Chapter 1

Introduction

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1.1 *Carbon nanotubes*

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. Nanotubes have been constructed with length-to-diameter ratio of up to 132,000,000:1[1]. It is called as aspect ratio and is significantly larger than that of any other material. These cylindrical carbon molecules have extremely unique and remarkable properties which find their use in various fields as bio-sensors, semi-conductors, electronics, optical sciences, nanotechnology, mechanical and materials science, astrology and thousands of other technologies. Carbon nanotubes have extraordinary mechanical strength, thermal and electrical conductivity, which make them useful as additives. CNT exhibits extraordinary mechanical properties: the Young's modulus is over 1 Tera Pascal. It is stiff as diamond. The estimated tensile strength is 200 Giga Pascal. These properties are ideal for reinforced composites, Nanoelectro-mechanical systems (NEMS).

Researchers have been working on using carbon nanotubes to make transistors instead of silicon. *Recently a team at USC has created a carbon nanotube transistor that has an extrinsic frequency (which defines its practical performance limit) of 25 GHz – 40% faster than the current record holder, which operates at 15 GHz. That makes the team's nanotube transistor the fastest in the world.* The extremely small lengths possible due to use of CNT reduce the time it takes for the electrons to travel through the transistors, thus making them faster by reducing the parasitic capacitance of the circuit and also decreasing the channel length of the transistor.

Nanotubes are members of the fullerene (Figure 1.1) structural family. Their walls are formed by one-atom-thick sheets of carbon, called graphene (sp^2 hybridized). These sheets are rolled at specific and

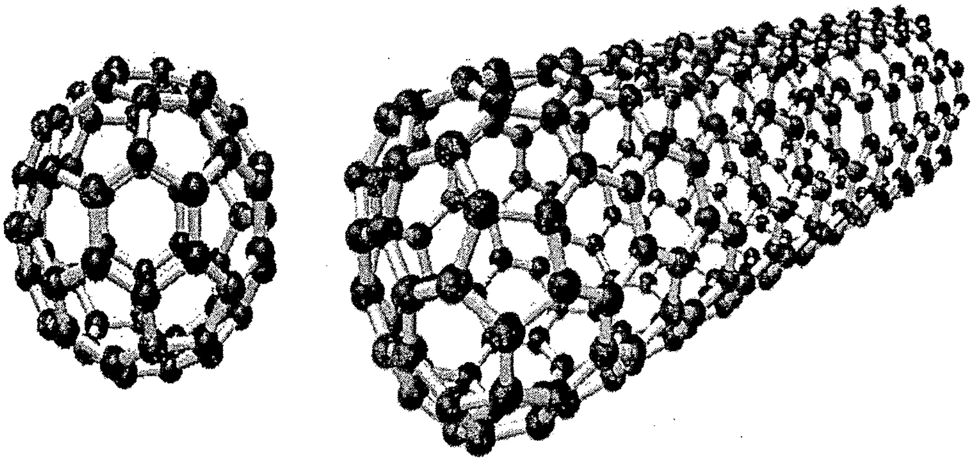

Figure 1.1 Bucky ball Fullerene and cylindrical nanotubes.

discrete ("chiral") angles, and the combination of the rolling angle and radius decides the nanotube properties; for example, whether the individual nanotube shell is a metal or semiconductor. Applied quantum chemistry, specifically, orbital hybridization best describes chemical bonding in nanotubes. The chemical bonding of nanotubes is composed entirely of sp^2 bonds, similar to those of graphite. These bonds, which are stronger than the sp^3 bonds found in alkanes and diamond, provide nanotubes with their unique strength.

The end cap of the nanotube can be thought as an incomplete fullerene with five and six membered carbon rings.Nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). Individual nanotubes naturally align themselves into "ropes" held together by van der Waals forces, more specifically, pi-stacking.

1.1.1 Single walled carbon nanotubes

The structure of a SWNT can be conceptualized by wrapping a one-atom-thick layer of graphite called graphene into a seamless cylinder. The way the graphene sheet is wrapped is represented by a pair of indices (n,m). The integers n and m denote the number of unit vectors along two directions in the honeycomb crystal lattice of graphene. If $m = 0$, the nanotubes are called zigzag nanotubes, and if $n = m$, the nanotubes are called armchair nanotubes (Figure 1.2). Otherwise, they are called chiral. The diameter of an ideal nanotube can be calculated from its (n, m) indices as follows

$$d = \frac{a}{\pi}\sqrt{(n^2 + nm + m^2)} = 78.3\sqrt{((n+m)^2 - nm)}\text{pm}.$$

where$a = 0.246$ nm.

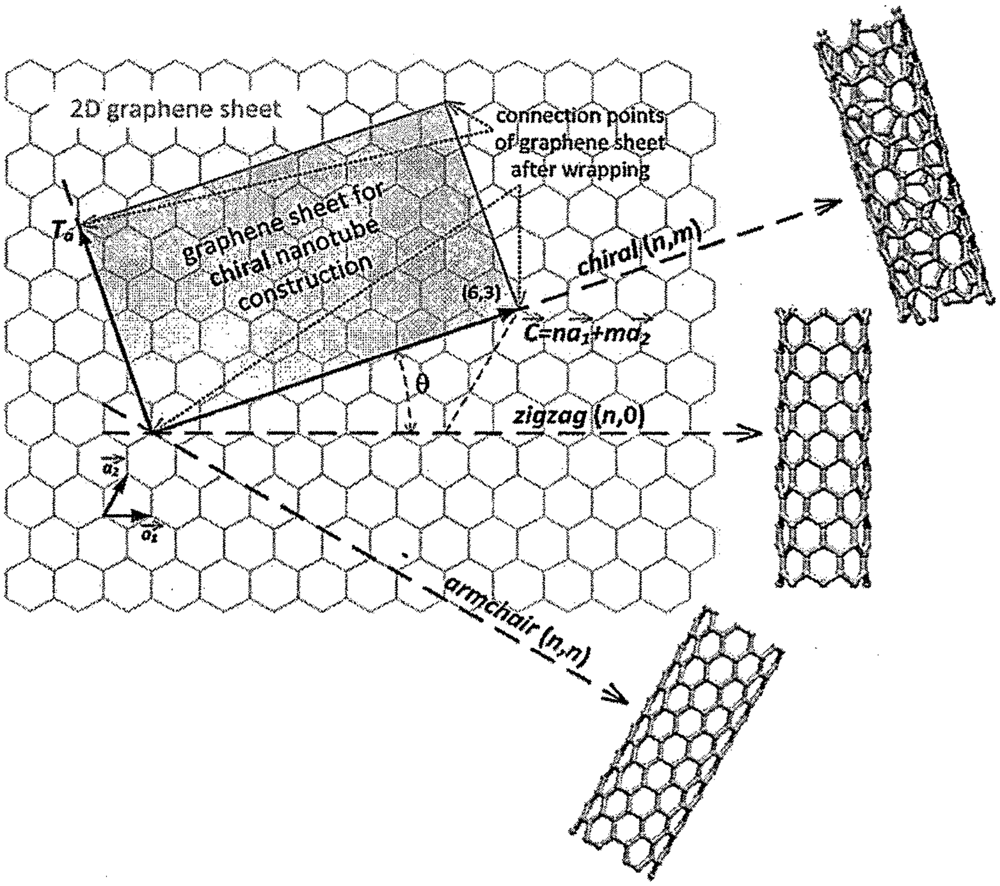

Figure 1.2 Rolling of graphene sheet along different directions to get different nanotubes.

1.1.2 Double walled carbon nanotubes

Double-walled carbon nanotubes (DWNT) form a special class of nanotubes (Figure 1.3) because their morphology and properties are similar to those of SWNT but their resistance to chemicals is significantly improved. This is especially important when functionalization is required (this means grafting of chemical functions at the surface of the nanotubes) to add new properties to the CNT. In the case of SWNT, covalent functionalization will break some C=C double bonds, leaving "holes" in the structure on the nanotube and, thus, modifying both its mechanical and electrical properties. In the case of DWNT, only the outer wall is modified. DWNT synthesis on the gram-scale was first proposed in 2003[2] by the CCVD technique, from the selective reduction of oxide solutions in methane and hydrogen.

The telescopic motion ability of inner shells[3] and their unique mechanical properties[4]will permit the use of MWNT and SWNT's as main movable arms in coming nanomechanical devices. Retraction force that occurs to telescopic motion caused by the Lennard-Jones interaction between shells and its value is about 1.5 nN [5].

1.1.3 Multi-walled carbon nanotubes

Multi-walled nanotubes (MWNT) consist of multiple rolled layers (concentric tubes) of graphene. Its individual shells can be described as SWNTs, which can be metallic or semiconducting. Because of statistical probability and restrictions on the relative diameters of the individual tubes, one of the shells, and thus the whole MWNT, is usually a zero-gap metal.

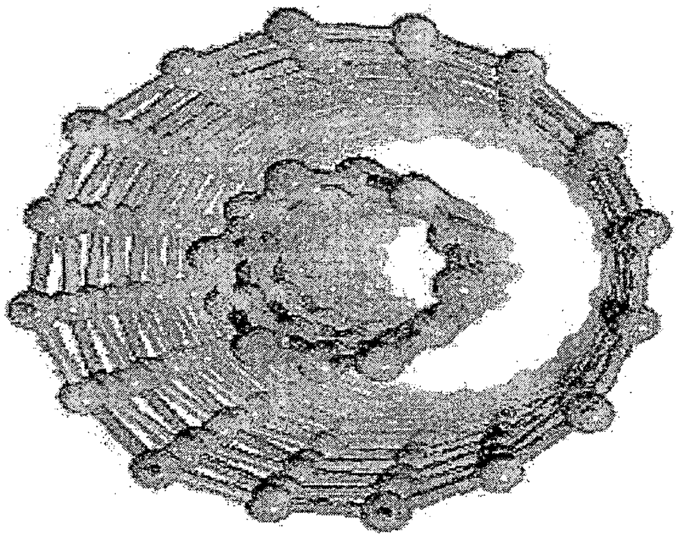

Figure 1.3 Double-walled carbon nanotubes.

1.1.4 Torus

In theory, a nanotorus is a carbon nanotube bent into a torus (doughnut shape). Nanotori (Figure 1.4) are predicted to have many unique properties, such as magnetic moments 1000 times larger than previously expected for certain specific radii[6]. Properties such as magnetic moment, thermal stability, etc. vary widely depending on radius of the torus and radius of the tube[6,7].

1.1.5 Nanobud

Carbon nanobuds are a newly created material combining two previously discovered allotropes of carbon: carbon nanotubes and fullerenes. In this new material, fullerene-like "buds" are covalently bonded to the outer sidewalls of the underlying carbon nanotube. This hybrid material has useful properties of both fullerenes and carbon nanotubes. In particular, they have been found to be exceptionally good field emitters. In composite materials, the attached fullerene molecules may function as molecular anchors preventing slipping of the nanotubes, thus improving the composite's mechanical properties.

1.1.6 Graphenated carbon nanotubes (g-CNTs)

Carbon filter papers(Hsu *et al.*)[10] and carbon nanotubes develop some leaf like structures on their sidewalls. These structures are produced following some special conditions of time and temperatures. These are graphene structures bonded chemically to CNT walls reported by Yu *et al.*[8]. Stoner *et al.*[9]

have made a detailed study on extraordinary supercapacitor performance of these structures known as "graphenated CNTs". The foliate density can vary as a function of deposition conditions (e.g. temperature and time) with their structure ranging from few layers of graphene (< 10) to thicker, more graphite-like[11].

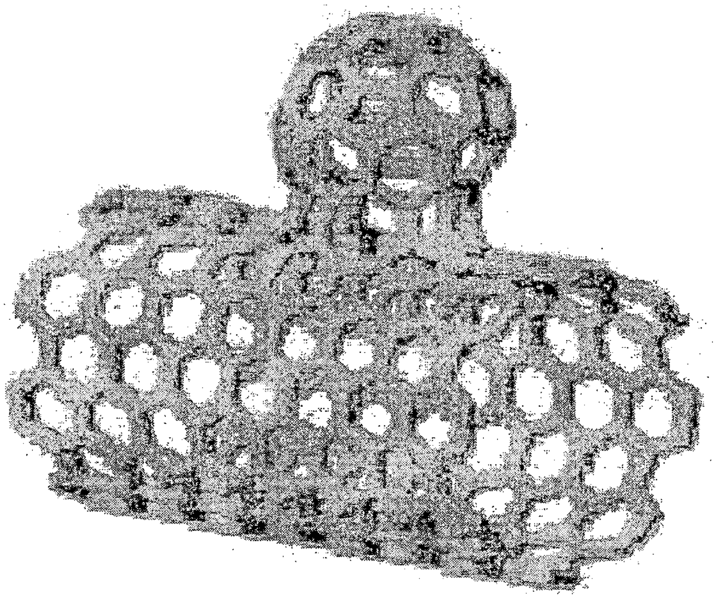

Figure 1.4 Torus.

Presence of these structures makes a very complicated structure with a three-dimensional arrangement, thereby increasing the reactive surface area. The graphene edges arising out are supposed to possess very high density. Graphene edges provide significantly higher charge density and reactivity than the basal plane, but they are difficult to arrange in a three-dimensional, high volume-density geometry. CNTs are readily aligned in a high density geometry (i.e., a vertically aligned forest) but lack high charge density surfaces[12].the sidewalls of the CNTs are similar to the basal plane of graphene and exhibit low charge density except where edge defects exist. Depositing a high density of graphene foliates along the length of aligned CNTs can significantly increase the total charge capacity per unit of nominal area as compared to other carbon nanostructures.

1.1.7 Nitrogen Doped Carbon Nanotubes

Nitrogen doped carbon nanotubes (N-CNT's), can be produced through 5 main methods, Chemical Vapor Deposition, high-temperature and high-pressure reactions, gas-solid reaction of amorphous carbon with NH_3 at high temperature[13] solid reaction, and solvothermal synthesis [14].

N-CNTs can also be prepared by a CVD method of pyrolysizing melamine under Argon at elevated temperatures of 800°C - 980°C. However synthesis via CVD and melamine results in the formation of bamboo structured CNTs. XPS spectra of grown N-CNT's reveals nitrogen in five main components, pyridinic nitrogen, pyrrolic nitrogen, quaternanry nitrogen, and nitrogen oxides. Furthermore synthesis temperature affects the type of nitrogen configuration.

Nitrogen doping plays a pivotal role in Lithium storage. N-doping provides defects in the walls of CNT's allowing for Li ions to diffuse into interwall space. It also increases capacity by providing more favorable bind of N-doped sites. N-CNT's are also much more reactive to metal oxide nanoparticle deposition which can further enhance storage capacity, especially in anode materials for Li-ion batteries. However Boron doped nanotubes have been shown to make batteries with triple capacity.

1.1.8 Peapod

A Carbon peapod is a novel hybrid carbon material[15] which traps fullerene inside a carbon nanotube. It can possess interesting magnetic properties with heating and irradiating. It can also be applied as an oscillator during theoretical investigations and predictions.

1.1.9 Cup-stacked carbon nanotubes

Cup-stacked carbon nanotubes (CSCNTs) differ from other quasi-1D carbon structures, which normally behave as quasi-metallic conductors of electrons. CSCNTs exhibit semiconducting behaviors due to the stacking microstructure of graphene layers[16].

1.1.10 Extreme carbon nanotubes

The observation of the *longest* carbon nanotubes (18.5 cm long) was reported in 2009. These nanotubes were grown on Si substrates using an improved chemical vapor deposition (CVD) method and represent electrically uniform arrays of single-walled carbon nanotubes.

The *shortest* carbon nanotube is the organic compound cycloparaphenylene, which was synthesized in early 2009.

The *thinnest* carbon nanotube is armchair (2,2) CNT with a diameter of 3 Å. This nanotube was grown inside a multi-walled carbon nanotube. Assigning of carbon nanotube type was done by combination of high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy and density functional theory (DFT) calculations[17].

Another structural aspect of tubes is their self-organization into *"ropes,"* which causes many (typically, 10-100) tubes held together by van der Waals forces.

Ropes are far longer than any individual tube in them (Tubes : 100-1000 nm in length, Ropes: endless, branching off from one another, then joining others). These ropes are useful in providing very long conductive pathways. These rope formation and interactive forces hinder, stable colloidal suspension in various protic and aprotic solvents. These forces overcome any other repulsive forces (e.g., electrostatic or steric), and make dispersed colloidal suspensions thermodynamically unstable, which limits the use of CNTs. However, surface active agents (surfactants, polymers or other colloidal particles) can modify the particles-suspending medium interface and change some rheological surface properties which contribute to increasing the stability of the colloidal suspension.

1.2 Synthesis techniques of nanotubes

Techniques have been developed to produce nanotubes in sizeable quantities, including arc discharge, laser ablation, high-pressure carbon monoxide disproportionation (HiPCO), and chemical vapor deposition (CVD). Most of these processes take place in vacuum or with process gases. CVD growth of CNTs can occur in vacuum or at atmospheric pressure. Large quantities of nanotubes can be synthesized by these methods; advances in catalysis and continuous growth processes are making CNTs more commercially viable.

1.2.1 High Pressure Carbon Monoxide Method

The high pressure carbon monoxide (HiPCO) method (Figure 1.5) can produce large quantities of carbon nanotubes. Catalysts for SWNT growth form in situ by thermal decomposition of ion pentacarbonyl in a heated flow of carbon monoxide at pressures of 1-10atm and temperatures of 800-1200°C. Previous methods for growing CNTs using hydrocarbons as source have resulted large

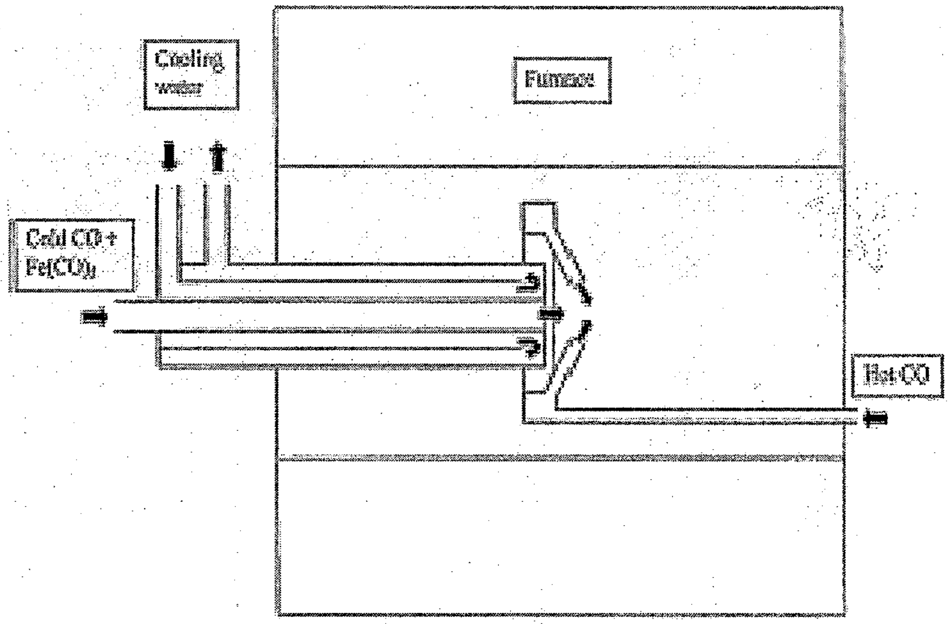

Figure 1.5 High Pressure Carbon Monoxide Method.

quantities of amorphous carbon and graphitic deposits due to the thermal breakdown of hydrocarbons at high temperatures. The amorphous carbon overcoating would have to be removed in subsequent steps. The HiPCO method uses carbon monoxide as the carbon feedstock and $Fe(CO)_5$ as the iron-containing catalyst precursor[18].

The products of the $Fe(CO)_5$ thermal decomposition react to produce iron clusters in gas phase. SWNTs nucleate and grow on these clusters. The solid carbon is formed through CO disproportionation, also known as the Boudouard reaction:

$CO+CO \Rightarrow C(s)+CO_2$

This reaction occurs catalytically on the surface of the iron particles. The iron particles promote the formation of the tube's characteristic graphitic carbon lattice.

1.2.2 Arc discharge

Nanotubes were observed in 1991,but first macroscopic production of carbon nanotubes was made in 1992 by two researchers at NEC's Fundamental Research Laboratory[19]. Arc discharge (Figure 1.6) belongs to the methods that use higher temperatures (above 1700°C) for CNT synthesis[20]which usually causes the growth of CNTs with fewer structural defects in comparison with other techniques.

A. MWNTs synthesis.

The arc discharge synthesis of MWNTs uses DC arc discharge between two graphite water-cooled electrodes with diameters between 6 and 12 mm in a chamber filled with helium at sub atmospheric pressure. Different atmospheres markedly influence the final morphology of CNTs. Wang et al.[21] used DC arc discharge of graphite electrodes in He and methane. By evaporation under high pressured CH_4 gas and high arc current, thick nanotubes embellished with many carbon nanoparticles can be obtained.

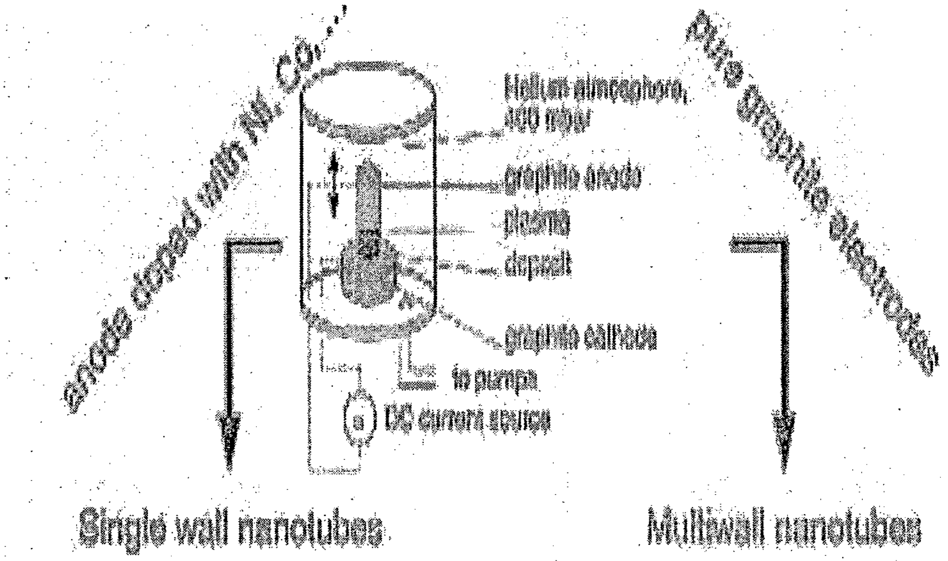

Figure 1.6 Arc discharge method.

Thin and long MWNTs can be obtained under aCH_4gas pressure of 50 Torr. Arc discharges in the three organic atmospheres (ethanol, acetone and hexane) produce more MWNTs, by two times at least, than those in the He atmosphere. Shimotani et al.[22]said that acetone, ethanol and hexane can be ionized and the molecules can be decomposed into hydrogen and carbon atoms. These ionized species may contribute the synthesis of MWNTs, so the higher yield of CNTs is produced. MWNTs obtained are are highly crystalline, with a well-ordered structure and free of defects. They obtained MWNTs with an outer diameter of10–20 nm and an interlayer distance of approximately 0.35 nm between graphene layers.

B. SWNTs synthesis

Usually the MWNTs are produced when no catalyst is used. On the other hand, the SWNTs are produced when the transition metal catalyst is used. The process of SWNTs growth in arc discharge utilizes a composite anode, usually in hydrogen or argon atmosphere. The anode is made as a composition of graphite and a metal, such as Ni, Fe, Co, Pd, Ag, Pt, etc.or mixtures of Co, Fe, Ni with other elements like Co–Ni, Fe–Ni, Fe–No, Co–Cu, Ni–Cu, Ni–Ti, etc. The metal catalyst plays a significant role in the process yield. To ensure high efficiency, the process also needs to be held on a constant gap distance between the electrodes which ensures stable current density and anode consumption rate. According to growth patterns and morphology of SWNTs, they divided the synthesis results into three groups: the tubes tangled with each other to form ‘‘highway junction’’ pattern for Co and Fe/Ni, long and thin tubes radially growing from Ni particles, and short and thick tubes growing from lanthanide compound particles[23].

1.2.3 Laser ablation

In the laser ablation process, a pulsed laser vaporizes a graphite target in a high-temperature reactor while an inert gas is bled into the chamber. Nanotubes develop on the cooler surfaces of the reactor as the vaporized carbon condenses. A water-cooled surface may be included in the system to collect the nanotubes. Laser ablation, as crucial step of PLD, is one of the superior methods to grow SWNTs with high-quality and high-purity. In this method, which was first demonstrated by Dr. Richard Smalley and co-workers at Rice University in 1995[24] the principles and mechanisms are similar to the arc discharge with the difference that the energy is provided by a laser hitting a graphite pellet containing catalyst materials (usually nickel or cobalt)[25].

The laser ablation method (Figure 1.7) yields around 70% and produces primarily single-walled carbon nanotubes with a controllable diameter determined by the reaction temperature. However, it is more expensive than either arc discharge or chemical vapor deposition.

1.2.4 Plasma torch

Single-walled carbon nanotubes can be synthesized by the induction thermal plasma method, discovered in 2005 by groups from the University of Sherbrooke and the National Research Council of Canada[26].The method is similar to the arc-discharge process in that both use ionized gas to reach the high temperature necessary to vaporize carbon containing substances and the metal catalysts necessary for the ensuing nanotube growth. The thermal plasma is induced by high frequency oscillating currents in a coil, and is maintained in flowing inert gas. Typically, a feedstock of carbon black and metal catalyst particles is fed into the plasma, and then cooled down to form single-walled carbon nanotubes. Different single-wall carbon nanotube diameter distributions can be synthesized.

The induction thermal plasma method can produce up to 2 grams of nanotube material per minute, which is higher than the arc-discharge or the laser ablation methods.

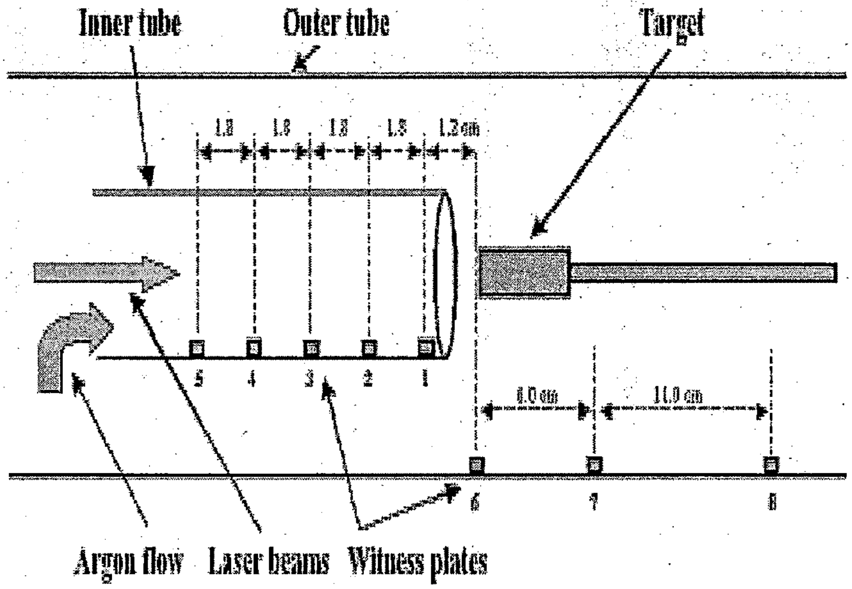

Figure 1.7 Laser ablation Process.

1.2.5 Chemical vapor deposition (CVD)

Carbon nanotubes were first prepared by this process in 1993, though the discovery of this process lies long back in 50's. For CVD (Figure 1.8) a substrate/reactor bed is prepared with a layer of metal catalyst particles, most commonly nickel, cobalt, iron, or a combination[27]. Size of the metal particles used decides the diameters of the nanotubes that are produced. The substrate is heated to approximately 700°C or high temperature annealing is done. A combination of two gases, inorganic or process gas, which is generally N_2 or H_2, and a organic gas, basically methane, ethene, or ethyne is used as initiator for growth of nanotubes at metal particles. The catalyst particles can stay at the tips of the growing nanotube during the growth process, or remain at the nanotube base, depending on the adhesion between the catalyst particle and the substrate[28].Thermal catalytic decomposition of hydrocarbon has become an active area of research and can be a promising route for the bulk production of CNTs. Fluidized bed reactor is the most widely used reactor for CNT preparation. A combination of metal nanoparticles such as MgO or Al_2O_3 and catalyst increases the surface area for higher yield. New water soluble catalyst particles are now preferred, due to the ease of their removal.

Use of a strong electric field during the growth process produces plasma (plasma enhanced chemical vapor deposition), and the nanotube growth follows the direction of the electric field. By adjusting the geometry of the reactor it is possible to synthesize vertically aligned carbon nanotubes[29] (i.e., perpendicular to the substrate), a morphology that has been of interest to researchers interested in the electron emission from nanotubes. CVD produces great interest because of its price/unit ratio, and because CVD is capable of developing nanotubes of desired diameters, length, and alignment and on desired catalyst support. In 2007, a team from Meijo University demonstrated a high-efficiency CVD technique for growing carbon nanotubes from camphor[30].

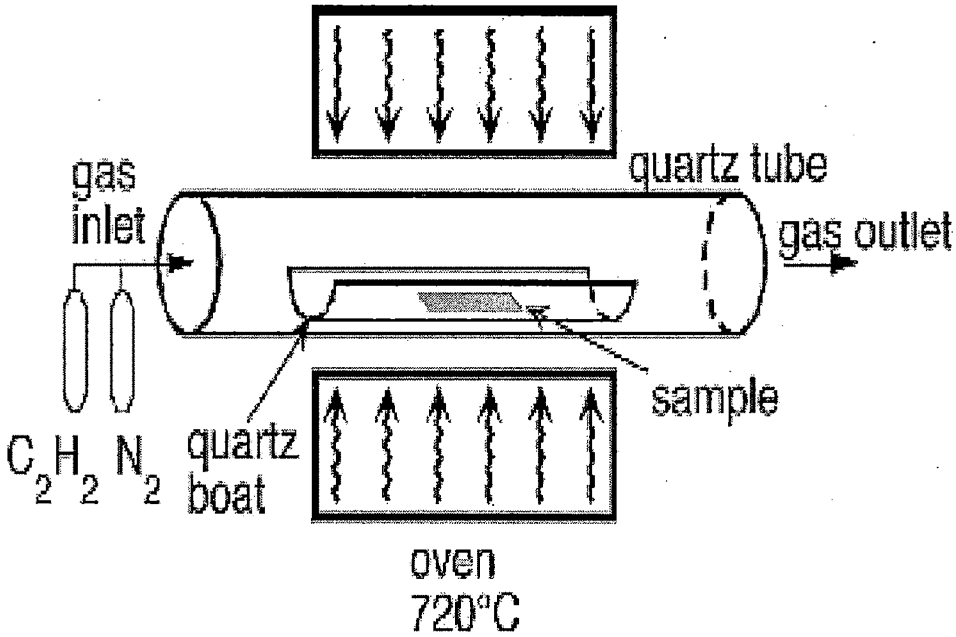

Figure 1.8 Chemical vapor deposition (CVD) process.

1.2.6 Super-growth CVD

Super-growth CVD (water-assisted chemical vapor deposition) process was developed by Kenji Hata, Sumio Iijima and co-workers at AIST, Japan[31]. In this process, the activity and lifetime of the catalyst are enhanced by addition of water into the CVD reactor.

Their specific surface exceeds 1,000 m^2/g (capped) or 2,200 m^2/g (uncapped), SWNT forests can be easily separated from the catalyst, yielding clean SWNT material (purity >99.98%) without further purification. Patterned highly organized single-walled nanotube structures were successfully fabricated using the super-growth technique.

The mass density of super-growth CNTs is about 0.037 g/cm^3. It is much lower than that of conventional CNT powders (~1.34 g/cm^3), probably because the latter contain metals and amorphous carbon.

The vertically aligned nanotube forests originate from a "zipping effect" when they are immersed in a solvent and dried. The zipping effect is caused by the surface tension of the solvent and the van der Waals forces between the carbon nanotubes. The packed carbon nanotubes are more than 1 mm long and have a carbon purity of 99.9% or higher; they also retain the desirable alignment properties of the nanotubes forest[32].

1.2.7 Flame pyrolysis

This technique is presented very uniquely by the research group of Liu et al.[33]as a new method for mass CNTs production using simple equipment and experimental conditions. The authors called it V-type pyrolysis flame. They captured successfully CNTs with less impurities and high yield using carbon monoxide as the carbon source. Acetylene/air premixed gas provided heat by combustion. Pentacarbonyl was used as the catalyst and hydrogen/helium premixed gas acted as diluted and protection gas. The diameter of obtained CNTs was approximately between10 nm and 20 nm, and its length was dozens of microns. Moreover they studied the effect of sampling time, hydrogen and helium to the CNTs growth process.

1.3 Potential applications

The strength and flexibility of carbon nanotubes makes them of potential use in controlling other nanoscale structures, which suggests they will have an important role in nanotechnology engineering. The highest tensile strength of an individual multi-walled carbon nanotube has been tested to be is 63 GPa[34].

1.3.1 Mechanical and structural applications

Carbon nanotubes have superior mechanical properties, and so find use and space in everyday items like clothes and sports gear to combat jackets and space elevators. Work done by Ray H. Baughman at the NanoTech Institute has shown that single and multi-walled nanotubes can produce materials with extremely high toughness[35].

Unmatched mechanical properties (~1 TPa in modulus, and ~100 GPa in strength) allowed them to be used to produce continuous CNT yarns from CVD grown CNT aerogels by Windle *et al.*[36]. With this technology, they fabricated CNT yarns with strengths as high as ~9 GPa at small gage lengths of ~1 mm, however, defects resulted in a reduction of specific strength to ~1 GPa at 20 mm gage length.

The fundamental properties of these extremely fine yarns are being studied using techniques borrowed from CSIRO's multi-fibre research and development (R&D) capability. They are also studying the production methods and properties of extruded fibres made from polymers blended with carbon nanotubes, with an emphasis on the uniform dispersal of the nanotubes in polymers, before extrusion into yarn.CNT's could help create stab-proof and bulletproof clothing. The nanotubes would effectively stop the bullet from penetrating the body.

1.3.2 Antiballistic materials

CSIRO is working with the Defence Science and Technology Organisation (DSTO), Defence Capability and Technology Demonstrator (CTD) Program to demonstrate the capabilities of carbon nanotubes as strong, lightweight antiballistic materials.

1.3.3 Medical

In the Kanzius cancer therapy, single-walled carbon nanotubes are inserted around cancerous cells, then excited with radio waves, which causes them to heat up and kill the surrounding cells. Researchers[37] at Rice University, Radboud University Nijmegen Medical Centre and University of California, Riverside have shown that carbon nanotubes and their polymer nanocomposites are suitable scaffold materials for bone cell proliferation and bone formation.

1.3.4 Electrical circuits

Nanotube-based transistors, also known as carbon nanotube field-effect transistors (CNTFETs), have been made to operate at using a single electron, at room temperature and that are capable of digital switching band gap. Semiconducting nanotubes can be used to build molecular field-effect transistors (FETs) while metallic nanotubes can be used to build single-electron transistors.

The recent CNFETs[38]are now built with top-gate geometry and resemble more conventional silicon CMOS devices. The SWNT transistors consist of a semiconducting carbon nanotube about 1 nm in diameter bridging two closely separated metal electrodes a top a silicon surface coated with SiO_2.

One major obstacle to realization of nanotubes has been the lack of mass production. IBM researchers demonstrated how metallic nanotubes can be destroyed, leaving semiconducting ones behind for use as transistors. Their process is called "constructive destruction". An approach[39] to produce transistors using random networks of carbon nanotube, that would help to average out all of their electrical differences was studied. Large structures of carbon nanotubes can be used for thermal management of electronic circuits. An approximately 1 mm–thick carbon nanotube layer was used as a special material to fabricate coolers, this material has very low density, ~20 times lower weight than a similar copper structure, while the cooling properties are similar for the two materials.

1.3.5 Solar cells

The different type of nanotubes, SWNT ,MWNT, and DWNT's have the capability to absorb various types of electromagnetic radiations such as Ultraviolet radiations, Visible and IR rays, making them useful in solar and radar panels. Solar cells[40] developed at the New Jersey Institute of Technology use a carbon nanotube complex, formed by a mixture of carbon nanotubes and carbon buckyballs (known as fullerenes) to form snake-like structures. The fullerenes or carbon nanotubes can be complexed with some polymers, which then results in structures which could trap electrons and cause them to flow. There are many types of photexcitable electron donors known like porphrin which when combined to fullerene and nanotube composition to create hybrid solar panels, would definitely give rise to increased efficiency.

1.3.6 Lighting Elements

Nanotubes are excellent electron sources, thus they are useful in the creation of light elements. The electrons produced by nanotubes are used to bombard a surface coated with phosphor in order to produce light. The brightness of this light is usually 2 times brighter than conventional lighting elements (due to the high electron efficiency).

1.3.7 Hydrogen Storage

Another property of carbon nanotubes is their ability to quickly adsorb high densities of hydrogen at room temperature and atmospheric pressure. The research group at the National Renewable Energy Laboratory already confirms that SWNTs are capable of storing hydrogen at densities of more than 63kg/m^3. Researchers have found that the interaction of hydrogen and SWNT is between the Van der Waals force of the SWMT and the chemical bonds of the hydrogen molecule (as opposed to being due to hydrogen dissociation)[41].

1.3.8 Memory device

Because of its ability to store information as a single electronic charge, nanotubes have the potential to be used in the design of memory devices. A single electron is discrete, and thus needs less energy in order to change the state of the memory. Such a design would also take advantage of the high mobility of SWMT, which is ten times greater than that of silicon.

1.3.9 Ultracapacitors

Ultracapacitors are storage devices which can store electric charges. The surface area available for storing electric charge plays a valuable role. Introduction of nanotubes to modify these capacitors has been challenging and has been worked upon by MIT Laboratory and Electronic Systems uses. The conventional ultracapacitors which use activated charcoal has many limitations such as, a significant fraction of the electrode surface is not available for storage because the hollow spaces are not compatible with the charge's requirements. With a nanotube electrode the spaces may be tailored to size—few too large or too small—and consequently the capacity should be increased considerably[42].

1.3.10 Radar absorption

Radars work in the microwave frequency range, which can be absorbed by MWNTs. Applying the MWNTs to the aircraft would cause the radar to be absorbed and therefore seem to have a smaller signature. One such application could be to paint the nanotubes onto the plane. Recently there has been some work done at the University of Michigan regarding carbon nanotubes usefulness as stealth technology on aircraft. It has been found that in addition to the radar absorbing properties, the nanotubes neither reflect nor scatter visible light, making it essentially invisible at night, much like painting current stealth aircraft black except much more effective. Current limitations in manufacturing, however, mean that current production of nanotube-coated aircraft is not possible. One theory to overcome these current limitations is to cover small particles with the nanotubes and suspend the nanotube-covered particles in a medium such as paint, which can then be applied to a surface, like a stealth aircraft[43].

1.3.11 Optical power detectors

A spray-on mixture of carbon nanotubes and ceramic demonstrates unprecedented ability to resist damage while absorbing laser light. Such coatings that absorb as the energy of high-powered lasers without breaking down are essential for optical power detectors that measure the output of such lasers. These are used, for example, in military equipment for defusing unexploded mines. The composite consists of multiwall carbon nanotubes and a ceramic made of silicon, carbon and nitrogen. Including boron boosts the breakdown temperature. The nanotubes and graphene-like carbon transmit heat well, while the oxidation-resistant ceramic boosts damage resistance. Creating the coating involves dispersing he nanotubes in toluene, to which a clear liquid polymer containing boron was added. The mixture was heated to 1,100°C (2,010 °F). The result is crushed into a fine powder, dispersed again in toluene and sprayed in a thin coat on a copper surface. The coating absorbed 97.5 percent of the light from a far-infrared laser and tolerated 15 kilowatts per square centimeter for 10 seconds. Damage tolerance is about 50 percent higher than for similar coatings, e.g., nanotubes alone and carbon paint.

1.3.12 Adsorption

Carbon nanotubes, functionalized or unfunctionalized have very high adsorptivity. Functionalization of Carbon nanotubes, generates active sites on the surface of nanotubes. These charged sites help to associate with the metal ions by chelate formation. Thus an added advantage of functionalization, increases the retention power of the nanotubes towards heavy metal ions.

HNO_3 treated Carbon nanotubes (CNTs) have been employed as adsorbent[44]to study the adsorption characteristics of some divalent metal ions (Cu, Co, Cd, Zn, Mn, Pb). Multi-walled carbon nanotubes have been used successfully for the removal of Copper(II), Lead(II), Cadmium(II), and Zinc(II) from aqueous solution, and effect of solution temperature on this process has been studied[45]. It has been confirmed that the % adsorption increases by raising the solution temperature due to the endothermic nature of the adsorption. The values of the free energies for the reactions are negative, which indicates that adsorption process is spontaneous, and this spontaneity increases by raising the solution temperature. The changes in entropy values are positive, which indicate the increase in randomness due to the physical adsorption of heavy metal ions from the aqueous solution to the carbon nanotubes surface. Enthalpy values are positive for all metal ions, but the free energies are negative, and the adsorption is a spontaneous one, which indicates that the heavy metal adsorption of Multi-walled carbon nanotubes is an entropy-driving process. Similar works on heavy metal adsorption has been done by Y. H. Li and co-workers[46].

Though most of the studies have been done with nanotubes containing carboxyl groups(-COOH), many studies have been done on nanotubes, developing different functional moieties containing different hetero atoms such as nitrogen, chlorine, sulfur, phosphorus etc. These hetero atoms increase the chelate formation tendency due to presence of lone pairs in hetero atoms and also due to their small sizes.

Multiwalled nanotubes functionalized with iminodiacetic acid (IDA) have been studied[47] for heavy metal detection in biological samples.Detection limit (3 s) was achieved at 1.3, 1.2, 0.70, 0.40, 2.5, 3.4, 0.79 ng L(-1), respectively. At the 1.0 μg L(-1) level, the precision (RSD, %) for 11 replicate measurements was from 1.0 to 4.0. this shows that carbon nanotubes could be used with good accuracy. A novel Schiff base-chitosan-grafted multiwalled carbon nanotubes (S-CS-MWCNTs) solid-phase extraction adsorbent has been[48]synthesized by covalently grafting a Schiff base-chitosan (S-CS) onto the surfaces of oxidized MWCNTs and used for detection of heavy metals.

Carbon nanotubes show a great affinity for protein adsorption and human complement activation[49] and thus interact with a part of the human immune system. Fibrinogen and apolipoproteins (AI, AIV and CIII) bound to carbon nanotubes in greatest quantity. Similarly light membranes composed of single-walled carbon nanotubes (SWNTs) can serve as efficient nanoscale vessels for encapsulation of tetrafluoromethane[50] on their surface as compared to currently used activated carbons and zeolites,

As an advancement procedure functionalized CNT sheets[51]synthesized by chemical vapor deposition of cyclohexanol and ferrocene have been studied as adsorbent for water treatment. Using the oxidized CNT sheets for waste water treatment without CNT leakage into water is economically feasible. Therefore, CNT sheets have good potential application in environmental protection. In some other research works Carbon nanotubes (CNTs) have been grown on the surface of microsized $A1_20_3$ particles in CH_4atmosphere at 700°C under the catalysis of Fe-Ni nanoparticles[52]. As grown CNTs have been tested for adsorbing heavy metals from test solutions and the results compared with active carbon powders, commercial carbon nanotubes, and Al_2O_3particles. The as-grown CNTs/Al_20_3, have demonstrated extraordinary absorption capacity with oxidation, as well as hydrophilic ability that unoxidized CNTs lacked.

The 1-D nanomaterials composed of various ratios of carbon nanotubes (CNT) and titanate nanotubes (TNT) (CNT/TNT) have been prepared[53] by alkaline hydrothermal method. The nanocomposites may have different shapes and morphologies as nanoparticles/nanosheets, nanotubes, nanowires and nanoribbon depending on used temperatures (60 - 230°C). In addition, the CNT/TNT nanomaterials have a good capability toward heavy metal adsorption. The Langmuirian maximum adsorption capacities of nanomaterials were in the range 83-124 mg/g for Cu^{2+} and 192-588 mg/g for Pb^{2+}, which is superior to that of CNT. Thus it could be said that nanocomposites are a promising nano-adsorbent for coupled removal of organic as well as heavy metal ions in solution.

CNTs also have found immense applications in nanocomposite science. CNT/polycarbonate matrix composite membranes have been found to have good hydrogen separation properties[54]. Unmodified MWCNT/polysulfone microporous conductive membranes have also been prepared by sonication technique[55]. *The use of carbon nanotubes in pure or composite forms the major base of present study. The nanosize materials also have the capacity of altering the pore diameters of polymeric membranes. This property has been used for heavy metal rejection studies using CNT/Polysulfone nanocomposite membranes, where effect of addition of CNTs to polysulfone has been recorded in terms of porosity and hydrophilicity variation.*

CNTs have also found use in chemisorptions of polymers and macromolecules[56,57], as well as in in situ ATRP "grafting from" approach to functionalize themselves[58]. *Apart from traditional initiators of ATRP, new macro initiators and some simple initiators have been used and reported as a part of study in the thesis.*

1.4 "Water" : Transparent Gold

"Water" is elixir to life. Survival is impossible without it. Population explosion, industrialization and globalization has made clean drinking water an "endangered requirement" for the world. There is water all around us, 10 x 10^8 billion cubic meters water, covering 75% of the surface of earth. Most of this is highly saline water and flows into rivers, seas and oceans making it unavailable for drinking. Out of the remaining 2.8%, a major portion is locked in polar ice and glaciers. Only 0.5% is available for human use. Access to clean water is increasingly becoming the most important issue around the world. A large population is dependent on rain water and stagnant water (at some places) for quenching their thirst. A large population lacks access to sufficient amount of clean water and adequate sanitation[59]. The combination of poor sanitation and unhealthy water quality is one of the largest causes of disease and death in the world.

World health organization (WHO),has set standards for potable water defining a permissible limit for various constituents as heavy metals, salts, organic chemicals, minerals, essentials metals ions, algae and various other suspended impurities. Concentrations above this permissible limit make water unfit for drinking [60].

With the growth of technology, the concentration of heavy metals in surface water has increased considerably. Metals ions allowed to pass into the environment are persistent, and cannot be biodegraded. These metals are adsorbed into the soil, runoff into rivers or lakes or leach in the ground water which is an important source of drinking water. These heavy metals tend to build their homes in animals, plants and humans tissues.

1.5 Toxic ions present in surface and ground water

The ions which are not metabolized by our body and accumulate in the soft tissues are referred as toxic ions. Arsenic, mercury, cadmium, chromium and lead are fall in this category. All over the globe tons oftoxic ions add to waters every year.

Agency for Toxic Substance and Disease Registry (ATSDR), Department of Health and Human Services (US), identified some ions as toxic ions and arranged them in the form of a list called ATSDR's "Top 20 List of Hazardous Substances"[61].

1.6 Sources and Health effects of Toxic Metals

The presence of heavy metals such as chromium, cadmium, copper, nickel, lead, mercury etc. in aqueous environment may result in a major concern due to their toxicity and carcinogenicity, which may cause damage to various systems of the human body.

1.6.1 Arsenic

A. Sources

Erosion from local rocks seeps into ground water and adds Arsenic to it. A large number of minerals and ores also are a source of arsenic to ground water[62].Whereas, the occurrence of arsenic in surface water is generally believed to be due to the domestic waste water. Other major sources include sewage sludge, manufacturing processes, and smelting and refining.

B. Health Effects

i. Toxicity

ATSDR placed arsenic, on number 1 in the "Top 20 List of Hazardous Substances". It is the most common cause of acute heavy metal poisoning in humans and characterized by central nervous system effects, leading to coma and eventual death. The respiratory tract, gastrointestinal tract and skin are also affected during the bouts of sever poisoning. Chronic intoxication results in neurological disorders, muscular weakness, loss of appetite, nausea, and skin disorders such as hyper-pigmentation and keratosis. Low level ingestion of arsenic (1-10 mg/L) over extended periods may leads to the onset of acute toxicity.

ii. Carcinogenicity

Inorganic arsenic was associated with the genesis of skin cancer as early as 1888[63]. The international agency for research on cancer currently classifies inorganic as in group1: Inadequate evidence for carcinogenicity in animals and sufficient evidence of carcinogenicity (skin and lungs) in humans. The earliest manifestation of arsenicosis such as pigmentation and lesions on skin have often played havoc in the social situation of those affected owing to ignorance and misleading information. In rural areas skin pigmentation caused by consumption of arsenic contaminated water is often believed to be contagious and hereditary. Further arsenicosis is often mistaken for leprosy or other highly communicable skin disease[64,65].

1.6.2 Cadmium

A. Sources

Among the toxic metals cadmium is of considerable environmental and health significance because of its increasing mobilization and human toxicity. The major sources for the introduction of cadmium in water are smelting and refining of nonferrous metals, manufacturing processes related to chemicals and metals and domestic waste water[66]. The atmospheric deposition which contributes about 15% cadmium contamination, from natural sources such as volcanoes, windborne soil particles and biogenic particles cannot be ignored.

B. Health Effects

i. Toxicity

In humans acute exposure to cadmium leads to nausea, vomiting, salivation, diarrhoea and muscular cramps. Sever to fatal cases may show the symptoms of liver injury, convulsions, shock, renal failure and cardiopulmonary depression.

ii. Carcinogenicity

The international agency for research on cancer has classified cadmium for carcinogenicity in humans and no evidence for carcinogenicity in animals since there is no or little evidence that it is carcinogenic via oral route [67].

1.6.3 Chromium

A. Sources

Chromium another common pollutant with its toxicity and mutagenic effect is introduced into natural waters from domestic waste water, sewage sludge and a variety of industrial processes such as electroplating, metal finishing industries (hexavalent chromium) and tanneries (trivalent chromium). Chromium occurs most frequently as Cr (VI) and Cr (III) in aqueous solutions. Both valences of chromium are potentially harmful but Cr (VI) possesses a greater risk due to its carcinogenic properties[68].

B. Health Effects

i. Toxicity

Compounds of hexavalent chromium are more toxic than trivalent chromium to humans. The toxic and genotoxic nature of Cr(VI) ion were established a long time ago[69,70]. Acute exposure to Cr(VI) produces nausea, diarrhoea, liver and kidney damage, internal haemorrhage, dermatitis and respiratory problems. Cases of acute poisoning by Cr(III) compounds are extremely rare, reflecting their low toxicity to human population.

ii. Carcinogenicity

The IARC (1980) has evaluated the carcinogenicity of chromium compounds and found the compounds of Cr(VI) cancer producing but not yet categorized it as carcinogenic groups due to insufficient evidences for its carcinogenicity to humans. R. Sanz has established that the workers exposed to Cr(VI) compounds in stainless steel welding, chrome pigment production and other industrial occupations can suffer skin lesions, lung disease and various forms of cancer[71].

1.6.4 Cobalt

A. Sources

Cobalt is introduced to water mainly by the burning of fossil fuels approximately 55 %. Municipal effluents may also contain relatively high residues, particularly in the cities dominated by the metal-working industries. Contribution of cobalt through fly ash and sewage sludge may not be ignored.

B. Health Effects

i. Toxicity

Water polluted with cobalt may result in asthma like allergy, damage to heart, causing heart failure damage to thyroid and liver. Acute exposure to cobalt may lead to depression to the iodine uptake. Neurotoxicological symptoms including peripheral neuritis and changes in reflexes have also been reported[72]. It may also cause mutation in living cells.

ii. Carcinogenicity

There does not appear to be any evidence for carcinogenicity of cobalt in humans, even those exposed occupationally through the inhalation route.

1.6.5 Lead

A. Sources

The primary sources of lead include manufacturing processes, atmospheric deposition and domestic wastewater. Combustion of leaded fuels, pyrometallurgical nonferrous metal processes and coal combustion are also responsible lead introduction in water stream.

B. Health Effects

i. Toxicity

Lead number 2 on the ATSDRs list, accounts for the most of the cases of paediatric heavy metal poisoning and targets the bones, brain, thyroid gland and kidney. Acute poisoning by it is rare and is generally restricted to occupational settings.

ii. Carcinogenicity

Some examples for carcinogenicity of lead are available but they are insufficient to prove are disprove its carcinogenicity[73]. The IARC classified lead into group 3: inadequate evidence for carcinogenicity in humans and sufficient evidence for carcinogenicity in animals.

1.6.6 Mercury

A. Sources

Mercury pollution of water occurs due to various reasons like discharge from coal burning power plants, chemical manufacturing processes and discharge from municipal and industrial sources etc. Its contamination of aquatic ecosystem is widespread globally due primarily to atmospheric deposition[74]. The majority of atmospherically deposited Hg is in the inorganic form which can be converted to highly bio-available methyl mercury (MeHg) through natural processes in water bodies and watersheds.

B. Health Effects

i. Toxicity

Mercury, placed on number 3 on ATSDR's "Top 20 List", exists in three forms; elemental mercury, organic mercury and inorganic mercury. It shows its harmful effects on brain and kidneys. Since mercury is one of the most hazardous heavy metals having very high binding capacity with proteins and mainly affects renal & nervous systems[75].

ii. Carcinogenicity

Although methyl mercury may cause chromosome aberrations, there are inadequate evidences for its carcinogenicity.

1.6.7 Nickel

A. Sources

Nickel, another pollutant is the major part of municipal wastewater followed by waste of smelting and refining of nonferrous metals Beucemma et al. reported that the total amount of nickel discharged into the Netherlands part of the North sea amounted to 1100 metric tons per year[76].

B. Health Effects

i. Toxicity

The primary acute effect of nickel exposure is dermatoses, including contact dermatitis, atopic dermatitis and allergic sensitization. No clinical epidemiological studies are available on the acute effects of oral ingestion of nickel.

ii. Carcinogenicity

Nickel in some forms is likely to be carcinogenic in humans and in fact statistically significant elevations in the incidence of respiratory cancers have been found in nickel refinery workers[77]. However, no evidence of carcinogenicity exists for ingestion of nickel in either food or water.

The harmful and toxic effects of these ions on human body compel the environmentalists, scientists and policy makers to work in the area of environmental protection in last three decades. All developed countries have initiated efforts for clean water supply to their population which is having these contaminants not more than permissible limits as decided by the WHO in 1980s.

1.7 Consumption guidelines by WHO & BIS

Bureau of Indian Standards (BIS), Indian Council of Medical Research (ICMR) and World Health Organization (WHO) have decided certain limits for different parameters such as pH, Hardness, Total Dissolved Solids, Turbidity, Colour, Odour, concentration of anions and cations including toxic metal ions. The potable water is the water in which these parameters present below permissible limits. Since our work is related to the removal of toxic ions from water for which the permissible limits decided by different agencies are shown in Table 1.1.

India, a large developing country is also making all out efforts for clean water supply to its population for quite some time. But lack of resources and place to place variation in surface and ground water quality due to large geographical area make this task difficult. Figure 1.9 insight on availability of fresh water in India and predict it as the acute scarcity region by year 2025. Rajasthan region is having large amount of nitrates in its ground water whereas West Bengal and some territories in UP are facing arsenic problem[78]. In present situation, therefore a need exists to develop technologies which can fulfil the needs of water purification at low cost and as par requirements of particular area. All of these goals can be achieved only when the cost effective and ion selective materials are developed and optimized for water purification.

Table 1.1 Permissible Limits of Different Metal Ions for Potable Water (in mg/L).

S. No.	**Metal**	**WHO**	**BIS**	**Other Agency**
1.	Arsenic	0.05	0.05	-
2.	Cadmium	0.005	0.01	-
3.	Chromium (VI)	0.05	0.05	-
5.	Lead	0.05	0.1	-
6.	Mercury	0.001	0.001	0.002 (EPA, US)
7.	Nickel	-	-	0.2 (EPA, US)

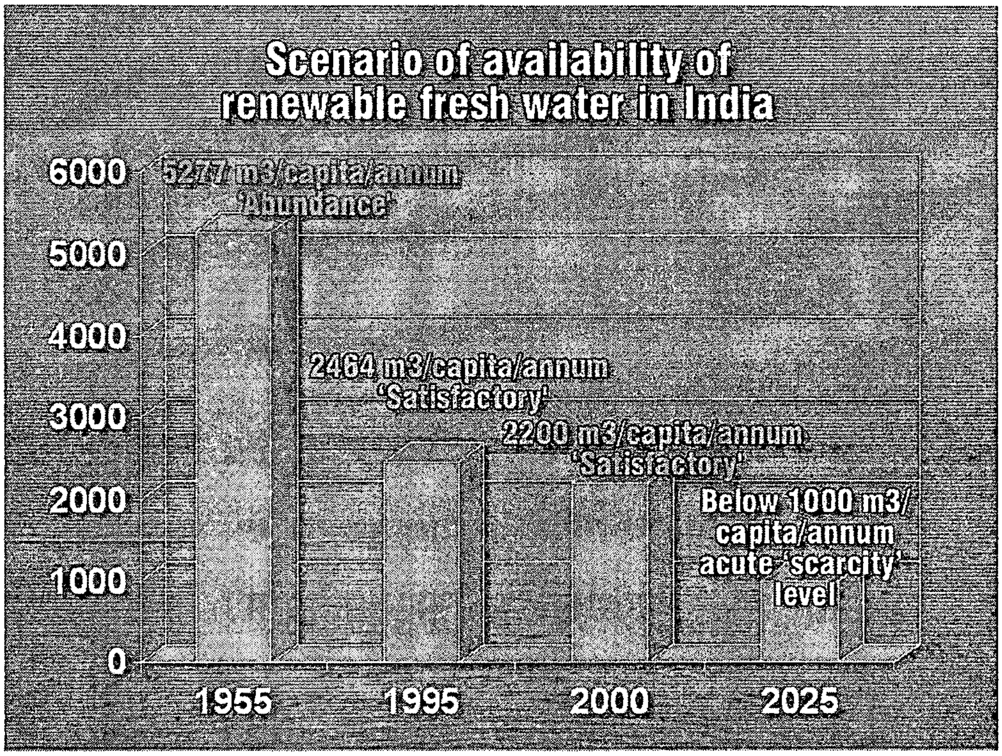

Figure 1.9 Availability of renewable fresh water in India.

1.8 Different technologies used in water purification

Many treatment processes such as chemical precipitation, evaporation, ion exchange, adsorption, electro-dialysis, reverse osmosis and ultra-filtration are currently used in various water treatment plants; but all of them are having their own limitations. The brief introductions of above processes are mentioned below:

1.8.1 Chemical precipitation

Precipitation of heavy metals as their hydroxides using lime, or sodium hydroxide, is widely used. Lime is generally chosen for precipitation purposes due to its low cost, ease of pH control in the range 8.0 – 10.0 and the presence of excess of lime also serves as an adsorbent for the removal of other metal ions[79]. The precipitation method has been used for the removal of iron, copper, zinc, tin, cadmium and nickel from the effluents of metal finishing industry and for the removal of aluminium and iron from sewage water[80]. Sorg.Et. al. Evaluated the use of lime for the removal of lead and cadmium from water and wastewaters and concluded that the effluents after treatment meet the requirements prescribed by Environmental Protection Agency (EPA), USA. But the major drawback with precipitation is sludge production[81].

1.8.2 Sulphide Precipitation

Excellent metal removal can be achieved by sulphide precipitation because most of the heavy metals form stable sulphides. The advantage of sulphide precipitation is that the solubility of metal sulphide is generally low resulting in a higher efficiency. In the sulphide precipitation method, the metal level is reduced to 0.01 mg/L for cadmium, copper and zinc and 0.05 mg/L for cadmium and nickel[82]. Mercury containing wastewaters have been treated using sodium sulphide in the pH range of 6.0 – 10.0 using ferric hydroxide as the collector[83].

1.8.3 Carbonate precipitation

The use of carbonate precipitation as a method for the removal of metals from wastewater is limited. Patterson et al.[84], used carbonate precipitation for cadmium (II) and lead (II) removal from electroplating effluents. At pH 7.5, the concentration of lead (II) and cadmium were reduced 0.6 and 0.25 mg/L respectively. Apart from low pH of precipitation, the relative filtration rates for carbonate precipitates were found to be approximately twice that of hydroxide precipitation[85].

1.8.4 Chemical Reduction

The hexavalent chromium in the chromate waste is reduced to trivalent chromium under acidic conditions (pH=3) followed by precipitation of Cr(III) hydroxide under slightly alkaline conditions[86], the removal of mercury, cadmium, lead, silver and gold by reduction process may be accomplished by use of sodium borohydride[87].

1.8.5 Solvent Extraction

Introduction of selective complexing agents has gained widespread usage for waste reprocessing and effluent treatment[88]. Liquid-liquid extraction of metals from aqueous solutions involves an organic and an aqueous phase. The aqueous solution containing the metal or metals of interest is mixed intimately with the appropriate organic solvent and the metal passes into the organic phase. In order to recover the extracted metal, the organic solvent is contacted with an aqueous solution whose composition is such that the metal is stripped from the organic phase and re-extracted into the stripping solution.

Knock et al[89], investigated the extraction of chromium (III), cadmium (II), copper (II), nickel (II) and zinc (II) from solutions containing 100 mg/L of each ion with 0.5 M solution of 8-Hydroxy quinoline into chloroform. At pH 5.4, 99 % of the cadmium (II) was reported to have extracted into chloroform layer. Back titration with dilute Hydrochloric acid solution showed that at pH 2.0, 79 % of the cadmium could be stripped into aqueous phase. The extraction of nickel into chloroform was 95 % at pH 2.0, while the extraction of Chromium (III) was poor at all pH conditions.

1.8.6 Cementation

Cementation is the displacement of a metal ion from aqueous solution by a metal higher in the electromotive series. The precipitation of silver from photo processing discharges, the precipitation of copper from printed etching solutions and the reduction of Cr (VI) in chromium plating and iriditing are some of the examples of cementation in wastewater treatment[90].

1.8.7 Electro-deposition

Recovery of metals found in waste solutions can be done by electro-deposition techniques using insoluble anodes, e.g. spent solutions resulting from sulphuric acid cleaning of copper may be saturated with the copper sulphate in the presence of residual acid. These are ideal for electro-winning where high quality copper cathode can be electrolytically deposited while free sulphuric acid is regenerated[91].

1.8.8 Ultrafiltration & Nanofiltration

Conventional ultrafiltration (UF, which can exclude particle size larger than 100 nm) and nanofiltration (NF, which can exclude the particle size larger than a few nanometers) filters for water treatments are based on porous membranes, typically manufactured by the phase immersion method[92]. These membranes have been reported for the removal of microbial contaminants from water due to their larger size and can efficiently remove heavy metal ions after complexation with appropriate complexing agents [93-95]. Polymer assisted ultrafiltration is another method to use UF membranes for toxic metal ion removal from water. Y. Uludag reported mercury removal by UF membrane using polyethyleneimine (PEI) as complexing agent , P. Canizares et al. has successfully used polyethyleneimine (PEI) and Poly (acrylic) acid (PAA) as complexing material for UF based separation of Cu(II), Ni(II), Pb(II) and Cd(II) ions from industrial wastewater[96]. Polyethyleneimine (PEI), poly (acrylic) acid (PAA) and poly (dimethylamine-co-epichlorohydrin-co-ethylenediamine) have been comparatively studied by R. Molinari for Cu(II) removal from wastewater using ultrafiltration[97]. Similarly many ultra and nanofiltration membranes have been reported by various workers which can be used for chelating enhanced or polymer assisted removal of heavy metals from wastewater [98,99].

Fibrous media in the form of non woven filters have been used extensively in water treatment as pre filters or to support the medium that does the separation. At present the use of non woven filter media is limited to pre filters and is not used further downstream as high performance filters. However it is expected that by reducing the fiber size in the nanometer range, higher filtration efficiency can be achieved. Non woven nanofibrous media is now introduced in liquid filtration with great possibility to replace the ultra filtration (UF that can exclude particle size larger than 100 nm) by nanofiltration (NF that can exclude particle size larger than few nm).

1.8.9 Electro dialysis

Electro-dialysis process works under the influence of electric current and separates the ions from water resulting in potable water. It is a well versed technique for ground and surface water treatment and can be used at TDS as high as 5000 ppm. The technique is used in SUJALAM, a joint project of DRDO and Rajasthan state government in which 64 water desalination plants have been installed in extreme desert areas of state to provide the potable water to its civilians[100].

1.8.10 Reverse Osmosis hyperfine filtration

Reverse osmosis are thin sheet-like materials forming barier in the feed water path. They are usually permeable to some species and impermeable to others. RO is the phenomenon of flow of solvent from concentrated side to dilute (pure) side through semi-permeable membranes by exerting external pressure. This technique is successfully applied for desalination purposes by various workers [101,102], used for removal of Cr, Pb, Fe, Ni, Cu and Zn from vehicle wash rack water[103], and now successfully used in large scale & domestic water purification systems.

1.8.11 Evaporation

Evaporators are used chiefly to concentrate and recover valuable plating chemicals in electroplating industries. In this process collected rinse stream is boiled till concentration and allowed to return to the plating bath. There are several evaporators available which permit the recovery of condensed steam for recycle as rinse water. Capital and operational, both costs of recovery systems are very high[104].

1.8.12 Xanthate process

Xanthates of cellulose and starch are commercially available, may be used for wastewater treatment. Wastewater containing lead, nickel, copper, chromium and iron when treated with cellulose xanthate resulted in minimum level of residual metals at pH range 6.5 to 9.5[105].

Most of these methods are associated with high capital and operational cost, complex handling and problems of disposal of the residual metal sludge.

1.8.13 Adsorption on Solid Surfaces

Sorption operations, including adsorption and ion exchange are potential alternatives for wastewater treatment. In an adsorption process, atom or ions (adsorbate) in a fluid phase diffuse to the surface of a solid (adsorbent), where they bond with the solid surface or are held there by weak intermolecular forces[106]. A number of investigators have studied the removal of inorganic metal ions namely cadmium, cobalt, zinc, silver, copper, mercury, chromium and lead from aqueous solution using different adsorbents[107-109].

1.8.14 Ion Exchange Resins

Ion exchange resins are potential alternatives for wastewater treatment. An ion exchange resin is an insoluble matrix (or support structure), normally in the form of small (1-2 mm diameter) beads fabricated from an organic polymer substrate. The material has sites with easily trapped and released ions. In the process simultaneous trapping and releasing of other ions takes place till the equilibrium is reached. Functionalization with chelating ligands enhances its efficacy due to complex formation in favorable conditions. However the improved ion exchange capacity of ion exchange resins may have advantages over such non specific adsorbents. In this regard, ion exchange resins hold great potential for the removal of heavy metals from water and industrial wastewater[110].

1.9 Advanced Materials Introduced in Water Purification

Presence of toxic ions in ground water and surface water above the permissible level decided by the WHO is the biggest problem facing the world. Lots of the people are suffering from supply of unhealthy drinking water which causes numerous disease and even death. Since water touches every aspect of human activity, from food, health and environment to local and global economies, the staggering importance of water treatment technologies cannot be ignored.

In present scenario due to advancement in technology it is easy to explore the utility of advanced nano materials in water purification as filter media and adsorbent as well. The pore size of filter media is obvious fundamental parameters as it determines the ability of the filter to trap particles of specific size range. The efficacy of water purification technology can be governed by reducing the size of filtration media or adsorbent from micro level to nano level and there surface modifications can be achieved by functionalizing them. Use of non woven nano fibrous filter media and functionalized carbon nanotubes are the new advancements in the water purification techniques with promising results. Nanotechnology opens new horizons for the researchers in the area of water purification.

Current water purification methods in wide use employ chemically intensive treatment that is relatively expensive, increases stress on watersheds and environment and is not translatable to the non industrialized world. This is the reason, which opens the door for material scientists and researchers for advanced materials and technology development. Some of the recent water purification advancements in the field of toxic ion removal from contaminated water are in R&D stage and showing promising results which are discussed below:

1.9.1 Resins Functionalized with Novel Chelating groups

Adsorption process has been and actually is the most frequently applied method in the industries and consequently the most extensively studied. S. Rangaraj et. al. reported IRN77 cation exchange resin as efficient adsorbent for the removal of Co(II), Cr(III) and Ni(II) from their aqueous solutions. Author has also carried out the comparison of IRN77 and SKN1 resin for the removal of cobalt from aqueous solution and nuclear power plant water. They have extensively utilised 1200H, 1500H and IRN77 for chromium removal from electronic process wastewater. A wide range of chelating ion exchangers has been tested for Zn, Ni, Cu and Cd removal from metal plating rinse water by Risto Koivula et.al.[111].

Though chelating ion exchangers are extensively used for water purification from long time and having great importance in selected ion removal, possibility exists for identification of new chelating ion exchangers and their property to selective complex formation can be explored in toxic metal ion removal from water at specific locations where there concentration in water is more than the permissible limit.

Chelating enhanced ultrafiltration membranes are also used extensively in toxic ion removal from water due to their complex forming capacity with toxic metal ions. K. Antonina et al have done work of cobalt and nickel removal using PEI (polyethylene imine) both branched and linear one.

1.9.2 Biomaterials and their scope in water purification applications

Biosorption of metal ions is also a good alternative and may be proved its potentiality due to easy availability and low cost. G. S. Agarwal et. al. has achieved better removal of chromium by tamarind seed powder, the chromium removal was also reported on different bio-sorbents by different workers. R.S. bai has successfully removed chromium from fungal biomass, S. E. Baily et. al. has reviewed the work on low cost sorbents thoroughly.

1.9.3 Carbon nanotubes

Carbon nanotubes (CNTs) rank amongst the most exciting developments in the modern science and engineering since their discovery by Iijima in 1991[112]. Carbon nanotubes are one of such type of material having vast scope in the future water purification technologies. CNTs possess hollow tubular structure, large surface area, show better suitability to work as supporting material for other molecules, ability to be functionalized with different groups and work as potential adsorbent. They have been used in many ways in water purification applications. CNTs have been predicted and experimentally proved to be a good material for the adsorption of gases and can be functionalized to explore their ability to adsorb metal ions from water also.

Adsorption heterogeneity and hysteresis are two widely recognized features of organic chemical-CNT interactions. Different mechanisms mainly hydrophobic interactions, pi-pi bonds, electrostatic interactions, hydrogen bonds, and adsorption of organic chemical adsorption on CNTs may account for adsorption behavior. Adsorption mechanisms will be better understood by investigating the effects of properties of both CNTs and organic chemicals along with environmental conditions. *Due to their adsorption characteristics CNTs have potential applications in separation sciences and water treatment.*

X. Peng et al. synthesized a novel adsorbent, ceria supported on carbon nanotubes (CeO2-CNTs) and successfully used the material in arsenate removal from water and suggest that it is a promising adsorbent for drinking water purification with having 94% regeneration efficiency[113].