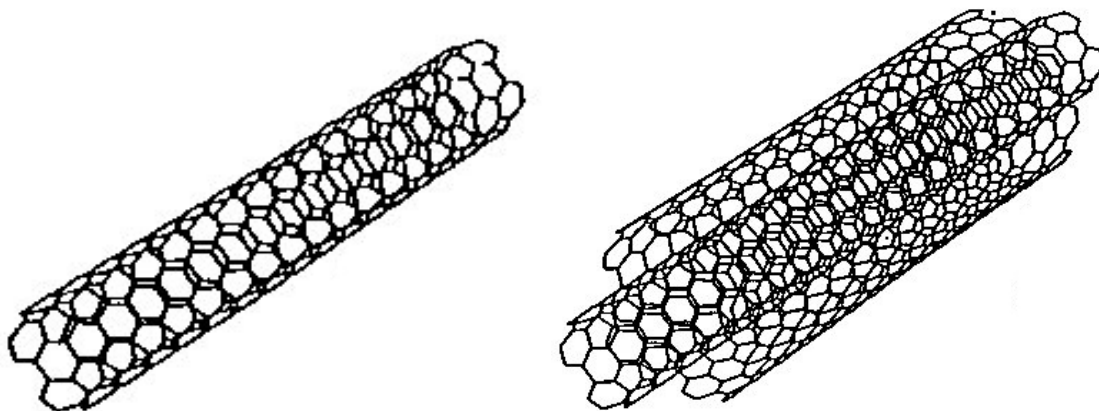
Figure 1. Single-walled (left) and multi-walled (right) carbon nanotubes.
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The angle at which the graphite sheet has been rolled imparts a characteristic "twist" to the structure of carbon nanotubes. This twist, known as the "chirality," can be represented by a chiral vector (n,m) that contains information on both the angle of twist as well as the diameter of the tube. The indices of this vector represent the number of unit vectors a_1 and a_2, relative to a graphite lattice, that define the diameter of an "unrolled" nanotube. These indices can also be used to find the diameter d, in angstroms, of a carbon nanotube

$$d = \frac{\sqrt{3}a_{C-C}}{\pi}\sqrt{m^2 + mn + n^2} \tag{1}$$

where $a_{c\text{-}c}$ is the carbon-carbon bond length of approximately 1.42 Å. Three examples of chiral vectors and their corresponding nanotubes are shown in Figures 2 and 3, respectively. The use of negative indices, while technically accurate, is not common practice, and this vector can be rotated about the origin to yield an equivalent chiral vector (8,2).

It should be noted that this relationship between the chiral vector and nanotube diameter assumes that the carbon-carbon bond length is the same constant 1.42Å found in graphite. In reality, however, the carbon-carbon bond in nanotubes is somewhat longer. Bonds in the direction of the tube axis are stretched by about 0.35%, and bonds in the direction of the tube diameter are stretched by 0.45% [2]. The exact length of each bond in a nanotube depends upon the chirality of the nanotube in question.

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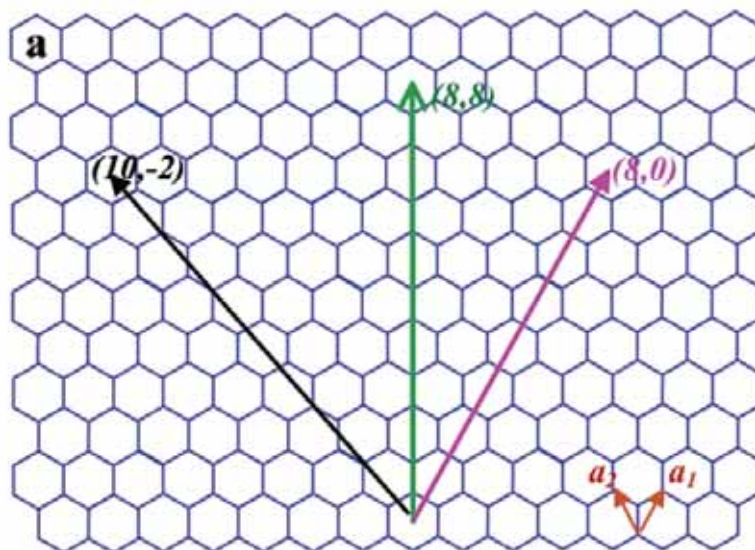
Figure 2. Graphite lattice shown with unit vectors and three chiral vectors [3].
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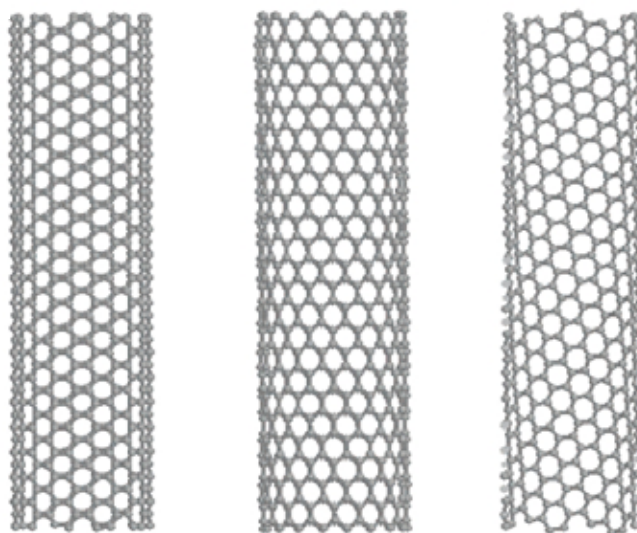
Figure 3. (8,8), (8,0), and (10,-2) single walled carbon nanotubes [3].
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In comparison to their mechanical properties, which are somewhat influenced by chirality but otherwise remain relatively consistent from tube to tube, the electrical properties of carbon nanotubes vary widely and are defined *purely* by chirality. Theoretical and experimental observations have confirmed that carbon nanotubes will act as metals or semi-metals when $|n - m| = 3q$, where q is an integer value. All other carbon

nanotubes will behave as semiconductors, with a band gap that is inversely proportional to their diameter. This also means that approximately one third of all carbon nanotubes within a random distribution will be metallic in character.

This important relationship between structure and electrical properties is the driving force behind the need for increased control over nanotube structure. For many applications it is important to use only nanotubes of a particular electronic type. It is therefore necessary to develop methods of controlling the structure of carbon nanotubes, in order also to control their properties.

3.0 Methods for Controlling the Structure of Carbon Nanotubes

The structure of carbon nanotubes can be examined in terms of three primary variables: morphology, length, and chirality. The morphology of a carbon nanotube describes its general structure, including the number of walls (SWNT or MWNT), as well as its shape (linearity, radius of curvature, etc).

Of the three structural variables, morphology is perhaps the easiest to control or influence. Synthesis processes have advanced sufficiently to allow one to selectively grow SWNTs, DWNTs, or MWNTs almost exclusively, thereby eliminating the need for post-synthesis morphological separation processes. This morphological discrimination can be achieved by altering reaction conditions such as precursor gas composition, catalyst composition and particle size, temperature, and atmospheric pressure and composition. Synthesis processes capable of morphological control are widely varied, well-established, and well-documented [4-9], and so will not be discussed here. This discussion will instead focus on techniques for separating carbon nanotubes by their length and electronic character (or metallicity), and will also address the manipulation of synthesis conditions to produce nanotubes of a desired structure. A summary of these techniques, including high-level assessments of their precision and scalability, is presented in Table 1.

3.1 Post-synthesis Separation of Carbon Nanotubes by Length

Some applications for carbon nanotubes – namely, those attempting to use nanotubes as reinforcing elements in composite materials or as continuous electrical conductors – require nanotubes of well-controlled and often extended lengths. The continuous refinement of synthesis processes in pursuit of controllable nanotube morphology has indeed resulted in nanotubes of ever-increasing lengths. Individual nanotubes as long as four centimeters have been synthesized, although lengths on the order of tens of microns are more common for large quantities of nanotubes. The manipulation of synthesis conditions to control nanotube length can vary widely and has been described in great detail [7, 10-13].

Table 1. Methods used to control the structure of carbon nanotubes

Chromatographic Methods	Structural Variable	Precision	Scalability	Section / Page
Size Exclusion Chromatography	Length	Poor	Poor	3.1.1 / 5
High Performance Liquid Chromatography	Length	Poor	Poor	3.1.1 / 5
Gel Permeation Chromatography	Length	Poor	Poor	3.1.1 / 5
Ion Exchange Chromatography	Diameter	Poor	Poor	3.2.3 / 11
Electrophoretic Methods				
Capillary Electrophoresis	Metallicity	Good	Average	3.1.2 / 5
	Length	Poor	Poor	
Alternating Current Dielectrophoresis	Metallicity	Good	Average	3.2.2 / 9
Gel Electrophoresis	Metallicity	Good	Poor	3.2.2 / 9
	Length	Poor	Poor	
	Diameter	Poor	Poor	
Dielectrophoresis Field Flow Fractionation	Metallicity	Good	Average	3.2.2 / 10
	Diameter	Poor	Average	
Fluid-based Methods				
Flow Field Fractionation	Length	Poor	Average	3.1.2 / 7
Nematic Liquid Crystal Extraction	Length	Poor	Average	3.1.2 / 7
Dielectrophoresis Field Flow Fractionation	Metallicity	Good	Average	3.2.2 / 10
	Diameter	Poor	Average	
Destructive Methods				
Current-induced Oxidation	Metallicity	Good	Poor	3.2.1 / 8
Fluorination and Annealing	Metallicity	Good	Good	3.2.1 / 8
Chemical Methods				
Amino Acid/Amine Adsorption	Metallicity	Good	Good	3.2.3 / 10
Photoelectrochemistry	Metallicity	Good	Average	3.2.3 / 11
Density-Gradient Ultracentrifugation	Metallicity	Good	Average	3.2.3 / 11
	Diameter	Average	Average	
Other Methods				
Phase Transfer Catalysis	Length	Poor	Average	3.1.2 / 7
Synthesis Variables				
Catalyst Particle Size	Diameter	Good	Good	3.4 / 13
Carbon Feed Rate	Diameter	Average	Average	3.4 / 14
Seeded Growth	Chirality	Unknown	Unknown	3.4 / 14
Specific Processes	Metallicity	Average	Good	3.4 / 14
	Chirality	Average	Good	

Some synthesis processes are capable of creating nanotubes of relatively uniform lengths; these processes, however, are not well-suited to large-scale production. Processes used to synthesize large quantities of nanotubes, on the other hand, can produce nanotubes of diverse lengths that may require additional processing if nanotubes of specific lengths are needed. This section will discuss methods for sorting or separating carbon nanotubes by their lengths.

3.1.1 Chromatographic Length Separation Techniques

One of the earliest examples of length discrimination of carbon nanotubes was actually the result of an attempt to remove soot and other impurities from as-synthesized multi-walled carbon nanotubes [14]. Research performed by Georg Duesberg and his colleagues at the Max Planck Institute for Solid State Research and the University of Dublin achieved length-based fractionation by subjecting water-dispersed MWNTs to size exclusion chromatography (SEC), a process that is commonly used to purify and analyze polymers or large biological molecules.

In SEC, a particle-containing liquid is introduced to and passed through a filtration column. The filtration column is packed with a porous medium with polydisperse pore sizes. In theory, larger particles are less likely to enter and interact with smaller pores, and should therefore traverse the filtration column more quickly. This can be observed experimentally by monitoring, over time, the sizes of the particles exiting the column. This principle has been used to purify and separate, on the basis of length, both MWNTs and SWNTs that were stabilized with a surfactant [15, 16].

Several other chromatographic methods have been used to separate carbon nanotubes by length. One approach, developed by Andrew Rinzler and his team at the University of Florida, used high performance liquid chromatography (HPLC), a pressure-fed variant of SEC, to separate cut, or shortened, surfactant-stabilized carbon nanotubes [17]. A different method used by Fotios Papadimitrakopolous's group at the University of Connecticut used gel permeation chromatography, an SEC variant that uses a porous gel as the filtration medium, to separate cut and functionalized SWNTs [18].

The stochastic nature of the particle-pore interactions, however, makes it difficult to predict the precise time that any given particle will exit the column. As a result, the product of chromatographic separation processes typically is a distribution of particle (and nanotube) sizes that resembles a Gaussian profile with a mean particle size and standard deviation that decreases with elution time [14] (see Figure 4). Ming Zheng and his colleagues at DuPont Central Research and Development have shown that serial HPLC processing of carbon nanotubes wrapped in single-stranded DNA can result in more sharply-defined nanotube length distributions [19]. However, chromatographic separation processes in general are not yet capable of extracting carbon nanotubes of specific lengths.
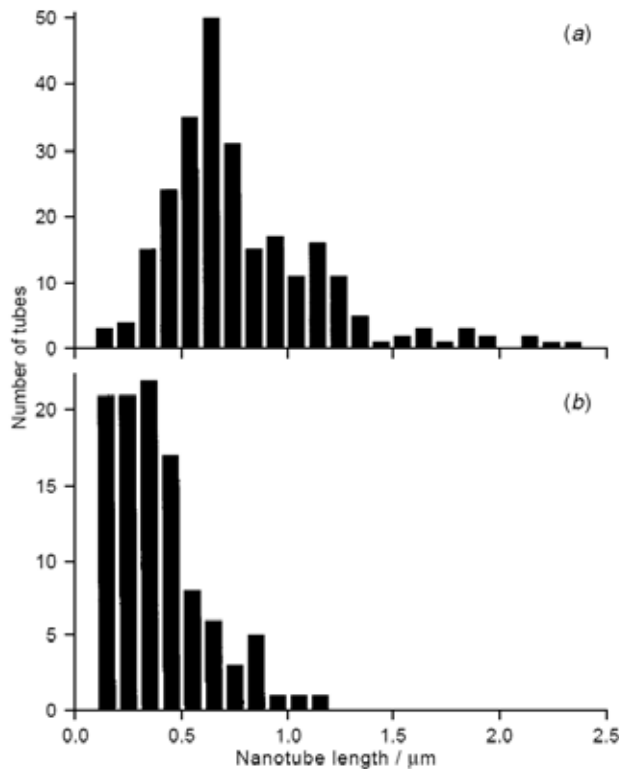
Figure 4. Length distribution of carbon nanotubes from early (top) and late (bottom) chromatographic elution fractions [14]. *Chemical Communications* **3, 435-436 (1998), reproduced by permission of The Royal Society of Chemistry.**

3.1.2 Other Length Separation Techniques

While electrophoretic processing is more commonly used to separate carbon nanotubes by their electrical properties, capillary electrophoresis (CE) also has been used to separate nanotubes by length. In most applications, CE is used to separate small ionic particles within an electrolyte-filled capillary by emphasizing differences in their size-to-charge ratios. Although Stephen Doorn and his team at the University of Kentucky did indeed propose that this principle could be used to separate carbon nanotubes by differences in their diameter and charge density [20], they instead achieved length-based separation using a different effect of CE.

In length-based separation of carbon nanotubes using CE, an electrostatic field is applied along the length of a fluid-filled capillary, and the outlet port is negatively charged with respect to the inlet. Carbon nanotubes within the fluid will tend to align themselves along the field lines parallel to the length of the capillary. However, Brownian motion and thermal agitation cause the alignment of the tubes to fluctuate, and shorter nanotubes experience greater fluctuations than longer tubes [20]. The longer nanotubes, therefore, experience lower hydrodynamic resistance and migrate more quickly toward the positively-biased inlet. The electro-osmotic counterflow of the entire

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solution toward the negatively-biased outlet, however, causes shorter carbon nanotubes to exit the capillary sooner [20]. Collectively, these two processes cause the length of the nanotubes exiting the capillary to vary as a function of time, with Gaussian length distributions similar to those discussed in section 3.1.1.

The application of a two-phase solution extraction process to selectively extract carbon nanotubes of characteristic lengths has also been demonstrated by researchers at Rice University led by the late Richard Smalley [21]. This was achieved by changing the concentration of a phase transfer catalyst – a chemical compound designed to promote migration of a solute from its original, compatible solvent phase into a second, otherwise-insoluble phase – in a nanotube-containing solution. Different length distributions of carbon nanotubes were able to be extracted from the insoluble phase at different catalyst concentrations.

Research performed by Bailin Chen and John P. Selegue at the University of Kentucky has shown that length-based separation also can be achieved using flow field-flow fractionation (FFF) of surfactant-stabilized, oxidatively-shortened MWNTs and SWNTs [22]. The operating principle of FFF relies on the viscous forces exerted on a suspended particle by a field applied perpendicular to the direction of flow. These forces will result in size-dependent differences in position, and therefore relative velocity, within a channel. Larger particles are expected to experience greater forces and be pushed to a region of lower flow velocity, and therefore will remain within the flow channel longer than smaller particles. Indeed, the mean length of nanotubes exiting an FFF channel has been found to increase as a function of processing time.

Recent efforts by Alan Windle and others at the University of Cambridge have demonstrated that nematic liquid crystals can be formed from dispersed multi-walled carbon nanotubes, and that these liquid crystals can be used for length fractionation of the nanotubes [23]. Differences in the mesogenicity, or affinity for the liquid crystalline phase, of the nanotubes leads to a relative enrichment of longer tubes with the crystalline phase and shorter nanotubes within the isotropic phase. Fractionated tubes can be extracted and re-processed to yield successively narrower length distributions within each phase.

3.2 Post-synthesis Separation of Carbon Nanotubes by Metallicity

Many processes have been developed that can discriminate between nanotubes of different electronic types, i.e. metallic vs. semiconducting nanotubes. Although we are not yet able to separate, extract, or produce carbon nanotubes with specific individual chiralities, both diameter and metallicity are related to chirality, and so these separation processes can be said to realize a sort of crude, chirality-based separation.

3.2.1 Destructive Separation Methods

The first reported separation of carbon nanotubes by their electrical properties was enabled by the selective and permanent destruction of metallic nanotubes from a mixed sample. Investigators at IBM's T. J. Watson Research Center, led by Phaedon Avouris, observed that when a large current was passed through a bundle or mat of carbon nanotubes, current-induced defect formation led to the rapid oxidation and destruction of the nanotubes [24]. However, the application of a gate voltage was used to deplete the charge carriers within the semiconducting nanotubes, thereby shutting off the flow of electrons and preventing these tubes' oxidation. Some metallic nanotubes also escaped destruction as a result of their containment and isolation within a larger bundle of semiconducting tubes.

More recently, a process capable of removing 100% of the metallic nanotubes from a mixture was developed in Hongjie Dai's lab at Stanford University [25]. Treatment of as-synthesized nanotubes using a low-temperature methane plasma was found to selectively destroy metallic nanotubes as well as all nanotubes with diameters outside of the range of 1.0 – 1.3 nanometers. Additional experiments using hydrogen plasma also showed diameter-dependent nanotube destruction, but did not consistently eliminate nanotubes of a particular metallicity. A large, multi-institutional team of Korean researchers has also shown that the fluorination of carbon nanotubes, when followed by an annealing step, is capable of a similar diameter-dependent elimination of metallic nanotubes [26].

3.2.2 Electrophoretic Separation Methods

Electrophoresis and its variants are among the most straight-forward techniques capable of differentiating nanotubes by their electronic character. These processes take advantage of the differences in the magnitude and direction of the electrophoretic forces experienced by particles with high (metallic nanotubes) and low (semiconducting nanotubes) dielectric constants.

Electrophoretic separation of carbon nanotubes was first demonstrated by Ralph Krupke and his team at Forschungszentrum Karlsruhe and Karlsruhe University. In this work the researchers used alternating current (AC) dielectrophoresis (DEP) to preferentially deposit metallic nanotubes onto an electrode array, while the semiconducting tubes remained in solution [27]. This is shown schematically in Figure 6. Later work showed that the AC frequency plays a critical role in determining the direction of the electrophoretic force on surfactant-stabilized nanotubes, with high frequency AC-DEP enabling separation by metallicity, and low frequency AC-DEP enabling "site-selective deposition of either tube type" [28]. This work also predicted that dielectrophoresis could be used to fractionate nanotubes based on their length and diameter. Further investigations by Michael Strano and others at the University of

Illinois identified a dependence between the choice of surfactant and the ability of DEP to differentiate between tubes of different metallicities [29, 30].
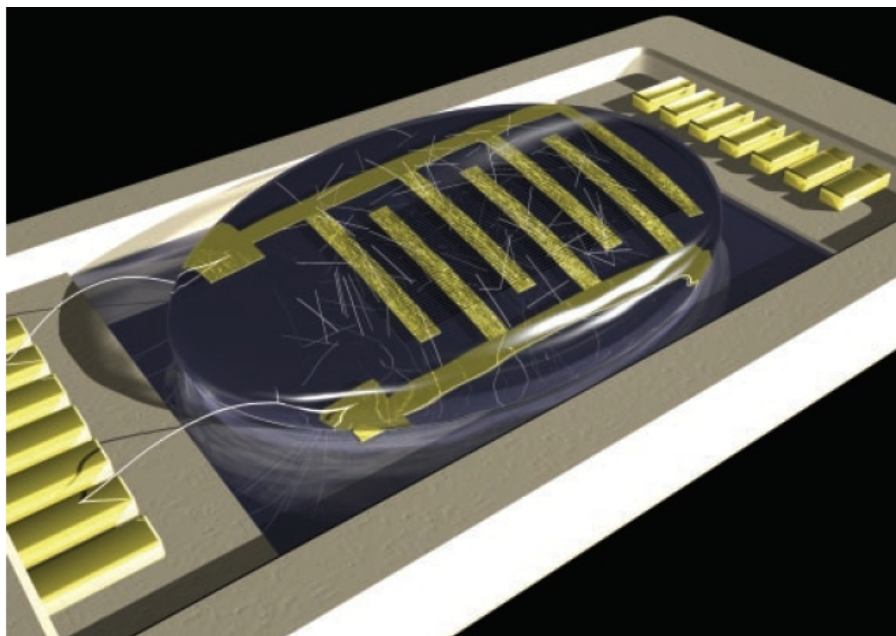

Figure 5. Dielectrophoresis of carbon nanotubes. Semiconducting nanotubes (white) remain in solution, while metallic nanotubes (black) are deposited on electrode array [27]. Reprinted with permission from Science 301, 344-347. © 2003 AAAS.

Additional research performed, in part, by Ray Baughman and Stephen Levene at the University of Texas at Dallas showed that gel electrophoresis, a technique commonly used in the biological and genetic sciences for analysis of macromolecules, could also be applied to carbon nanotube fractionation [31]. The addition of a nucleic acid coating to carbon nanotubes introduces a surface charge, and the nanotubes are driven through an agarose gel by the application of a potential. It has been observed that semiconducting nanotubes have higher electrophoretic mobilities than their metallic counterparts, and that shorter tubes migrate through the gel more quickly, as well. The electrophoretic mobility has also been shown to depend on nanotube diameter [31, 32].

Most recently, Howard Schmidt and his team at Rice University combined dielectrophoresis with field-flow fractionation to achieve separation according to metallicity as well as diameter fractionation [33]. Metallic nanotubes accumulated on the electrodes, while the semiconducting nanotubes exiting the flow chamber were observed to fractionate according to their diameter. Since the bandgap of semiconducting nanotubes is inversely related to their diameter, such a separation process may be useful in the eventual development of nanotube-based nanoelectronic devices.

3.2.3 Chemical Methods

Chemically-based separation processes have been demonstrated that use differences in the reactivity or chemical affinity of certain nanotubes to enhance their solubility, density, or other physical properties. These processes have been most successful at differentiating carbon nanotubes by their metallicity [34]. It also has been observed that the reactivity of carbon nanotubes is inversely proportional to their diameter due to the increased bond strain caused by the smaller radius of curvature, thus also enabling a degree of diameter-based separation [35].

Several of these chemical modification processes exploit the preferential absorption of amines to semiconducting or metallic nanotubes to enhance some aspect of the reaction. One such process, developed by Papadimitrakopolous and his team., involves treating a nanotube-containing solution with octadecylamine (ODA, a solublizing/functionalizing agent), followed by an amine-destabilization step that disrupts the weaker adsorption of ODA to metallic nanotubes [36]. This leads to the precipitation of the now-insoluble metallic nanotubes, while semiconducting nanotubes remain in solution.

Papadimitrakopolous later showed that this amine-assisted separation of metallic from semiconducting tubes was even more dramatic in nanotubes with diameters smaller than one nanometer [37]. Further research has shown that different amines can also be chosen to promote enrichment of either semiconducting or metallic nanotubes [38]. Other studies have attempted to identify the underlying mechanisms responsible for the metallicity-selective interactions of amines with carbon nanotubes [39].

A similar process developed by Rinzler's team utilizes the tendency for bromine to preferentially form charge-transfer complexes with semiconducting nanotubes [40]. The addition of bromine atoms to the carbon structure increases the density of semiconducting tubes, which are then precipitated during centrifugation. Although the separation efficiencies for these, and other, solution-based separation techniques may not be 100%, they are generally well-suited for scaling and may be used to separate larger quantities of carbon nanotubes.

Additional work by Rinzler, Zheng, and others has shown that single-stranded DNA (ssDNA) not only can act as an effective dispersant for carbon nanotubes, but also can be used to separate nanotubes on the basis of metallicity [41] and diameter [42, 43]. Separation by metallicity has been achieved through ion exchange chromatography, where differences between the surface charges of ssDNA-wrapped metallic and semiconducting nanotubes lead to differences in their chromatographic mobility [41]. Diameter differentiation has been achieved, as well, through ion exchange chromatography, where a gradual increase in nanotube diameter can be observed in processed samples [43].

It has also been suggested that metallic nanotubes can be enriched through a photoelectrochemical process. A patent held by the Intel Corporation suggests that when a mixture of metallic and semiconducting SWNTs is treated with a strong acid, the metallic tubes are cathodically protected while the semiconducting SWNTs are dissolved [44]. The application of photon energy can be used to further promote this metallicity-specific dissolution.

Finally, recent experimental results from Hersam's group at Northwestern University have shown that carbon nanotubes can be independently separated by their metallicity or fractionated by their diameter by using carefully-selected surfactants to disperse them prior to centrifugation [45]. The surfactants introduce subtle variations in density to the suspended nanotubes, and these differences in buoyancy can be emphasized through ultracentrifugation. In addition to separating metallic from semiconducting tubes with high selectivity, diameter distributions as narrow as >97% of nanotubes within ±0.01 nm were achieved. The results of this separation process can be seen in Figures 7 and 8.
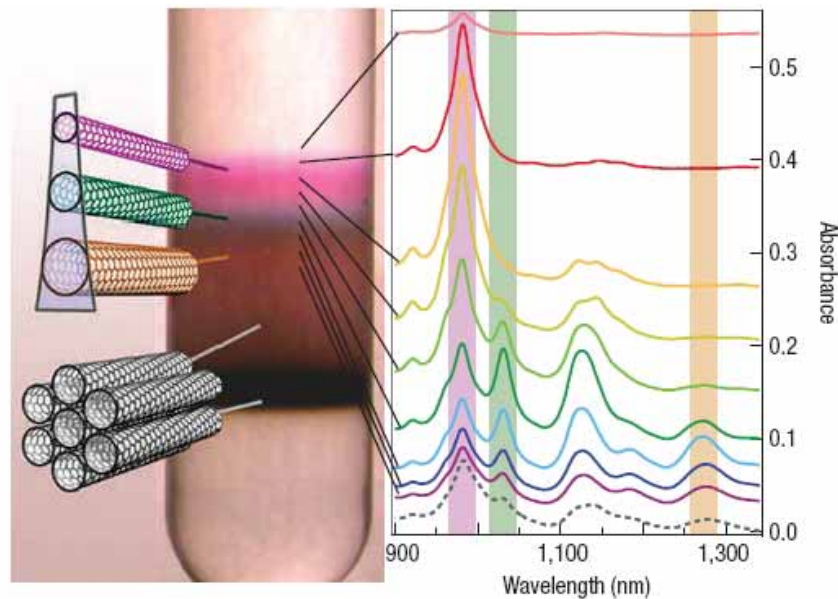

Figure 6. Diameter-based separation of carbon nanotubes by density-gradient centrifugation. Absorbance spectra show the gradual change in band gap within the sample, which can also be seen in the change in color [45]. Reprinted by permission from Macmillan Publishers Ltd: *Nature Nanotechnology* **1, 60-65. © 2006.**
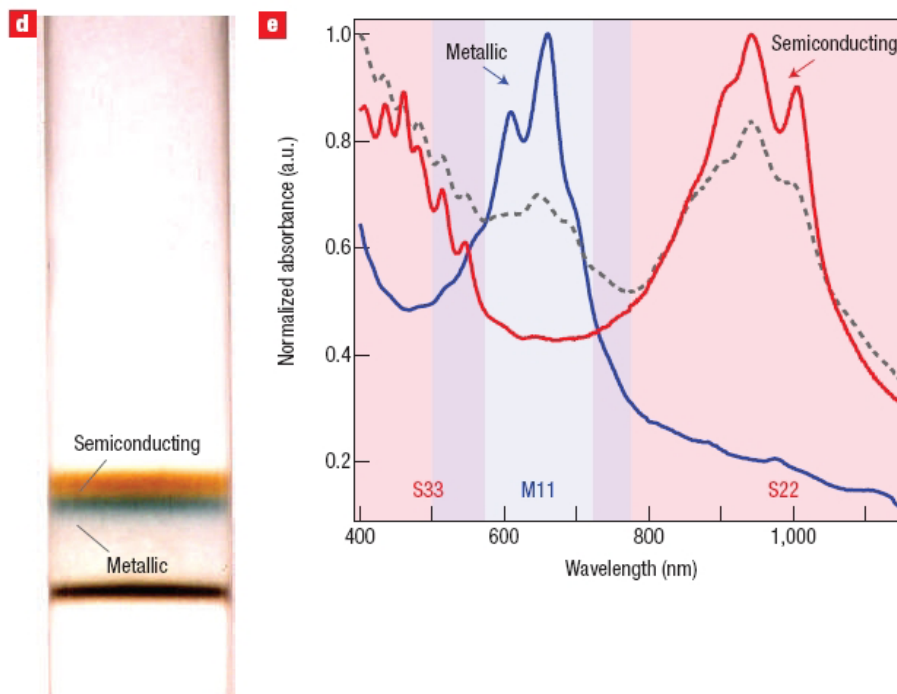
Figure 7. Metallicity-based separation of carbon nanotubes by density-gradient centrifugation. Absorbance spectra taken from different locations show differences in the relative quantities of metallic and semiconducting nanotubes [45]. Reprinted by permission from Macmillan Publishers Ltd: *Nature Nanotechnology* **1, 60-65. © 2006.**

3.3 Separation of Carbon Nanotubes by Chirality

Chirality is the most difficult, and arguably the most important, of the three structural variables to control. Many new applications could be enabled by the ability to obtain or produce carbon nanotubes with consistent and predictable electrical characteristics. Although separation of carbon nanotubes purely on the basis of chirality has not yet been achieved, some techniques for achieving this goal have been proposed.

Research has found that for many nanotube-material systems there exist chirality-specific minimum energy configurations. It has been predicted that carbon nanotubes deposited on a highly-oriented pyrolytic graphite surface should exhibit preferred orientations relative to the lattice of the graphite [2]. These preferred orientations are dependent on the chirality of the nanotubes, and arise from the physical similarities between the hexagonal carbon lattices of both materials. A separation process based on this orientation-dependent energy minimization, using graphite or other crystalline materials, could potentially be used to extract carbon nanotubes of a single chirality from a mixture [46].

The serial application of fractionation processes could also be used to separate carbon nanotubes on the basis of chirality. This fractionation could be brought about through a density-gradient centrifugation process [45] or through pH-dependent

protonation followed by electrophoresis [47]. It should be noted, however, that fractionation-based approaches will not immediately isolate specific nanotubes. Rather, the potential of these approaches lies in their prospective ability to refine nanotube samples, successively and continuously, until desired levels of purity have been reached.

3.4 Manipulation of Synthesis Conditions to Control Nanotube Chirality

There are many ways by which the output of carbon nanotube synthesis processes may be influenced. Templates can be used to influence nanotube shape, size, distribution, and alignment. Magnetic or electric fields may be applied to manipulate the growth direction. Catalysts can be lithographically patterned so that nanotubes grow only in specific, desired locations. However, only limited progress has been made in controlling the chirality or electrical properties of carbon nanotubes by varying the synthesis conditions. Synthesis processes have not yet been developed that allow us to predict the precise chirality or metallicity of the nanotubes that will be produced. However, processes have been developed that allow some control over carbon nanotubes' diameter, and research efforts dedicated to achieving complete chiral selectivity continue to approach this goal.

It has often been observed that the diameter of carbon nanotubes is influenced by the diameter and composition of the catalyst particles [48-50] used during synthesis [51]. The relationship between particle size and nanotube diameter for three different particle sizes is represented graphically in Figure 9. It is unlikely, however, that our control over catalyst particle diameter will ever improve enough to allow preferential synthesis of carbon nanotubes with a specific chirality [40]. This is because the difference in diameter between, e.g., a (10,10) metallic tube and a (9,11) semiconducting tube is only 0.003 nm. Moreover, thermal vibrations at the temperatures required for nanotube growth are not insignificant, and may further degrade any attempts at precision synthesis through diameter control.
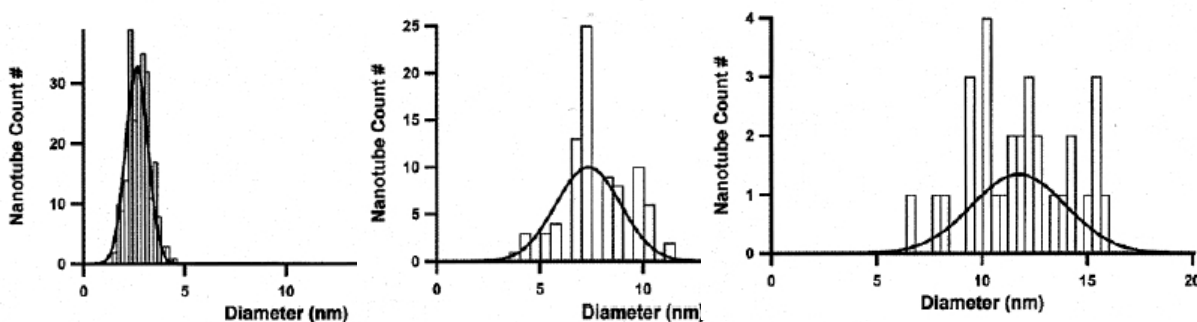

Figure 8. Distribution of nanotube diameter for average initial Fe catalyst particle sizes of 3 (a), 9 (b), and 13 nm (c) [49]. Reprinted with permission from *Journal of Physical Chemistry B* 106, 2429-2433. © 2002 American Chemical Society.

Some synthesis techniques seem to produce, preferentially, carbon nanotubes with certain electrical properties. Early analyses of carbon nanotubes produced by laser ablation done by Smalley's group suggested that metallic nanotubes are produced in larger-than-expected quantities [52], while Dai and his team found that some chemical vapor deposition processes appear to prefer semiconducting nanotubes [53, 54]. One such process has reportedly produced samples in which 90% of the carbon nanotubes exhibited semiconducting characteristics.

Interestingly, recent investigations have determined that the carbon feed rate in chemical vapor deposition processes can be used to influence the diameter of carbon nanotubes, even when the size of the catalyst particles is highly polydisperse [55]. Catalyst particles of sub-optimal diameter can be over-fed and poisoned, resulting in a growth-prohibiting layer of graphitic material. Large catalyst particles, on the other hand, do not reach the carbon concentrations necessary for the nucleation and growth of nanotubes. In this way the size range of active catalyst particles, and therefore the diameter of the nanotubes that will be produced, can be tuned.

Most synthesis processes produce nanotubes with a large number of different chiralities – as many as 50 different chiralities have been observed in nanotubes produced by high-pressure disproportionation of carbon monoxide (HiPCO) [56]. However, synthesis processes have been developed that predominantly produce nanotubes of only a few chiralities. Research from the lab of Daniel Resasco at the University of Oklahoma has revealed that approximately 50% of the semiconducting nanotubes grown using silica-supported Co-Mo catalysts (the CoMoCAT process) were of the (6,5) or (7,5) chirality [57]. Further investigations in which the growth temperature, gas composition (see Figure 10), and catalyst supports were systematically varied showed that the proportion and distribution of these chiralities could be controlled to some degree. In some cases the chiral angle was able to be preserved despite a change in the diameter of the nanotubes [58].

In a somewhat different approach to the problem of controlling the chirality of carbon nanotubes, research also has been conducted into duplicating and amplifying nanotubes of a known chirality or chiral distribution. Research at Rice University has recently shown that a single, short nanotube fragment can be used to seed the growth of a longer nanotube of the same diameter and surface orientation [59]. It has yet to be demonstrated, however, whether or not the seed-grown nanotube exactly matches the chirality of the seed fragment. Should this nanotube duplication process prove successful, the "cloned" nanotube could be broken apart and the fragments used to seed the growth of even more nanotubes.
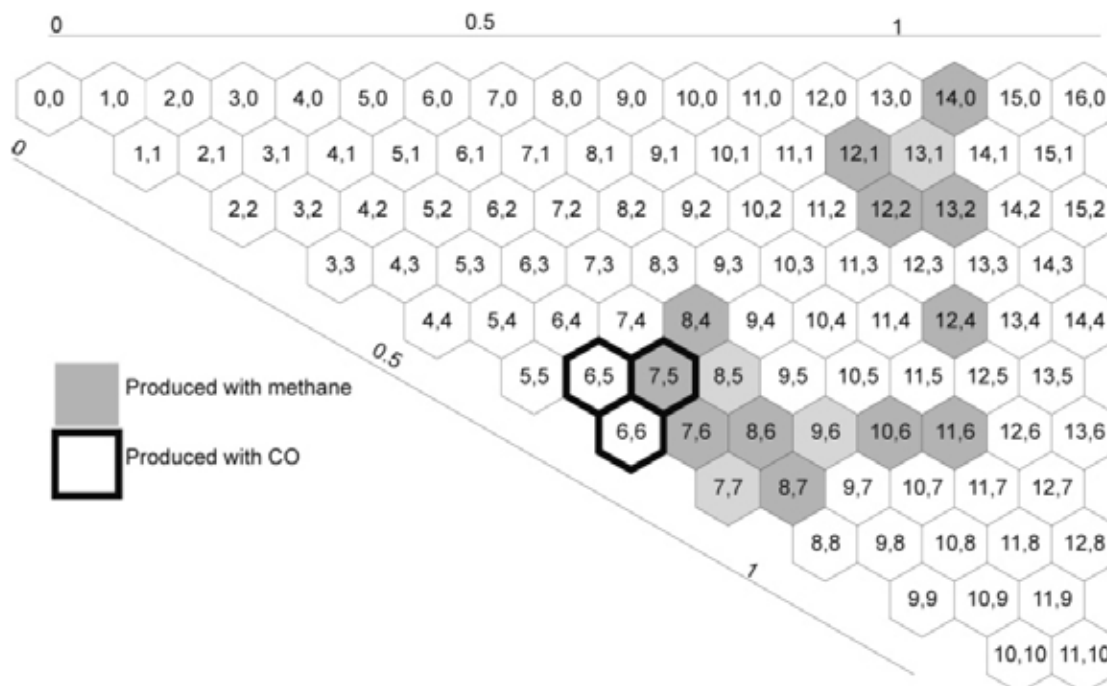
Figure 9. Chirality map showing effects of gas composition on nanotube chirality in CoMoCat-synthesized carbon nanotubes [58]. Reprinted with permission from Journal of Physical Chemistry B 110, 2108-2115. © 2006 American Chemical Society.

4.0 Assessing the Efficacy of Structural Control and Isolation

Carbon nanotube length is perhaps the easiest of the three structural variables to quantify, and is also not difficult to measure. Most electron and scanning probe microscopes, such as atomic force microscopes, scanning tunneling microscopes, and scanning electron microscopes, are capable of resolving at least the length, if not the diameter, of carbon nanotubes. Nanotubes need only be dispersed and deposited on a surface to allow the collection of length-related data. This can be achieved by suspending the nanotubes in a solution, applying the solution to a surface, and allowing it to evaporate. One can then image the surface and acquire statistical data concerning the lengths of the deposited nanotubes.

Surface-deposited samples also can be used to determine the tubes' metallicity through electron transport measurements. An electrode array can be patterned over the deposited nanotubes to establish electrical contact, although it is difficult to ensure that the electrodes will contact only a single nanotube and many of the electrodes will not form useful circuits. However, if a dilute nanotube solution is deposited over a large enough area, the number of single-nanotube devices can be increased significantly. These devices can then be used to characterize the tubes' electrical properties.

Raman spectroscopy is a technique that is commonly used to study carbon nanotubes. Monochromatic light is used to probe a sample of material, and the change in

wavelength of inelastically-scattered photons can be used to derive structural information. It is well-known that for a carbon nanotube the radial breathing mode (the radial resonant frequency of vibration) is inversely proportional to the diameter [60]. Measurement of this frequency can be used to assign (n,m) indices to individual nanotubes [56]. Raman spectroscopy can thus be used to assess the degree of structural control that has been achieved during synthesis or separation processes [32]. Scanning tunneling and transmission electron microscopy also can be used to identify the chirality of individual carbon nanotubes, but these procedures are elaborate and time-consuming, and are not well-suited to large-scale evaluations.

5.0 Summary

In order to take advantage of the unique electrical properties of carbon nanotubes it is first necessary to develop a reliable means of extracting or producing nanotubes with homogeneous physical, and thus electrical, characteristics. As carbon nanotube R&D has matured, processes have been developed that are capable of separating carbon nanotubes on the basis of length, diameter, and metallicity. Chromatographic separation techniques, in particular, are well-suited to generating length-fractionated solutions of carbon nanotubes, and electrophoretic processes are capable of separating and fractionating carbon nanotubes on the basis of both diameter and metallicity. Processes leveraging minute differences in the reactivity of specific nanotubes also have been developed and shown to effect separations. A recently-developed process based on density-gradient ultra-centrifugation of surfactant-stabilized nanotubes, in particular, is a promising candidate for the eventual realization of chiral separation.

Synthesis processes have also undergone continuous refinement and are now capable of producing nanotubes of only a handful of chiralities. These advances have been achieved through improved control of the size, shape, distribution, and composition of catalyst particles, as well as through careful selection and tuning of reaction conditions. Preliminary results have recently suggested that it may even be possible to clone carbon nanotubes, thus preserving the distribution of chiralities within a sample.

Although none of these advances has yet achieved the ultimate goal of producing carbon nanotubes of a single chirality, progress continues to be made. It may be that several processes could be combined in series in order to produce nanotubes of controlled and well-defined properties. This area of research remains an active one, and bulk quantities of such nanotubes may well be available commercially within five to ten years.

6.0 Acknowledgements

7.0 Glossary of Terms and Acronyms

AC-DEP – Alternating Current Dielectrophoresis

As-synthesized – the state of a material immediately following its creation, prior to any additional purification or processing steps.

CE – Capillary Electrophoresis

CoMoCat – Cobalt Molybdenum Catalyst, a process for synthesizing carbon nanotubes

DEP – Dielectrophoresis

Elution – the process of extracting an adsorbed substance by washing it with a solvent. The solvent is called the eluent, and the solution of the solvent and the desired substance is called the eluate.

FFF – Field Flow Fractionation

Fractionate – to separate into ingredients or into portions having different properties

HiPCO – High Pressure Disproportionation of Carbon Monoxide, a process for synthesizing carbon nanotubes

HPLC – High Performance Liquid Chromatography

MWNT – Multi-Walled Carbon Nanotube

Nematic – of or relating to the oriented (non-random) phase of a liquid crystal

ODA – Octadecylamine

Protonate – to add protons to

SEC – Size Exclusion Chromatography

SWNT – Single-Walled Carbon Nanotube

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