REVIEW PAPER

Carbon Nanomaterials: Applications in Physico-chemical Systems and Biosystems

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ABSTRACT

In the present article, various forms of carbon and carbon nanomaterials (CNMs) and a new approach to classify them on the basis of sp^2-sp^3 configuration are presented. Utilising the concept of junction formation (like $p:n$ junction) a concept is developed to explain the special reactivity of nanosized carbon materials. Geometric consideration of chiral and achiral symmetry of single-walled carbon nanotubes is presented which is also responsible for manifesting special properties of carbon nanotubes. A brief introduction to various common synthesis techniques of CNMs is given. These is increased chemical and biological activities have resulted in many engineered nanoparticles, which are being designed for specific purposes, including diagnostic or therapeutic medical uses and environmental remediation.

Keywords: Carbon nanomaterials, nano-carbon forms, single-walled carbon nanotubes, carbon solar cells, fullerene

1. INTRODUCTION

Carbon is a vital constituent of all living organisms. Organic chemistry branches out with carbon chains in addition to many organometallic compounds, π-bonded complexes and carbonyls, while inorganic chemistry includes large quantity of carbon black, coke, graphite, carbon dioxide, calcium carbide, etc. In the Periodic Table, carbon stands at the sixth place and is the first element of column IV. Out of its six electrons, four electrons in its valence shell play significant role of forming three hybridisations, viz., sp, sp^2 and sp^3, leading to the formation of many stable forms of carbon in all dimensions. Figure 1 shows a pictorial view of different hybridisations seen in carbonaceous materials. Carbon differs from remaining elements of group IV because of its smaller size, higher electronegativity and non-availability of d-orbital.

Carbon is unique in forming π-π multiple bonds, such as $C=C$, $C≡C$, $C=O$, $C=S$, and $C≡N$, which is not observed by any other element of this group. Carbon due to its strong tendency to form bond with its own atom (bond energy of $C–C$ bond is 348 kJ/mol) leads to form a long network of carbon structures. However, sp^3 and sp^2 bonding carbon atoms are the main building blocks of all the carbonaceous structures available so far. Though both diamond (made from sp^3 carbon) and graphite (made from sp^2 carbon) are constituted from the same basic element (carbon), their properties are different. This makes the science of carbon all the more interesting with the discovery of its new allotropic forms.
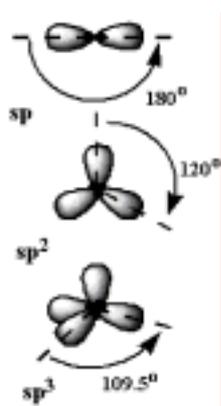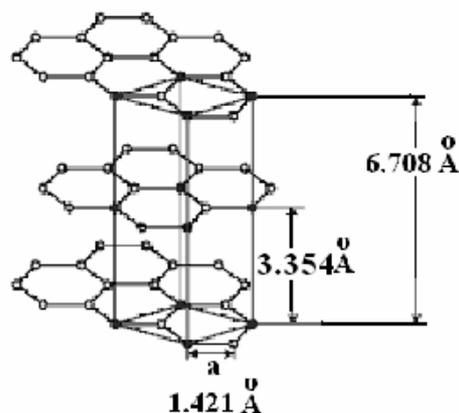
Figure 1. Hybridisation of carbon.

Figure 2. Hexagonal graphite structure.

2. VARIOUS FORMS OF CARBON

2.1 Diamond

In diamond all the four valence electrons orbital (one s and three p) of carbon intermixes with each other and give four sp^3 hybrid orbitals of equal energy, which upon overlapping with neighboring carbon hybrid orbital, create isotropically strong diamond structure. Diamond-like carbon (DLC), though has great similarity to diamond, is amorphous or in a partly crystalline phase in the lattice of carbon structures.

2.2 Graphite

By sharing three sp^2 electrons with three neighboring carbon atoms, carbon forms a layer of honeycomb network of planar structure called graphite and the fourth π-electron of carbon is delocalised over the whole plane of graphite. As π-electrons are mobile, graphite conducts electricity in the plane. This conduction of electricity can occur only in plane, but not from one plane to another. This sp^2 carbon-build layered structure (Fig. 2) has very strong in-plane bonding (covalent) but weak out-of-plane bonding (van der Waals). Due to this weak interplaner bond spaced at 3.35 Å, graphite sheets can slide upon each other. That is why graphite is been used as lubricant and is considered a soft material.

2.3 Carbon Fibres

Carbon fibres[1] are very strong and lightweight, hence used in many sports goods, musical instruments, brake discs of aircraft, rocket nozzle, heating elements, etc.

2.4 Carbon Blacks

Carbon black is another synthetically produced form of carbon having spherical fine particles. These are used as fillers for improving the electrical, mechanical, and optical properties of different materials. Thermal black, charcoal black, acetylene black, plasma black, and furnace black are different types of carbon blacks obtained from the respective synthesis process or precursor.

2.5 Activated Carbon

Activated carbon is an amorphous solid of varying shapes with a large internal surface area of specific pore size which is generally controlled by different activation processes. Activation is done by both physical and chemical methods. In physical activation, carbon is exposed to steam or CO_2 around 1000 °C. In the chemical method, carbon is mixed with activating chemical like potassium hydroxide, phosphoric acid or zinc chloride and then pyrolysed at 400–800 °C, leading to the formation of complex arrays of mesopores or micropores on the carbon; which is widely used as adsorbent (for removal of SO_2/NO_x, volatile organic compounds from air, toxic gases, in water purification).

3. VARIOUS FORMS OF NANOCARBON

3.1 Buckminster Fullerene

A group at Rice University along with Harry Kroto, the Nobel Laureate from Sussex University found an unusual symmetrical structure of carbon synthesised by laser vaporisation of graphite and gave the name Buckminster fullerene (C_{60}) after an architect-engineer, R. Buckminster Fuller who

designed geodesic domes. At the same time, they disproved the very truth of fundamental physical properties of two allotropic forms of carbon (diamond and graphite). Fullerene is the most stable cage-cluster structure, in which 12 pentagons are present as required by famous Euler's theorem and all the pentagons are separated by hexagons (the isolated pentagon rule). There are no other ways these pentagons and hexagons can be arranged to form a closed-cage structure of C_{60}. So in C_{60} molecule, carbon atoms are bonded in an icosahedral structure which is made up of 20 hexagons and 12 pentagons. The bonding between carbons atoms in fullerene are sp^2 type with some sp^3 character due to its high curvature. Later on other types of fullerene C_{70}, C_{76}, C_{78}, C_{80}, etc. (Fig. 3) have also been
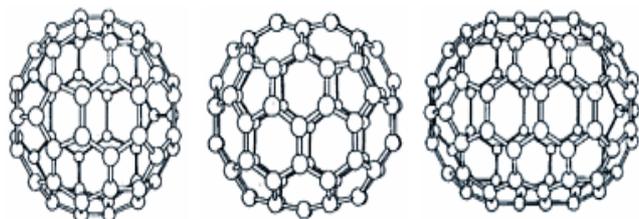

Figure 3. Structural models of fullerene.

discovered which are all constituted with different number of pentagonal, hexagonal, and heptagonal rings. Fullerenes are related more closely to graphite, as the bond distance between carbon-carbon atoms in fullerene are only 1-2 per cent larger than graphite.

3.2 Carbon Nano-onion

The carbon nanomaterials (CNMs) and carbon nanotubes (CNTs), (from cathode soot obtained from arc-vapourisation of graphite) under < 300
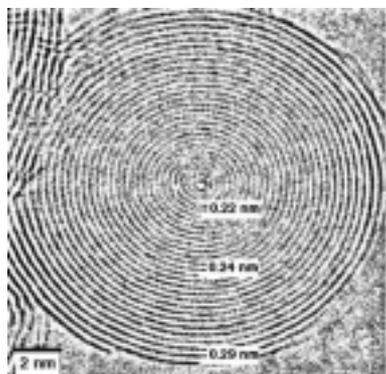

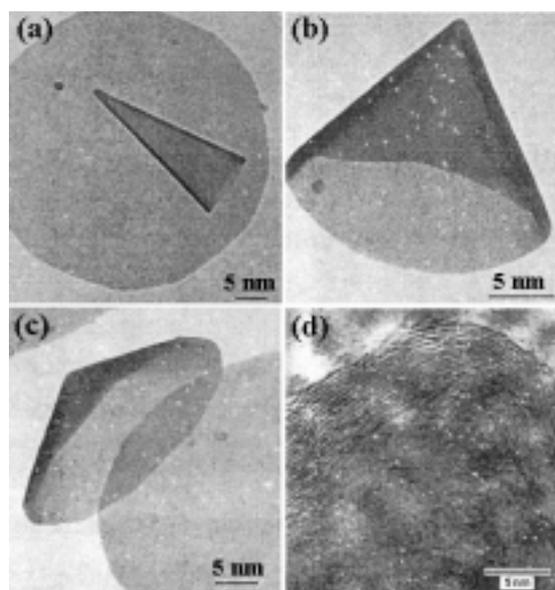Figure 4. TEM image of carbon onion.

Figure 5. TEM images of carbon nanocones at an angle of: (a) 19.2°, (b) 60°, (c) 112.9°, and (d) HRTEM image of cone tips (Krishnan, 1997).

kV. The TEM produced spheres made up of concentric fullerenes called carbon onion (Fig. 4). Most of the onions diameter corresponds to C_{60} or C_{240} and smallest have been C_{28} or C_{32}.

3.3 Carbon Nanocone

Carbon nanocone was obtained by pyrolysis of hydrocarbon in carbon arc plasma generator with plasma temperature around 2000 °C. Samples formed from this pyrolysis had large number of conical structures, disks, open nanotubes and disordered material. Figure 5 shows the nanocones having different tip angles. The graphitic conical structure has pentagonal rings (1–5) depending on the angle of cones. Open disk does not have any pentagonal ring.
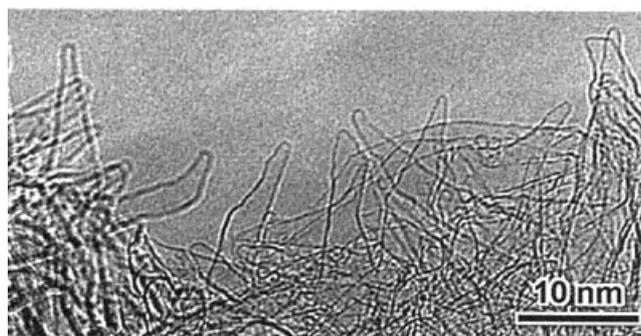

Figure 6. TEM image of carbon nanohorn (Iijima, 1999).

3.4 Carbon Nanohorn

Ablating graphite by CO_2 laser in the absence of catalyst in argon pressure of 760 Torr resulted in theformation of a new kind of aggregates of single-walled carbon sheath called nanohorns (Fig. 6).

3.5 Carbon Nanotubes

At the crossroad of traditional carbon fibres and fullerene, the CNTs emerged as an important material in the nano-scale science. CNTs are simply matchless to any other CNM due to their unique properties, such as smaller dia (4 nm–300 nm), long length (μm to cm), high mechanical strength, high thermal and chemical stability, and good heat conduction. Electrical properties of CNTs are even more fascinating. When a single layer of graphene sheet is rolled to form a cylindrical shape, it is single-walled carbon nanotube (SWCNT). If multiple layers of graphene sheets are rolled to form a hollow cylindrical shape, it is multi-walled carbon nanotube (MWCNT). These graphene sheets are separated by of 3.4 Å (Fig. 7). These can be semiconducting or metallic depending, upon the diameter of the tube. The MWCNTs are complex due to number of walls, interaction between the walls, disorderliness and the nonuniformity. In many ways, SWCNTs are superior to MWCNTs, e.g., these are defect- free, can be either semiconducting or metallic, have better mechanical strength, etc. The MWCNTs have very good mechanical character with high Young Modulus of around 1-terapascal.

3.6 Carbon Nanobeads

A special type of carbon nanobead (CNB) has been synthesised from camphor by CVD method[2] (Fig. 8). The circumference of bead is made of broken graphene sheet of about 80 nm thickness.
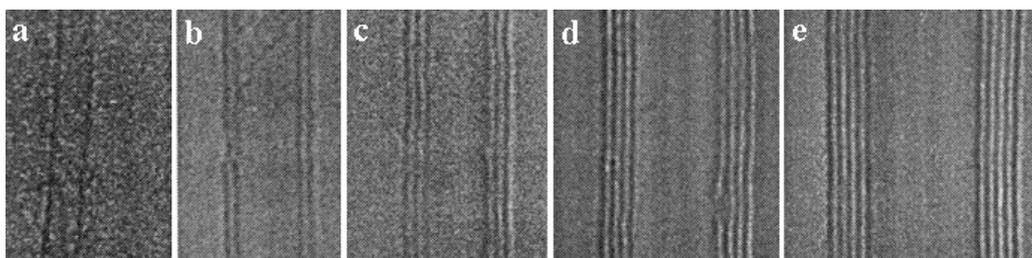
The inner portion of the bead is made of amorphous carbon.

3.7 Carbon Nanofibres

Both CNTs and CNFs appear almost the same under the SEM. Both are like hollow cylinder. The outer layer of CNT is made of unbroken graphene sheet whereas CNFs are made of broken graphene sheet (Fig. 9).
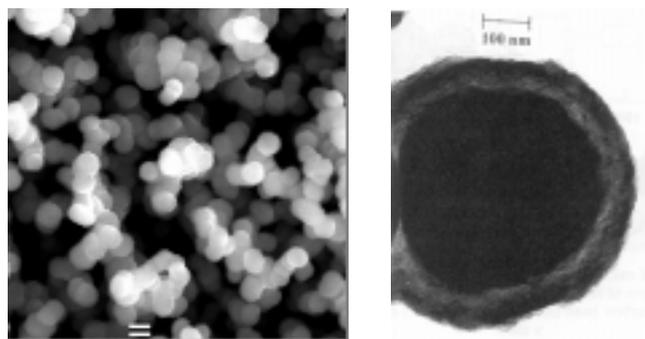

Figure 8. Carbon nanobeads synthesised from camphor by CVD process.
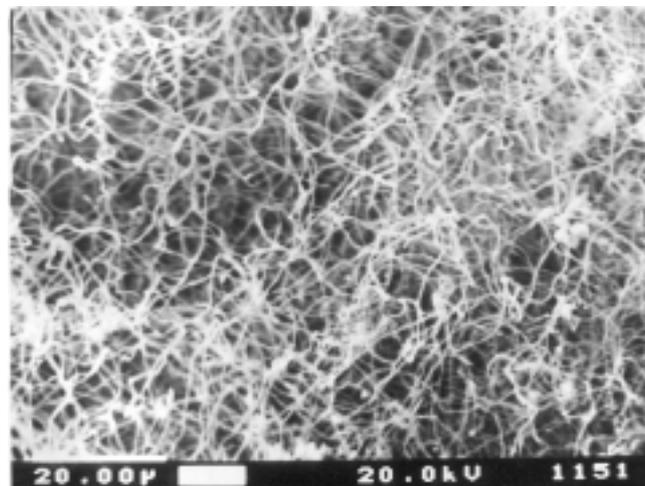

Figure 9. Carbon nanofibres of around 100 nm dia synthesised from camphor.

Figure 7. TEM images of: (a) single-walled CNT, (b) double-walled CNT, (c) triple-walled CNT, and (d) and (e) multi-walledCNT.

3.8 Octopus-like Carbon Nanofibres

Depending on the raw material and nano catalyst used for synthesis of the CNMs, different types of CNFs have been reported, e.g., CNFs grown by CVD process from camphor using nickel powder catalyst[3] of 20–50 nm size have resulted in the formation of octopus-shaped CNFs (Fig. 10).

3.9 Cactus-type Carbon Nanofibres

Cactus- type CNFs were fabricated by pyrolysing camphor using nanosized nickel electroplated over copper as catalyst[3]. When large-sized nickel particles were used as catalyst, then vertically growing cylindrical CNFs were formed.

3.10 Y-junction and Bamboo-shaped Carbon Nanofibres

Camphor and turpentine on pyrolysis have produced Y-junction and bamboo-shaped branched-CNTs (Fig. 11), respectively[4].

4. SYMMETRY OF SINGLE-WALLED CARBON NANOTUBES

Graphene sheet is made of six-membered carbon ring attached to each other. To form a symmetrical cylinder, this sheet rolls along an axis, such that throughout the length of the cylinder, its radius remains the same (Fig.12). Under such process, both ends of the cylinder appears open. The aspect ratio for SWCNTs will be in the range 10^4–10^5 (i.e., 10^{-6} nm /10^{-10} nm = 10^4). Such a nanotube is considered as 1-D nanostructure.
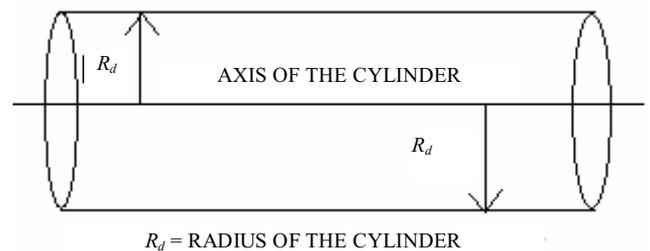

R_d = RADIUS OF THE CYLINDER

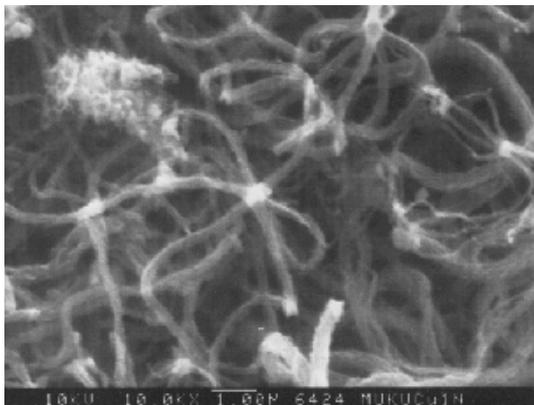**Figure 12. A graphene sheet rolled into a cylindrical form of radius, R_d.**

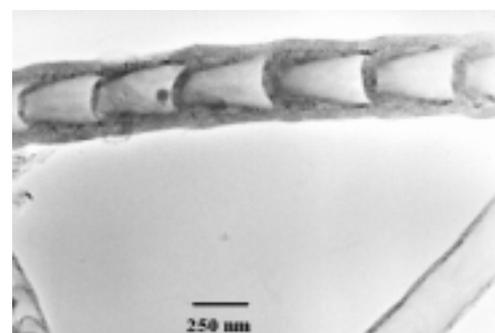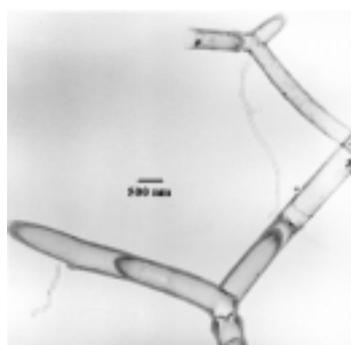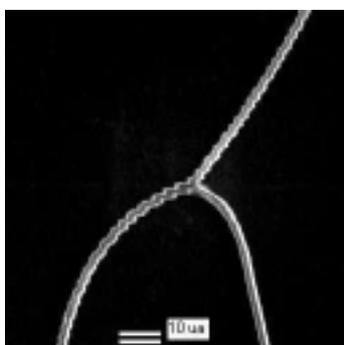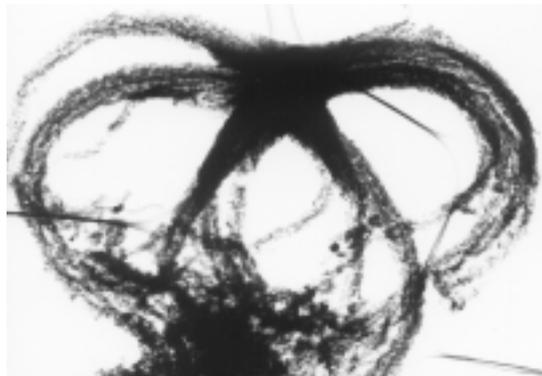**Figure 10. Octopus-type carbon nanaofibre synthesised from camphor using nickel as catalyst.**

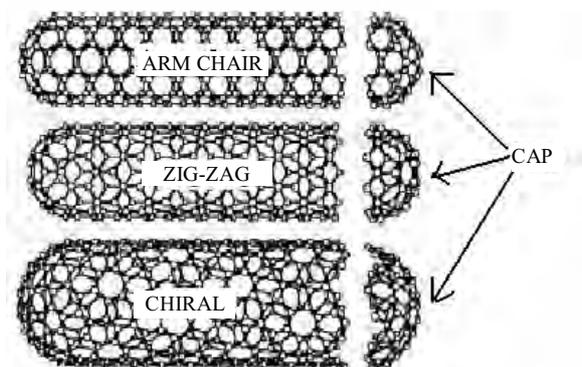**Figure 11. Y-junction and bamboo-shaped CNF synthesised from camphor.**

Figure 13. Three types of CNT cylinders.

Geometrically, the graphene sheet can be rolled in such a way that three different types of configurations are achieved (Fig. 13). One end of the cylinder is shown as open separated by a cap which consists of a hemisphere of a fullerene. The cap consists of pentagonal carbon atoms. The number and the orientation of pentagonal carbon are arranged in such a way that it can fit with the cylinder without creating any distortion. Geometrically, it can be calculated. Thus by a geometric consideration, the primary symmetry classification of CNT can be either achiral (symmorphic, i.e., symmetrical) or chiral (non-symmorphic). The CNTs whose mirror images have an identical structure are considered as having an achiral symmetry. There are only two types of achiral nanotubes: armchair and zig-zag. Both these structures posses mirror symmetry. On the other hand, chiral nanotubes exhibit a spiral symmetry whose mirror image can not be superimposed on to the original nanotube.

The arrangement of pentagonal carbon in caps decides the shape the CNT will take during synthesis. In other words, the seeding of carbon starts with the formation of pentagonal carbon; over which the entire structure is built, forming any of these three types of symmetries. Extending this logic further, since the cap of CNT contains pentagonal carbon (which contains sp type of carbon) and the rest of the CNT contains hexagonal carbon (which contains only sp^2 type of carbon), it is the ratio of carbon atoms with configuration of sp^3/sp^2 carbon which controls the formation of any of these three types of symmetries. Moreover, the number of pentagonal carbon atoms present in the cap also

controls the diameter of the tube. Thus, the ratio of sp^3/sp^2 carbon actually controls the diameter of the tube. Though this geometrical classification in principle is useful, for practical application, it is of little help, e.g., it would be extremely difficult to suggest which form of CNT has been synthesised in a laboratory, unless one takes high-resolution tunnelling microscope (HRTM). The TEM micrograph or Raman spectroscopy measurement, are useful in confirming the CNM to be CNT and getting information about its diameter which can also be experimentally determined by measuring the concentration of sp^3 or sp^2 carbon present in the CNT or its band-gap[5].

5. CLASSIFICATION OF CARBON NANOFORMS

As per conventional classification there are only three allotropes of carbon: graphite, diamond, and fullerene. Then to which class of allotrope other forms of carbon, belong to? A classification based on the nature of carbon atoms present in the carbonaceous material, may be appropriate. Diamond has 100 per cent sp^3 type of carbon, while graphite has 100 per cent sp^2 type of carbon atoms. These two examples immediately suggests that there is a possibility of millions of permutation and combinations of sp^3 and sp^2, giving innumerable variety of carbon with varied band gaps in the range 0.25 eV to 5.5 eV. The DLC, glassy carbons, etc are few examples which can not be classified as diamond or graphite. Therefore, classification of carbon on the basis of ratio of sp^3 and sp^2 carbon atoms present in the material may be more appropriate than the conventional classification. All forms of carbon can be classified into the following three groups:

(i) Diamond (100 % sp^3)

(ii) Intermediate carbon (with different ratio of sp^3/sp^2 carbon atoms)

(iii) Graphite (100 % sp^2).

The CNB, CNT, CNF, active carbon, charcoal, fullerenesall of these fall in the intermediate group of carbon because these contain different ratios of sp^3/sp^2.

6. CARBON NANOMATERIALS SYNTHESIS

Some of the commonly used techniques for the synthesis of CNMs are distributed below:

6.1 Arc-discharge

In an arc-discharge unit, two graphite rods are used as the cathode and anode, between them arcing occurs when dc voltage is supplied (Fig. 14).
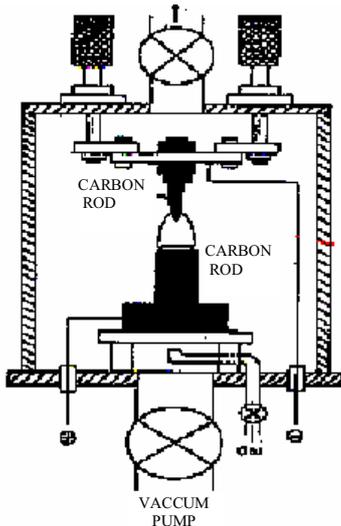

Figure 14. Schematic diagram of dc arc-discharge apparatus for preparing carbon nanotubes with graphite rod.

A large quantity of electrons from the arc-discharge moves to the anode and collide into the anodic rod. Carbon clusters from the anodic graphite rod caused by the collision are cooled to low temperature and condensed on the surface of the cathodic graphite rod. The graphite deposits condensed on the cathode contain CNT, nanoparticles, and clusters. Arc-discharge method is being used for the synthesis of fullerenes, MWCNTs and SWCNTs and binary metal catalysts (Fig. 14).

6.2 Chemical Vapour Deposition Method

The chemical vapour deposition (CVD) process involves passing a hydrocarbon vapour through a quartz tube kept in the furnace in which a catalyst material is present at sufficiently high temperature to decompose the hydrocarbon. The CNTs grow over the catalyst in the furnace, which are collected upon cooling the system to room temperature. In the case of a liquid hydrocarbon (benzene, alcohol, etc.), the liquid is heated in a flask and an inert gas purged through it carries its vapour into the (Fig. 15) reaction furnace: Vapourisation of a solid hydrocarbon (camphor, naphthalene, etc.) is conveniently achieved in another furnace (low-temperature) before it reaches the main reaction furnace. Catalyst is either placed inside the furnace or fed from outside. Pyrolysis of the catalyst vapour at a suitable temperature liberates metal nanoparticles *in-situ* (such a process is known as floating catalyst method). Alternatively, catalyst-plated substrates can be placed in the hot zone of the furnace to catalyse CNT growth.

6.3 Pulsed Laser Deposition Technique

The pulsed laser deposition (PLD) technique is used for the synthesis of CNMs. In this process, graphite or pellet of carbon soot is hit by a pulsed laser beam of 10–50 ns pulsed duration producing a flux of evaporated/ablated material which condenses on a substrate to form a film. The strongly forward
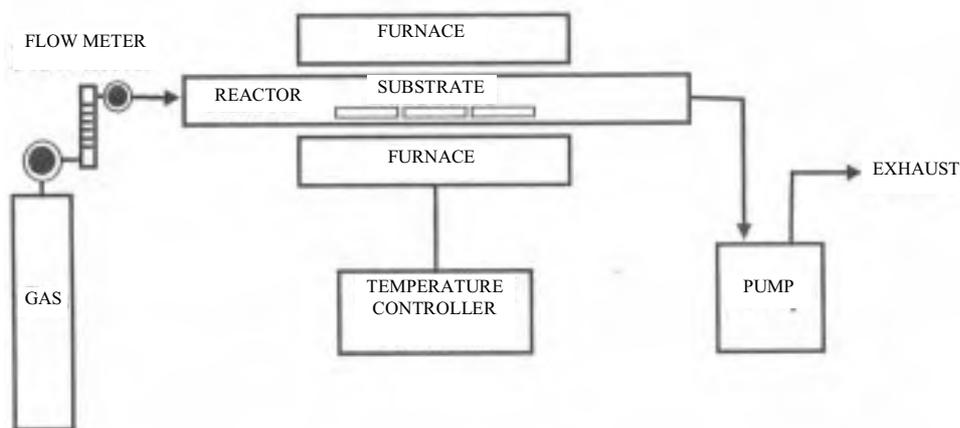

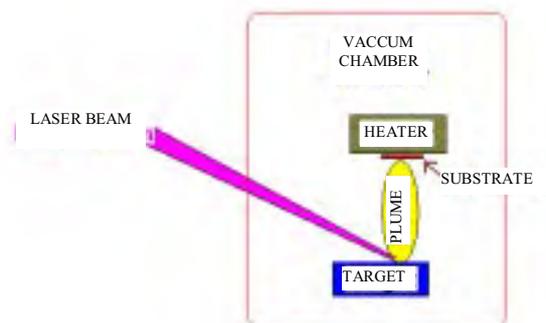**Figure 15. Schematic diagram of a typical CVD setup**

Figure 16. Schematic diagram of a pulsed laser deposition system.

directed flux of material is called plasma plume. A set of optical lenses is used to focus laser beam over the target surface (Fig. 16). The deposition can be carried out in the presence of a reactive environment as well as in an inert atmosphere. This can also be operated in conjunction with other types of deposition techniques, e.g., laser- arc deposition[6] and magnetron assisted PLD[7].

6.4 Thermal Flash Evapouration Technique

In this technique, a quartz boat containing the substrate is placed inside the tungsten coil (used for heating). The source material is heated by passing current through the tungsten coil to evaporate the substrate. Vacuum is required to allow the molecules to evaporate freely in the chamber and subsequently condense on the substrate kept near the coil (Fig. 17).

7. CHARACTERISATION OF CARBON NANOMATERIALS

Standard methods of characterisation of the CNMs mainly include SEM, TEM, high-resolution TEM (HRTEM), XRD, Raman spectroscopy, TGA, and DTA, etc.

7.1 SEM and TEM for Characterising Various Forms of CNMs

The SEM has contributed immensely in characterising various forms of CNMs, viz., CNF, CNB, CNTs (SWCNTs and MWCNTs). The SEM is used to observe the morphology of a sample at higher magnification, higher resolution, and higher depth of focus compared to an optical microscope.

However, SEM has limited applications in characterising SWCNT. The main problem is difficulty in differentiating SWCNT and MWCNT, mostly due to the tendency of SWCNTs to strongly adhere to each other, forming bundles of 5–20 nm dia. In contrast to TEM, the SEM cannot resolve the internal structure of SWCNT bundles. Nevertheless, the SEM can yield valuable information regarding the purity of a sample as well as an insight on the degree of aggregation of raw and purified SWCNT materials and presence of impurities like catalysts or amorphous carbon. For getting information about the arrangement of carbon atoms in the CNM, HRTEM is used. It works at high operating voltage (in the range 400 kV) as compared to normal TEM operating in the range of 100 kV to 300 kV.

7.2 XRD for Structural Information

One of the advantages of XRD is getting the structural information about the nature of CNT. Crystalline CNT gives a sharp peak for plane (002). Sometimes, CNT formed by the pyrolysis of plant-
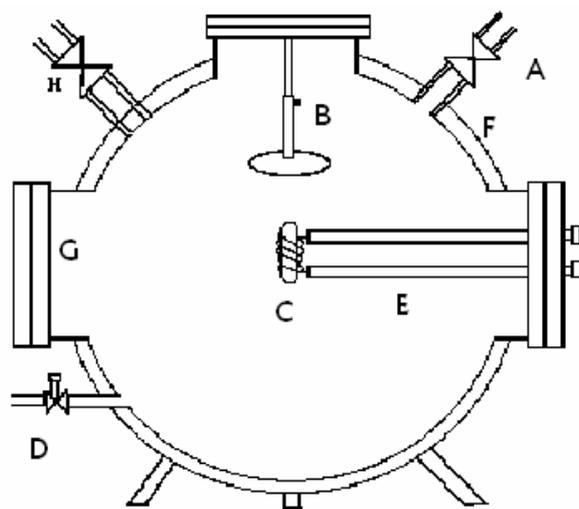
Figure 17. Schematic diagram of the thermal flash vapour deposition unit. A & H are the two valve systems to be connected to vacuum pump and pressure gauge unit. B is a substrate holder to which a thermocouple is attached, C is the tungsten coil holding a quartz boat for keeping a precursor, D is a valve to allow any reactive gas into the chamber, E is the electric power supply connections, F is the chamber of flash vapourisation unit, and G is the glass window to view the deposition process.

derived precursor does not give well-defined peak corresponding to any specific plane [Fig. 18(a)]. However same materials after sintering, plane corresponding to diamond like carbon can be obtained [Fig. 18(b)]. This is how XRD can help to find out the structural properties of CNMs prepared under different conditions.

(a)

(b)
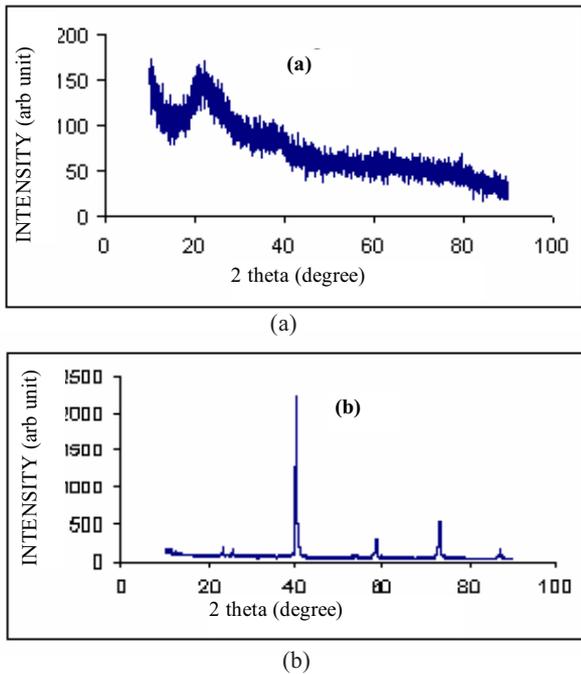
Figure 18. XRD pattern of carbon film prepared by flash evaporation: (a) substrate temperature 650 °C: showing amorphous carbon, and (b) after sintering at temperature 750 °C: showing well-defined crystalline structure of the thin film having (111) plane of diamond-like carbon.

7.3 Raman Spectroscopy for Identification of SWCNTs

Based on the symmetry of the CNMs, A_{1g}, E_{1g}, and E_{2g} modes are Raman active. Number of Raman active modes is independent of the diameter of CNTs. However, the frequencies of these modes do vary with the CNT's diameter. The strong lines between 1550 cm^{-1} and 1600 cm^{-1} are assigned to three E_{1g}, E_{2g} and A_{1g} modes in CNTs with different diameter and in special, strong modes of 1567 cm^{-1} and 1593 cm^{-1} have been assigned to the E_{2g} and E_{1g} or A_{1g}, respectively.

Raman intensity for graphite in the 1300–1600 cm^{-1} region is sensitive to sample quality. Generally, the intensity of E_{2g} modes of graphitic materials is sharp and strong when the sample is highly crystalline and defect-free. Disordered graphite and carbons show broad features around 1350 cm^{-1}. The 1347 cm^{-1} signal may come from a symmetry-lowering effect, due to defects or nanotubes caps, bending of the nanotubes, or the presence of carbon nanoparticles and amorphous carbon.

Raman spectra of pure diamond show one sharp peak around 1350 cm^{-1} and pure graphite shows one peak around 1550 cm^{-1}. Raman peak around 1350 cm^{-1} (known as D-band) is an indication of sp^3 carbon and peak around 1550 cm^{-1} (known as G-band) corresponds to sp^2 carbon. Raman peak around 1350 cm^{-1} in graphite is considered as disorder created in graphite. Disorder in graphite

(a)

(b)

Figure 19. Raman spectra of: (a) SWCNT (radial breathing mode) and (b) MWCNT at higher frequency showing *G*-band at 1561.32 cm^{-1} and *D*-band at 1351.07 cm^{-1}.

can be due to the presence of sp^3 carbon. In other words, intensity of peak (or peak areas) around 1350 cm^{-1} obtained with graphite may be considered as equivalent to amoun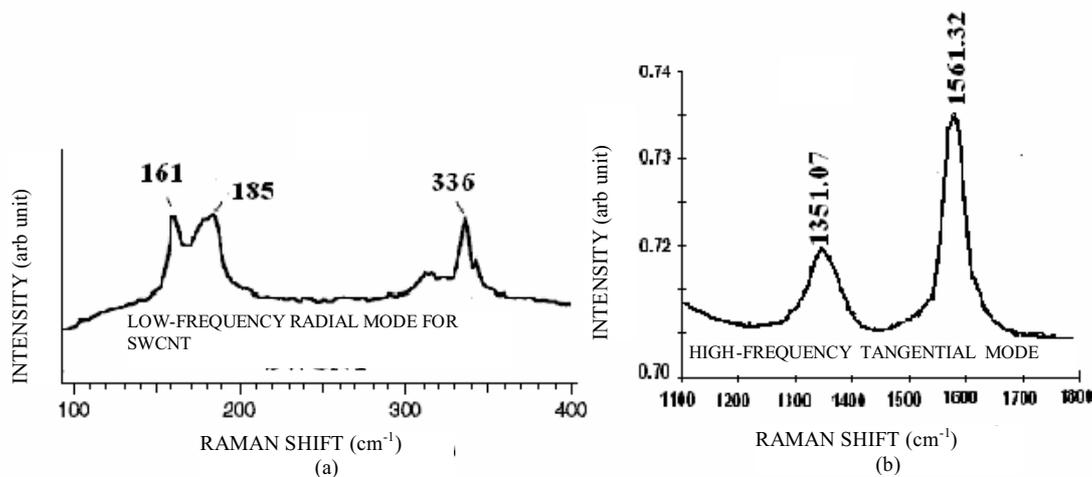t of sp^3 carbon present in the graphite. Similarly, presence of peak around 1550 cm^{-1} in diamond materials should be considered as the amount of sp^2 disordered present in the diamond. In DLC, Raman spectra shows the presence of both bands, i.e., peaks at 1350 cm^{-1} and 1550 cm^{-1} suggesting the presence of both these configurations.

At 186 cm^{-1}, a strong A_{1g} breathing mode is found. This peak has strong dependence on (i.e., the frequency of the A_{1g} breathing mode) on nanotubes diameter. Raman features of the SWCNTs are: (a) the radial breathing mode [Fig. 19(a)], whose frequency varies according to the dia of the tube; (b) the tangential G-band [Fig. 22(b)] in the range of 1550–1605 cm^{-1}; and the disordered-induced D- band [Fig. 19(b)] at about 1350 cm^{-1} and its second order harmonic (G-band) at about 2700 cm^{-1}. The radial breathing mode has been found to be inversely proportional to the dia of the tube ($\upsilon = 248/d_t$), where υ is in units of cm^{-1} and d is the nanotube diameter in nm.

7.4 Thermogravimetric Analysis and Differential Thermal Analysis

The TGA and DTA are done to find whether the CNT contains only CNT or some impurities like amorphous carbon, because the CNT decomposes at higher temperature ($\sim 600\ ^o$C) than amorphous carbon which decomposes at lower temperature ($\sim 300\ ^o$C). In DTA, the change in thermoelectric emf. is measured at various temperatures, which gives the information about any phase change in the sample at any specific temperature.

8. PROPERTIES OF CARBON NANOTUBES

8.1 Size and Reactivity of CNMs

Why particles of smaller size are more reactive than particles of larger size? Such behaviour is possible only if the electron transfer in nanosized particles follow a different mechanism than the electron transfer in bulk materials.

Reactivity of any material refers to reactivity of a material which is in contact with any other material. The reaction would depend upon the ease with which electron transfer could take place between the two materials. Each material possesses its specific work function, i.e., Fermi energy. In other words, like $p{:}n$ junction formation, there is a possibility to form a junction potential if two types of particles are in contact.

Therefore, it may be appropriate to explain the reactivity of nano-size materials by probing the effect of formation of depletion region between the two reactants. Figure 20 shows the condition of formation of a depletion region. Within the depletion region (d), a very strong electric field exists.

If particle of size almost equal to the depletion region is used for any charge-transfer reaction [Fig. 21(a)], due to the presence of depletion region, it will allow the transfer of electrons only through the surface and not through inside of the
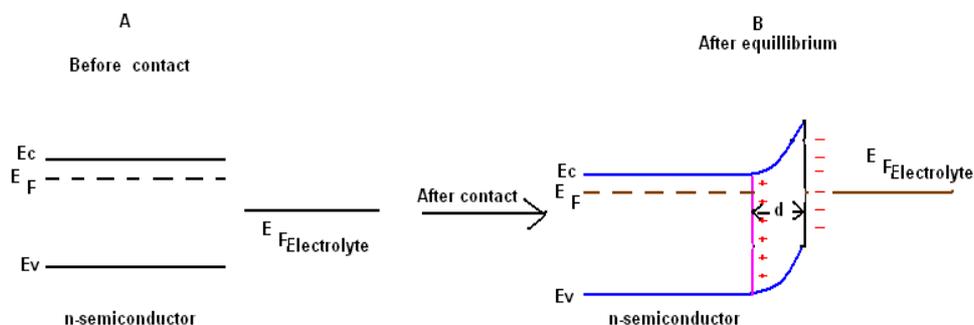

Figure 20. Schematic diagram showing formation of depletion region by making contact of an *n*-semiconductor with an electrolyte. (*Ec* = conduction band, *Ev* = valence band, E_F = Fermi level, and *d* = depth of the depletion region.
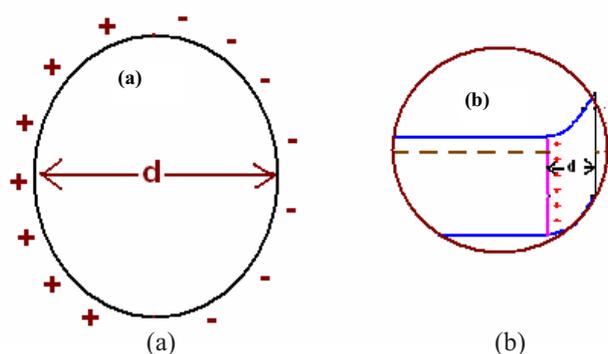
Figure 21. Schematic diagram showing: (a) charge distribution at the surface of a particle of size equal to the depletion depth *d*, and (b) particle size larger than depletion region.

material. However, if the size of the particle is larger than the depletion region [Fig. 21(b)], transfer of electrons will depend upon the resistance of the material as it has to be transferred through the material. Thus, with nanosized particles (i.e., the particle of size almost equal to depletion region depth), the electron transfer takes place only through the surface, and hence, it does not depend upon the resistance or the band gap of the material whereas in electron transfer with large sized particles, resistivity of the bulk or the band gap of the material becomes an important factor to control the reactivity of the materials. That is why nano-sized particles show better chemical reactivity than large-sized particles of the same materials. Theoretical calculation suggests that particles of 60–100 nm size would show high reactivity as compared to larger-sized particles of the materials. Moreover, such calculations also suggest that particles of any material composed of about 10,000 atoms or less would show special reactivity as compared to particles containing larger number of atoms[8].

8.2 Electronic Properties

The unique electronic properties of CNTs are due to the quantum confinement of electrons normal to the CNT axis. The delocalised electrons in CNMs are free to move about the entire structure, rather than remain with its donor atom, giving rise to the metallic-type electrical conductivity. Thus, the CNTs can be either metallic or semiconducting in their electrical behaviour, depending upon their diameters.

In the radial direction, electrons are confined by the monolayer thickness of the graphene sheet. Around the circumference of the CNT, periodic boundary conditions come into play. Because of this quantum confinement, electrons can only propagate along the CNT axis. The conductivity of CNTs has been shown to be a function of their chirality (degree of twist) as well as their diameters.

8.3 Thermal Conductivity and Expansion

The CNTs may be the best heat-conducting material man has ever known. Ultra-small SWCNTs have even been shown to exhibit superconductivity below 20 K. Many applications of CNTs, such as in nanoscale molecular electronics, sensing and actuating devices, or as reinforcing additive fibres in functional composite materials, have been proposed. It is expected, that the CNT reinforcements in polymeric materials may also significantly improve the thermal and thermomechanical properties of the composites.

8.4 Light Emission by CNMs

A MWCNT can carry a current density as high as 10^{13} A/cm^2, which is about 1000 times larger than that of copper. The CNTs can emit fluorescent light when excited by a laser light source. Recently, it has been demonstrated that
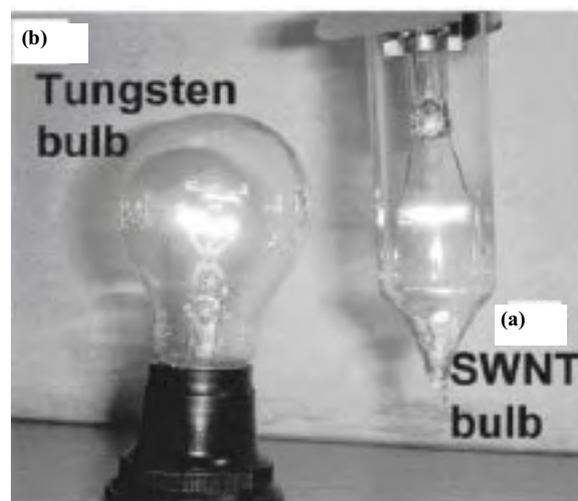

Figure 22. (a) Illuminated SWCNT bulb and (b) a tungsten filament bulb; both showing light emission at the same applied voltage of 20 V (Wei, *et al.*, 2004).
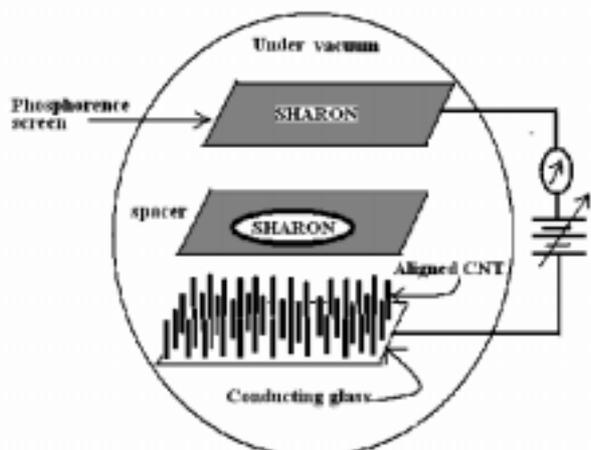
Figure 23. Schematic diagram of a electron field emission setup.

lighting[9] from SWCNT and MWCNT can take place (Fig. 22). SWCNT was first immersed in alcohol, and then assembled into long filaments to which a dc potential was applied under vacuum. Its intensity was compared with conventional tungsten bulb. It is reported that both gave light intensity equivalent to 40 W.

8.5 Electron Field Emission by CNTs

Field emission is a quantum mechanical tunneling phenomenon in which electrons escape from a solid surface into the vacuum. In contrast to the commonly used thermionic emission from hot filaments, field emission occurs at room temperature from unheated cold cathodes under an electric field, so it is also termed as cold cathode emission.

A schematic diagram of an electron field emitter (Fig. 23) shows CNTs acting as anode and releases the electrons which travel towards the cathode through a separator. When electron strikes the cathode which is made of phosphorescence material, it produces the image (e.g., Sharon). The entire set up is kept under vacuum to make large mean–free path of electrons and to stop any corrosion of electrode.

9. PHYSICO-CHEMICAL APPLICATIONS OF CARBON NANOMATERIALS

9.1 Field Emission Display

The field emission display (FED) is one of the main applications attracting technologist to make the electron field emission practical for market-oriented application like flat-panel displays.

9.2 Carbon Solar Cells

Carbon has the properties similar to that of silicon. Unlike silicon, carbon can provide the possibility of getting various band gaps in the range 0.25 eV to 5.5 eV. This variation can be controlled by manipulating the concentration of sp^3/sp^2 carbon ratio into a carbon material. This freedom does not exist with silicon as its configuration is fixed (i.e., sp^3 configuration only). Fortunately unlike silicon, semiconducting-grade carbon has also been made at much lower temperature, i.e., 600–800 °C as compared to 1700 °C needed for silicon[2,10,11]. These special properties of carbon make it a strong candidate for making a carbon solar cell. However, the main hurdle with carbon materials is in finding the exact condition to get carbon with a desired band gap of 1.4 eV. Because for ideal solar cell, the band gap should be 1.4 eV (direct). The other problem associated with carbon is its low mobility of carriers. In addition, most of carbon materials show p-type character even without any external doping. Hence, preparation of an extrinsic semiconducting carbon is a challenge.

Nevertheless, in spite of these constrains and some of the advantages of carbon, a homojunction carbon solar cell of configuration $Au/n-C/p-C/Au$ with an efficiency of 2.1 per cent has been developed for the first time by the Research Group of Sharon[2, 8-19]. It is postulated that this cell will cost Rs 20 per peak watt as compared to silicon solar cell which costs Rs 300 per peak watt.

A flexible transparent conducting electrode has been developed by printing films of SWCNT networks on plastic[20]. Cells were fabricated on the SWNT/plastic anodes on ITO/glass. Efficiencies, 2.5 per cent at air mass 1.5 AM, have been reported. There are many references in the literature explaining the possibility of making hetrojunction carbon solar cells. But unfortunately all of them have used silicon as one component of the cell, which defeats the purpose of lowering the price of the solar cell.

There is a need to develop a carbon solar cell which does not use silicon at all. Since semiconducting carbon can be synthesised with different band-

gaps (in the range 0.25 eV to 5.5 eV), efforts should be made to make cascade-type carbon solar cell so that the entire spectrum of solar radiation could be covered. If a cascade solar cell technology is developed, the efficiency of carbon cascades-type solar cells can be as high as 100 per cent, which can never be even thought of for any other material.

9.3 Microwave Absorption Capacity

Morphology of CNTs has attracted scientists to use it as an absorber of microwaves. Microwave-
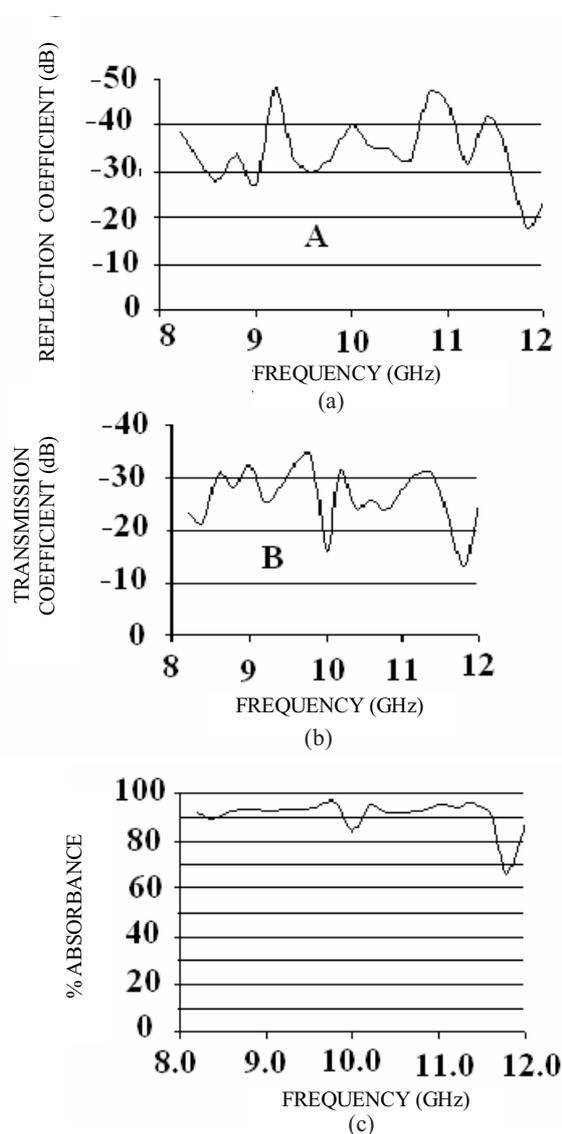
Figure 24.(a) Variation in reflection coefficient (dB) versus frequency, (b) transmission coefficient versus frequency, and (c) per cent absorbance *vs* frequency for a thin film of CNM synthesised from plant precursor.

absorbing materials and their composites are mostly used in military applications, such as reduction of radar visibility in different types of vehicles. This is also known as stealth technology. The most known vehicle with this technology is the Lockheed F-117A Nighthawk, which is one of the first stealth aircraft ever produced. To develop economically cheap microwave absorbers, efforts have been made to develop CNMs for absorbing microwaves in the range 8 GHz to 24 GHz[8,21]. Figure 24 shows the plot of the reflection coefficient versus frequency; transmission coefficient versus frequency; and absorbance versus frequency for CNFs obtained from plant-based precursor. From the graph it is clear that the CNFs have reflection coefficient in the range – 30 dB to – 40 dB for frequency range 8 GHz to 12 GHz (– 30 dB reflection coefficient corresponds to ~ 99 % absorption). This CNM shows that the loss of microwave energy incident on the sample as reflection and transmission is in very less quantity, which indicates that the energy is fully absorbed by the sample. Research Group of Sharon is trying to study the microwave absorption covering the entire range 8 GHz to 24 GHz.

9.4 Hydrogen Absorption

Hydrogen can be stored into the CNT through chemisorptions or physisorption. The methods of trapping hydrogen are not known accurately but density functional calculations have shown some insights into the mechanisms. Hydrogen can be adsorbed at the exterior of the tube wall by *H–C* bonds with a *H/C* coverage 1.0 or inside the tube by *H–H* bonds with coverage up to 2.4. The adsorption into the interior wall of the CNT is also possible but not stable. The hydrogen relaxes inside the CNT forming *H–H* bonds.The MWCNT can adsorb hydrogen between the SWCNTs. The hydrogen causes the radius of the tubes to increase and thus makes a MWCNT less stable[22]. Hydrogen can also be adsorbed in between two layers of the MWCNT[23].

Theoretically, SWCNT can adsorb up to 14 Wt per cent of hydrogen and a MWCNT about 7.7 Wt per cent of hydrogen. Dillon[24], *et al.* reported their work on high hydrogen uptake by CNT. They estimated that hydrogen could achieve a density

of 5–10 Wt per cent. Chen[25], *et al.* have reported that alkali-doped CNTs are able to store even 20 Wt per cent under ambient pressure, but are unstable and require elevated temperatures. The result has shown to be in great disagreement with other results and has been considered to be incorrect.

Recent results on hydrogen uptake of SWCNT are promising. At 0.67 bar and 600 K, about 7 Wt per cent of hydrogen has been adsorbed and desorbed with a good cycling stability[25]. Another result at ambient temperature and pressure shows that 3.3 Wt per cent can be adsorbed and desorbed reproducibly and 4.2 Wt per cent with slight heating.

10. BIOLOGICAL APPLICATIONS

Nano forms of materials and functioning of living being at nano-level have existed in nature much before mankind was able to identify them. Advances in synthetic chemistry and physical equipments have been one of the driving forces in the integration of biology and nanoscience. In the last decade, enormous progress has been made in developing new fabrication techniques and materials for producing nano-devices. The biosciences today, are characterised by irreconcilable demands where the CNM is poised to contribute immensely as diagnostic tools and devices, in water purification, use of CNT as sterilant, use in probes, quantum dots, bio-pharmaceutics, and medicines, scaffold for fabricating tissues, as implantable materials, in the cosmetic industry, and in the food and agro-industry.

10.1 Diagnostic Tools and Devices

10.1.1 Radiation Oncology

In the traditional x-ray machine, when a metallic filament (cathode) is heated (resistively) to a very high temperature, it generates electrons. The accelerated electrons are bombarded on a metal target (anode) to generate x-rays. But this x-ray equipment consumes high energy and has limited lifetime. Recent research has reported that field emission is a better mechanism of extracting electrons compared to thermionic emission[26]. Moreover, electrons are emitted at room temperature and the output current is voltage-controllable. In addition, giving the cathode in the form of tips increases the local field at the tips and as a result, the voltage necessary for electron emission is lowered[27].

An optimal cathode material should have high melting point, low work function, and high thermal conductivity. The CNTs meet all these requirements, hence are used as a cathode material for generating free-flowing electrons. Electrons are readily emitted from their tip when a potential is applied between a CNT surface and an anode[28,29]. This generates continuous and pulsed x-rays. The advantage of CNT-based x-ray devices is that these have fast response time, fine focal spot, low power consumption, possible miniaturisation (hence portability), longer life, and low cost. The field emission x-ray tube can produce sufficient x-ray intensity to image the human anatomy. Moreover, it minimises the need of cooling required by the conventional method[28-30]. Miniaturised x-ray devices can be inserted into the body by endoscopy to deliver precise x-ray doses directly at a target area without damaging the surrounding healthy tissues.

10.1.2 Sensors

The CNTs have been used in pressure, flow, thermal, gas, chemical, biological, and piezo-resistive pressure sensors[31]. As the CNTs have temperature coefficient almost two orders of magnitude lower than that of silicon and have increased sensitivity, highly efficient pressure sensors incorporating CNTs can be fabricated. Pressure sensors can be used in eye surgery, for hospital beds, as respiratory devices, for patient monitors, as inhalers, and kidney dialysis machines[32,33]. Pressure-sensing technology is used in both invasive and non-invasive blood pressure monitoring. The CNTs can also be used in flow sensors[36,37] because the flow of a liquid on bundles of SWCNTs induces a voltage in the direction of flow.

10.1.2.1 Biosensors

Biosensor incorporates a biological element as bio-recognition system, e.g., enzymes, proteins, antibodies, nucleic acids, bacteria, single-cell organisms, whole tissues of higher organisms. Bio-recognition system is immobilised onto the surface of physico-chemical transducers. Use of the CNTs as immobilisation matrix for the development of an amperometric biosensor was initiated by growing aligned MWCNTs on platinum (*Pt*) substrates[34] which served as the transduction platform for signal monitoring, whereas

opening and functionalisation of large CNT arrays allowed for the efficient immobilisation of the model enzyme (glycine decarboxylase, in this case). Biosensors can also be used for blood analysis[35].

10.2 Water Purification

The CNTs have shown promises in water purification by three different methods:

(a) *Photocatalytic degradation of pollutants*: Composite photo-catalytic membranes prepared by using the CNT in a pilot plant have already been tested[38] for their efficacy in degrading triazine herbicides in the presence of sunlight.

(b) *Adsorbent for various chemicals*: The CNMs can be used to adsorb or *sequester* pollutants and remove them from water. Inclusion of nanosorbents can be much more effective because of their larger surface area. Various functional groups can also be attached to nanoparticles to improve their specificity in removing pollutants. The MWCNTs can adsorb three-four times more amount of heavy metals (copper, cadmium, and lead) than activated carbon. The CNT and nanoporous activated carbon fibres have been found to effectively adsorb organic pollutants such as benzene, and the fullerenes could adsorb polycyclic aromatic compounds such as naphthalene[39].

(c) *Ultra-filtration unit for water purification*: Nanotechnology can enhance the effectiveness of ultrafiltration and reverse osmosis, thus removing bacteria and viruses from water.

10.3 Sterilant and Anti-microbial Agent

Hydrogen-free CNT-composite films, that possess unusual free-radical generation properties, can nonspecifically kill bacterial cells hence can be used to sterilise a surface[40]. These composites have been formed by simultaneous pulsed-laser ablation of carbon and bombardment of nitrogen ions generated by a Kaufman ion source at high temperatures (600–700 °C). The results suggest the creation of a new form of carbon that is predominantly trigonally-coordinated, with small fractions of carbon-nitrogen bonds. The TEM studies show that the material

consists of sp^2-bonded ribbons wrapped approximately +/-15° normal to the surface. Plan-view the TEM specimens demonstrate layers with curvature similar to that seen in the MWCNT structures. In addition, the interlayer order extends to approximately 15–30 nm. These novel structures result from the use of energetic ions, which create nonequilibrium conditions that alter the growth mode of graphitic planes. Applications include use on the functional surfaces of dialysis equipment, sterile equipment, nano-structured bandages and in surfaces sterilisation.

10.3.1 Anti-microbial Activity

In broad terms, an anti-microbial kills or slows the growth of microbes like bacteria, fungi, viruses, or parasites. Certain nanoparticles are distruptive to bacteria and viruses simply by virtue of their physical nature. The versatile properties of the CNMs are used for killing the harmful micro-organism[41]. Some of the studied antimicrobial or anticellular effects of the CNM are:

- *In vitro* action of carboxy-fullerene compounds shows avid reactivity with free radicals. The trimalonic acid derivative of fullerene is one of the water-soluble compounds that has been found to be an effective antioxidant. *Streptococcus pyogenes* A-20 was killed rapidly by intercalation of carboxy-fullerene into the cell wall[42].

- Solubilisation of fullerene (by sonication or tetrahydrofuran) increased the toxicity of nC_{60}, the nC_{60} to fresh-water crustaceans and fish[43].

- Effects of the CNMs have also been studied on plant cells which unlike microbes have cell walls made up of cellulose and lectins. It was observed that the cell walls of the plant cells get ruptured totally when in contact with the CNMs. Moreover the CNMs are found to destroy the plant cells effectively in the presence of sunlight[44]. This property has application in killing undesired algal cells that accumulate during rainy season on floor and walls.

10.3.1.1 Anti-microbial Activity Mechanism of CNMs

Illumination of the interface between the semiconductor and electrolyte with photon of band

gap energy equal to or greater than the band gap energy of a semiconductor results in the transient formation of photo-generated electron/hole pair. These holes function as powerful oxidants while electrons function as a powerful reductant. It has been reported that tumor cells and bacteria get killed by these oxidants/reductants produced at the illuminated surface of powdered semiconductor CNM.

10.4 Use as Probes

The CNTs have been used as probes[45,46], e.g., in atomic force microscopy (AFM). Since the AFM-generated image is dependent upon the sharpness of the tip and surface structure of the sample a probe should have vertical sides with tip of radius of atomic proportions. The AFM tips made of silicon or silicon nitride are pyramidical in shape and have a radius of curvature around 5 nm. Compared to these, nanoprobes made of CNTs have high resolution, as their cylindrical shape and small tube diameter enable imaging in narrow and deep cavities. In addition, the CNT probe tips have mechanical robustness and low buckling force which lessens the imaging force exerted on the sample, hence can be applied for imaging soft biological samples. Use of the CNTs in AFM enhances the life of probes by minimising sample damage during repeated hard crash-esontosubstrates[47].

10.5 Quantum Dots

Quantum dots are tiny light-emitting particles of 2–10 nm size. These are a new class of biological labels. Semiconductor quantum dots can be used for quantitative imaging and spectroscopy of single cancer cells, for disease diagnostics, cancer imaging, molecular profiling, drug and biochemical discovery, disease staging, targeted therapeutics, and high-throughput drug screening because of their dimensional similarity with biological molecules such as nucleic acids and proteins and their size-tunable properties.In addition, these allow longer periods of observation and do not fade when exposed to UV light. These can also be used for tracking many biological molecules simultaneously, as their colour can be tailored by changing the size of the dot. The SWCNTs have been shown to form quantum dots[48,49]. The MWCNTs can also form quantum dots where the level of

separation exceeds the charging energy[50]. Recently, a structure has been proposed to fabricate a quantum well of a few nm using the electromechanical properties[51] of SWCNTs. When embedded in biological fluids and tissues, the quantum dot excitation wavelengths are often quite constrained. Hence it should be selected carefully for a particular application[52].

10.6 Bio-pharmaceutics and Healthcare

10.6.1 CNTs as Molecular Carriers

The diversity of available chemistry and cell-penetrating structures makes CNTs viable candidates as carriers for the delivery of drugs, DNA, proteins, and other molecular probes into cells. The CNTs are adept at entering the nuclei of cells, hence can be used as nano-delivery vehicle[53]. The prerequisite for such a task is the ability of the carrier to bind to biologically-relevant molecules. For this purpose the CNT were modified by heating for several days in di-methyl formamide, which enabled these to attach short linking chains of triethylene glycol (TEG). Then a small peptide can be bonded to the TEG molecule. When the modified CNTs were mixed with cultures of human fibroblast cells, these rapidly enreed and migrated towards the nucleus. At the low doses, the CNTs appeared to leave the cells unharmed, but as the concentration was increased, the cells began to die. Studies regarding interactions between MWCNTs and protein revealed the self-organisation of streptavidin molecules and the growth of its helical crystals on the nanotube surface. Similarly, DNA molecules have been found to get adsorbed on MWCNTs and small protein molecules such as cytochrome c and ß-Lactose[54]. Vaccine delivery by the CNT was tried by linking the antigen to CNT while retaining its conformation, and thereby inducing antibody response with the right specificity.

10.6.2 Malignancy Prevention and Treatment

For solving the cancer problem, there are four directions in which nanotechnologists are working. The prevention of precancerous cells can be done by imaging agents and diagnostics from becoming malignant at early stages. Two landmark achievements using CNTs are:

(a) *Development of highly-sensitive immuno-detection of cancer biomarkers by amplifying CNTs*[55]: In an attempt to increase the sensitivity of cancer biomarker detection and to decrease the need for large samples from which to detect those molecules, a forest of SWCNTs is used to detect lower levels of the prostate-specific antigen (PSA) which is a biomarker protein produced by the cells of the prostate gland. When the prostate gland enlarges, the PSA level in the blood rises. To the bundles of SWCNT, the chemically reactive groups (enzymes or antibodies capable of reacting or binding to any PSA present in the serum sample) are attached. Using electrical impulses the number of PSA molecules bound to CNTs can be measured. It can detect PSA at levels as low as 4 pg/ml in a sample size of 10 µl of serum. Whereas the existing standard assay has detection limits of 10–100 pg/ml and requires as much as 50–150 µl of sample. In addition, this system can provide quantitative detection of PSA from laser micro-dissected tissue samples of 1,000 cancer cells, something that current technology cannot achieve.

(b) *Fabricating a protein-coated nano-cantilever*[56] *to cancer detection at an early stage*: Cylindrical and hollow tube shape; number of walls enclosing a nanotube making it SWCNT or MWCNT, and the arrangement of carbon atoms wrt tube axis (there are many kinds of chiral tubes) make the CNT a suitable material for preparing a cantilever. Using unique mechanical (such as bending or bucking and high resilience to mechanical strains) and thermal properties of CNTs cantilevers are fabricated from these[57]. Moreover, MWCNTs can adsorb light energy selectively depending on light polarity. Nano-cantilevers coated with molecules capable of binding specific substrates–DNA complementary to a specific gene sequence can detect a single molecule of DNA or protein. The change in the surface stresses that bend the nano-cantilever, helps in detection by using optical techniques.

10.6.2.1 Killing Cancerous Cells

The CNTs have excellent electrical conductivity, hence attempts are being made to develop nanotube-based therapeutics and imaging agents that can detect the earliest signs of cancer from a pinprick of blood and using electrodes modified with CNTs to create highly sensitive devices capable of detecting specific sequences of DNA, including those associated with the breast-cancer-gene BRCA1[58]. In another effort antibodies are attached to the surfaces of CNTs that can bind molecules shed by tumors into the bloodstream [59]. In both the cases, the idea is to incorporate the tumor-sensing nanotubes into a small electrical circuit, which would signal the presence of the tumor-marker with a change in electrical conductivity.

Nanobombs have also been tried to kill the cancerous cells[60]. The nanobomb was made up of bundles of CNTs which on exposure to light and host of different liquids such as alcohol, de-ionised water, and phosphate-buffered saline solutions generate heat. With a single nanotube, the heat generated is dissipated to the surrounding air. But in bundles of CNTs, heat cannot dissipate as quickly and the result is an explosion on the nanoscale. Nanobombs are created due to the thermal-energy confinement in SWCNT bundles and subsequent vaporisation of liquids between SWCNT in bundles, creating pressures that cause the eventual explosion. Nanobombs can be created to explode in cancer cells with highly localised precision and minimum collateral damage to neighbouring cells. Furthermore, this technique, which uses low laser power compared to competing techniques, can produce larger explosions that may ensure complete destruction of cancer cells. Short-CNTs, (20–100 nm) are best-suited for this purpose. In this size range, the nanotubes are readily taken up by cells and also rapidly cleared from the body.

10.6.2.2 Targeted Drug-delivery Device

Antibodies attached to the CNTs can diagnose cancer by detecting specific proteins found only on the surface of cancer cells. The CNTs can ferry a protein (cytochrome-C) across the cell-

membrane[61]. For targeted drug-delivery to cancer cells, folic acid was attached to the surface of the nanotubes. Folic acid binds to a folic acid receptor protein found in abundance on the surfaces of many types of cancer cells. It was suggested that when attached to a CNT, the antibody plays the role of a Trojan horse[62].

10.6.2.3 Carbon Nanomaterials Toxicity

The CNTs and bucky-balls have shown promise as drug-delivery tools, killing cancerous cells, and imaging agents. But toxicity associated with these has raised questions about their utility in clinical oncology. Studies of CNM toxicity have produced apparently conflicting results. Mechanism of CNM toxicity at molecular level[63] has proved that apoptosis (programmed cell-death), cell-cycle delay, cellular transport, and inflammation are linked to the exposure to the nanotubes and nano-onions; which activated the genes involved in cellular transport, metabolism, cell-cycle regulation, and stress response. The MWCNT-induced response by genes related to a strong immune and inflammatory, whereas nano-onions-induced changes in gene were related to external stimuli. The CNTs appeared to be ten-time more toxic than the nano-onions.

While assessing the cytotoxicity of unpurified CNT using keratinocyte cells (HaCaT), adverse effects of SWCNT was found within 18 h of exposure[64]. Oxidative stress and cellular toxicity forming free radicals, peroxidative products, antioxidant depletion, and loss of cell viability were envisaged as the causes for damaging effect, resulting in morphological changes in the ultra-structure of the keratinocytes.

Although both fullerene and CNTs have been demonstrated to accumulate to cytotoxic levels within organs of various animal and cells, the molecular and cellular mechanisms for cytotoxicity of this class of CNM are not yet fully apparent. To address this question, molecular characterisation of the cytotoxic mechanism of MWCNT and nano onions on human skin fibroblast was done[65]. Whole genome expression array analysis and high content image analysis-based phenotypic measurements on fibroblast cell populations exposed to carbon nanoonions and MWCNTs have

shown that cell cycle arrest and increased apoptosis/necrosis was induced in fibroblast cells.

Movement of the CNT across the outer membrane of cells occurs so easily that it gives a concern that if higher amount of CNT is administered these may not only become toxic but also clog the pathway. The cellular toxicity of CNM as a function of their aspect ratio and surface chemistry was tested *in vitro* on lung tumor cells. The results have indicated that toxicity is size-dependent. Moreover, cytotoxicity is enhanced when CNM is functionalised by acid. Increasing concentrations of MWCNT, CNF, or carbon nanoparticles caused changes in cell proliferation and cellular health of cultured human lung tumor cells. It was suggested that dangling bonds could be responsible for the toxicity of the CNMs. Highly reactive dangling bonds (carbon atoms not bonded to the other carbon atoms) available to react with biomolecules are more prevalent in the carbon nanoparticles than in nanofibres or nanotubes[66].

There are reports that functionalisation of CNM may induce non-toxicity in the CNTs. Moreover, when lower concentration of nanotubes is used in biomedical applications, toxicity has not been an issue[67]. Toxic effect of the CNM was observed in unpurified CNM which possibly had left-over metal catalysts as well as amorphous carbon. Such toxicity was not encountered in highly purified CNTs. The CNTs functionalised to make them water-soluble, show very little toxicity even at very high concentrations. Cells that had taken up as many as 70,000 functionalised CNTs showed no signs of toxicity[68]. Two types of functionalised CNTs, by 1, 3-dipolar cyclo-addition reaction and the oxidation/amidation treatment, have been found to be taken up by *B* and *T* lymphocytes as well as macrophages *in vitro*, without affecting cell viability.

11. CARBON NANOTUBES AS SCAFFOLD FOR FABRICATING TISSUES

Tissue engineering or fabricating tissues is a discipline which involves replacement of anatomic structure of the damaged, injured, or missing tissue or organs by agglomerating biomaterials, cells, and biologically-active molecules[69-71] materials are

3-D scaffolds which provide mechanical support to the growing cells or tissue, guiding them in a microenvironment, mimicking the biological system. These can then be transplanted into the system. The principal function of a scaffold is to direct the cell behaviour such as migration, proliferation, differentiation, maintenance of phenotype, and apoptosis, by facilitating sensing and responding to the environment, via, cell-matrix communications and cell-cell communications[72]. Such scaffold should have the capacity to give highly porous surfaces allowing seeding of cells at high densities as well as facilitating proper cell-cell interaction through a regulated molecular myriad[73, 74].

Fusion of nanotechnology and micro-engineering can be the best options for designing biomaterials to generate scaffolds for tissue engineering. The SWCNT and MWCNT possess ordered structures with high aspect ratio, ultralightweight, high mechanical strength, high electrical and thermal conductivity, metallic or semi-metallic behaviour, and high surface area hence these have been found to be potential nanomaterial for tissue engineering[75, 76]. A scaffold-CNT has significant relevance for tissue engineering, because it can help in the following:

11.1 Cell Tracking and Labelling

- *By optical labeling*: because CNTs possess optical transitions in the near-infrared (NIR) region[77, 78].

- *By magnetic resonance imaging (MRI) contrast agent*: Fullerenes and CNTs are composed entirely of carbon, thus providing poor contrast in MRI, hence require functionalisation to make them more readily detectable, which is done by attaching a heavy metal such as gadolinium to the surface of the fullerene or caging the heavy atom[79, 80]. Gadolinium loading into ultra short (20–100 nm long) nanotubes through side wall defects, displays 40 time greater proton relaxivities than the standard gadolinium clinical contrast agent. With such a large contrasting capability, such materials can be dispersed throughout an engineered tissue allowing the complete process monitoring.

- *By radio-labelling technique*: The specific radioisotopes are covalently bound to the CNT and then administered into the biological system to measure the biodistribution of nanotubes. Study with BALB/c mice, such functionalised SWCNTs have shown that they do not accumulate in any specific organ and rapidly get cleared from the blood system through the renal excretion without any toxic side effects or mortality and were observed in the urine[81].

11.2 Monitoring Cellular Physiology

Continuous monitoring of the engineered tissues; with biosensors provided real-time data related to the physiological relevant parameters such as pH, pO_2, and glucose levels. The SWCNTs are promising candidates for the development of nanoscale biosensor, because of their capability to provide strong electrocatalytic activity and minimise surface fouling of the sensors[82]. The SWCNTs were reported to have high ability to promote electron-transfer reactions in electrochemical measurement[61]. The CNTs have very strong potential to address the needs of even label-free sensing for protein arrays[83]. They are functionalised and their conductance is modulated as the target molecules bind to the functionalised CNTs. This sensing technology has been used to detect the binding of small virus particles[84], small molecules binding to proteins[85], streptavidin[86], and anti-biotin immunoglobulin binding to immobilised biotin[87].

11.3 Regulating Cellular Behaviour

The CNTs made an impact in tissue engineering in controlling the production or delivery of tissue-inducing substances such as growth factors, localised drug delivery[75], transfection[80], and ion-channel blockers[81] by taking the advantage of the large aspect ratio and ease of functionalisation of CNTs. The end- and side-walls of CNTs possess different chemical reactivities that can facilitate a dual functionalised drug delivery platform. They can be functionalised to attach either electrostatically or covalently to DNA and RNA, and the remaining unfunctionalised and hydrophobic portions of the nanotubes can be attracted to the hydrophobic regions of the cells. This hydrophobicity explains non-specific binding between nanotubes and proteins[82]. In addition, they can be functionalised with bioactive proteins to

help cross the cellular membrane, e.g., biotin functionalised CNTs bound to fluorescent dyes were capable of intercellular transport of fluorescent streptavidin[80]. Nanotubes can also be functionalised with cationic components capable of penetrating human and murine cell types. Such nanotubes can be complexed with plasmid DNA to facilitate transfection of cells[80]. In addition, DNA or siRNA can be bound to nanotubes with cleavable disulshide bonds and delivered to mammalian cells[87].

Besides heterogeneous functionalisation, the CNTs could provide localised delivery of therapeutic agents triggered by external sources. Previously it was shown that the CNTs absorb NIR light at wavelengths that are optically transparent to native tissue, e.g., irradiation with 880 nm laser pulses can induce local heating of SWNTs *in vitro* thereby releasing its molecular cargo without harming cells or can be internalised within a cancer cell and with sufficient heating to kill the cell[88]. This could allow selective delivery of drugs to certain cell types, helping to control the distribution of such cells throughout the engineered tissue.

11.4 Structural Support for Tissues Engineering

The CNTs have the potential for providing the needed structural and mechanical reinforcement for tissue scaffolding[89]. CNTs can be grown on a patterned bed of catalysts, thus creating 3-D array having complete control in size, shape, and periodicity. This can be exemplified when L929 mouse fibroblasts and neurons have been grown on such scaffolds[90]. Mechanical immobilisation of Hela cells on aligned CNTs array through insertion of the nanotube tips into the cell have already been demonstrated[90]. Since the CNT is not biodegradable and is not readily dispersed in aqueous solutions, they are blended with polymers, e.g., the MWCNTs mixed with chitosan brings significant improvement in mechanical properties, Young's modulus and tensile strength can be compared to neat chitosan[91]. Scaffolding agent like collagen blends with SWNT to support smooth muscle cell growth[92]. The CNT can also be functionalised to release bioactive factors like glucose oxidase which can be attached to nanotubes and still retain the enzymatic activity[93].

Bio-compatibility of CNM can be demonstrated as:

- Heart valves made of pyrolytic carbon were highly compatible, with good adherence of endothelial cells and minimal adherence and activation of platelets[94].

- The diamond-like carbon was biocompatible and used as coatings for many orthopedic and cardiovascular applications[85,97,98].

- The CNTs have been found to be biocompatible for neural applications[99-102].

- Investigation of the proliferation and function of osteoblast cells seeded onto four variant of compacted CNFs (of dia > 100 nm or <100 nm) showed that there was increased osteoblast proliferation on the nanophase (< 100 nm) CNFs and increased alkaline phosphatase activity, intracellular protein synthesis and deposition[103].

12. IMPLANTABLE MATERIALS AND DEVICES

12.1 Implantable Nanosensors and Nanorobots

These can be useful in monitoring pulse, temperature, and blood glucose[104]. The CNT-based nanosensors are thousand-time smaller than even micro-electromechanical systems (MEMS) sensors and consume less power[105,106]. Possible applications of implanted nanorobots are to cure skin diseases; to protect the immune system by identifying unwanted bacteria and viruses and puncturing them to end their effect; to ensure that the right cells and supporting structures are at the right place; and as a mouthwash to destroy pathogenic bacteria and lift food, plaque, or tartar from the teeth to rinse them away.

12.2 Actuators

Actuators convert electrical energy to mechanical energy. The direct conversion of electrical energy to mechanical energy through a material response is crucial for many biomedical applications such as microsurgical devices, artificial limbs, artificial ocular muscles, or pulsating hearts in addition to robotics, optical fibre devices, and optical displays. The main technical requirements of these actuators are low

weight, low maintenance voltage, large displacements, high forces, fast response, and long life cycle, hence the CNTs have been suggested[51,107,108] as actuators. The CNT actuators can work under physiological environment, low voltages, and temperatures as high as 350 °C. The CNT electromechanical actuators (known as artificial muscles) generates higher stresses than natural muscles and higher strains than high-modulus ferroelectrics. The MWCNTs are excellent candidates for electromechanical devices because of large surface area as well as their high electrical conductivity[109,110].

12.3 Surgical Aids

Nanotweezers (that can be used for manipulation and modification of biological systems such as structures within a cell) have already been created using CNTs. They have the potential to be used in medical nanorobotics, for manipulation and modification of biological systems such as DNA and structures within a cell or as nano-probes for assembling structures or for removing the brain tumor. Nested-CNTs have made exceptionally low-friction nano-bearings that can be used in many surgical tools[111].

13. USE IN COSMETICS

Without being aware, several thousands of years ago Egyptians, Greek, and Romans used nano-sized formulations to dye their hair[112]. Most remarkably claimed property of fullerenes used in cosmetic industry is antioxidant (elimination of free radicals linked to aging and cell death) property; which is being exploited in the cosmetic and food industry which serves to mop up free radicals due to their structure of the cage, bonding configuration and high number of available bonding sites, effectively neutralising the power of the free radicals to damage tissue. They have shown to be up to 100 times more effective than such commonly used compounds as vitamin E and co-enzyme Q10. The chemical property of CNTs aids in carrying out reaction at the nanoscale where the nutrient (vitamin D, co-enzyme Q10) are precisely targeted to the cells of the skin.

14. USE IN FOOD AND AGRICULTURE

14.1 In Food Industry

Use of CNM in food industry is till in its infancy, though the impact of nanotechnology is being felt in basic food to food processing, from nutrition delivery to intelligent packaging. Potential applications of functionalised nanotubes can be:

* *Anti-microbial packaging*: It will scavenge the oxygen molecules and other microorganisms from entry into the food product and thereby keeping it fresh. By heating the CNTs in a closed vessel microwave oven, they were chemically modified without damaging their essential structure. This novel method of functionalising improves the solubility of CNTs, leading to new types of packaging[113].

* *Embedded sensors in nanotubes*: In electronic tongue technology, the sensors can detect substances in ppt and would trigger a colour change in the packaging to alert the consumer if a food has become contaminated or if it has begun to spoil, and hence detect the entry of food-borne pathogens.

* *Intelligent food packaging*: The nanotubes in the packaging material will release a preservative if the food within begins to spoil. This preservative release is operated by means of a bio-switch developed by nanotechnology.

* *Super sensors*: It will lead to instantaneous detection of certain bacteria and hence would play a crucial role in the event of a terrorist attack on the food supply.

14.2 In Agriculture

As per data from Rice University nanotechnology can be used[114] to reduce use of pesticides and fertilizers by their slow release using CNM; to improve plant and animal breeding and new nano-bioindustrial products; to culture CNTs into seeds which can sprout new nanotubes, making them self-replicating bodies; and to use sensors having CNM to detect infection and the nutrient level in the plants and soil.

15. INDIAN SCENARIO

Nano-bug has bitten the scientific world of India. There are many R&D and academic institutes taking initiative in this direction. That's because they have realised that the next generation evolution of all the disciplines of science is going to be based and backed by the knowledge of nanoscience and nanotechnology.

The convergence of nanotechnology and biotechnology has created an opportunity for the innovative development of medical advances spanning the continuum of drug discovery and development. Convergence of nanotechnology, a functional engineering on an extremely small scale with biotechnology, will not only produce high-tech products at low cost but will also prolong life via preventing illness and improving the health.

The industries are also exploring the opportunities in nanotechnology. There are very few industries involved in production of nanomaterials in India but about 100 odd pharmaceutical/biotechnology and biomedical companies in India are working on nano-based technologies. The private sector too is spending on nanotechnology but to a small extent. Considering the huge market potential for nanoparticles in India, companies from China, Japan, and Iran are trying to enter the domestic market through tie-ups.

Though leading companies like Reliance, Tata Group, and Mahindra and Mahindra are also making investments in this upcoming space, but they have not covered the CNMs in their plans so far.

Narayan Kulkarni of *Biospectrum Magazine* has written that Monad Nanotech is another company producing the CNM commercially using low cost production technology developed by Prof Maheswar Sharon's group at IIT Mumbai, who has two patents and 38 research publications to his credit on CNMs. The team has been working on not only synthesis of CNMs; but also on their futuristic applications. Monad Nanotech has been supplying many nanomaterials- MWCNT 1-3 nano-beads 1-2, nanofibres 1-4, fibrous carbon nanosize metals and porous carbon gas diffusion fuel cell electrodes to the research organizations in India. Dr Madhuri Sharon, Managing Director,

Monad Nanotech, feels the market for nanotech particle is very huge and growing very fast. Besides doing research and development and producing nanomaterials, Monad Nanotech has taken up the agency of Shenzhen Nanotech Port Co Ltd (NTP), China, for sales rights in India and Canada. Similarly Monad has taken the agency of Meijo Nano Carbon, Nagoya, Japan, for world marketing rights for its products excluding Japan.

16. GLOBAL SCENARIO

Summing up, the activities in the field of CNM at the global level in this review article would be beyond the scope. However, considering the applications of nanotechnology in the various fields, the next ten years will see nanotechnology playing the most dominant role in the global business environment and is expected to go beyond the billion dollar estimates and cross the figure of $ 1 trillion. The market share for nanotechnology products such as nanomaterials will be about $ 340 billion, electronics and semi conductors will be $ 300 billion, pharmaceutical will be around $ 180 billion, and aerospace, chemical plants and tools will be around $ 200 billion. In BRICS countries, the market for nanotechnology is expected to be about $ 1 billion. Similarly research arena is expected to give very high output in all the disciplines of science; scientists working on nanotechnology have opened a broad net of discoveries that does not leave any major research area untouched in physical, biological, and engineering sciences.

Dr Abdul Kalam has said, "I am confident that the Indian nanotechnology initiatives are maturing into marketable products for worldwide applications. Industries from abroad and India are keen to take our technologies and to commercialise. Indian industries should now take the lead and become a partner in the nanoscience and technology ventures to capture the international market." He has also proposed the establishment of 'world knowledge platform' which will combine the core competence of the partners in the area of convergence of technologies in bio-info-nano technologies for the design, development, and product realisation.

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