

# Manufacturing, Characterization and Use of Single Walled Carbon Nanotubes



Richard Jansen and Philip Wallis\*  
SouthWest NanoTechnologies, Inc.  
2501 Technology Place  
Norman, OK 73071  
\*Email: pwallis@swentnano.com

## Introduction

Carbon nanotubes are materials that possess remarkable properties and offer extraordinary possibilities. This article gives a brief overview of the physico-chemical nature and characterization of single-walled nanotubes (SWNTs). We describe the current state of efforts to explore the SWNT promise and the status of their commercialization. Except for a brief introductory comparison, we do not cover their "cousins", the multi-walled carbon nanotubes (MWNTs).

Since their discovery in 1991 by Iijima<sup>1</sup>, single walled carbon nanotubes have stimulated a great deal of activity in both the global research community and industry, and have inspired much investment in manufacturing methods, characterization and application development. The reasons for this are quite clear, given the remarkable properties these materials possess and the diversity of distinct species, each with its own unique variations in those properties.

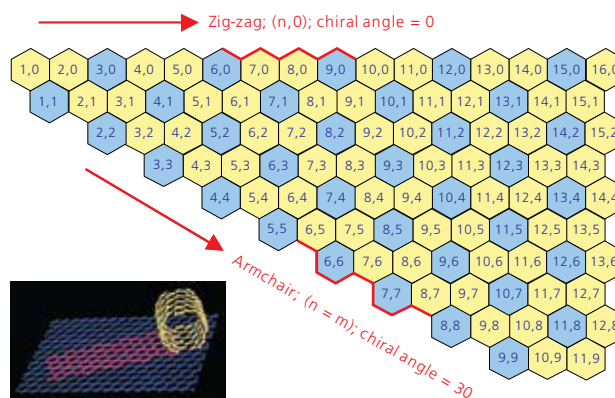
SWNTs and MWNTs share some similarities, but also striking differences. MWNTs can be thought of as a series of single walled tubes nested within one another. There may be as few as 2, or as many as 100 plus concentric walls. Their diameters may, therefore, be as great as 50nm as opposed to 0.7 - 2.0 nm for a typical SWNT. Only the outer wall generally contributes significantly to the electrical and mechanical properties of MWNTs when used in composites, for example, affording the opportunity for much lower loading of SWNTs versus MWNTs. Of the two carbon nanotube types, single walled nanotubes are the more remarkable. They have outstanding strength, can be highly electrically conducting or semiconducting, may be as thermally conductive at room temperature as any other known material, have a very large surface area per unit mass, and have unique optical properties. This range of unique properties has opened the doors to advances in performance in a wide range of materials and devices.

## Structure of Carbon Nanotubes

Single walled carbon nanotubes are an allotrope of  $sp^2$  hybridized carbon, similar to fullerenes. The structure can be thought of as a cylindrical tube comprised of 6-membered carbon rings, as in graphite. The cylindrical tubes may have one or both ends capped with a hemisphere of the buckyball or fullerene structure.

An understanding of SWNT structure requires familiarity with the concept of nanotube chirality, since the chirality of a SWNT dictates many of its properties. A concept known as a Chirality Map, illustrated in **Figure 1**, has been developed as a tool for understanding chirality and its implications.

A SWNT can be envisioned as a sheet of graphite one atom thick rolled into a tube (see inset in Figure 1). The chirality describes both the orientation and diameter to which the sheet is rolled. Each SWNT on the chirality map is defined by two integers,  $(n,m)$ . As indicated previously chirality defines many of the properties of the individual SWNT. For example, SWNT shown on the chirality map in blue are metallic in nature. These are tubes where  $n=m$  (armchair) or  $n - m = 3i$ , (where  $i$  is any integer.) Those depicted in yellow are semiconducting, displaying different band gaps depending on the length of the chiral vector.



**Figure 1.** A graphic displaying a Chirality Map which shows the various types of SWNTs that can be formed. The properties are governed by the way in which they are rolled as shown in the insert. The SWNT will be metallic in the armchair configuration, or when  $m-n$  is a multiple of 3.

## Unique Properties of Single Walled Carbon Nanotubes

### Mechanical

Individual SWNTs are significantly stronger than steel. Calculated values for tensile strengths of SWNTs are ~ 100 times greater than steel at 1/16th the weight. The highest measured value is approximately half of the predicted theoretical strength,<sup>2</sup> possibly due to defects in the structure.

### Electrical

Individual SWNTs, have current carrying capacities of  $10^9$  amp/cm<sup>2</sup>, higher than those of copper or gold,<sup>3</sup> and semiconducting species exhibit higher electron mobility than silicon.

### Optical

SWNTs have a distinct optical absorption and fluorescence response, with each chirality demonstrating its own characteristic absorption and fluorescence spectrum. In general, coating formed with SWNT are highly transparent in the visible and IR regions of the spectrum, making SWNT an ideal candidate to replace ITO as the transparent conductor of choice for applications such as displays, solar cells and electroluminescent lighting etc.

### Thermal

Room temperature thermal conductivity of a single nanotube may be comparable to that of diamond or in-plane graphite, which are generally thought to display the highest measured thermal conductivity of any known material at moderate temperatures.



## The Challenges of Single Walled Carbon Nanotubes (SWNTs)

Technical hurdles in the areas of purity, selectivity and dispersibility have so far limited the widespread application of SWNTs. Much recent progress has been made to address each of these obstacles.

### Purity

The various manufacturing processes used in the production of SWNTs lead to products which are contaminated to varying degrees with residual catalyst and other forms of carbon. For many applications, secondary processes are necessary to remove these contaminants to provide product of sufficient purity. More recently, methods of synthesis that minimize the 'as manufactured' impurities have become commercially available.

### Selectivity

As described earlier, the SWNTs are a mixture of tubes of different chiralities, some of which are electrically conducting and some are semiconducting. It is desirable, for many applications, to isolate the types of tubes from one another, such as metallic from semiconducting, and for some applications, tubes with well-defined individual chiralities (see previous section for an explanation of SWNT chirality). Laboratory scale methods designed to achieve a very high degree of selectivity have been reported,<sup>4</sup> and efforts to develop scalable processes are underway. In particular, manufacturing processes such as the CoMoCAT<sup>®</sup> catalytic CVD process have been shown to provide a substantial degree of selectivity toward certain chiralities in as-synthesized SWNTs, making the yield of secondary purification processes substantially higher.

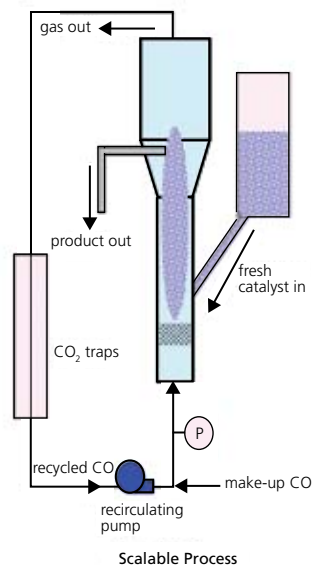
### Dispersibility

SWNTs can be difficult to disperse, partly because of their well-known tendency to form ropes or bundles due to natural Van der Waals attraction between the tubes. However, they can be dispersed in aqueous solutions with the aid of suitable surfactants either as small bundles or as individual tubes. Exfoliation of bundles can be achieved by sonication of aqueous solutions of SWNTs in the presence of surface active molecules such as DNA, sodium deoxycholate (**Aldrich Prod. No. D6750**) and sodium cholate (**Aldrich Prod. No. 270911**). To quantify the degree of nanotube exfoliation obtained in a given dispersion, Tan and Resasco<sup>5</sup> defined the concept of resonance ratio from the optical absorbance spectrum. The area of the resonant band divided by the area of the non-resonant background in this ratio allows easy comparison of results independent of the absolute absorption. Dispersants can then be ranked for their effectiveness using this parameter.

Additionally, dispersions of SWNTs in resins and thermoplastics is limited by a dramatic build up in viscosity caused by the entanglement of the SWNT bundles. Various proprietary methods exist to circumvent this problem, and new hybrid forms of SWNTs are being developed to address this issue.

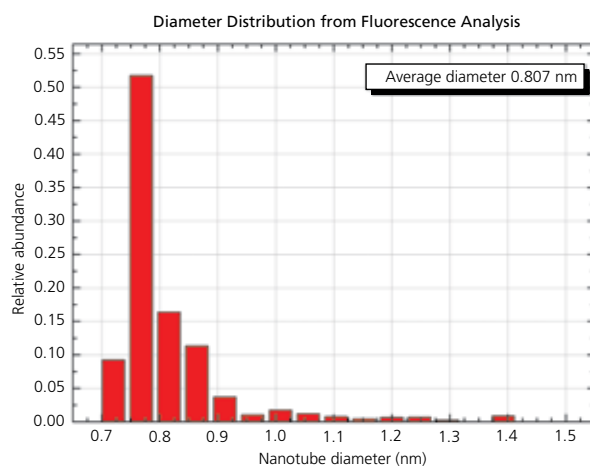
## SWNT Synthesis

Various methods have been used in the manufacture of SWNT. These include Laser Ablation, Carbon Arc and CVD processes, either involving a gaseous catalyst as in the HiPCo<sup>®</sup> process or using a supported catalyst as in the CoMoCAT process. The laser ablation process is used primarily for research materials. The Carbon Arc process produces long tubes with diameters in the range 1.4 to 2.0nm, but carbon arc material has a very large amount of impurity and for most applications will require extensive purification. The CVD processes offer the best approach to the manufacturing of larger SWNT quantities, with perhaps the most scalable being the CoMoCAT process which uses a fluidized bed reactor (**Figure 2**) similar to those used in petroleum refining, albeit, on a much smaller scale.



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

In this CoMoCAT method, SWNT are grown by CO disproportionation (decomposition into C and CO<sub>2</sub>) at 700-950°C in flow of pure CO at a total pressure that typically ranges from 1 to 10 atm. In a three-year research program of catalyst and reactor development, which included detailed characterization and testing of a large number of catalyst formulations and operating conditions, we developed a process that is able to grow significant amounts of SWNT in less than one hour, keeping a selectivity towards SWNT better than 90 percent. We discovered a synergistic effect between Co and Mo that is critical for the performance of the catalyst. The catalyst is effective when both metals are simultaneously present on a silica support with a low Co:Mo: separated, they are unselective. **Figure 3** shows the selective synthesis of a SWNT using the CoMoCAT method.



**Figure 3.** The Histogram for SG 65 material shows the very narrow distribution of SWNT diameters possible with the CoMoCAT process. 90% of the tubes have a diameter between 0.72 and 0.92 nm. 52% of the tubes are (6,5) chirality.

Two of the unique characteristics of the CoMoCAT process are that it is readily scalable and its intrinsic high selectivity is preserved as the reactor size is scaled up. These characteristics impart the SWNT product of the CoMoCAT process the dual benefit of low cost and high product quality. This supported catalyst approach also offers the unique ability to provide a substantial degree of chirality control during synthesis.

## Characterization of SWNTs and Quality Assurance Parameters

As discussed above the properties of carbon nanotubes vary with the individual SWNT chirality. Since at this time all SWNTs are produced as a mixture of chiralities, the properties of the material will depend on the proportions of chiralities present. Many analytical techniques have been deployed to elucidate the structure of SWNT materials. These range from observational techniques such as SEM, TEM, AFM and STM to spectroscopic techniques such as UV-Vis-NIR, Photoluminescence, and Raman spectroscopy. In addition to these methods, X-ray diffraction has been used by Miyata et. al.<sup>6</sup> to confirm the chirality assignments in the optical spectrum of SWNTs. Thermogravimetric analysis (TGA) has been used extensively to determine the onset of oxidation, maximum oxidation rate and the mass of catalyst retained in the product. In some cases it is possible to obtain a reasonable estimate of purity from the TGA curve.

TEM and SEM have been widely used to assess SWNT purity. However, these are unreliable for any quantitative estimation of purity. A typical TEM or SEM image uses ~ 1pg of material over an area of 1 to 4  $\mu\text{m}^2$  and it would therefore take the analysis of many micrographs imaged randomly throughout a macroscopic sample to obtain any meaningful results of the overall purity. Furthermore, there are no suitable algorithms for objectively determining the relative proportions of the different species seen in typical unpurified SWNT material. Thus, while TEM and SEM can give good information on the structure of the product, they must be used with caution and considered only as qualitative indicators of purity.

There are three relatively straightforward and commonly available techniques that can be used in combination to ensure that consistent high quality SWNTs are produced, namely Raman spectroscopy, Absorbance spectroscopy and Thermogravimetric analysis (TGA). Combined, these three methods give a good measure of purity and consistency of the SWNT. However, as SWNT applications are developed further, functional testing, such as electrical conductivity measurements, will be needed to link the purity data to SWNT performance.

### Analysis by Raman Spectroscopy

Raman spectroscopy has been widely used for determining both the detailed combination of chiralities present in the SWNT material and for assessing purity. There are three areas of the Raman spectrum of primary interest for SWNTs. The Radial Breath Mode (RBM) from approximately 120 to 300  $\text{cm}^{-1}$  is unique to SWNTs and can be used to determine tube diameter from the equation:

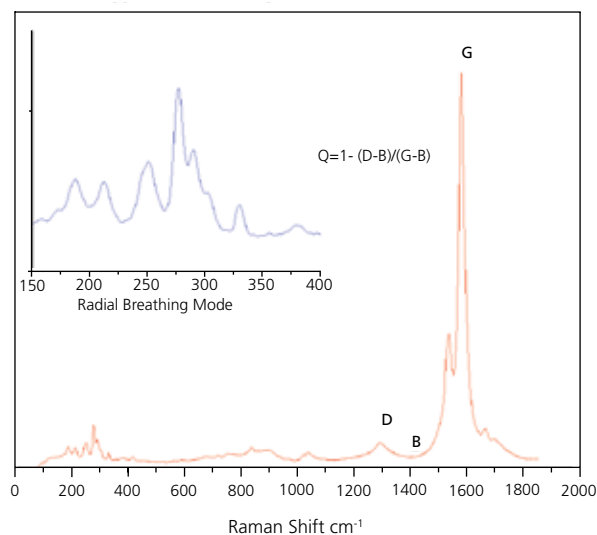
$$\nu = \frac{238}{d^{0.93}}$$

where,  $d$  is the SWNT diameter in nm and  $\nu$  is the wavenumber in  $\text{cm}^{-1}$ .

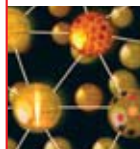
It is important to note that to get a complete picture of the chiralities present, several lasers of different excitation frequency must be used. Using a continuously variable laser to excite the SWNT, Jorio, et.al. have mapped the chiral structure of SWeNT<sup>®</sup> SG 65.<sup>7</sup>

There are two additional bands seen in the Raman spectrum of SWNT: the D band at 1300 to 1350  $\text{cm}^{-1}$  is indicative of disordered carbon, multiwall tubes and microcrystalline graphite, and the G band at 1500 to 1586  $\text{cm}^{-1}$  is a result of the tangential stretching mode from graphitic-like materials. The ratio of the height of the G band to that of the D band has been widely used as a measure of the purity of SWNT. However, caution must be used when measuring this ratio as the G band is a resonant band and is therefore much stronger than the D band. It is probably best used by stating that a high G:D ratio is a necessary condition for high purity SWNT, but it is an insufficient assurance of purity since other methods must be used in conjunction with this parameter. For example, other forms of graphitic carbon may contribute to a strong G band.

The Raman G:D ratio, with the cautions listed above can be used as a first measure of purity. A typical Raman Spectrum for SWeNT SG 65 is shown in **Figure 4**. For quality assurance purposes, the RBM region can be used as a rough purity fingerprint.



**Figure 4.** Typical Raman spectrum of SWeNT SG 65, obtained with 633 nm laser excitation.

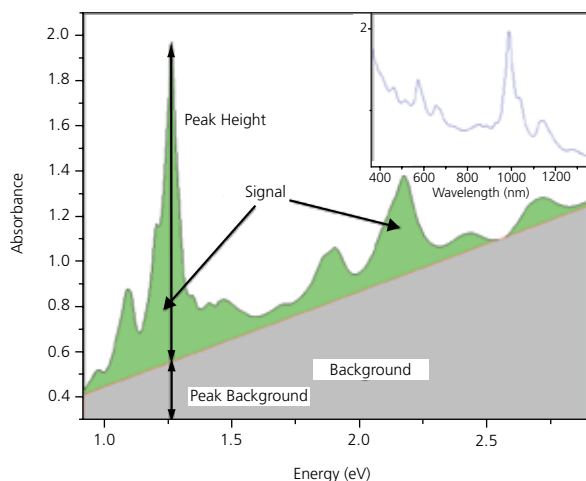


### Analysis by Optical Absorbance Spectroscopy

Optical absorption (OA) measurements in the UV-Vis.-NIR region show peaks which are characteristic of individual (n,m) species superimposed on the  $\pi$ -plasmon background. For example,<sup>8-9</sup> the (6,5) species absorb at 566 and 976 nm and in response fluoresce at 983 nm. A (7,6) SWNT absorbs at 645 and 1024 nm and fluoresces in response at 1030 nm. These individual peaks have been used as a basis for estimating the purity of SWNT.<sup>10</sup> Nair et. al.<sup>11</sup> have developed a method for computing the baseline for the spectrum, which then enables a calculation of peak heights and areas for the individual (n,m) species. For simplicity, we usually transform the measured OA spectrum to the energy domain, where the background becomes linear in the area of interest for SWNT characterization. **Figure 5** shows a typical OA spectrum for SWeNT® SG 65. The inset shows the spectrum in the more conventional form with the absorption plotted as a function of wavelength, while Figure 5b shows the same spectrum converted to the energy domain. Measurements of the height of the strongest peak, (P2B) and integration of the overall signal, S2B can be used to ensure that the product is consistent. We primarily use P2B as a control parameter for SWeNT® SG 65 and SG 76 nanotubes where one particular tube type is dominant. P2B is defined as the height of the highest peak in the spectrum between 350 and 1,350 nm divided by the background at that wavelength

$$P2B = \frac{\text{Height of (6,5) or (7,6) Signal Peak}}{\text{Height of Background Peak}}$$

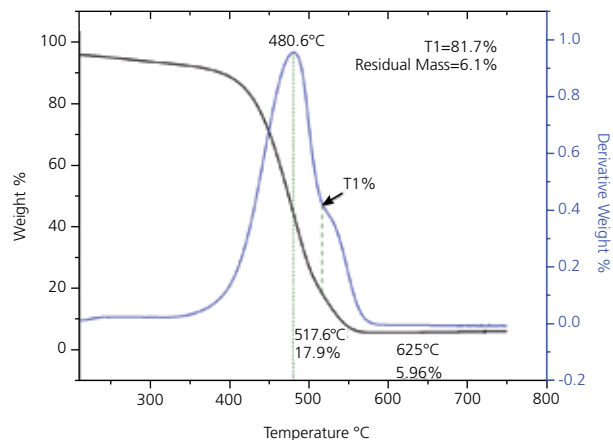
It should be noted that the OA methodology as described here uses the OA spectrum measured after dispersing and centrifuging the SWNT sample. It is used as a measure of chirality control rather than overall purity. Measurement of the absorbance at a particular wavelength before and after centrifugation gives a measure of the dispersability of the SWNTs.



**Figure 5.** Optical Absorbance spectrum for SWeNT® SG 65. The highest peak corresponds to the (6,5) tubes.

### Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is used to assess the purity of the material. A typical TGA curve for SG 65 SWNT is shown in **Figure 6**. Studies have shown that the first peak in the derivative curve of the TGA trace represents the oxidation of SWNT, while the second peak is indicative of the presence of other forms of carbon. The quality parameters determined from the TGA analysis are T1% and residual mass at 625 °C.



**Figure 6.** Thermogravimetric (TGA) Analysis for SWeNT® SG 65. The small peak in the derivative curve about 625 °C is due to changes in the residual catalyst as the material is heated.

T1%, as shown in **Figure 6**, is measured as a control parameter. It has been shown that this measurement typically underestimates the SWNT content by 3-5%. The position for T1 is taken at the minimum between the two peaks in the derivative curve. In the absence of a second distinct peak in the derivative curve, T1 is taken at the point of inflection. The weight loss % is recorded and the final value of T1% as a percentage of the carbon in the sample, corrected for the initial weight loss due to moisture in the sample is calculated from the following equation:

$$T1\% = \frac{\text{Initial weight} - T1\% \text{ measured}}{\text{Initial weight} - \text{residual mass}}$$

The measurement of residual mass at 625 °C gives a measure of the non-carbon content of the material. The residual mass is expressed as a percentage normalized for the weight loss at 200 °C.

$$\text{Residual Mass} = \frac{\text{Weight Loss at } 625\text{ }^\circ\text{C}}{\text{Initial Weight Loss}}$$

### SWNT Applications

The numerous unique properties of SWNTs have led to their application in a wide range of technological problems.<sup>12</sup> Their extraordinary mechanical strength is exploited in enhanced carbon fiber<sup>13</sup> and reinforced resins and elastomers; their highly conductive nature and large surface areas are utilized to prepare conductive polymer blends and films, improved lithium ion batteries, and super capacitors. Unique optical properties allow for their use as electrodes in displays, solarcells, and emerging solid state lighting technologies. The semiconducting nature of some SWNT species allow their adaptation to logic devices, non-volatile memory elements, sensors and security tags. It seems that new SWNT applications emerge regularly, limited only by the creativity of scientists and engineers working in the field.

## Conclusion

Despite early excitement about SWNT materials and the extraordinary amount of research inspired by their discovery, to date, commercial exploitation of the technology has been disappointing. Perhaps there is insufficient understanding of the practical hurdles to their commercialization. However, momentum seems finally to be building, driven by substantial recent progress in these fundamental areas:

**Metrology and Quality Control:** The concept of “if you can measure it, you can improve it” applies here. The means are now available to adequately characterize SWNTs and to assure consistency of the materials needed for commercialization. Supporting this is the soon to be available offerings by NIST of Standard Reference Materials for calibration purposes.

**Improved selectivity:** Driven by applications that require more than a near-random distribution of tube chiralities, there has been a demonstration of the means to substantially narrow the ‘as produced’ chirality distributions of commercial scale production products. There is also promising work toward achieving further selectivity through secondary processing.

**Dispersion:** Recent years have seen the emergence of improved aids to disperse SWNTs for formulation in inks and composites.

**Scale-up of manufacturing process:** The last five years have seen development and a maturing of scalable SWNT manufacturing processes, which can provide commercial quantities of SWNT with high purity, controlled properties and consistent quality.

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### References:

- (1) Iijima, S. *Nature*, **1991**, 354, 56. (2) Meo, M.; Rossi, M. *Composite Science and Technology*, **2006**, 66, 1597. (3) Tans, S.J.; Devoret, H.; Thess, A.; Smalley, R.E.; Geerligs, L.J.; Dekker, C. *Nature*, **1997**, 386, 474. (4) Arnold, M.S.; Green, A.A.; Hulvat, J.F.; Stupp, S.I.; Hersham, M.C. *Nature Nanotechnology*, **2006**, 1, 60. (5) Tan, Y.; Resasco, D.E. *J. Phys. Chem. B*, **2005**, 109, 14454. (6) Miyata, Y.; Yanagi, K.; Maniwa, Y.; Tanaka, T.; Kataura, H. *J. Phys. Chem. C*, **2008**, 112, 15997. (7) Jorio, A.; Santos, A.P.; Ribeiro, H.B.; Fantini, C.; Souza, M.; Viera, P.M.; Furtado, C.A.; Jiang, J.; Balzano, L.; Resasco, D.E.; Pimenta, M.A. *Phys. Rev. B*, **2005**, 72, 075207. (8) Bachtlo, S.M.; Strano, M.S.; Kitrell, C.; Hauge, R.H.; Smalley, R.E.; Weisman, R.B. *Science*, **2002**, 298, 2361. (9) Lolli, G.; Zhang, L.; Balzano, L.; Sakulchaicharoen, N.; Tan, Y.; Resasco, D.E. *J. Phys. Chem. B*, **2006**, 110, 2108. (10) Itkis, M.E.; Perea, D.E.; Jung, R.; Niyogi, S.; Haddon, R.C. *J. Amer. Chem. Soc.*, **2005**, 127, 3439. (11) Nair, N.; Usrey, M.; Kim, W.-J.; Braatz, R.D.; Strano, M.S. *Anal. Chem.*, **2006**, 78, 7589. (12) Rensselaer Polytechnic Institute. Ajayan and Zhou. <http://www.rpi.edu/locker/38/001238/pdfs/applications%20of%20nanotubes.pdf>. (accessed Mar 03 2009). (13) Jorio, A.; Dresselhaus, G.; Dresselhaus, M.S. (Eds.). *Carbon Nanotubes, Topics in Applied Physics*, Springer-Verlag, New York (2008).

## Non-functionalized Carbon Nanotubes

For a complete list of nanotubes please visit [sigma-aldrich.com/nanocarbon](http://sigma-aldrich.com/nanocarbon)

### Carbon Nanotubes, Single-Walled (SWNTs)

SWCNT Grade	Description	CNT Purity	Production Method	CNT Size	Cat. No.
SWeNT® CG-100	-	>75% carbon basis, carbon > 90%	Produced by CoMoCAT® catalytic CVD process	L 450-2300 nm (mode: 800nm; AFM), diameter 0.7 - 1.3 nm	<a href="#">704113-250MG</a> <a href="#">704113-1G</a>
SWeNT® SG-76	(7,6) chirality	>80% carbon basis, carbon > 90%	Produced by CoMoCAT® catalytic CVD process.	L 300-2300 nm (mode: 800nm; AFM), diameter 0.7 - 1.1 nm	<a href="#">704121-250MG</a>
SWeNT® SG-65	(6,5) chirality	>75% carbon basis, carbon > 90%	Produced by CoMoCAT® catalytic CVD process.	L 450-2000 nm (mode: 900nm; AFM), diameter 0.7 - 0.9 nm	<a href="#">704148-250MG</a>
CarboLex AP-grade	-	50-70% carbon basis, carbon 50-70%	Produced by Arc method	diam. x L 1.2-1.5 nm x 2-5 µm (bundle dimensions)	<a href="#">519308-250MG</a> <a href="#">519308-1G</a>
-	-	40-60 wt. % carbon basis, carbon ≥ 70%	Produced by Arc method	diam. x L 2-10 nm x 1-5 µm (bundle dimensions) 1.3-1.5 nm (individual SWNT diameter)	<a href="#">698695-1G</a> <a href="#">698695-5G</a>

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### Carbon Nanotubes, Multi-Walled (MWNTs)

CNT Type	CNT Purity	Production Method	CNT Size	Cat. No.
Carbon nanotube, double-walled	50-80% carbon basis, carbon > 90% (trace metal basis)	Produced by CVD method	O.D. x I.D. x L 5 nm x 1.3-2.0 nm x 50 µm	<a href="#">637351-250MG</a> <a href="#">637351-1G</a>
Carbon nanotube, multi-walled	>90% carbon basis, carbon > 90%	Produced by CVD method	diam. x L 110-170 nm x 5-9 µm	<a href="#">659258-2G</a> <a href="#">659258-10G</a>
Carbon nanotube, multi-walled	>90% carbon basis, carbon > 90% (trace metal basis)	Produced by Catalytic Chemical Vapor Deposition (CCVD)	O.D. x I.D. x L 10-15 nm x 2-6 nm x 0.1-10 µm	<a href="#">677248-5G</a> <a href="#">677248-25G</a>
Carbon nanotube, multi-walled	>95% carbon basis, carbon content > 95% (trace metal basis)	Produced by CVD method.	O.D. x I.D. x L 7-15 nm x 3-6 nm x 0.5-200 µm, bundled	<a href="#">694185-1G</a> <a href="#">694185-5G</a> <a href="#">694185-25G</a>
Carbon nanotube, multi-walled	>99% carbon basis, carbon > 99% (total metals impurities)	CVD followed by HCl demineralization	O.D. x L 6-13 nm x 2.5-20 µm 12 nm (average diameter, HRTEM) 10 µm (average length, TEM)	<a href="#">698849-1G</a>

