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Carbon Nanotubes

Description & properties

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CARBON NANOTUBES – Description and Properties

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DISCOYERY

Late 1950s:	Observation of carbon layered tiny tubes, R. BACON (Union Carbide)
1976:	Carbon Nanotubes? A. OBERLIN, M. ENDO, T. KOYAMA M. ENDO (Journal of Crystal Growth 32 (1976))
1885:	Fullerenes H. W. KROTO, R. F. CURL, R. E. SMALLEY
1991:	Multi-walled carbon nanotubes S. IIJIMA *(Nature 354 (1991))*
1993:	Single-walled carbon nanotubes S. IIIJIMA, D. BETHUNE *(Nature 363 (1993))*

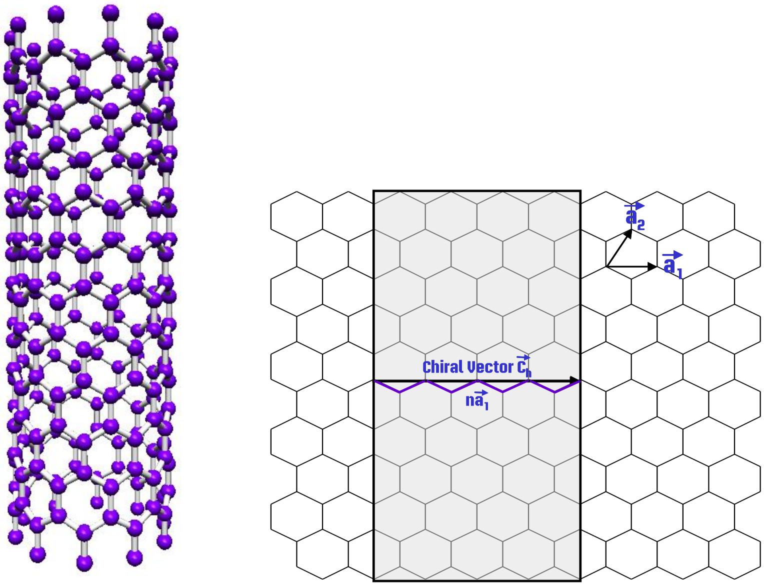
The history of Carbon Nanotubes starts in the late 1950s with the observation of carbon layered tiny tubes by R. BACON at Union Carbide as well as by RADUSHKEVICH and LUKYANOVICH (Russian *Journal of Physical Chemistry*). In 1976, OBERLIN, ENDO, and KOYAMA published TEM images of hollow carbon fibres synthesised by a chemical vapour-growth technique (*A. Oberlin, M. Endo & T. Koyama, Filamentous Growth of Carbon Through Benzene Decomposition, JOURNAL OF CRYSTAL GROWTH 32, at 335-49 (1976)*). The term “carbon nanotube” was applied for the first time by IIJIMA to describe hollow cylinders he observed in arc-discharge soot *(Nature 354 (1991))*. The discovery of single-walled carbon nanotubes (SWCNTs) is attributed to IIJIMA and BETHUNE who independently published in 1993 the synthesis of monolayered hollow graphite nanostructures.

STRUCTURE

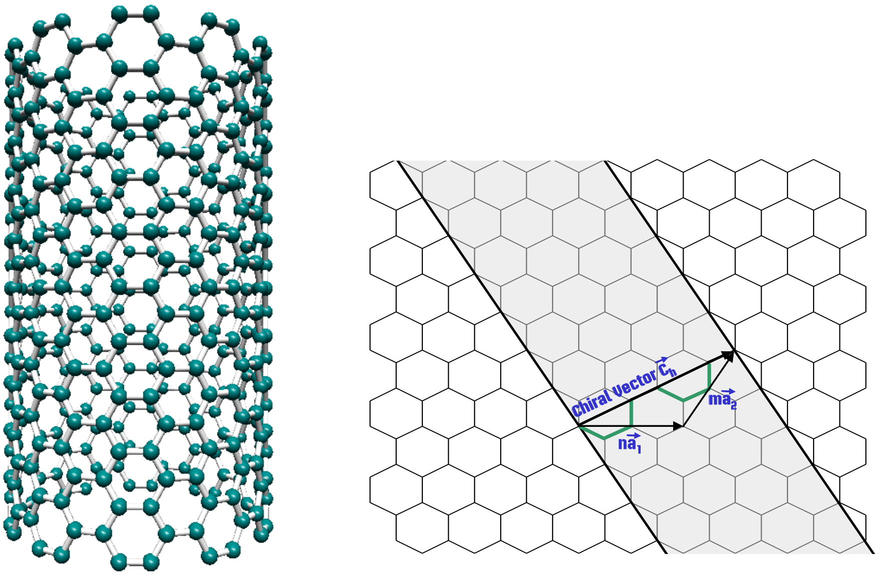
Carbon nanotubes can be described as graphitic sheets, also called graphene sheets, rolled into a tube. Those tubes, or cylinders, can be closed at both extremities due to the introduction of pentagons into the hexagonal graphitic lattice. Two types of carbon nanotubes are known:

Single-Walled Carbon Nanotubes (SWCNT) and Multi-Walled Carbon Nanotubes (MWCNT).

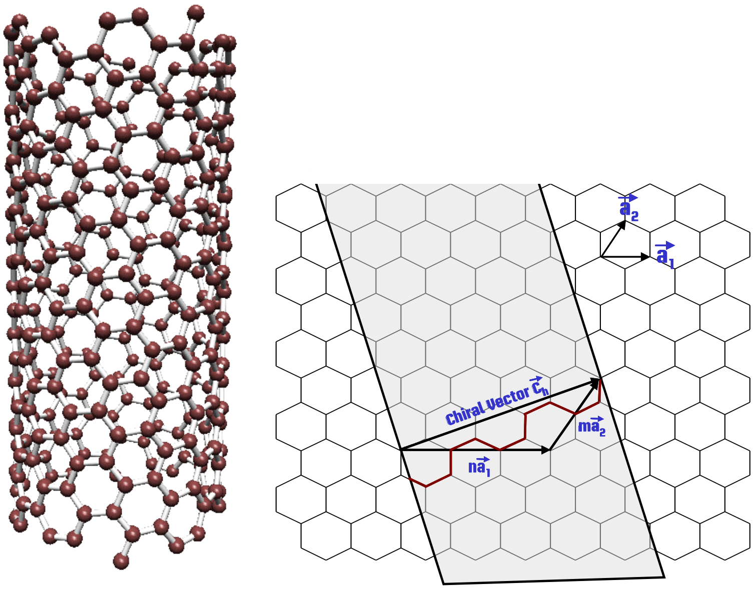
Depending on how the grapheme sheet is wrapped into a tube, three different types of single-walled carbon nanotubes are built: zig-zag, armchair, and chiral. This structural feature is called *chirality* and describes the twist of a tube. In order to determine in which way a tube is twisted, or, in other words, its chirality, one has to count the number carbon atoms moving along the unit vectors a_1 (n) and a_2 (m) from a carbon atom to its equivalent one on the lattice.



Left: Zig zag (10,0) carbon nanotube. Right: projection of a rolled up (4,0) nanotube on the crystal lattice of graphene.

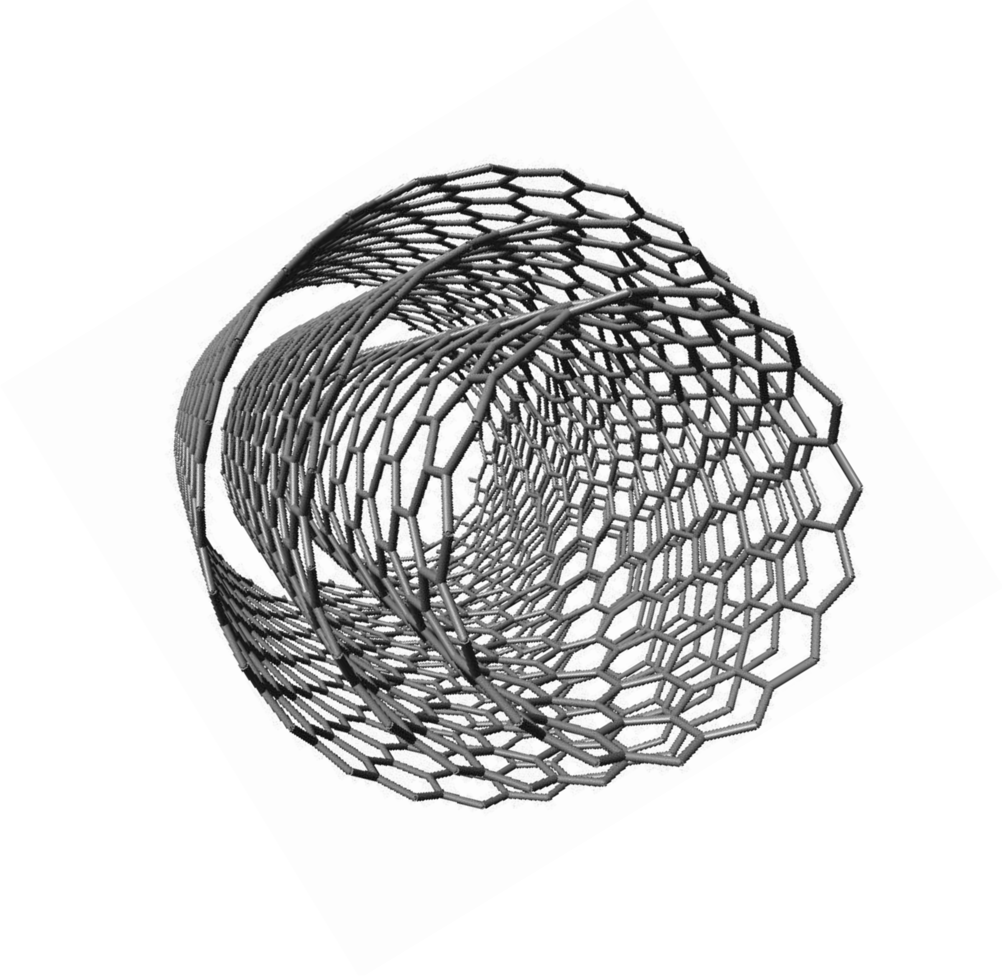


Left: Armchair (10,10) carbon nanotube. Right: projection of a rolled up (2,2) nanotube on the crystal lattice of graphene.



Left: Chiral (10,6) carbon nanotube. Right: projection of a rolled up (3,2) nanotube on the crystal lattice of graphene.

Multi-walled carbon nanotubes can be described as an assembly of concentric single-walled carbon nanotubes with different diameters and chiralities.



Computer image of a MWCNT

The chirality is an important parameter since it affects certain physical properties of a nanotube, such as conductance and density. For example, a SWCNT is considered metallic if the value $n - m$ can be devised by three. In all other cases, the nanotube is semiconducting. Thus, all armchair carbon nanotubes are metallic.

Diameter of carbon nanotubes typically run from less than 1 nm up to 50 nm.
Given the chiral vector (n,m), the diameter of a carbon nanotube can be determined using the relationship
$d_t = (\sqrt{3}/\pi)a_{c\text{-}c}(m^2 + mn + n^2)^{1/2}$; where $a_{c\text{-}c}$ is the distance between the nearest neighbouring carbon atoms in the flat sheet.

Byron Pipes et al. (*Comp. Sci. and Techn. 63, 1349-1358 (2003))* calculated that the density of individual SWCNTs having diameters between 1 to 14 nm decreases with increasing diameter from roughly 0.2 to 2.0 g/cm^3.

PROPERTIES

Mechanical properties

Due to the sp^2 bonds between the individual carbon atoms, which is the strongest known covalent bond, carbon nanotubes are extremely stiff and resistant to physical forces.
The Young's modulus of perfect CNTs has been theoretically calculated using different models (*R. Byron Pipes et al., Comp. Sci. and Techn. 63, 1349-1358 (2003); J-P. Salvetat, Phys. Rev. Let. 82(5), 944-947 (1999); C. F. Cornwell, L. T. Wille, Sol. State Com. 101(8), 555-558 (1997); R. S. Ruoff, D. C. Lorents, Carbon 33(7), 925-930 (1995)*). Commercially available SWCNTs have estimated Young's moduli in the range of 400-600 GPa. The precise value is depending on the diameter (chirality) and the amount of disorder in the nanotube walls.
The maximum tensile strength of SWCNTs has been reported to be 30 GPa (*M.-F. Yu et al., Phys. Rev. Lett.* ***84****, 5552 (2000)*). The same authors found a tensile strength of 63 GPa for MWCNTs (*Min-Feng Yu et al., Science 287, 637-640 (2000)*), while Demczyk et al. estimated the tensil strength of MWCNTs to be 150 GPa.
Due to the nonlinearity of the radial compression, moduli from 9.7 to 80.0 GPa where found by Shen et al. when compressing a 10 nm tube from 26 to 46%.

Electrical Properties

As discussed above, the electrical properties of carbon nanotubes are strongly influenced by their physical structure. For a given (n,m) nanotube, if $n + m=3q$ (where q is an integer), then the nanotube is metallic, if $n + m=3q \pm 1$ the nanotube is a semiconductor. Thus all armchair ($n=m$) nanotubes are metallic, and nanotubes (7,0), (8,3), (9,1), etc. are semiconducting. Statistically, two-thirds of as produced carbon nanotubes are semi-conducting, while the other third is metallic.
Due to ballistic transport of electrons, which means that there is no or only negligible scattering by atoms or impurities, the electrical resistance of carbon nanotubes is extremely low.
Further, nanotubes have a current carrying capacity of 10^9 A/cm², for comparison, copper wires burn out at 10^6 A/cm².

Thermal Properties

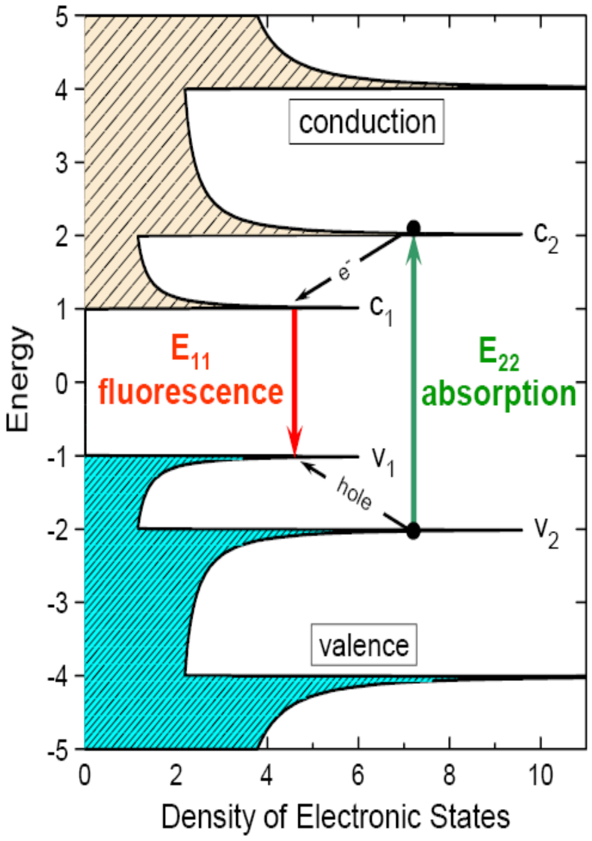
The thermal conductivity is depending on the temperature and the large phonon main free path. Tomanek et al. suggested a value of 6600 W/m·K for the room temperature thermal conductivity (*S. Berber, Phys. Rev. Lett. 84 (2000)*). 3000 W/m·K has been measured using a microfabricated suspended device (*P. Kim et al., Phys. Rev. Lett. 87 (2001)*).
It has been reported that carbon nanotubes can readily conduct heat by ballistic phonon propagation (*E. Brown et al., Appl. Phys. Lett. 87 (2005); H.-Y. Chiu et al., Phys. Rev. Lett. 95 (2005)*).

Optical Properties

Due to their quasi one-dimensional structure, carbon nanotubes show several remarkable optical properties. The density of states of the highest occupied energy level, known as Fermi Level, is zero for semiconducting and closed to zero for metallic CNTs. While conventional metals have a smooth density of states, these nanotubes are characterized by a number of sharp peaks, the Van Hove singularities, that appear at higher energies. Each peak corresponds to a single quantum subband. Those Van Hove singularities lead to optical transitions which are sensitive to the chirality of the tubes. The calculated allowed optical transitions of the different tube chiralities can be plotted against the tube diameter, the resulting diagram is referred to as "Kataura plot". As a first approximation, the diameter-absorption energy relationship for each pair of Van Hove singularities can be described by a simple equation:

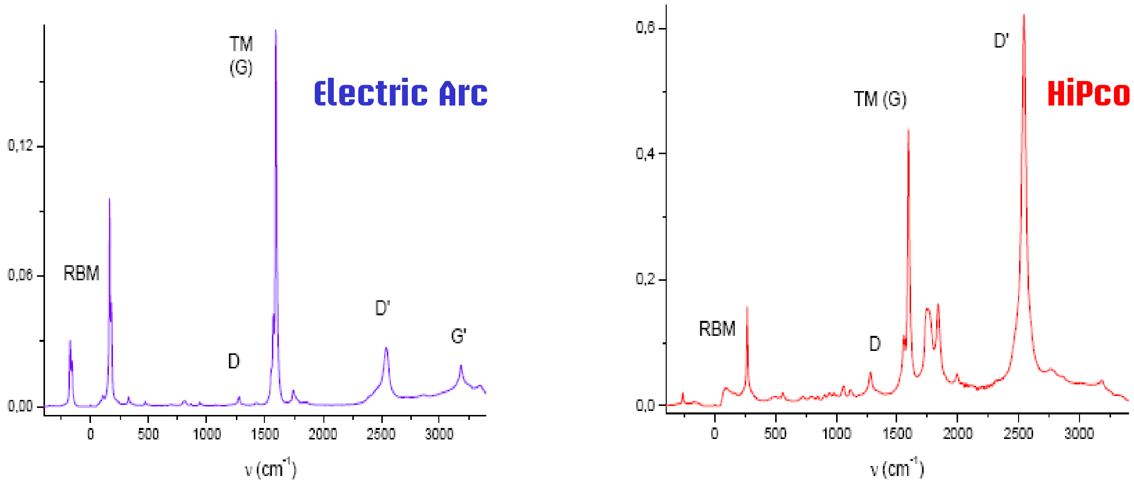
$\Delta E = 2k\gamma_0 a_{cc} / d$,

in which k, γ_0, a_{cc}, and d are an integer (1,2,4,8 for semi-conducting and 3,6 for metallic CNTs), the overlap energy of neighbouring carbon atoms (2.7-3.0 eV), the distance between neighbouring carbon atoms (about 0.14 nm), and the nanotube diameter, respectively.
Therefore, the diameter of individual semiconducting SWCNTs can be determined using excitation photoluminescence (*S. M. Bachilo et al., Science 298, 2361 (2002)*).



Energy absorption and fluorescence due to electron-hole recombination in SWCNTs

Raman spectroscopy has been proven a powerful tool to study the length of SWCNT, their diameter distributions, their electronic type (metallic or superconducting), and whether nanotubes are separated or in bundle (*A. M. Rao et al., Science 275, 187 (1997)*). Practically important excitations in carbon nanotubes are the phonons (carbon vibration modes). Raman scattering from phonons is always mediated by electrons via electron-phonon coupling. The Raman spectra of carbon nanotubes show four main signals: at around 1500-1600 cm^{-1} (G band, corresponding to the tangential vibration modes), at around 1300 cm^{-1} (D band, due to structural sidewall defects), and low-frequency radial breathing modes (RBM) in the range of 100-300 cm^{-1}. A less nanotube specific second order band (D*) can be observed at ~2650 cm^{-1}.



∅ 1.0 – 1.5 nm **∅ 0.7 – 1.3 nm**

Typical Raman spectra of SWCNTs

As mentioned above, tubes with different chiralities have different allowed optical transfer energies. Thus, both the RBM and the TM region of the RAMAN spectra of a SWCNT sample change in function of the incident laser energy. By varying the laser excitation wavelength, the Kataura plot allows to predict the diameter distribution and the electrical behaviour (metallic or semi-cinducting) of a CNT sample.

MANUFACTURING

Manufacturing methods

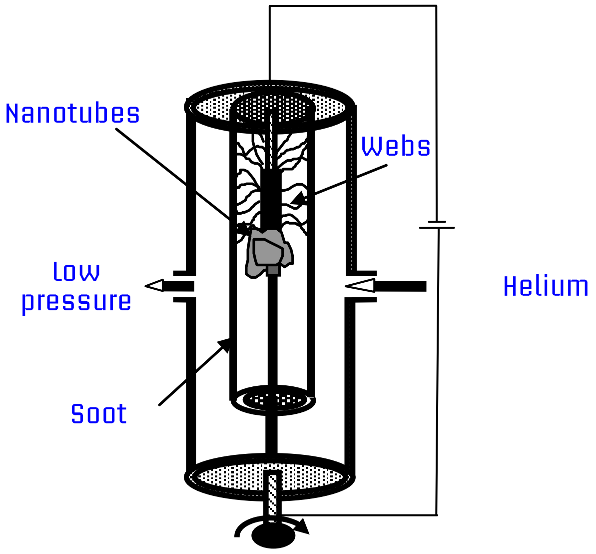
Carbon nanotubes can be produced by various physical and chemical methods. Most promising processes for large-scale production of high-quality CNTs include Arc-discharge, Chemical Vapour Deposition (CVD), and – to a lesser extend – Laser-Ablation.

Laser-Ablation produces only single-walled carbon nanotubes where a high-energy laser beam vaporizes a target carbon-catalyst (growth onset temperature ~1350°C) followed by an annealing step. The resulting SWCNTs contain very few defects and contaminants. SWCNT diameter control may be more easily achieved in comparison to other methods. The main limitation of Laser-Ablation is that large-scale production would require substantial financial investment associated with high production costs.

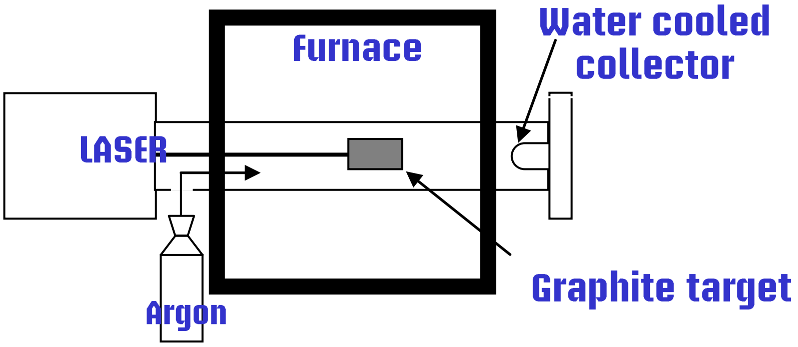
Arc-discharge involves condensation of hot gaseous carbon atoms generated from evaporation of catalyst-doped graphite. Growth temperature in the Arc-discharge is considerably higher than other CNT production methods (2000-3500°C, or even 6000°C). Consequently, crystallinity and structural perfection of arc-produced CNTs are higher and a significantly higher yield per unit time is obtained in comparison to other methods.

CVD is a relatively simple and economic technique allowing synthesis of both single- and multi-walled carbon nanotubes. Several differing methods, such as Plasma-Enhanced CVD (PECVD), or Low Pressure CVD (LPCVD), have been developed over the last few years. Most are based on thermal decomposition of hydrocarbons or alcohols in the presence of metal catalysts. The growth temperature varies in function of the method from approximately 450 to 1200°C. Disproportionation of carbon monoxide (CO) catalyzed by metal particles or high-pressure catalytic decomposition of CO (HiPco) are further CVD derivatives. Even if CVD methods are mainly used for the synthesis of MWCNTs, SWCNTs can be produced as well. CVD offers the possibility of growing aligned CNTs for specific applications (orientation control) and, to a certain extent, synthesis of small-diameter CNTs. Industrial scale-up of CVD is generally considered to be relatively easy.

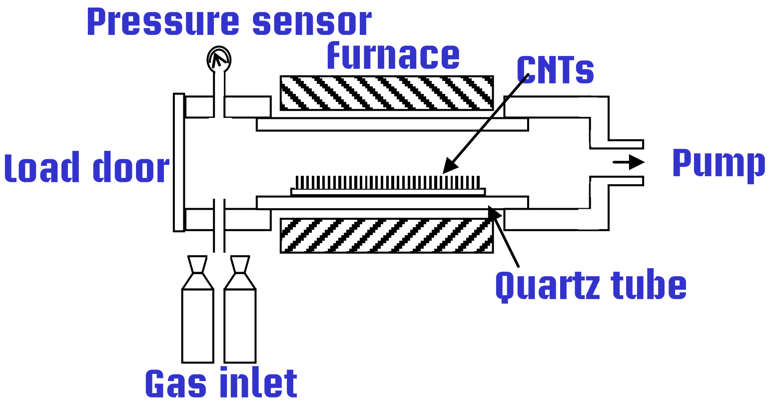
Photograph of the inner chamber of an experimental arc-discharge reactor



Electric arc-discharge reactor



Laser-ablation device



Apparatus for Chemical Vapour Deposition

Purification

Carbon nanotubes produced by CVD and Arc-discharge contain metal nanoparticles and other impurities and hence require a post-synthesis purification step. The same characteristics that give carbon nanotubes their outstanding properties (high specific surface and aspect ratio, structural perfection) make their processing and purification extremely difficult. Significant progress has been made in this field and highly pure material is currently available. Most known approaches for pure CNT production involve a combination of two or more of the following procedures: wet chemical oxidation, gas- or vapour-phase oxidation, filtration and centrifugation. However, all off these purification methods deal with relatively small quantities. To date, no treatment of contaminated material in more than a few kilogram scale has not been realized and considerable effort has to be made for effective and economic purification processes. It should be emphasized that the very first purification step consists of producing raw material which contains less impurity. Beside purification the separation of the raw material into fractions with defined geometries and chiralities is another approach to render CNTs more useful in industrial applications. Methods for separating metallic from semiconducting SWNTs, which is of great interest for realization of nanoelectronic devices, field-emission displays, nanosensors, etc. are just now beginning to be realized.

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