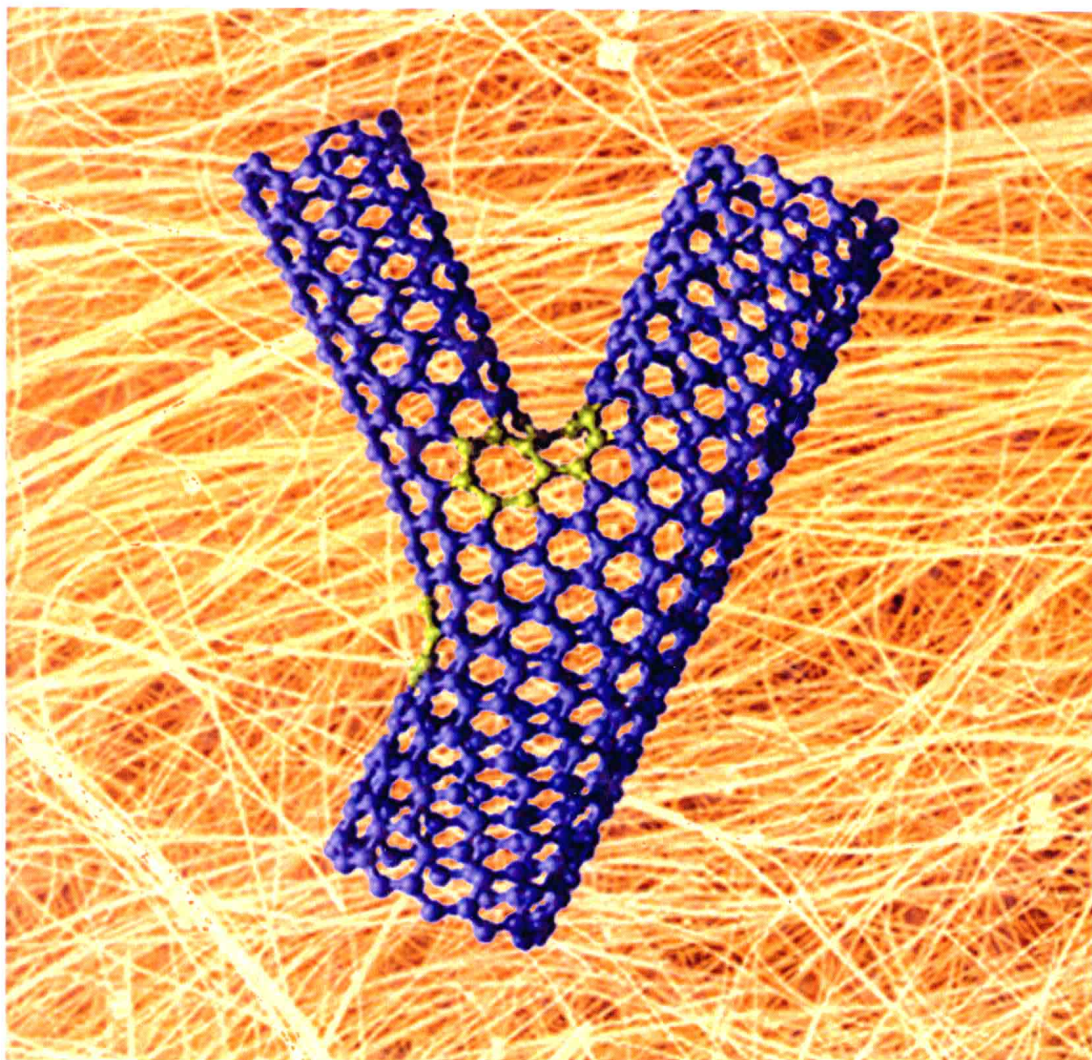


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CNR Rao, FRS and A Govindaraj

Nanotubes and Nanowires



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Nanotubes and Nanowires

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Preface

The science of nanomaterials has become the flavour of the day, with research being driven both by academic curiosity and the promise of useful applications. Amongst the nanomaterials, nanocrystals, nanowires and nanotubes constitute three major categories, the last two being one-dimensional. Since the discovery of the carbon nanotubes in 1991, interest in one-dimensional nanomaterials has grown remarkably, and a phenomenal number of research articles has been published on nanotubes as well as nanowires. The nanotubes are not only those of carbon but also of inorganic materials. Several strategies have been developed for the synthesis of these materials and a range of interesting properties reported. Thus, the electronic and mechanical properties of carbon nanotubes have been studied extensively, and several of them directly relate to potential applications. Typical of the important properties of carbon nanotubes are high mechanical strength, good electrical and thermal conductivity and excellent electron emission characteristics. The electronic and Raman spectra of carbon nanotubes have helped immensely in characterization as well as in understanding some of the intrinsic structural characteristics.

While nanotubes of several inorganic materials, many of which possess layered structures, have been synthesized and characterized, the literature on inorganic nanowires is much more extensive. Every conceivable inorganic material seems to have been prepared in nanowire form. Properties and possible applications of these inorganic one-dimensional materials have been investigated to some extent, but there seems to be ample scope for study.

This monograph provides an up-to-date survey of various aspects of carbon nanotubes, inorganic nanotubes and nanowires. Nanotubes of lipids, peptides, polymers and DNA are known, but they have not been discussed in this monograph due to its limited scope. We have found it difficult to cover the entire gamut of properties and applications of the nanotubes and nanowires in detail in view of the immense literature that has accumulated in the last three to four years. We have been selective, emphasizing more the chemical aspects of nanotubes and nanowires, especially those related to synthesis and characterization to a greater extent. We have provided an extensive list of references to enable those who would like more complete information on the properties and other aspects of these

materials. It is possible that we have failed to cite some important references by oversight or error in judgement, and we would like to be excused for such omissions. We have done our best to make the monograph contemporary and we hope that students, teachers and practitioners of nanoscience will find it useful.

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About the Authors

C.N.R. Rao obtained his PhD degree from Purdue University and DSc degree from the University of Mysore. He is the Linus Pauling Research Professor and Honorary President of the Jawaharlal Nehru Centre for Advanced Scientific Research and Honorary Professor at the Indian Institute of Science (both at Bangalore). His research interests are mainly in the chemistry of materials (e.g., transition-metal oxides, open-framework structures, and nanomaterials). He has authored nearly 1000 research papers and edited or written 30 books in materials chemistry. A member of several academies including the Royal Society, US National Academy of Sciences, Japan Academy, French Academy of Sciences, and the Pontifical Academy of Sciences, he is also Distinguished Visiting Professor at the University of California, Santa Barbara. He was awarded the Einstein Gold Medal by UNESCO, the Hughes Medal by the Royal Society, and the Somiya Award of the International Union of Materials Research Societies (IUMRS). In 2005, he received the Dan David Prize for materials research from Israel and is the first recipient of the India Science Prize.

A. Govindaraj obtained his M.Sc and Ph.D degrees from the University of Mysore. His main research interests are in fullerenes, nanowires and nanotubes in which areas he has published extensively. He is a Senior Scientific Officer at the Indian Institute of Science and Honorary Faculty Fellow at the Jawaharlal Nehru Centre for Advanced Scientific Research.

Abbreviations

AAM	Anodic Alumina Membrane
AFM	Atomic Force Microscope (Microscopy)
BNNTs	Boron Nitride Nanotubes
c.m.c.	Critical Micelle Concentration
μ CP	Microcontact Printing
CNTs (or CN)	Carbon Nanotubes
CSR	Carrot-shaped Rods
CTAB	Cetyltrimethylammonium Bromide
CVD	Chemical Vapour Deposition
DOS	Density of States
DWNTs	Double-walled Carbon Nanotubes
EDX	Energy Dispersive X-ray Spectroscopy
FE	Field Emission
FEED	Field-emitted Electron Energy Distribution
FET	Field-effect Transistor
F-N	Fowler–Nordheim (plot)
F-SWNTs	Fluorinated Single-wall Nanotubes
HFCVD	Hot-filament Chemical Vapour Deposition
HiPco	High-pressure CO Disproportionation Process
HOPG	Highly Oriented Pyrolytic Graphite
HREM	High-resolution Electron Microscope (Microscopy)
IF	Inorganic Fullerenes
IMJs	Intramolecular Junctions
ITO	Indium Tin Oxide
MFP	Mean-free Path
MR	Magnetoresistance
MWNTs	Multi-wall Nanotubes
NR	Nanoribbons
NSP	Nebulized Spray Pyrolysis
NT-FETs	Nanotube Field-effect Transistors
NW	Nanowires (often prefixed by an elemental symbol, <i>e.g.</i> BiNW for Bismuth Nanowires)

PANI	Polyaniline
PDMS	Polydimethylsiloxane
PEG	Poly(ethylene glycol)
PEI	Polyethyleneimine
PFO	Poly(9,9-di- <i>n</i> -octylfluorenyl-2,7-diyl)
PL	Photoluminescence
PMMA	Poly(methyl methacrylate)
PPV	Poly(<i>p</i> -phenylene vinylene)
PVD	Physical Vapour Deposition
PVP	Poly(vinylpyrrolidone)
SAED	Selected-area Electron Diffraction
SDS	Sodium Dodecyl Sulphate
SEM	Scanning Electron Microscope (Microscopy)
SET	Single Electron Tunnelling
SFLS	Supercritical fluid–Liquid–Solid
SLS	Solution–Liquid–Solid
SHG	Second-harmonic Generation
sscm	Standard Cubic Centimetres per Minute
STM	Scanning Tunnelling Microscopy
STS	Scanning Tunnelling Spectroscopy
SWNTs	Single-wall Nanotubes
s-SWNTs	Shortened Single-wall Nanotubes
TB-DFT	Tight-binding Density Functional Theory
TEM	Transmission Electron Microscope (Microscopy)
TEP	Thermoelectric Power
THG	Third-harmonic Generation
VLS	Vapour–Liquid–Solid
VS	Vapour–Solid
XRD	X-ray Diffraction

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CHAPTER 1

Carbon Nanotubes

1 Introduction

Diamond and graphite are the two well-known forms of crystalline carbon. Diamond has four-coordinate sp^3 carbon atoms that form an extended three-dimensional network, whose motif is the chair conformation of cyclohexane. Graphite has three-coordinate sp^2 carbons that form planar sheets, whose motif is the flat six-membered benzene ring. The new carbon allotropes, the fullerenes, are closed-cage carbon molecules with three-coordinate carbon atoms tiling the spherical or nearly-spherical surfaces, the best known example being C_{60} , with a truncated icosahedral structure formed by twelve pentagonal rings and twenty hexagonal rings (Figure 1.1a). Fullerenes were discovered by Kroto *et al.*¹ in 1985 while investigating the nature of carbon present in interstellar space. The coordination at every carbon atom in fullerenes is not planar, but slightly pyramidalized, with some sp^3 character present in the essentially sp^2 carbons. The key feature is the presence of five-membered rings, which provide the curvature necessary for forming a closed-cage structure. In 1990, Krätschmer *et al.*² found that the soot produced by arcing graphite electrodes contained C_{60} and other fullerenes. The ability to generate fullerenes in gram quantities in the laboratory, using a relatively simple apparatus, gave rise to intense research activity on these molecules and caused a renaissance in the study of carbon. Iijima³ observed, in 1991, that nanotubules of graphite were deposited on the negative electrode during the direct current arcing of graphite for the preparation of fullerenes. These nanotubes are concentric graphitic cylinders closed at either end due to the presence of five-membered rings. Nanotubes can be multi-walled with a central tubule of nanometric diameter surrounded by graphitic layers separated by ~ 3.4 Å. Unlike the multi-walled nanotubes (MWNTs), in single-walled nanotubes (SWNTs), there is only the tubule and no graphitic layers. A transmission electron microscope (TEM) image of a MWNT is shown in Figure 1.1(b). In this nanotube, graphite layers surround the central tubule. Figure 1.1(c) shows the structure of a nanotube formed by two concentric graphitic cylinders, obtained by force-field calculations. A single-walled nanotube can be visualized by cutting C_{60} along the centre and spacing apart the hemispherical corannulene end-caps by a cylinder of graphite of the same diameter. Carbon nanotubes are the only form of carbon with extended

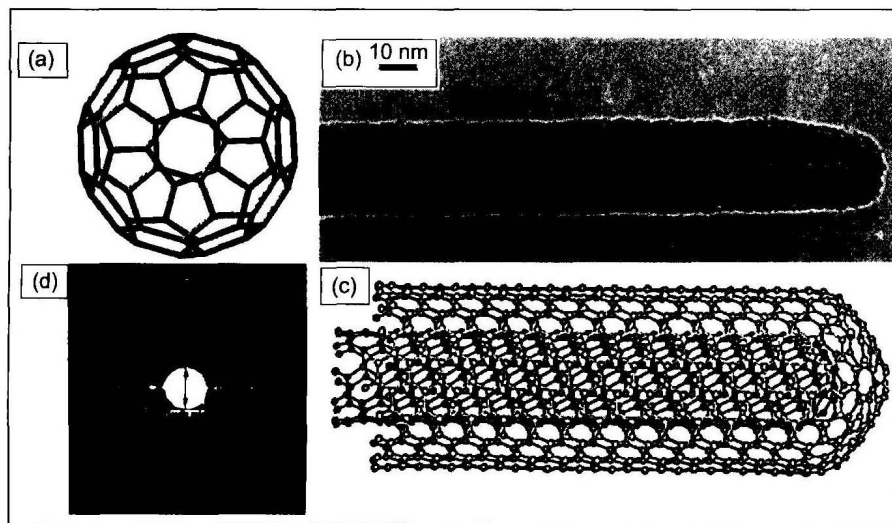


Figure 1.1 (a) Schematic diagram of a C_{60} molecule; (b) A TEM image of a multi-walled carbon nanotube; (c) Minimum energy structure of a double-walled carbon nanotube; (d) Electron diffraction pattern of a multi-walled carbon nanotube (Parts (a–c) reproduced from ref. 20a; part (d) reproduced from ref. 20c)

bonding and yet with no dangling bonds. Since carbon nanotubes are derived from fullerenes, they are referred to as tubular fullerenes or bucky tubes.

Ever since the discovery of the carbon nanotubes,^{4,5} several ways of preparing them have been explored. Besides MWNTs, SWNTs have been prepared by various methods, including electrochemical synthesis⁶ and pyrolysis of precursor organic molecules.⁷ The structure of carbon nanotubes has been extensively investigated by high-resolution electron microscopy.^{8–10} The nanotubes, prepared by arc vaporization of graphite, are closed at both ends, but can be opened by various oxidants.^{11,12} There has been considerable success in filling nanotubes with various materials.¹³ Apart from opening and filling, carbon nanotubes have been doped with boron and nitrogen, giving rise to p-type and n-type materials, respectively. By employing carbon nanotubes as removable templates, oxidic, carbidic and other nanostructures have been prepared. One of the developments is the synthesis of aligned nanotube bundles for specific applications. Various properties and phenomena as well as several possible and likely applications of carbon nanotubes have been reported. Unsurprisingly, therefore, these nanomaterials have elicited great interest. Several review articles, special issues of journals and conference proceedings^{14–20} have dealt with carbon nanotubes. Some of the reviews present possible technological applications, with focus on the electronic properties,^{19,20} the recent book of Reich *et al.*²¹ being devoted to a detailed presentation of the basic physics of carbon nanotubes. There are several other reviews and books as well, some of which are cited as references.^{22–27}

Since the discovery of the carbon nanotubes, there has been considerable work on inorganic layered materials such as MoS_2 , WS_2 and BN to explore the formation

of nanotubes of these materials. Indeed several have been synthesized and characterized.^{28–31} Inorganic nanotubes are discussed at length in Chapter 2. Here, we shall present several aspects of carbon nanotubes, such as their preparation, structure, mechanism of formation, chemical substitution, properties and applications. We briefly examine the three fundamental aspects of CNTs, namely, their electronic structure and related properties, their vibrational and thermal characteristics and their mechanical properties. These aspects are interrelated, since both thermal and mechanical properties reflect the chemical bonding in the carbon network, which controls their electronic structure as well.

2 Synthesis

Multi-walled Nanotubes

Carbon nanotubes are readily prepared by striking an arc between graphite electrodes in ~ 0.7 atm (~ 500 Torr) of helium, which is considerably larger than the helium pressure used to produce fullerene soot. The schematic diagram of the apparatus is shown in Figure 1.2. A current of 60–100 A across a potential drop of about 25 V gives high yields of carbon nanotubes. The arcing process can be optimized such that the major portion of the carbon anode gets deposited on the cathode as carbon nanotubes and graphitic nanoparticles.^{32a} Arc evaporation of graphite has been carried out in various kinds of ambient gases (He, Ar, and CH_4).^{32b} Hydrogen appears to be effective in producing MWNTs of high crystallinity. Arc-produced MWNTs in hydrogen also contain very few carbon

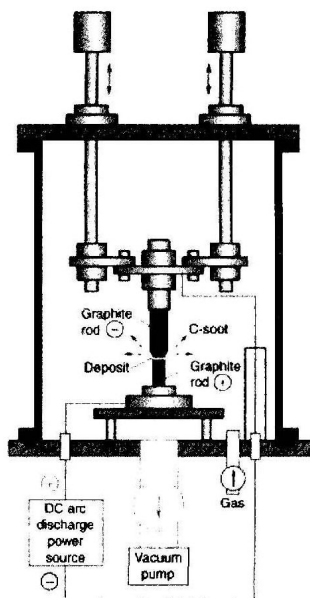


Figure 1.2 Schematic diagram of an arc discharge apparatus (Reproduced from ref. 32b)

nanoparticles. Carbon nanotubes have been produced in large quantities by using plasma arc-jets by optimizing the quenching process in an arc between a graphite anode and a cooled copper electrode.^{33,34} If both the electrodes are of graphite, MWNTs are the main products, along with side products such as fullerenes, amorphous carbon, and graphite sheets.

A route to highly crystalline MWNTs is the arc-discharge method in liquid nitrogen.³⁵ In this method, vacuum is replaced with liquid nitrogen in the arc discharge chamber. Typically, direct current was supplied to the apparatus using a power supply. The anode is a pure carbon rod (8 mm diameter) and the cathode is a pure carbon rod (10 mm diameter). The Dewar flask is filled with liquid nitrogen and the electrode assembly immersed in nitrogen. Arc discharge occurs as the distance between the electrodes became less than 1 mm, and a current of ~ 80 A flows between them. When the arc discharge is over, carbon deposits near the cathode are recovered for analysis. Liquid nitrogen prevents the electrodes from contamination with unwanted gases and also lowers the temperature of the electrodes. Furthermore, CNTs do not stick to the chamber wall. The content of the MWNTs can be as high as 70% of the reaction product. Analysis with Auger-spectroscopy revealed that no nitrogen was incorporated in the MWNTs. Synthesis in a magnetic field gives defect-free and high purity ($>95\%$) MWNTs, which can be used as nanosized electric wires for device fabrication.³⁶ Here, the arc discharge is controlled by a magnetic field around the arc plasma, created by using extremely pure graphite (purity $>99.999\%$) electrodes (Figure 1.3a and 1.3b). MWNTs can be mass produced economically by

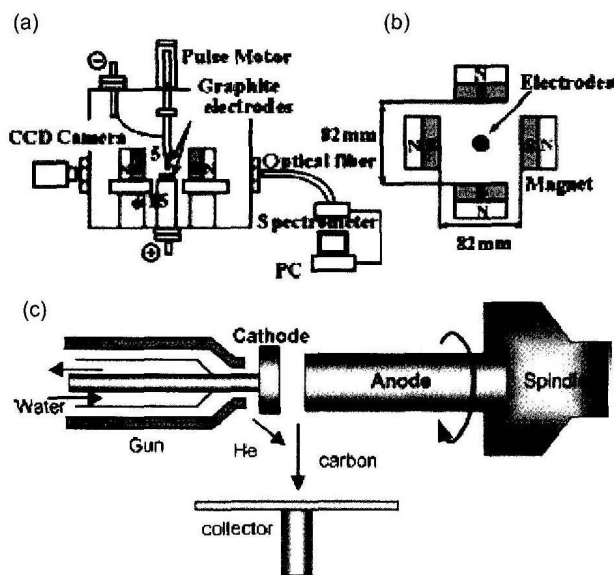


Figure 1.3 (a) and (b) Schematic diagrams of the system for the synthesis of MWNTs in a magnetic field (c) Schematic diagram of a plasma rotating electrode system (Parts (a) and (b) reproduced from ref. 36; part (c) Reproduced from ref. 37)

the plasma rotating arc discharge technique.³⁷ The centrifugal force caused by the rotation generates turbulence and accelerates the carbon vapour perpendicular to the anode (Figure 1.3c). Rotation also distributes the micro discharges uniformly and generates a stable plasma. Consequently, it increases the plasma volume and raises the plasma temperature. At a rotations of 5000 rpm, a yield of 60% is obtained at 1025 °C (without the use of a catalyst). The yield increases up to 90% if the rotation speed is increased at 1150 °C. The MWNTs obtained generally have an inner diameter of 1–3 nm and an outer diameter of ~10 nm.

Deposition of carbon vapour on cooled substrates of highly oriented pyrolytic graphite affords tube-like structures.³⁸ Carbon nanotubes are also produced by electrolysis in molten halide salts with carbon electrodes under argon.^{39a} MWNTs with well-ordered graphitic structures have also been obtained under hydrothermal conditions around 800 °C, under 60–100 MPa pressure, using a polyethylene–water mixture in the presence of a nickel catalyst.^{39b} Besides the conventional arc-evaporation technique, carbon nanotubes are produced by chemical vapour deposition (CVD), by the decomposition of hydrocarbons such as C₂H₂ under inert conditions around 700 °C over Fe/graphite,⁴⁰ Co/graphite⁴¹ or Fe/silica⁴² catalysts. Transition metal particles are essential for the formation of nanotubes by the CVD or pyrolysis process, and the diameter of the nanotube is generally determined by the size of the metal particles.⁴³

Chemical Vapour Deposition (CVD)

The chemical vapour deposition (CVD) method uses a carbon source in the gas phase and a plasma or a resistively heated coil, to transfer the energy to the gaseous carbon molecule. Commonly used carbon sources are methane, carbon monoxide and acetylene. The energy source cracks the molecule into atomic carbon. The carbon then diffuses towards the substrate, which is heated and coated with a catalyst (usually a first row transition metal such as Ni, Fe or Co) and binds to it. Carbon nanotubes are formed in this procedure if the proper parameters are maintained. Good alignment⁴⁴ as well as positional control on a nanometric scale⁴⁵ are achieved by using CVD. Control over the diameter, as well as the growth rate of the nanotubes is also achieved. Use of an appropriate metal catalyst permits preferential growth of single-walled rather than multi-walled nanotubes.⁴⁶

CVD synthesis of nanotubes is essentially a two-step process, consisting of a catalyst preparation step followed by synthesis of the nanotube. The catalyst is generally prepared by sputtering a transition metal onto a substrate, followed by etching by chemicals such as ammonia, or thermal annealing, to induce the nucleation of catalyst particles. Thermal annealing results in metal cluster formation on the substrate, from which the nanotubes grow. The temperature for the synthesis of nanotubes by CVD is generally in the 650–900 °C range.^{44–47} Typical nanotube yields from CVD are around 30%. Various CVD processes have been used for carbon nanotubes synthesis, including plasma-enhanced CVD, thermal chemical CVD, alcohol catalytic CVD, aerogel-supported CVD and laser-assisted CVD.

Plasma-enhanced Chemical Vapour Deposition

The plasma-enhanced CVD method involves a glow discharge in a chamber or a reaction furnace through a high-frequency voltage applied to both the electrodes. Figure 1.4 shows a schematic diagram of a typical plasma CVD apparatus with a parallel plate electrode structure. A substrate is placed on the grounded electrode. To form a uniform film, the reaction gas is supplied from the opposite plate. Catalytic metals such as Fe, Ni and Co are deposited on a Si, SiO₂, or glass substrate using thermal CVD or sputtering. After the nanoscopic fine metal particles are formed, the carbon nanotubes grow on the metal particles on the substrate by the glow discharge generated from a high frequency power source. A carbon-containing gas, such as C₂H₂, CH₄, C₂H₄, C₂H₆ or CO is supplied to the chamber during discharge.⁴⁸ The catalyst has a strong effect on the nanotube diameter, growth rate, wall thickness, morphology and microstructure. Nickel seems to be the most suitable catalyst for the growth of aligned MWNTs by this technique.⁴⁹ The diameter of the MWNTs is around 15 nm. The highest yield of carbon nanotubes achieved by Chen *et al.* was about 50%, at a relatively low temperature (<330 °C).⁴⁸

Thermal Chemical Vapour Deposition

In this method, Fe, Ni, Co or an alloy of these metals is initially deposited on a substrate. After the substrate is etched by a dilute HF solution, it is placed in a quartz boat, positioned in a CVD reaction furnace. Nanometre-sized catalytic metal

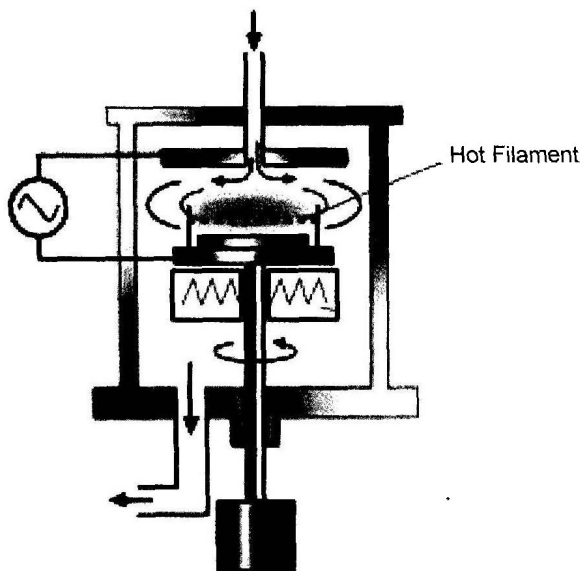


Figure 1.4 Schematic diagram of a plasma CVD apparatus
(Reproduced from ref. 48)