NANOMATERIALS Biomedical, Environmental, and Engineering Applications

Edited by Suvardhan Kanchi Shakeel Ahmed Myalowenkosi I. Sabela Chaudhery Mustansar Hussain



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Preface

Nanostructure science and technology is a broad and interdisciplinary area of research and development that has been growing explosively in the past decades. Nanomaterials can be obtained either naturally or incidentally or can be manufactured. They are crystalline or amorphous of organic or inorganic materials having sizes in the range of 1-100 nm, which exist in unbound state or as an aggregate or agglomerate. Nanomaterials are classified as nanostructured and nanophase/nanoparticle materials. Their properties are significantly different and they can be significantly improved relative to those of their coarser-grained counterparts. Most benefits of nanomaterials depend on the fact that it is possible to tailor the essential structures of materials at the nanoscale to achieve specific properties. Hence, the evolution of nanotechnology represents an ever improving process in the design, discovery, creation, and novel utilization of artificial nanoscale materials. Research on variety of chemical, mechanical, and physical properties is beginning to yield a glimmer of understanding on how this interplay manifests itself in the properties of these new materials.

To meet the major challenges in environmental sustainability, these nanomaterials in various hierarchical fashions are stimulating various important practical applications in the environmental sector. Their applications involve addressing the existing environmental problems, preventive measures for future problems resulting from the interactions of energy and materials with the environment.

In comparison to their larger counterparts, nanomaterials also have unique physico-chemical and biological properties. Therefore, nanomaterials properties, such as size, shape, chemical composition, surface structure and charge, aggregation and agglomeration, and solubility, have been investigated for advancement of diagnostic biosensors, drug delivery, and biomedical imaging.

The contents of the book includes mainly the fundamentals of nanoparticles, state-of-the-art in synthesis and characterization of nanomaterials and their influence of nanomaterials on the analytical systems (macro to micro & lab-on-a-chip) for biomedical and environmental applications. The evolution in the nanotechnology world clearly signifies a need for broader understanding and, therefore, we hope this book with contribute to this effort.

Part I

SYNTHESIS AND CHARACTERIZATION

Synthesis, Characterization and General Properties of Carbon Nanotubes

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Abstract

Carbon is among the most abundant elements found on Earth, forming different carbonaceous materials by bonding with various atoms, starting with hydrogen and ending with most of the elements on the periodic table. Besides, carbon atoms can react with each other to form different structures by using various types of hybridization: sp, sp², and sp³. The most important hybridization for carbon atoms is sp², which can form amazing and rare structures such as graphite, graphene, and fullerene. These carbonaceous nonomaterials have drawn great attention throughout the world as a result of their particular nano- and micro-structures, their unique physiochemical properties, and their potential unprecedented application in many fields. The most important nanostructures made of carbon material are carbon nanotubes (CNTs); the molecular structure of carbon nanotubes consists of pristine carbon atoms linked together to look like a polymer in a hexagonal arrangement in a monolayer of carbon atoms. This new carbon material consists of CNTs, which appear to become a reality for science, thanks to Iijima who synthesized one type of carbon nanotube and called it a single wall in 1991 with Ichihashi. This was a challenge and temptation at the same time due to its physiochemical properties being unknown to some extent, and the variety of types of single-walled carbon nanotubes (SWNTs), double-walled carbon nanotubes (DWNTs), few-walled carbon nanotubes (FWNTs), and multi-walled carbon nanotubes (MWNTs). Extensive studies and research were done on these materials due to their many specific physiochemical properties and representing

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The most abundant element in nature. There are three primary methods that are used for the synthesis of CNTs: chemical vapor deposition (CVD), arc-discharge, and laser ablation. In recent years, carbon nanotubes have been prepared under different labels for the various techniques used, and in fact represent the development of methods and techniques for the three methods mentioned above, with new titles. In any industrial application, the most important issues in the production process are represented by substrate cost, quality, and yield of product. The economic feasibility of the production of carbon nanotubes is seen in the CVD method, whereby hydrocarbon is pyrolyzed or dissociated in the presence of suitable metal catalysts. This has attracted attention due to the possibility of producing nanotubes on a large commercial scale. For various kinds of deposition processes, many materials are used as carbon sources, such as ROH or many unsaturated hydrocarbons, which are used as sources of energy in addition to many industrial purposes; thus, a lot of these sources are at risk of depletion in the near future in addition to the high cost of these materials compared with many other materials that can be used for the same purpose. Therefore, many attempts have used natural hydrocarbon precursors, which are interesting because of the possibility of the synthesis of CNTs from the bank of hydrocarbon compounds that are being renewed by nature that is available and low cost, such as essential oils, sucrose, or plant and animal waste. In this work, the waste from date palms is used as a source of carbon to synthesize CNTs. It is rare to find literature or books, which deal with carbon nanotubes without mentioning lijima, but the story of carbon nanotubes started before that; therefore, a section specifically about their history before lijima has been included here. A variety of techniques are used to characterize the surface chemistry or structure of CNTs after covalent functionalization. These characterizations may be classified to qualitative, semi-quantitative, and quantitative analyses.

Keywords: carbon nanotubes, synthesis, chemical vapor deposition

1.1 Introduction

The molecular structure of carbon nanotubes (CNTs) consists of pristine carbon atoms linked together to look like polymer in a hexagonal arrangement of a monolayer of carbon atoms [1-3]. The carbon atoms react with each other to form different structures using various types of hybridizations: sp, sp², and sp³.

The most important hybridization for carbon atoms is sp^2 , which can form amazing and rare structures such as graphite, graphene, and fullerene [1]. The most important nanostructures made of carbon material are CNTs. The CNTs appear to become a reality for science, thanks to Iijima [4], who synthesized the single-wall carbon nanotubes in 1991 with

Ichihashi [5]. This was a challenge and temptation at the same time due to its physiochemical properties [6], being unknown to some extent, and the variety of types. The common types are single-walled carbon nanotubes (SWNT), double-walled (DWNT), few-walled (FWNT), and multi-walled (MWNT). Extensive studies and research were done with these materials due to their many specific physiochemical properties and representing the most abundant element in nature.

Generally, there are three primary methods that are used for the synthesis of CNTs: chemical vapor deposition (CVD) [7], arc-discharge [8], and laser ablation [9]. In recent years, CNTs have been prepared under different labels for various techniques [10, 11]. The economic feasibility of the production of carbon nanotubes is seen in the CVD method, whereby hydrocarbon is dissociated in the presence of suitable metal catalysts. This has attracted attention due to the possibility of producing nanotubes on a large commercial scale [12]. For various kinds of deposition processes, many materials are used as carbon sources, such as ROH or many unsaturated hydrocarbons, which are used as sources of energy in addition to many industrial purposes. It is rare to find a literature or a book that deals with CNTs without mentioning lijima, but the story of CNTs started before that; therefore, a specific section deals with the history before lijima.

1.2 The History of Carbon Nanotubes

The first event where CNTs appeared was the Paris Universal Exposition [13] in 1889 in a patent by Edison that proposed the use of filaments in light bulbs. The filaments consisting of carbon atoms that were formed during thermal decomposition experiments that involved passing of cyanogens over red-hot porcelain. This may represent the first mention of the possibility for the preparation of CNTs. At that time, it was impossible to identify nanostructures because the resolutions of optical microscopes were only able to see filaments of a few micrometers, which prevented finding out more about these structures. Thus, the decision to synthesize CNTs remained hidden and without confirmation. But the evidence for the process and conditions of pyrolysis refer to MWNTs. The decision still remained hidden until specific, advanced technology appeared able to scan on the nanoscale. In 1939, the Siemens company succeeded in producing the first version of transmission electron microscopy, which opened new horizons to discover many details about CNTs. The first recorded attempt to study CNTs was done by two Russian researchers, Radushkevich and Lukyanovich [14] in 1952. The two researchers published the carbon

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filaments in the Journal of Physical Chemistry of Russia, which were produced from the decomposition of carbon monoxide on the surface of iron at 600 °C. The images that were obtained from transmission electron microscopy (TEM) showed tubular structures with diameters around 50 nm. They inferred from these images that the dissolution of carbon in iron resulted in the formation of iron carbide at first, and then the deposition of carbon over the iron carbide, which led to the formation of a graphene sheet. In 1953, two Russian scientists Tesner and Echeistova [13] published that lampblack particles of carbon were exposed during the burning of methane, benzene, or cyclohexane at temperatures above 977 °C. These results were not available globally due to the cold war and the article being published in the Russian language, which prevented Russian publications from reaching America and Europe. It is believed that Russian scientists succeeded in preparing CNTs before this time, but their publication depended on the discovery of TEM as we reported earlier. The first version of TEM had a resolution only in the nanometer range, which prevented scientists from finding out the nature of graphene sheets in CNTs, whether to be their concentric, herringbone, bamboo, or platelet. In 1953, Davis et al. [14] reported that carbon nanofibers had been grown from the reaction of CO and Fe₂O₄ at 450 °C in a brickwork blast furnace. The product was identified using electron micrographs and XRD spectroscopy, which postulated that iron and iron carbide behave as a support to precipitate carbon atoms in layers of carbon that varied in thickness from 10 to 200 nm. Hofer *et al.* (1955) found that the diameter of the carbon layers was $(0.01-0.2) \,\mu\text{m}$ at 390 °C [15]. In 1958, Hillert and Lange [16] reported two textures of graphene filaments: the first was a concentric composition that was determined by electron diffraction, and the second was a bamboo composition. In 1973, Baker et al. [17] showed that during the chemical vapor deposition for C₂H₂ onto surfaces that contained iron, cobalt, and chromium, filaments of graphene were deposited onto the surfaces of the catalyst.

In 1976, Oberlin *et al.* [18] prepared carbon fibers that had various external shapes and contained a hollow tube with a diameter ranging from 20 to more than 500 Å along the fiber axis. This work referred to MWNTs without referring to the tubular form, as in CNTs. All of these attempts did not attract any real attention. However, the real revolution in the carbon field occurred when researchers became interested in this new allotropic form of carbon in 1985. During this year, Kroto *et al.* [19] published in *Nature* Journal the formation of clusters consisting of carbon atoms in ball shapes, which were called Fullerene C_{60} . In 1991, the schematic for CNTs was completed when Iijima [4] repeated the reaction that was done by Kroto and his colleagues. Mostly, the aim was to study the reaction by a characterization

process. The surprise was the identification of carbon structures in the form of C₆₀ and other fullerenes, when Arc-Discharge was done in graphite with Ar gas atmosphere. Iijima reported the preparation of a new type of finite carbon structure filaments of graphene consisting of needle-like tubes. After that, on April 23, 1993, Iijima and Ichihashi succeeded in synthesizing single-wall CNTs [5], which represented the first paper about the synthesis of SWNTs. At the same time, on May 24, Bethune et al. from IBM in California published [20] a second paper about SWNTs. The discovery of SWNTs was incidental without any preparation in advance in both cases. The SWNTs were formed during failed attempts to produce MWNTs, with different transition metals. Perhaps the most important reason [21] for the late appearance of this material was that filaments of graphene represented a byproduct from the production processes of the coal and steel industries that hindered them. These filaments also represented an important problem for cooling systems in nuclear reactors; thus, the study of these materials was limited to prevent or at least reducing their formation.

1.3 Graphene

The first publication on graphene was in 1947 by P. R. Wallace [22], who studied the band structure and explained the semimetallic behavior of this material. A typical example of a sp² hybridized crystal structure graphite represents one of the softest materials, consisting of bonding and antibonding π - and π *-orbitals. It consists of carbon atoms bonded with three neighboring atoms in a honeycomb lattice with a lattice constant or the distance between carbon atoms *a* = 0.142 nm [23]. From Figures 1.1 and 1.2, this value is compared with single (C–C = 0.147 nm) and double (C=C = 0.135 nm) bands between carbon atoms representing their average. The distances between carbon atoms refer to the unit cell of a lattice structure that consists of two atoms of carbon. The lattice vectors can be defined as

$$a_1 = \frac{a}{2} \left(3, \sqrt{3}\right) \tag{1.1}$$

$$a_2 = \frac{a}{2} \left(3, -\sqrt{3} \right) \tag{1.2}$$

The length of the lattice spacing (a) can be found by the equation:

$$a = |a_1^{\rightarrow}| = |a_2^{\rightarrow}| = \sqrt{3} \ a_{c-c} = 0.246 \text{ nm}$$
 (1.3)

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Figure 1.1 Honeycomb lattice structure of graphene, consisting of two triangular lattices a_1 and a_2 , which are the lattice unit vectors, and δ_1 , δ_2 , δ_3 , which are the nearest-neighbor vectors.



Figure 1.2 Honeycomb lattice structure of graphene, the Brillouin zone. The Dirac cones are located at the K and K⁻ points.

The reciprocal honeycomb lattice vectors are given as

$$b_1 = \frac{2\pi}{3a} \left(1, \sqrt{3} \right) \tag{1.4}$$

$$b_2 = \frac{2\pi}{3a} \left(1, \ -\sqrt{3} \right) \tag{1.5}$$

The Brillouin zone of the reciprocal lattice in graphene refers to the planes mediating for vectors to the nearest reciprocal lattice points as bounded. The distribution was the same form as the original hexagons of the honeycomb lattice, but rotated as compared to them by a vector $\pi/2$. Figure 1.2 shows that the Brillouin zone for graphene consists of six points in the corner, divided into two equivalent groups with about three points known by the symbols K and K⁻. The values of K and K⁻ can be explained [24] by two equations:

$$K = \frac{2\pi}{3a} \left(1, \frac{1}{\sqrt{3}} \right) \tag{1.6}$$

$$K^{-} = \frac{2\pi}{3a} \left(1, -\frac{1}{\sqrt{3}} \right)$$
(1.7)

The vectors of the three nearest neighbors in real space can be represented by the following equations.

$$\delta_1 = \frac{a}{2} \left(1, \sqrt{3} \right) \tag{1.8}$$

$$\delta_2 = \frac{a}{2} \left(1, -\sqrt{3} \right) \tag{1.9}$$

$$\delta_3 = -a(1,0) \tag{1.10}$$

The positions of the second six nearest are located in the following equations:

$$\delta_1^- = \mp a_1 \tag{1.11}$$

$$\delta_2^- = \mp a_2 \tag{1.12}$$

$$\delta_3^- = \mp (a_2 - a_1) \tag{1.13}$$

Graphene can take on many forms, and every one of these forms is characterized by specific and unique physiochemical properties, as shown in Figure 1.3.

Graphene represents a two-dimensional (2-D) material, sp² in nanocarbon systems, which can be understood when recalling the graphene edge energy γ . The edge energy for the graphene scheme includes the position of armchair (A) to zig-zag (Z) and all the intermediate orientation chiral angles. Saito *et al.* [23] found that the inter-sheet distance in a multi-sheet nanotube is 0.344 nm, which is close to the value of the distance between two layers of graphene in graphite, which equals 0.335 nm [24].



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Figure 1.3 The structure of graphene in nature.

1.4 Graphite

This three-dimensional material consists of many sheets of graphene bonded with each other by weak van der Waals forces, which occur as a result of the π -orbitals that are distributed over all the surfaces of the sheets. Kiselev et al. reported that graphite was discovered by Borrowdale in Cambria, England, in the 16th century [24]. The literature refers to graphite as a stack of many 2-D graphene layers combined through layer-bylayer orientation to form a 3-D structure. The distance between the layers is approximately d = 0.34 nm [25], with the arrangements of carbon atoms in two layers bonded from the centers of the hexagons for one of these two layers. This organization makes the translation between the layers possible with two probabilities. The first happens if the translation between the layers produces a rhombohedra configuration; thus, 6 atoms per unit cell will extend in three dimensions along the *z*-axis, which produces β -graphite. The second probability occurs if the stacking between the layers behaves like a hexagon; in this case, 4 atoms per unit cell will extend in two dimensions along the z-axis, which produces α -graphite [26]. Generally, the crystalline *a*-graphite occurs more often in nature compared to β -graphite. Although different in terms of the crystal structure, these two forms have identical physical properties. The alpha forms can be converted into the

beta by mechanical treatment, while the opposite process is more difficult which requires heating above 1000 °C.

1.5 Fullerene

The 0-D graphitic allotope (fullerene) was discovered in 1985 by Kroto *et al.* [19]; its most prominent representative is the C_{60} molecule, which has the form of a football and is also called a "buckyball." It consists of a graphene sheet, where some hexagons are replaced by pentagons, which causes a crumbling [27–28] of the sheet and the final formation of a graphene spherical. Its existence had been predicted before, by Ozawa and Ōsawa [28], in 1970, when described fullerenes as a class of closed-cage molecule, containing 12 pentagonal structures with the complete ball structure of hexagons [29]. The number of hexagons in the structure can be determined by using a simple relation [30], which is

$$Hexagons = [(carbon atoms) - 20] /2$$
(1.13)

The most common consists of a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. Fullerenes are characterized by high reactivity and strain energies, which decrease during saturation of the pi-bonds. The steric hindrance with reduced Pi-bonds causes a reduction in the electrophilic. The activity of fullerenes behaves like electrophiles in nucleophilic reactions and can be a legend in organometallic reactions. Fullerenes without functional groups behave positive effects and act as antioxidants, while functional groups can be converted into a highly toxic material. Fullerenes in the environment can be dangerous because they are soluble in organic solvents such as benzene, toluene, or chloroform.

1.6 Rehybridization

Common factors between graphene, carbon nanotubes, and fullerenes of all types include hybridization, which is represented by sp² and the carbon atoms; thus, the length and angle between the carbon atoms may be the same. But the truth is the opposite of this because the linear bond in space will behave differently in a tubular structure or in a circular ball. Theoretically [31–32], if the sheet of graphene is rolled or contorted into CNTs or fullerenes, the length of the sigma band should be reduced in spite of using the same hybridization and the same carbon atoms. The π bond is

distributed over a 2-D sheet of graphene up and down the sheet in equal value, while with regard to the distribution for 0-D and 1-D, the structures will change outside and inside when the outer sites are much higher than the inner cities.

From Figure 1.4, two regains can be seen: the first inside the rings and the second outside the rings. The part inside the rings looks like a continuous dark color, which refers to the δ bond only without the clouds of π bonding. The change in the arrangements of the δ and π bonds makes the surface able to capacitance all of π with δ bond, so that it shows two different bonds on the surfaces that are referred by two different colors. This is caused by the appearance of two hybridizations sp² and sp³ that are mixed together and can be seen by using Raman spectroscopy as a Δ and G band [3,33]. However, the degree of hybridization could be obtained by the equation

Degree of hybridization =
$$sp^{2+\eta}$$
, (1.14)

where η refers to a number between 0 and 1; in this description, one can specify the ratio between the sp² and sp³ hybridization. The important factor that play a major role in enhancing the distribution was the tilting angle



Figure 1.4 Distribution sigma δ (blue color) and pi π (bright color) bonds.

(δ) contributing to the bending of the π -orbitals outside the CNTs [20], which depend on the diameter (d) and chirality of the curved wall:

$$\delta = a/2\sqrt{3d} \tag{1.15}$$

while *a* refers to a lattice constant.

1.7 Structure of Carbon Nanotubes (CNTs)

The most promising materials from nanotechnology are CNTs, which refer to one-dimensional material consisting of carbon atoms only bonded with each other. The sp² hybridization in a graphene sheet or graphite is closely related to the honeycomb arrangement or the carbon atoms making a network of hexagons. As mentioned before in the rehybridization section, the p orbital on the carbon atoms form an extended π system that allows for a lattice of graphite to conduct. The simplest images of a CNT can be imagined as a sheet of graphene that has been rolled up to form a seamless cylinder with a hollow core [32,33], which may be opened or closed from two ends such as fullerenes. CNTs have two types or structures. The first is single-walled carbon nanotubes (SWNTs), which are made up of a monolayer of carbon atoms in a graphene sheet rolled into a cylinder structure. The SWNTs behave as either metal or semiconductor depending on the tube's diameter, the direction of the wrap, and the helicity [33]. The second type is multi-walled carbon nanotubes (MWNTs), graphene sheets rolled into a cylinder. Recently, few-walled carbon nanotubes (FWNTs) [34], which are a special kind of MWNT that consist of two to six layers of graphene sheets, can be considered as an intermediate structure between SWNTs and MWNTs. They have a diameter in the range of nanometers from 0.3 up to 100 nm [35], but their length might reach to more than 18 cm [34]. The diameter of a typical single-walled CNT (SWNT) is around 1 nm and for multi-walled CNTs (MWNTs) it could reach 10 nm [35], while for FWNTs their diameter is around 4–7 nm [36–37].

1.8 Classification of CNTs

A classification of the material represents the common ways to understand and make the studies more clear and easy. A carbon nanotube was classified according to many physical and chemical properties such as chirality, conductivity, or number of graphene layers [34–37].

1.8.1 Classification by Chirality

The chirality of a carbon atom refers to molecules that are non-super impossible on their mirror image, or chiral molecules are those that include different groups attached to the central atom. For carbon nanotubes, this type of classification depends on how the carbon sheet is wrapped into a tube; however, the chiral [33] can be described by the chiral vector which indicates the direction in which the tube rolls up:

$$C_h = na_1 + ma_2 \tag{1.16}$$

where a_1 and a_2 are the unit vectors of graphene and n and m are integers. The values of n and m have important indicators for the electronic properties of CNTs. Figure 1.5 shows that two different categories of nanotubes depend on the simple expression $C_h = (n, m)$: the first being achiral. This includes two types: one refers to (n = m) the nanotube that has the characteristics of an armchair nanotube within ($\theta = 30^\circ$), and the other appears when (m = 0); the nanotube in this case is called a zigzag nanotube within $(\theta = 0^\circ)$. The second category of nanotubes is chiral nanotubes that occur when $(m \neq n \neq 0)$.



Figure 1.5 Graphene map chirality of (n, m) chiral vectors that give three structures armchair, zig-zag and chiral nanotubes

1.8.2 Classification by Conductivity

According to these phenomena, carbon nanotubes include two types: metallic and semiconducting, which are mainly affected by the chirality [33] of the CNT, when the chiralities are determined by the n and m values. It is mathematically possible to predict the type of carbon nanotube according to two probabilities; the first is when n-m is a multiple of 3 or an armchair, then the nanotube is metallic; the second refers to n-m not being a multiple of 3 or a zig-zag or chiral, then the nanotube is a semiconductor.

1.8.3 Classification by Layers

These types of classifications depend on the number of graphene layers that form a tubular structure and which commonly include two types:

- i. Single-walled carbon nanotubes: This type consists of one layer of graphene (SWNTs).
- ii. Multi-walled carbon nanotubes. Many layers of graphene sheet are wrapped around to form it (MWNTs).

In recent years, two other types have been added, which are doublewalled carbon nanotubes (DWNTs) [35], which consist of two layers of graphene, and few-walled carbon nanotubes (FWNTs) [34], which consist of (2–6) layers of graphene sheets.

1.9 Crystal Structures of Carbon Nanotubes

Carbon nanotubes can be defined as a sheet of graphene that is wrapped from side to side, producing a tubular structure; this expression refers to the transformation of the material from 2-D to 1-D. The two characteristic morphologies depend on establishing a complete understanding of the crystal structures of carbon nanotubes, which are SWNTs and MWNTs. The graphene layer consists of a hexagonal carbon network; the nature of how the sheet is wrapped will decide the physical and chemical properties of the carbon nanotubes [35–39]. Figure 1.6 shows [40] that (XRD) patterns on a (*Rigaku Rotalflex*) (*RU-200B*) X-ray diffractometer for SWNT and MWNT were measured by using Cu K α radiation (wavelength 0.15405 nm) with a Ni filter. The tube current was 100 mA with a tube voltage of 40 kV. The 2 θ angular regions between 10° and 80° were explored at a scan rate of 5°/min. For all XRD tests, the resolution in the 2 θ scans was kept at 0.02°.



Figure 1.6 The X-ray diffraction patterns of SWNT (red color) and MWNT (green color).

The red spectrum refers to SWNT that consists of one sheet of graphene; therefore, one isolated tube cannot be seen easily by using X-ray diffraction. The absence of the repeating planes prevents or at least reduces the ability to detect one tube of SWNTs; thus, many noises can be seen. The green spectrum of MWNTs, which are many monolayers of graphene repeated in the same center with different radii, makes the Bragg equation very sensitive for these structures. Thus, creating the typical peaks shown clearly with MWNTs at $2\theta = 25.3^\circ$, with the Miller index (002) and a spacing value equal to 0.35 nm. It is possible that the preparation conditions or the process of purification does not allow for the filaments of the tubes to be isolated. In the best conditions, carbon nanotubes consist of micronsize aggregates, referring to many groups of CNTs together due to Van der Waals interaction [41-42]. Further research has found that the methods of preparing carbon nanotubes have an influence on the degree of crystallization of the as-grown carbon nanotubes. The common literature is interested in the fact that XRD forms a scattering angle of between 15° and 30°, which refers to the Miller index (002). The wider root of the (002) peak centered at 23° is induced by the disordered carbon, and the higher sharp peaks centered at 26° mostly on the characterization and identification of carbon nanotubes [43]. By comparing the relative magnitude of the (002) profiles of the graphite and disordered carbon, XRD can provide some information on the average degree of crystallization of the entire sample. Khani and Morad [41] reported that after treating the MWNTs with different oxidants, a clear decrease in the nanotube diameters along the tube

walls was observed. The decrease in the degree of crystallization starts with the full width at half maximum (FWHM) widening of the XRD diffraction peaks. The particle size (d_{002}) calculated by Bragg's law increases depending on the kind of oxidants; the procedure can be performed using a mixture of HNO_3/H_2SO_4 on the surface of the MWNTs with an outer diameter 10 to 20 nm. However, the diffraction patterns of pristine and oxidized MWNTs are similar. Therefore, the MWNTs that undergo the oxidation process are able to preserve the first features of their structures, even though some narrowing of their outer diameters and decreasing in the crystallization occurs. Generally, the observed narrow and sharp reflections have suggested good crystallinity and structural integrity. Also, the crystal structures of the CNTs, which represent one of their physical properties, are influenced by the diameters of the tubes with ratios of defects and deformations on their surfaces [43–45].

1.10 Synthesis Methods

The main methods reported commonly depend on the synthesis of carbon nanotubes including three types. All of these methods are economically feasible for large-scale production; however, they all produce many byproducts that all need the purification process. The purification techniques still have to be developed. Improvements include varying the temperature, the catalyst composition, and other process parameters. Consequently, the average diameter and length of the carbon nanotubes can be varied.

1.10.1 Arc-Discharge

Iijima [4] used the arc-discharge method to produce fullerenes, when an electric arc between two graphite rods is placed in an inert atmosphere. Carbon evaporation is initiated by a high-intensity electric current passing through the two rods, which are placed near to each other approximately 1 mm in order to initiate the arc production. Figure 1.7 shows a simple scheme for this method, which includes a direct current of 50 to 100 amp. Driven by approximately 20 V, thus creating a high temperature and low pressure (between 50 and 700 mbar) [5], the high yield production of the carbon nanotubes depends on the homogeneity of the plasma arc and the temperature of the deposit on the two electrodes. Normally, multiwalled nanotubes will be produced if the two electrodes include graphite only without a catalyst. If holes are bored into the graphite rods and then filled with appropriately proportional composites of graphite powder and