Structure and Applications of Single-Walled Carbon Nanotubes (SWCNTs) Synthesized Using the CoMoCAT® Method

Daniel Resasco, Ph.D.
D. and H. Bourne Chair and George Lynn Cross Professor
School of Chemical, Biological and Materials Engineering
University of Oklahoma

Ricardo Silvy, Ph. D.
SouthWest Nanotechnologies
2501 Technology Place
Norman, OK 73071-1102

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Structure

The unique properties of single-walled carbon nanotubes are a direct result of their distinctive structure, which is composed of C-C bonds more closely related to those in graphite than to those in diamond. That is, while diamond has a coordination number of four with sp^3 hybridization, graphite involves three-coordinated carbons, in which three electrons are in sp^2 hybridization and one is delocalized. Fullerenes and nanotubes also have carbon bonds with sp^2 hybridization such as graphite, but unlike the graphite structure, which is made up of flat planar honeycomb, the structures of fullerenes and nanotubes involve a high degree of curvature.

The intrinsic strength of the sp^2 carbon-carbon bonds and the special structure of nanotubes result in high mechanical strength and a very large Young's modulus (values near 1,000 GPa have been predicted or measured on individual nanotubes, which is around 50 times higher than the modulus of steel). Depending on their geometric structure, they can either be metallic or semiconducting since , slight changes in the geometric configuration can result in significant changes in electronic structure. This offers materials scientists the opportunity to design -- at the nanoscale -- the best material for each specific application.

As illustrated in **Figure 1**, a single-walled carbon nanotube (SWNT) is a seamless cylinder with a diameter in the nanometer range that can be visualized as a rolled up sheet of graphene (i.e. two-dimensional graphite plane). The structure of any given nanotube is determined by its diameter and the relative orientation of the carbon hexagons with respect to the axis of the tube. Consequently, each SWNT is uniquely identified by two indices, n and m, which are the two integers that determine the chiral vector (also known as “wrapping vector”) in terms of the primitive vectors of the hexagonal lattice (a_1 and a_2). The chiral vector $C_h = n\,a_1 + m\,a_2$, connecting two crystallographically equivalent sites on a graphene sheet, determines the circumference of the nanotube’s circular cross-section.

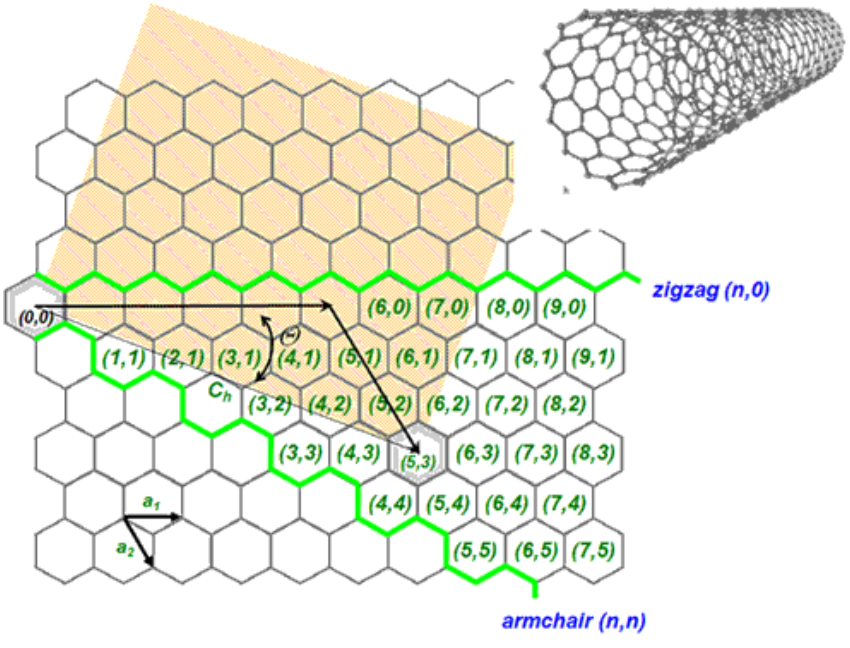

Figure 1. Schematic to show the chiralities of SWNTs based on the relative orientation of the carbon hexagons with respect to the orientation of the nanotube.

Starting at the (0,0) site on the plane, the (n,m) point is reached by moving n units in the a_1 direction and m units in the a_2 direction. Connecting (0,0) and (n,m), the chiral vector Ch is generated, and if a semi-infinite rectangle with base C_h is cut and wrapped, the (n,m) nanotube is obtained. The angle that is formed between the vectors C_h and a_1 is called the chiral angle. It ranges between 0 and 30° for all the possible structures that vary from zigzag (m= 0, angle = 0) to armchair (n=m, angle = 30°). All other nanotubes with chiral angles between 0° and 30°, are known as chiral nanotubes because their mirror images are not identical, and therefore, they have enantiomeric pairs. The diameter of a nanotube can be calculated from its (n,m) indices according to the following expression:

$$d = a_0 \bullet (m_2 + mn + n^2)^{1/2}/\pi \qquad \textbf{(1)}$$

Where a_0 is the atomic lattice constant (= 0.246 nm).

Similarly, the chiral angle (Θ shown in **Figure 1**) can be calculated in terms of the (n,m) indices according to the following expression:

$$\tan \Theta = (n \sqrt{3}) / (2m + m) \qquad \textbf{(2)}$$

Electronic and Optical Properties

Theoretical calculations of the electronic band structure of single-walled carbon nanotubes have predicted that nanotubes can be ***metallic*** or ***semiconductor*** in nature depending on their (n, m) indices. The nanotube will be metallic whenever the density of states (DOS) at the Fermi level is non-zero and it will be semiconducting when there is a band gap at this energy level. In a graphene plane, each C atom is connected to other C atoms via an sp^2 planar bond, which comprises of three σ bonds formed from the hybridization of the 2s, $2p_x$ and $2p_y$ orbitals, while the remaining $2p_z$ orbital, pointing perpendicular to the graphene plane, generates covalent π bonds by overlapping with the $2p_z$ orbitals of the neighbor C atoms. The energy of the system formed by the more stable σ bonds has a lower energy than that of the system formed by the π bonds. As a result, the energy bands for the π system lie in the region of the Fermi level. Therefore, the π system plays a major role in determining the electronic transport properties.

In a first approximation, a direct analysis of the π system indicates that either when n=m (i.e., armchair) or when (n-m) is a multiple of 3, the DOS at the Fermi level is non-zero and the nanotubes are metallic. In fact, a closer analysis taking into account the curvature of the tube has shown that mixing of the *π* system with the *σ* system for both the bonding and anti-bonding orbitals can slightly alter the original picture and instead of a non-zero DOS at the Fermi level, these calculations revealed the presence of small gaps.[1] The magnitude of these gaps decreases as the tube diameter increases. However, in the case of (n,n) tubes, this gap remains on the sub-band of the nanotube, so they are considered to be metallic.

Synthesis of SWNTs with Controlled Structures using the CoMoCAT® Process

For large-scale production of nanotubes, the use of a particulate, high-surface area catalyst is very advantageous. In a typical supported catalyst, the active species (e.g. a metal cluster) is stabilized in a high state of dispersion over the surface of a refractory support such as alumina, silica or magnesia. This catalyst type is similar to those used in the chemical and petrochemical industry in the production of polymers, fuels, solvents, etc. One of the key advantages of using supported catalysts is that the engineering aspects of the possible reactor designs (fluidized bed, fixed bed, transport bed, rotary kiln, etc.) are well-known in industry and scaling-up is a mature technology.

It is widely recognized that in an unrestricted state (e.g. during laser ablation) the growth rate of single-walled carbon nanotubes is at least higher than several microns-per-second. By contrast, when the growth occurs via catalytic decomposition of carbon-containing molecules on high surface-area catalysts, the overall growth process continues in a scale of minutes to hours. It is clear that while the amount of carbon deposits slowly increases with time, this does not necessarily mean that the growth of a given nanotube is that slow. That is, the slow rate observed for the overall rate of carbon deposition comprises an induction period followed by a fast nanotube growth rate. Accordingly, new nucleation sites will appear on a high-surface area material and

each site will give rise to a nanotube that grows relatively fast. The nanotubes that grow later will be constricted by the presence of those grown earlier.

To have a high selectivity towards SWNT, nucleation of the nanotube embryo needs to occur before the metal particle sinters. Several approaches have been followed to avoid rapid sintering. The strategy used in the CoMoCAT® method is to keep the active Cobalt species (Co) stabilized in a non-metallic state by interaction with Molybdenum oxide (MoO_3) before it is reduced by the carbon-containing compound (CO). When exposed to carbon monoxide, the Co-Mo dual oxide is carburized, producing Molybdenum carbide and small metallic Co clusters, which remain in a high state of dispersion and result in high selectivity towards SWNT of very small diameter. Lower temperature syntheses and stabilization of small metal clusters yield a CoMoCAT® nanotube product with a smaller average diameter and a narrower distribution of structures compared to other synthesis methods.[2] The CoMoCAT® process utilizes fluidized bed reactors (**Figure 2**) to maintain precise control of the temperature and flow rates, resulting in high (n,m) selectivity.[3]

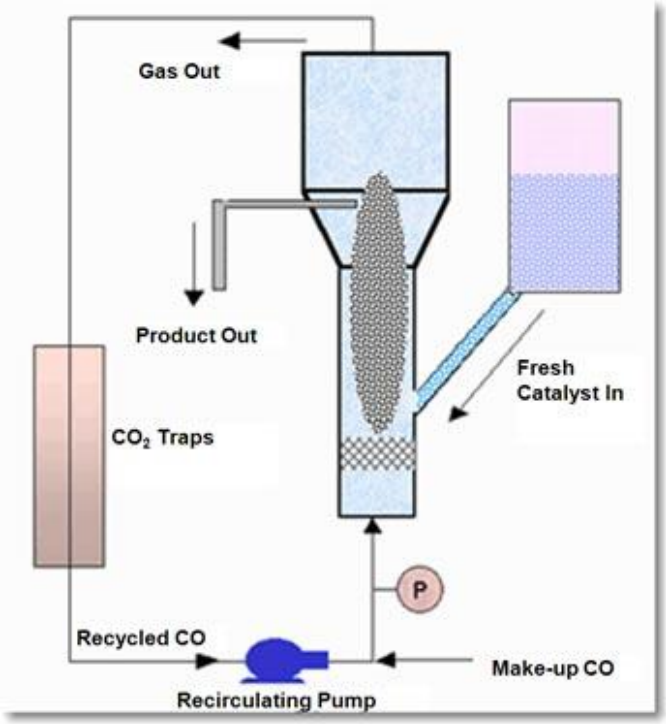

Figure 2. An illustration of a fluidized bed reactor, which is able to scale up the production of SWNTs using the CoMoCAT® process.

Characterization of the geometric and electronic structures of SWNT

In addition to the usual microscopy techniques such as TEM, SEM, and AFM typically employed in nanotechnology research, several techniques are particularly suitable for characterizing the geometric and electronic structures of SWNT. Structural information, electronic, and optical information about SWNT can be obtained from scanning tunneling microscopy and spectroscopy (STM/STS), Raman spectroscopy, optical absorption, and photoluminescence.

Optical absorption can be used to evaluate the distribution of (n,m) species in a given sample. The spectrum in **Figure 3** corresponds to a sample produced by the standard CoMoCAT® method at 725°C, which exhibits a high concentration of the specific (6,5) nanotube type and a narrow range of diameters and chiral angles (around 0.76 nm and 27 degrees, respectively). In this product, the concentration of semiconducting nanotubes is higher than 90%.[2]

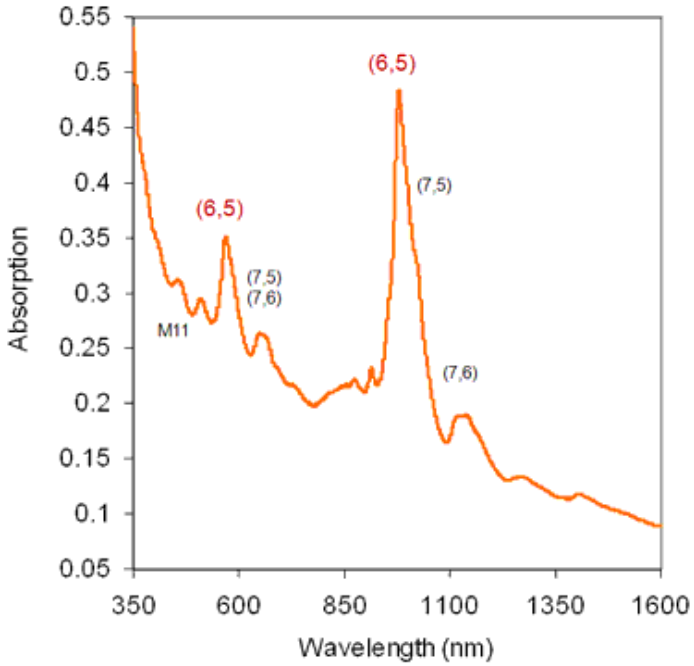

Figure 3. Optical Absorption Spectra showing the predominance of the (6,5) nanotube when the CoMoCAT® method is carried out at 725°C.

The spectrum shown in **Figure 4** corresponds to a sample obtained at 850°C on the same Co-Mo catalyst at varying pressures exhibits a broader range of diameters (0.75-1.22 nm) and chiral angles (19-30 degrees). In this sample, the metallic/semiconducting type ratio is close to the statistical ratio, that is 0.5.[4]

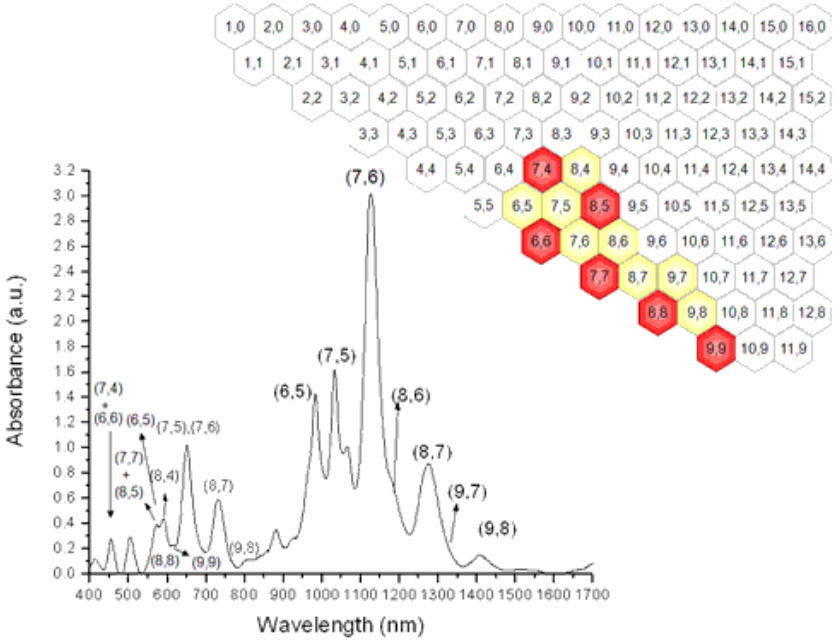

Figure 4. Optical Absorption Spectra showing a wider geometric range of nanotube materials when the CoMoCAT® method is carried out at 850°C and at various pressures.

Applications of SWNTs

Important applications of nanotubes have been extensively investigated during the last 10-15 years. A summary of the range of applications related to the specific properties where carbon nanostructure present a distinctive advantage is given in **Figure 5**. Some of these applications have advanced to become commercial products and others are still in the developmental stage.

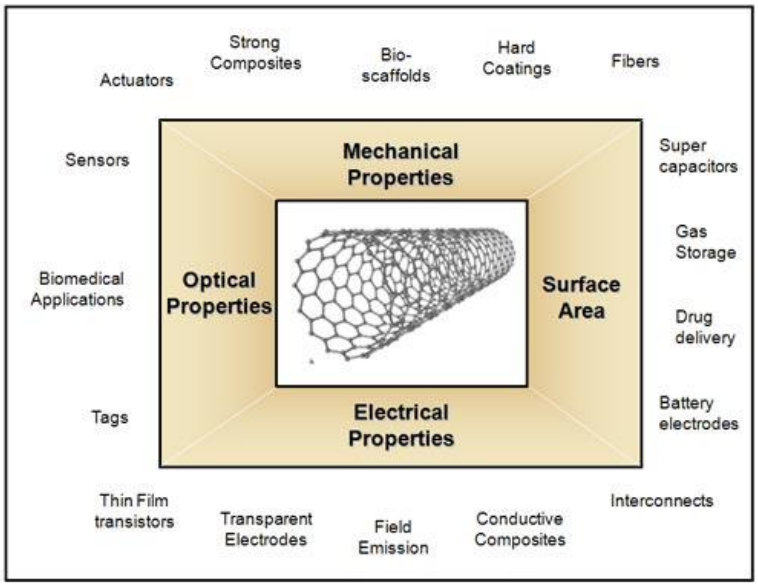

Figure 5. A chart to show the diversity of applications possible using the various attributes of carbon nanotubes.

It is expected that the cost and availability of nanotubes of consistent quality will soon become more in line with the industrial needs, and consequently the pace of development will greatly accelerate. Some of the most widely investigated applications include conductive and high-strength nanotube/polymer composites, transparent electrodes, sensors and nanoelectromechanical devices, additives for batteries, field emission displays and radiation sources, semiconductor devices (e.g. transistors) and interconnects.

CoMoCAT® carbon nanotubes available from Aldrich® Materials Science

Listed below are the high-purity carbon nanotubes produced using the CoMoCAT® method as described above. These products are manufactured by SouthWest Nanotechnologies, Inc. and are available in research quantities exclusively from Aldrich Materials Science.

Aldrich Prod. No.	SWeNT Product	Product Name	Features
704113	CG 100	Carbon nanotube, single-walled ≥70% (carbon as SWCNT), 0.7-1.3 nm diameter	• High purity single-walled carbon nanotubes • Uniform chiral distribution
724777	CG 200	Carbon nanotube, single-walled ≥90% (carbon as SWCNT), 0.7-1.4 nm diameter	• High purity single-walled carbon nanotubes • Large diameter • High metallic tube content

			• High electrical conductivity
704148	SG 65	Carbon nanotube, single-walled (6,5) chirality, ≥77% (carbon as SWCNT), 0.7-0.9 nm diameter	• High purity single-walled carbon nanotubes • Small diameter • Precise chirality and diameter control • >90% semiconducting character
704121	SG 76	Carbon nanotube, single-walled (7,6) chirality, ≥77% (carbon as SWCNT), 0.7-1.1 nm diameter	• High purity single-walled carbon nanotubes • Precise chirality and diameter control • Good conductivity
724769	SMW 100	Carbon nanotube, multi-walled 98% carbon, 6-9 nm diameter	• High purity multi-walled carbon nanotubes • Few-walled • Small diameter • Lower cost (compared to SWNTs)

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