1

An Introduction to Carbon Nanofiber

Maheshwar Sharon

Walchand Center for Research in Nanotechnology and Bionanotechnology, WCAS, Solapur, Maharashtra, India

The goal of education is not to increase the amount of knowledge but to create the possibilities for a child to invent and discover, to create men who are capable of doing new things.

Jean Piaget

1.1 Introduction

Carbon (Latin word: *carbo* "coal") is a chemical element with symbol **C** belongs to group 14 of the periodic table. Its atomic number is 6 and has the electronic structure of $1s^2 2s^2 2p^2$. The valence of carbon will depend upon the arrangement of electrons in 2s and 2p orbitals. 2s orbitals are supposed to house maximum of 2 electrons and 2p can possess a maximum of 6 electrons. The energy of electrons in 2s and 2p orbitals is not much different from each other. Therefore, depending upon the condition of the electronic arrangement, carbon atom can show valence of 2 due to hybridization of $2s^1 2p^1$ orbitals. The 2s2p orbital can also be hybridized as $2s^1 2p^2$ showing a valence of 3. Likewise, 2s2p orbital can be hybridized to show $2s^1 2p^3$ configuration making a carbon valence of 4. Carbon compound with $2s^1 2p^1$, i.e., with valence of 2, is rarely seen, and if some carbon compounds are made with such configuration, they are not stable. Most common compounds with configuration of $2s^1 2p^2$ (like graphite) and $2s^1 2p^3$ (like diamond) are found in nature. Angles between each carbon for $2s^1 2p^1$, $2s^1 2p^2$ and $2s^1 2p^3$ are shown in Figure 1.1.

Email: sharonmaheshwar@gmail.com

Madhuri Sharon and Maheshwar Sharon (eds.) Carbon Nanofibers: Fundamentals and Applications, (1–20) © 2021 Scrivener Publishing LLC

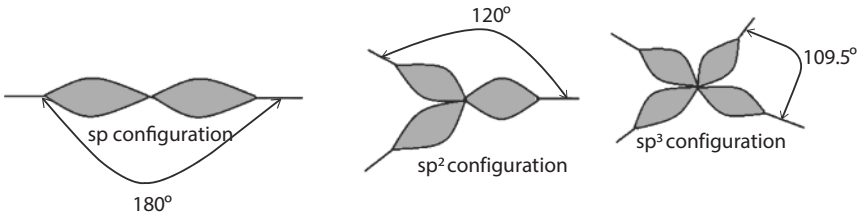

Figure 1.1 The formation angle between the carbon for sp, sp^2 and sp^3 configuration.

In this chapter we shall restrict our discussions to carbon with configuration of sp^2 and sp^3. In addition, we shall also restrict our discussions especially regarding carbon fiber (discussed in detail in later on), though we may touch upon carbon nanotube.

It will not be the scope of this chapter to discuss diamond or graphite, mainly because information about these materials are available in almost all textbooks dealing with carbon. Our discussion will be confined to materials like carbon fiber, carbon nanofibers and to some extent carbon nanotubes for making a clear distinction between these materials.

1.1.1 History of Carbon Fiber

The development of carbon fibers dates back as early as the 18th century but its applications were only realized after 1960, making it possible to develop carbon fibers with high strength. Some landmarks in the development of carbon fibers are given here. In 1860, Joseph Swan first produced carbon

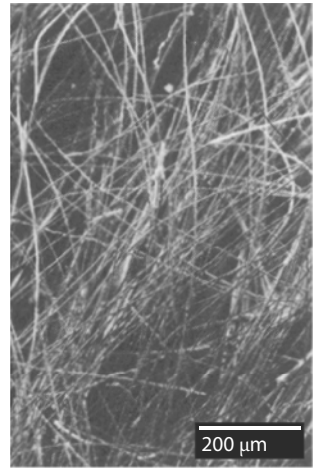

Figure 1.2 SEM image of carbon fiber.

fibers. In 1879, Thomas Edison carbonized cotton threads or bamboo slivers to produce carbon fiber. He used it as wire filament which glows under electric current. Roger Bacon prepared carbon fiber containing about 20% carbon in 1958 by carbonizing rayon. The process of carbonizing rayon was later improved in 1960 by Richard Millington (US Patent No 3,294,489) [1] to get carbon fiber with almost 99% carbon. During the 1960s, a Japanese firm produced carbon fibers from a petroleum pitch which contained 85% carbon and had excellent flexural strength. After 1960, it seems various efforts were made to prepare carbon fibers (Figure 1.2) from different types of precursors to improve the quality of carbon fibers; for example, giving tensile strength 4,000 MPa and a modulus of 400 GPa to be used in aircraft.

1.1.2 What Is a Carbon Fiber?

Carbon fibers are classified symbolically as CF. These fibers are of size about 5–50 μm in diameter and composed mostly of carbon atoms. They are also known as graphite fiber. Graphite is made of pure carbon arranged into big sheets of hexagonal aromatic rings (Figure 1.3X). The structure of carbon fibers is like the structure of graphite arranged in layers of long graphite sheets of length about 5–50 μm and each layer of graphite is stacked together forming a ribbon-like structure. Depending upon the precursors used to synthesize carbon fibers and the manufacturing processes, each layer planes may be either turbostratic graphitic, or a hybrid structure. In graphitic crystalline regions, the layer planes are stacked parallel to each

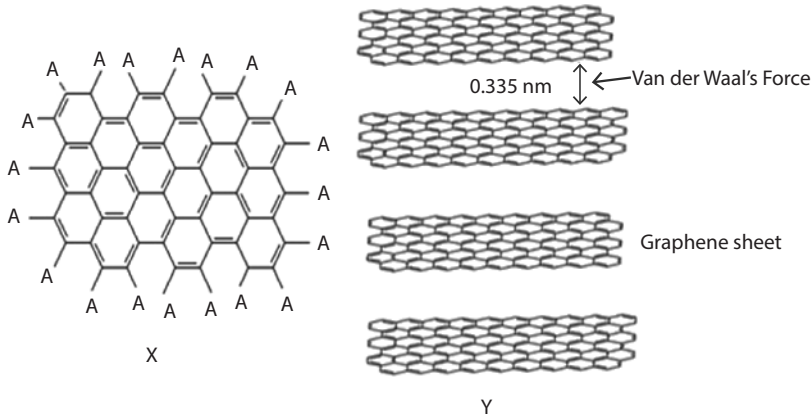

Figure 1.3 (X) A sheet of graphite showing free edges A, which are reactive and can be functionalized, (Y) shows four layers of graphene sheet separated by van der Waals forces. In graphite this separation distance between two consecutive layers is 0.335 nm.

other in a regular fashion. The atoms in each layer are covalently bonded through sp^2 bonding while the interaction between each layer is relatively weak van der Waals forces. In a single graphitic crystal, *d*-spacing between two graphene layers (d002) is about 0.335 nm (Figure 1.3Y).

If carbon content in the fiber is 92 wt% then it is considered as *carbon fiber*. However, if carbon content is more than 99 wt% then the fiber is known as *graphite fiber*. This classification depends on the percentage content of carbon, process of synthesis and precursors; Carbon fibers can possess excellent tensile strength, low densities, high electrical conductivities, high temperature tolerance, low thermal expansion and chemical stabilities. High tensile strength and lightweight carbon fiber can be developed by making its composite with suitable polymers. Because of these properties, carbon fiber has found its place in aerospace, civil engineering, the military, and motorsports, along with other areas like sports.

Classification of carbon fibers based on precursor used to make them:

- PAN-based carbon fibers (90% of fibers made from this precursor)
- Pitch-based carbon fibers (about 10% or less are made from this precursor)
- Mesophase pitch-based carbon fibers
- Isotropic pitch-based carbon fibers
- Rayon-based carbon fibers (this also falls under the category of pitch-based (10% are made from this precursor)
- Gas-phase-grown carbon fibers

***Classification of carbon fibers based on heat treatment temperature*:**

- **Type-I**, High-heat-treatment carbon fibers (HTT)
  Carbon fibers obtained after heat treatment at temperature above 2000 °C. These fibers are associated with high-modulus type fiber.

- **Type-II**, Intermediate-heat-treatment carbon fibers (IHT)
  Carbon fibers obtained after heat treatment at temperature around 1500 °C. These fibers are associated with high-strength type fiber.

- **Type-III**, Carbon fibers obtained with low-heat-treatment.
  Carbon fibers obtained with heat treatment at temperature around 1000 °C show low modulus and low strength.

1.1.3 Structures of Carbon Fibers

Some carbon fibers synthesized by the author [2, 3] and his research group from camphor under different but specific conditions are shown in Figure 1.4. These are grown by chemical vapor deposition technique. It is observed that though precursor was the same, i.e., camphor, by altering the nature and form of catalyst, carbon fibers of different morphologies are obtained. For this growth, nickel in different forms was used as a catalyst. Nickel plate, cleaned by acid followed by acetone, gave carbon fiber as shown in Figure 1.4a. When the top surface of nickel was oxidized and then cleaned, it gave carbon fiber as shown in Figure 1.4b. It grew from one point on the catalyst surface in a cauliflower-like shape. In another experiment, camphor was pyrolyzed without using any catalyst. Under this condition, plate type (cactus type) carbon fiber was obtained (Figure 1.4c). These fibers also contained some small beads attached to the fiber. In one experiment nickel powder of size 20 nm spread over nickel plate was used. Under this condition, branched carbon fiber as shown in Figure 1.4d was obtained, with Ni catalyst sitting at the center. Vapor-grown carbon fibers (VGCFs) (Figure 1.4e) were obtained by pyrolysis on the Ni coated quartz substrate. All these experiments were carried out under argon atmosphere at temperature 750 °C.

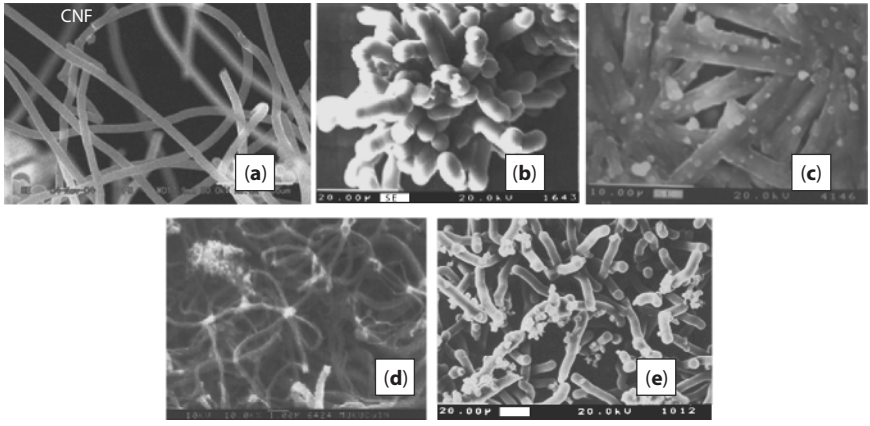

Figure 1.4 SEM images of carbon fibers (CF) synthesized from camphor as precursors by pyrolyzing them at 700 °C in presence of argon under varying conditions: (a) Long tube-like CF over nickel plate, (b) cauliflower-like CF over oxidized nickel plate, (c) CF grown without using any catalyst, (d) branched carbon fibers obtained at temperature 750 °C, with Ni sitting at the center, and (e) VGCFs obtained by pyrolysis on the Ni coated quartz substrate (Source: Debabrata Pradhan, 2003) [4].

1.1.4 Synthesis of Carbon Fibers

The process of synthesis of carbon fibers is patented and each company has its own trade secret. It is difficult to provide a detailed and very accurate process. It is therefore only possible to discuss an overall process without providing the intricacies of the actual process. Hence, the synthesis process of the most popular carbon fibers prepared from polyacrylonitrile (PAN) precursor is discussed here.

1.1.4.1 Carbon Fibers from PAN

Before carbon fibers are made from PAN, some pretreatments are made, like mixing Acrylonitrile powder with a suitable plastic (e.g., methyl acrylate, methyl methacrylate) and a catalyst to form a polyacrylonitrile plastic. This plastic is then spun to form the internal atomic structure of the fiber. These fibers are stabilized by heating them in air at about 200–300 °C for about 30–120 minutes. During this process some oxidation of carbon takes place, which helps to rearrange their atomic bonding pattern. These fibers are then carbonized at temperature 1000–3000 °C for several minutes in gas like argon (but in absence of any oxygen). By this process most of the non-carbon atoms and a few carbon atoms as well are lost in the form of gas like CO_2, CO, N_2 NH_3, water vapor H_2, etc. This process helps to form strongly bonded carbon atoms that are aligned parallel to the long axis of the fiber. Due to losing different types of material during the carbonizing process, the surface of the fiber is very rough. Hence, to obtain better bonding properties, surfaces are oxidized in a controlled manner by techniques like exposing them in oxygen environments or by performing some chemical treatments like dipping them into some oxidizing solutions like nitric acid. In order to protect the fibers from environmental oxidation, they are coated with epoxy, polyester, nylon, urethane, and others.

1.1.5 Properties of Carbon Fibers

It is difficult to give the properties of carbon fibers by quantity because that depends on how the fiber was made and what treatments were done to the fiber. Here we give properties qualitatively only. Specific strength of carbon fiber (which is the ratio of strength to weight) is very high. Strength of material is the ratio of the force per unit area applied to fiber at which it breaks to its density. Carbon fiber is very rigid, i.e., its Young's

modulus is high. In other words, it needs high force to deflect it. The fiber is chemically stable and resistant to corrosion. Carbon fiber is electrically conductive and is resistant to fatigue, especially its composites. Carbon fiber has good tensile strength, which means it can stand maximum stress while it is stretched or pulled. Carbon fibers are normally fire resistant/nonflammable in the absence of oxygen. They are a good thermal conductor. Carbon fibers have a unique property of low coefficient of thermal expansion. They are nonpoisonous, biologically inert and X-ray permeable. These properties are especially good for any medical applications.

Some general properties of PAN-based fiber are given below, but these values may be different if PAN-based fibers are prepared under some specific condition. Hence, these data can be taken as approximate values.

- Density: 1750–1870 kg/m^3
- Tensile strength: 0.9–6.37 kN/mm^2
- Young's modulus: 40–588 kN/mm^2
- Elongation: 0.7%–2.2%
- Filament diameter: 4.4–7.2 μm
- Tensile strength of carbon fiber: 4127 MPa
- Carbon fiber reinforced epoxy (thermal conductivity): 24 W/(m.K)

1.2 Properties of Carbon Nanofiber and How It Differs from Carbon Nanotube

Intrinsically, there is not much difference between carbon nanofiber and carbon nanotube. When a single layer of graphene sheet is rolled into a cylinder (Figure 1.5a) it takes the shape of a single-walled carbon nanotube. When a multiple number of graphene sheets separated by a distance of 0.335 nm are rolled into a cylindrical shape it takes the shape of multi-walled carbon nanotubes (Figure 1.5b). However, when broken sheets of multiple graphene sheets are rolled into a cylinder it takes the shape of carbon nanofiber (Figure 1.5c). In other words, carbon nanofibers appear as cylindrical nanostructures with graphene layers organized as packed cones, cups or plates. The surface area of CNF is much larger compared to MWCNT of the same dimension, because the former has many broken graphene sheets which are not aligned as that of MWCNT (well-defined layer, as shown in the TEM image in Figure 1.5b).

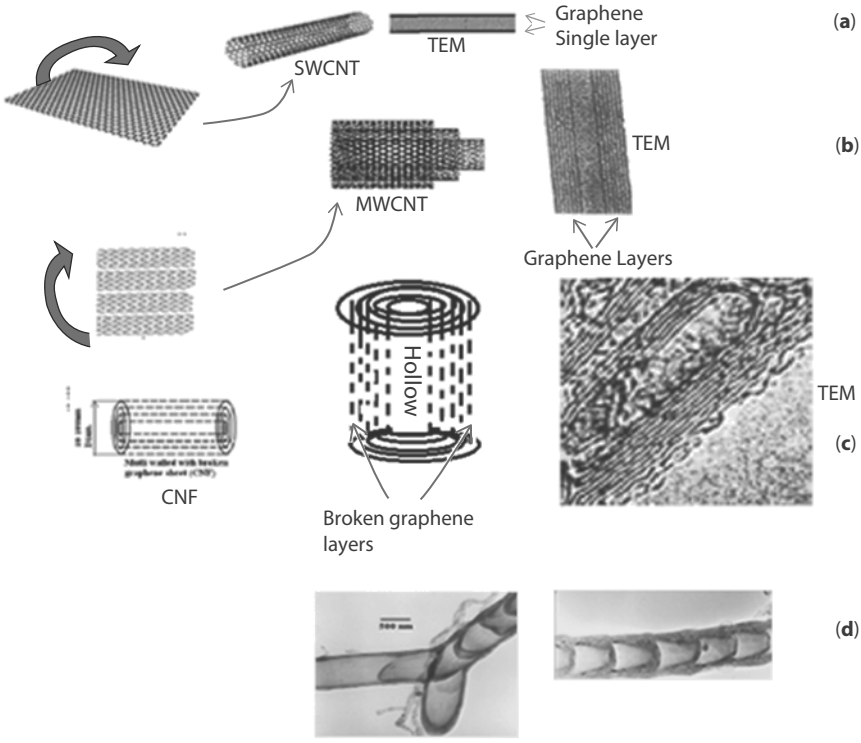

Figure 1.5 Schematic illustration of (a) how single layer of graphene folds to make a single-wall carbon nanotube; (b) how multilayers of graphene fold together to form a multi-walled carbon nanotube; and (c) sketch of how broken graphene layers fold to form a carbon nanofiber, and TEM image of CNF with broken graphene layers, and (d) TEM image of packed cones, cups.

1.2.1 History of CNF

Carbon nanofibers (CNFs) were first reported by Hughes and Chambers in a patent in 1889 [5] while carrying out the synthesis of filamentous carbon. Pyrolysis of methane/hydrogen gaseous mixture yielded carbon nanofibers in the form of a filament growth. The first electron microscopy observations of hollow carbon nanofibers of 50 nm in diameter was reported in the early 1950s by the Soviet scientists Radushkevich and Lukyanovich. Then, in 1988 Morinobu Endo [6] at Shinshu University, Japan, reported carbon nanofibers with a diameter of 1 μm and length of above 1 mm. In 1991, Yoshinori Ando [7] synthesized carbon nanomaterial by Arc process which was examined by Sumio Iijima while working

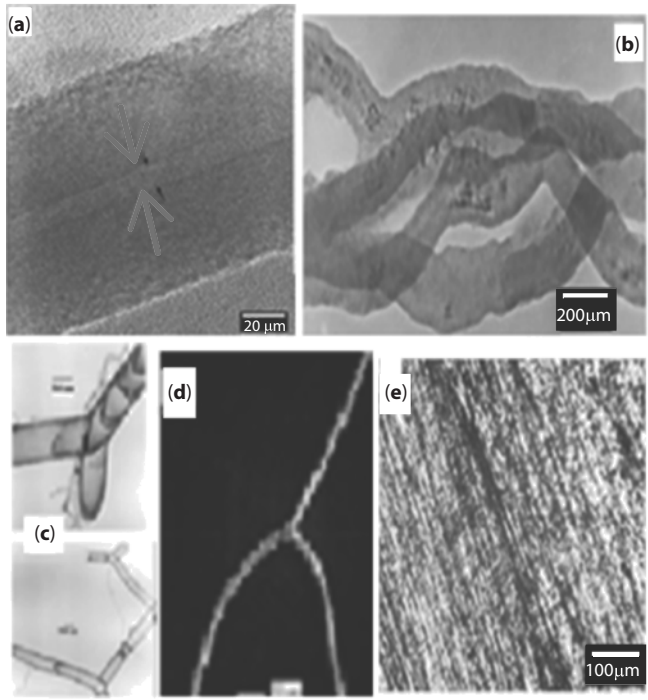

Figure 1.6 (a) TEM image showing graphene layers of (b) entwined carbon nanofibers synthesized at 1100 °C in presence of Ni: Al catalyst and n-hexane; (c, d) TEM images of open-ended bent, V-shaped inner novel growth of carbon nanotubes at 1000 °C in presence of nickel particles; and (e) SEM micrograph image of straight VGCFs (Source: Debabrata Pradhan, 2003) [4].

at NEC as a new form of carbon nanotube. Pradhan synthesized carbon nanofibers by the pyrolysis of precursor camphor. Some of the peculiar shaped carbon nanofibers synthesized are shown in Figure 1.6.

1.2.2 Role of Surface States in Controlling the Properties of CNFs

Carbon nanofibers possess excellent mechanical properties, high electrical conductivity, electromagnetic shielding and high thermal conductivity. Carbon nanofibers have average diameters ranging from 125–150 nm depending upon the precursors and technique used to manufacture them and have lengths ranging from 50–100 μm. They can form composites with various types of polymers and can be easily functionalized due to the presence of unique surface states (Figure 1.7).

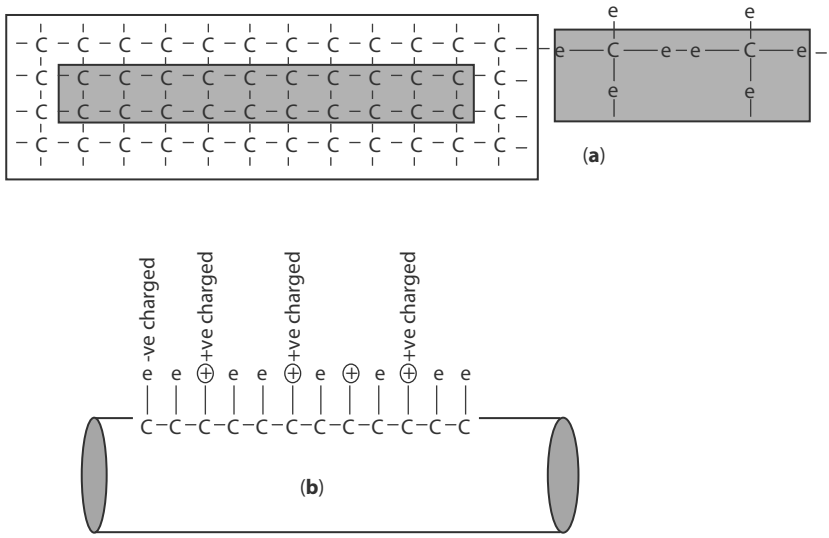

Figure 1.7 Schematic illustration showing (a) the formation of bonds of carbon atoms present at different layers of carbon fiber's surface and missing of electrons from the top layer of carbon atoms; and (b) the effect of the missing electrons from the surface of top layer atoms, creating positive and negative charges which are responsible for making the carbon fibers reactive.

Each layer of carbon nanofiber or nanotubes, contains a set of carbon atoms arranged in one plane. In x-y direction, each carbon is attached with σ-bonds. Bottom layers of carbons (in z direction) are also arranged in the same fashion, such that each carbon shares its electron with bottom layers of carbon by either σ-bonds or π-bonds as the case may be (Figure 1.7a). However, electrons of carbon atoms present in the top layer are not satisfied with its electron due to the absence of any carbon atoms above its layer. These carbon atoms are dissatisfied with electrons. As a result, these carbon atoms would either behave as positively charged (lost its electron) or negatively charged (contains more than its normal electron). However, these distributions of charges would be such that overall the carbon tube will behave like a neutral particle. These unsatisfied carbon atoms are more reactive as compared to carbon atoms present in the layers below the top layer. These carbon atoms are said to possess active sites which are designated as a surface state. The presence of surface state depends upon the types of graphene layers present on the top layers of carbon tube. Its broken graphene layers will show a large number of surface states as well as surface areas. It is for this reason that carbon nanofibers are more reactive as compared to carbon nanotubes.

1.3 Synthesis of Carbon Nanofiber (CNF)

Catalytic chemical vapor deposition (CCVD) or simply CVD is the foremost commercial technique for the fabrication of CNF as well as CNT. This is a batch process. This technique also produces CMF known as vapor-grown carbon nanofiber (VGCNF). In this type of process, precursor near its boiling temperature is converted into gas-phase molecules and is transported by some carrier gas to decompose at high temperatures in the presence of a transition metal catalyst kept on a substrate. A subsequent growth of the fiber around the catalyst particles is achieved. The nanofiber diameter depends on the catalyst size. There can be different designs of a CVD unit.

1.3.1 Chemical Vapor Deposition (CVD) Method

A typical CVD setup is shown in Figure 1.8. A long quartz tube (C) is inserted into two ceramic tubes (D). Electrical heating wire is wrapped over two ceramic tubes (D). These two ceramic tubes are arranged to maintain two different temperatures (A1 and A2). In the quartz tube (C) two quartz boats (B1 and B2) are kept. In boat B1 a known amount of precursor which is to be pyrolyzed is kept. In boat B2 catalyst powder is spread over the boat. Two gas cylinders (K and H) are connected to the long quartz tube (C) via two controllers (E) and flow meter (F). The outlet of tube C is connected to two bubblers (G). Temperature of A1 is maintained at a value which can boil the precursor kept in quartz boat B1, which is normally kept at around 400 °C. Temperature of furnace A2 is maintained at a suitable temperature where the precursor gas can be decomposed in the presence of the catalyst to get the CNF. Before setting the temperatures of two furnaces, inert gas like argon gas (H) is purged through the quartz tube (C) to remove the presence of oxygen. The temperature of furnace A2 is set to a required temperature (which could be in the range of 600–1000 °C). When the required temperature has attained the temperature of the furnace, A1 is set to boiling temperature of the precursor. During this process the flow of carrier gas is maintained which helps to carry the vapor of precursor to the furnace A2 for completing the process of pyrolysis. Undecomposed gas and carrier gas are allowed to escape to atmosphere through the bubblers (G). At the end of pyrolysis CNF is collected from the furnace (A2).

It is possible to control the length of carbon nanofibers by controlling the rate of gas flow in the quartz tube (C). In addition, direction of fiber growth can also be controlled by adjusting the direction of gas flow. If adjusted properly, the variable parameters of the process can yield CNF with submicrometer diameters and lengths of a few to 100 μm.

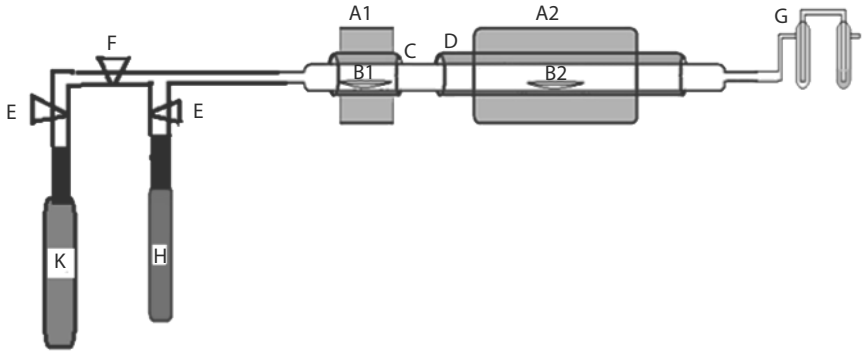

Figure 1.8 A sketch of a typical CVD unit. A1 and A2 are two furnaces operating at two different temperatures. B1 and B2 are two quartz boats used for keeping precursor and catalyst respectively. CNF is grown on the boat B2 as well as over the entire area covering the furnace A2, C is the quartz tube in which growth of CNF takes place, D is ceramic tube over which heating wire is wrapped to create required temperature, E and F are gas valves and flow meter to regulate flow rate of gas. G is a gas bubbler to prevent backflow of gas into the quartz tube and allow the escape of unreacted gas into the atmosphere, H is the gas cylinder containing the carrier gas and K is precursor gas like methane or acetylene.

1.3.2 Precursors for CNF

Precursor for synthesizing CNF can be several types of hydrocarbons such as natural oils like mustard oil, pure fatty acids (liquid or solid), camphor, terpene oil, acetylene, ethylene, methane, natural gas, benzene, etc. Introduction of carbon monoxide (CO) into the gas flow can increase the carbon yield, hence yields a greater amount of CNF. It is also possible to use plant seed materials like mustard seed, stem of any plant, plant leaves, bamboo, rice straw, bagasse, etc. It is also possible to use some gasses directly like methane, acetylene, etc. When using solid materials like plant leaves, there is no need to use the furnace (Figure 1.8A1). These precursors can be kept directly in the boat (Figure 1.8B2) along with any catalyst (if needed). If gases like methane are to be used as a precursor then there is also no need to use the furnace (Figure 1.8A1). Gas from the cylinder (Figure 1.8K) can be sent to the furnace (Figure 1.8A2) where suitable catalyst is kept in the boat. The precursor gas can either be directly fed into the unit or is mixed with carrier gas in the required proportion.

1.3.3 Use of Catalyst in the Synthesis of CNF

There are variations in the type of catalyst used for the synthesis of CNF. There are some catalysts which are solid like ferrocene, cobaltocene, etc.

These catalysts vaporize in the temperature range of 300 to 400 °C. Such catalysts are kept in a boat (Figure 1.8B1) in the furnace (Figure 1.8A1) along with the precursor like oil. The vapor of oil and the vapor of catalyst like ferrocene are carried with carrier gas to the furnace (Figure 1.8A2). Catalyst decomposes into its metal oxide and *in-situ* reaction takes place with the vapor of oil to produce CNF. These CNFs are collected in the boat (Figure 1.8B2).

Catalyst can be used either in the form of powder or as a thin film deposited on a substrate like quartz glass, alumina plate, or as a metal plate like nickel, iron metal, etc. Normally, after scratching a metal plate with diamond powder it is cleaned with water and dried with acetone, which is also used as a catalyst. Scratching the plate creates more roughness of the metal, which produces more surface states and surface area over which the reaction of vapor of precursor reacts more favorably with catalyst. The preferred size of catalyst particles should be in the range of 5–25 nm in diameter. Some examples of the role of different types of catalysts and their effect on the carbon nanomaterials produced are shown in Figure 1.4.

There is no hard and fast rule to suggest which type of catalyst will produce better CNF. Better CNF means the value of its diameter, length, surface area and surface states. Selection of catalyst and its type depends upon the type of precursor and size of catalyst powder, which can only be decided by carrying out some specific experiments. Powder or thin films of Fe/Ni, Ni, Co, Mn, Cu, V, Cr, Mo, Pd, MgO, and Al_2O_3 are used as catalyst. But most popular catalysts are powder or thin film of organometallic compounds of iron or nickel or cobalt. Details of the use of different catalysts are presented in Chapter 3 of this book.

1.3.4 Selection of Variable Parameters for Growth of CNF

Variable parameters of pyrolysis under the CVD units are: precursor (oil, solid materials like plant materials, camphor, etc.), temperature (Figure 1.8A1 and A2), type and size of catalyst (usually nickel, iron and cobalt), carrier gas (argon, nitrogen, etc.), reactive gas (hydrogen), and duration of pyrolysis. Due to the large number of variables, it becomes very time-consuming to reach a suitable condition to obtain the desired type of CNF.

It is advisable that one should adopt the Taguchi method, which can provide information of effective variables to produce the required type of CNF [1–3]. For example, with 4 variables (requires 24 experiments) one needs to carry out only 9 sets of experiments; whereas, with 6 variables (requires 720 experiments) one needs to carry out only 16 sets of experiments.

1.3.5 Epitaxial Growth of Aligned CNF

Afre *et al.* [8] have developed a CVD with spray techniques (Figure 1.9A) to get epitaxial growth of aligned, continuous (Figure 1.9B), catalyst-free carbon nanofiber from vapor of turpentine oil. Aligned CNF possesses properties like high mechanical strength, high directional electrical conductivity, and high thermal conductivity. The main difference between the CVD unit described in Figure 1.8 and 1.9 is the inclusion of a spray facility so that solution containing precursor and the catalyst sprays its liquid in the furnace like a cloud of material.

1.3.6 Mechanism of CNF Synthesis

There are different mechanisms suggested to explain the role of catalyst but none of them can explain why CNFs are formed over the entire reaction tube in a larger amount than the amount of catalyst used for the purpose. The author of this chapter suggests that vapor of precursor at high temperature breaks down into lower very reactive carbon fragments and this decomposition is catalyzed by the catalyst. These reactive fragments move around the furnace (Figure 1.8A2) with the help of the carrier gas. Since these fragments are highly reactive, they recombine to give CNF. The process of recombination giving the product depends upon the variable conditions used for the synthesis of CNF. The nature of CNF formed thus depends upon variables like temperature, the flow rate of carrier gas, etc. It is for this reason one finds deposition of CNF not only in the boat (Figure 1.8B2) but

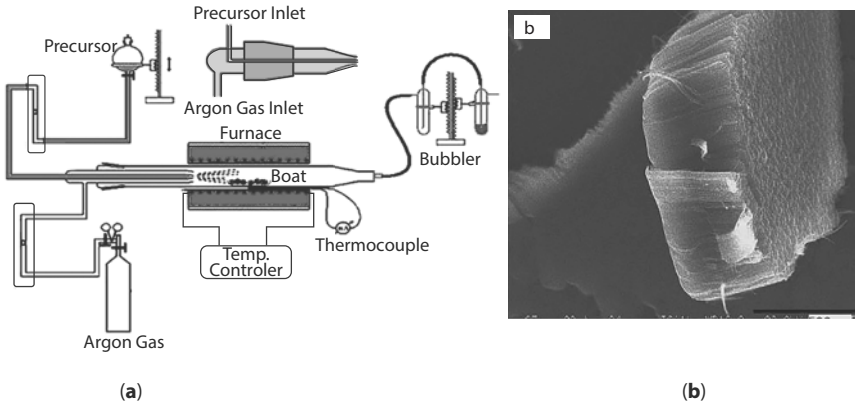

Figure 1.9 (a) typical sketch of CVD unit with a spray system and (b) the aligned carbon nanofibers produced from this process using turpentine oil.

throughout the quartz tube (Figure 1.8C). Moreover, the amount of CNF formed are far in excess of the amount of catalyst used for the purpose.

1.4 Properties of CNF and Its Composites

Electrical conductivity in CNF/polymer composites depends upon the nature of the network and their alignment in the matrix. Therefore, for good electrical conductivity a good fiber dispersion and the continuation of the network of carbon nanofibers is necessary. Also, by controlling the loading amount of CNF in the composite different electrical resistivity values can be achieved. CNF/polymer composite can increase the tensile strength (gain of 50 to around 300%), compression strength (50–100%), Young's modulus (almost 100%), inter-laminar shear strength (with 1% CNF increases in the range of 20–50%), fracture toughness (with 1% CNF increases in the range of 30–50%), and vibration damping of the base polymer. These improvements depend upon the nature of polymer, extent of dispersion, etc. [9–15]. Thermal conductivity of CNF with 20 wt% epoxy resin has been observed to increase from 0.2 W/m-K to 2.8 W/m-K [15]. CNF composite with thermoplastic material is found to retard fire properties like delay in burning when exposed to flame and slow heat transmission [16, 17]. Polymeric composites with carbon nanofibers have shown substantially lower coefficients of thermal expansion as compared to graphite. Details of CNF and its composites are presented in Chapter 4 of this book.

1.5 Applications of CNF

Some of the applications of CNF are enumerated here:

- Scientists, after understanding the properties of carbon fibers, have started using this material in various engineering applications to reinforce concrete, replace steel with carbon fibers, as material for bridge work, etc. CNFs are being applied or are thought to apply for strengthening of structures with carbon fiber composites in precast concrete and plastic, and fiber-cement. The traditional method of strengthening the reinforcement of brick is by utilizing steel clamps, which provide strength but also become heavy and are prone to corrosion. CNFs are being thought of to use in

place of steel to get almost the same strength. Carbon fibers in precast concrete has also become popular since 2003. Carbon fiber grid reinforcement is applied in the wall panel face, which allows the use of less concrete, reducing weight and raw material.

- CNF composites with a conductive polymer, polypyrrole (PPy), in N,N-dimethylformamide (DMF) solvent increases its strength.
- The non-corrosive nature of carbon fibers prevents the rusting and staining which otherwise occur with steel reinforcing. Carbon fiber composites have low thermal conductivity, thus reducing the transfer of heat or cold from outside to inside. Carbon fiber composites used for building works provide the benefit from long-term energy savings. CNF is used in bridge construction because CNF-reinforced plastic provides reduction in bridge weight and economy of lifting equipment. Carbon fibers possess the property of repelling water, hence are used by mixing with grits and coal tar to give more life to the road.
- CNFs are used as additive for anode and cathode materials in energy conversion and storage systems because they possess properties like good chemical stability, thermal stability, and electrical conductivity, high specific surface area and good charge transport properties.
- CNF is used for the delivery of therapeutic drugs. It has been proposed that when a needle-shaped carbon nanofiber is loaded with therapeutic drugs and embedded into an elastic material (which can be inflated to form a balloon) and inserted next to the diseased site, the needle-shaped CNF penetrates the diseased cell and delivers the therapeutic drugs.
- Since CNF has large surface area and good electrochemical properties, it is observed that it increases the capacity of lithium battery more than graphite. CNF is used to improve overall energy capacity and cycling stability of anode material of lithium-ion battery. Because of its reversible electrochemical properties, it increases good charging/discharging cycles of lithium battery. Metal/CNF composites, like carbon/TiO_2, Carbon/SnO_2, etc., have been found to enhance the capacity of lithium-ion battery.

- CNF is used to develop gas mask sensor because it changes its color after absorbing chemical.
- Since the electrical conductivity in CNF is highest along its length, it can be used as electron field emitter if aligned CNF is grown along its length.
- Supercapacitors (electric double-layer capacitors) are gaining in popularity because they can provide high energy density and better power density than normal batteries. There has been increasing interest in the use of porous carbon nanofibers to develop supercapacitors because of their higher specific surface area (1200 m^2/g or more). The electrode (e.g., CNF/V_2O_5 composite) has given specific capacitance of 150 F/g and energy density of 18.8 W h kg^{-1} over a power density range of 400–20,000 W kg^{-1}. Number of operating cycles with CNF supercapacitor has also been found in the range of 2000 cycles.
- Because of their low-cost, dye-sensitized solar cells (DSSC) are being thought of to replace silicon solar cells. DSSC consists of a photoanode and a counter electrode separated by a redox electrolyte (iodide/triiodide). CNFs are highly stable against electrochemical corrosion in either alkaline or acidic media, hence are found to possess significant catalytic activity and power conversion efficiency in DSCs. This material is expected to replace expensive counter electrode made of noble metals like platinum.
- CNF can be used as catalyst due to its high specific surface area, high chemical resistance, outstanding electrical properties, and suitable mechanical properties. Because of good electrical properties, it is developed for high loaded active enzymes and for fast kinetics at electrode surface, especially for enzymatic cathodes in biofuel cell devices. Carbon of CNF acts both as catalyst and adsorbent for the catalytic oxidation of NO into NO_2 or reduction of NO into N_2.
- In developing electrodes for fuel cell, it is essential to replace platinum with some other materials which are inexpensive. CNFs loaded with nickel, iron and nitrogen are found to be suitable material for use as an electrode in alkaline fuel cell.
- Microbial fuel cell (MFC) is a bio-electrochemical cell that uses microorganisms to utilize organic substrates at anodes to generate electricity. For this purpose, it is necessary to

develop biocompatible electrode materials with high surface area and long-term stability to support the maximum growth of bacteria and enhance electron transfer rate. CNFs are finding their use as anode in MFC [18].

- CNFs have generated interest in the area of sensors and biosensors because of their functionalization ability, electrochemical property, mechanical flexibility, and biocompatibility. They have exhibited a good response for developing glucose biosensor. Metal-loaded CNFs are gaining in popularity in developing biosensors. For example, palladium-loaded CNFs exhibit good electrochemical catalytic activities for determining dopamine (DA), uric acid (UA), and ascorbic acid (AA). These three chemicals can be determined simultaneously from their mixture because of their difference in overpotential [19].
- CNFs are used as good adsorbent material especially in the field of adsorption/separation because of their high specific surface area and high porosity. Removal of dissolved impurities, such as dyes and metals present in drinking and industrial water, is being tried using CNFs. There are several chapters devoted to different applications of CNF presented in this book.

1.6 Health Hazards of CNF

Though many studies are being conducted with CNFs, some studies have indicated that there are health hazards associated with CNFs especially due to their sizes [20, 21]. One of the hazards associated with CNF is that it is expected to cause respiratory damage such as pulmonary inflammation, granuloma, and fibrosis. These effects are observed with mice. There seem to be no studies available on its effect on human beings. However, it is proposed to wear some type of mask when working with CNF so that it is not inhaled. Sharon and his research team have observed that CNF of a particular band gap if spread over skin affected by cancer cells, and simultaneously exposed to visible light, can kill cancerous cells, suggesting that this material can be used in dermatology for killing the growth of cancer cells grown over skin. However, this experiment was done with mice only [22–25].

1.7 Summary

In this chapter an effort was made to discuss the various aspects of carbon fibers and carbon nanofibers, including their synthesis, properties and applications. An effort was also made to explain the basic differences between carbon fibers, carbon nanofibers and carbon nanotubes.

References

1. R. Millington, of H.I. Thompson Fiberglas Co. (US Patent No. 3,294,489) Process for producing a high carbon content (99%) fibre using rayon as a precursor, 1960.
2. Sharon, M., Apte, P.R., Purandara, S.C., Zacharia, R., Application of the Taguchi Analytical Method for optimization of Effective parameters of the chemical vapour deposition controlling the production of nanotube/nanobeads. *J. Nanosci. Nanotechnol.*, 5, 2, 288–295, 2005.
3. Sharon, M., Mishra, D.K., Bejoy, N., Application of Taguchi Methodology for Optimization of Parameters of CVD Influencing Formation of a Desired Optical Band gap of Carbon Film. *Carbon Sci.*, 6, 2, 96–100, 2005.
4. Debabrata, P., Synthesis of carbon nanomaterials and their applications, PhD thesis, IIT Bombay, Powai, Maharashtra, India, 2003.
5. Hughes TV, Chambers. Manufacture of 0 N Filaments, No. 405,480. v I Patented June 18, 1889. //TFH5,. 74 2772 anew. ww Z 42 3}.
6. Endo, M., Grow carbon fibers in the vapor phase. *Chemtech*, 18, 568–576, 1988.
7. Iijima, S., Helical microtubules of graphitic carbon. *Nature*, 354, 56–58, 1991.
8. Afre, R.A., Soga, T., Jimbo, T., Kumar, M., Ando, Y., Sharon, M., Growth of vertically aligned carbon nanotubes on silicon and quartz substrate by spray pyrolysis of a natural precursor; turpentine oil. *Chem. Phys. Lett.*, 414, 1–3, 6–10, 2005.
9. Finegan, I.C., Tibbetts, G.G., Glasgow, D.G., Ting, J.M., Lake, M.L.J., Surface treatments for improving the mechanical properties of carbon nanofiber/thermoplastic composites. *Mater. Sci.*, 38, 3485, 2003.
10. Kumar, S., Doshi, H., Srinivasarao, M., Park, J.O., Schiraldi, D.A., Fibers from polypropylene/nano carbon fiber composites. *Polit. Commun.*, 43, 170, 2002.
11. Tibbetts, G.G. and McHugh, J.J., A review of the fabrication and properties of vapor-grown carbon nanofiber/polymer composites. *Mater. Res.*, 1999, 14, 1999.
12. Sadeghian, R., Minaie, B., Gangireddy, S., Hsiao, K.-T., In *50th International SAMPE Symposium Proceedings*, Long Beach, CA, May 1-5, 2005.
13. Li, B., Wood, W., Baker, L., Sui, G., Leer, C., Zhong, W.H., Synergistic effects of hybrid graphitic nanofillers on simultaneously enhanced wear and mechanical properties of polymer nanocomposites, *Polym. Sci. Eng.*, 210, 50, 1914.

14. Peng, H., Liu, X., Wang, R., Jia, F., Dong, L., Wang, Q., Emerging nanostructured materials for musculoskeletal tissue engineering. *Nanomater.*, 32, 803, 2006.
15. Lafdi, K. and Matzek, M., In *48th International SAMPE Symposium Proceedings*, Long Beach, CA, May 11-15, 2003.
16. Koo, J., *Polymer Nanocomposites: Processing, Characterization and Applications*, McGraw-Hill, Boston, 2006.
17. Zammarano, A.M., Kramer, R.H., Harris, R., JR., Ohlemiller, T.J., Shields, J.R., Rahatekar, S.S., Lacerda, S., Gilman, J.W., Flammability reduction of flexible polyurethane foams via carbon nanofiber network formation. *Polym. Adv. Technol.*, 19, 588, 2008.
18. Patil, S.A., Chigome, S., Hagerhall, C., Torto, N., Gorton, L., Electrospun carbon nanofibers from polyacrylonitrile blended with activated ographitized carbonaceous materials for improving anodic bioelectrocatalysis. *Bioresour. Technol.*, 132, 121, 2013.
19. Huang, J., Liu, Y., Hou, H., You, T., Simultaneous electrochemical determination of dopamine, uric acid and ascorbic acid using palladium nanoparticle-loaded carbon nanofibers modified electrode. *Biosens. Bioelectron.*, 24, 632, 2008.
20. Wu, M., Wang, Q., Liu, X., Liu, H., Biomimetic synthesis and characterization of carbon nanofiber/hydroxyapatite composite scaffolds. *Carbon*, 51, 335, 2013.
21. Yang, Q., Sui, G., Shi, Y.Z., Duan, S., Bao, J.Q., Cai, Q., Yang, X.P., Osteocompatibility characterization of polyacrylonitrile carbon nanofibers containing bioactive glass nanoparticles. *Carbon*, 56, 288, 2013.
22. Maheshwar, S., Pal, B., Kamat, D.V., Photocatalytic killing of pathogenic bacterial cells using nanosize Fe2O3 and carbon nanotubes. *J. Biomed. Nanotechnol.*, 1, 3, 365–368, 2005.
23. Sharon, M., Datta, S., Shah, S., Sharon, M., Soga, T., Afre, R., Carbon material from natural sources as an anode in lithium secondary battery. *Carbon Lett.*, 8, 3, 184–190, 2007.
24. Sharon, M., Pal, B., Subbarayan, M., Application of Photocatalytic Process to inhibit the growth of cancerous cells. *Int. J. Nanosyst.*, 1, 2, 973–979, 2008.
25. Sharon, M., Photocatalytic treatment to inhibit the growth of skin cancerous cells. *J. Adv. Phys.*, 13, 3, 4735–4739, 2017.