

## Chapter

# Synthesis and Purification of Carbon Nanotubes

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## Abstract

In this chapter, we will evaluate the synthesis and purification of carbon nanotubes. Carbon nanotubes are cylindrical molecules that consists of graphene (rolled up of a single-layer carbon atom). A wide variety of synthesis techniques such as arc discharge synthesis, laser ablation of graphite/laser vaporization synthesis method, chemical vapor deposition (CVD), high pressure carbon monoxide synthesis and flame synthesis techniques, have been implemented to grow single and multi-walled carbon nanotubes for technological applications. All of the above methods exploit transition metals, like iron, cobalt, and nickel, as a catalyst. There are number of methods (filtering, chromatography and centrifugation) used to purify the carbon nanotubes, but the degree of purity remained questionable in these methods. In order to enhance the purification extent, alternate techniques such as Gas phase purification, Liquid phase purification and Purification by Intercalation are introduced. Here we will discuss the advantages and disadvantages of these purification routes. It will help researchers in selecting appropriate and effective method for synthesis and purification of carbon nanotubes.

**Keywords:** Graphene, Carbon Nanotubes, Synthesis, Purification, Laser Vaporization, Arc Discharge, Chemical Vapor Deposition, Gas Phase Purification, Liquid phase Purification, Intercalation

## 1. Introduction

Carbon atom contains six electrons with an electronic configuration of  $1s^2, 2s^2$  and  $2p^2$ . In its purest form, it crystallizes into graphite and diamond allotropes having different mechanical and optical properties. In former crystalline shape, the carbon atoms display  $sp^2$  hybridization, where each carbon atom is covalently bonded with three other neighboring carbon atoms, making an angle of  $120^\circ$  in x-y plane along with a pi ( $\pi$ ) bond available in z-direction [1]. This makes honeycomb like hexagonal crystal structure of graphene and this structural pattern shows the basis for other materials like fullerenes [2]. In diamond allotrope of carbon, carbon atoms unveil  $sp^3$  – type of hybridizing character, forming a regular tetrahedron [1]. Apart from existing allotropes of carbon (diamond, graphite and fullerenes).

With the emergence of the field of nanotechnology, the carbon material (graphene, fullerenes and carbon nanotubes) where  $sp^2$  hybridization prevails have

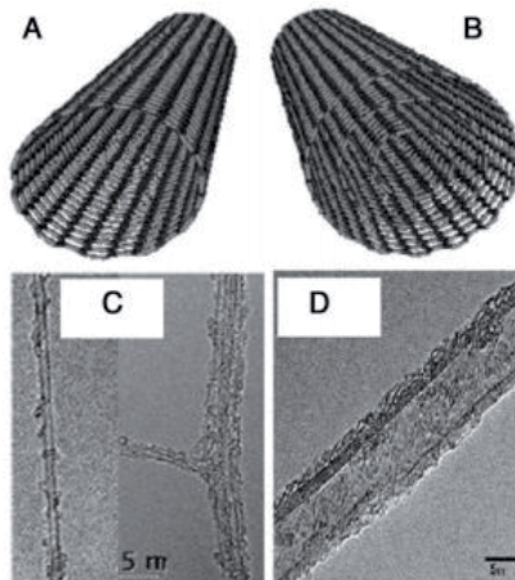
attracted extreme focus from research community. Following the similar hierarchy, carbon nanotubes depict physical properties just like the graphene. Carbon nanotubes also offer  $sp^2$  hybridization scheme and seems like a cylindrical coated graphene sheet in single and multiple wall patterns (**Figure 1a** and **b**).

Nanotubes with single walls are named as single-wall carbon nanotubes (SWCNTs), firstly discovered in 1993 [5], while the nanotubes having multiple walls are termed as multi-wall carbon nanotubes (MWCNTs) discovered earlier in 1991 by Iijima et al. [6].

Immense interest in CNTs lies in their fascinating mechanical [7], electrical and optical properties [8] and hence are widely used in multiple applications such as field effect transistors [9], fuel cells [10], hydrogen energy storage applications [11], quantum computing [12] nanosensors [13–15] and battery electrodes [16]. The superior mechanical properties of CNTs are attributed to the higher values of tensile strengths and young modulus, thus revealing their potential use as a composite material to be used in futuristic Mars operation by NASA. Its use in such type of missions is subjected to its 50 times higher specific strength than the steel and hence creates exceptional load-bearing supports when integrated in composites. Field emission properties of CNTs have noticed enough attention from the research community, where the generation of electrons takes place under extreme conditions of electric field similar to thermionic emission. In addition, CNTs have also offered excellent chemical stability, higher electrical conductivity, nanosize and structural smoothness and are potentially used in flat display panels [8]. One can also attribute the use of CNTs in energy storage and energy production application to their smaller size, higher electron transfer rates, and superior surface topology in nanotubes.

As discussed above, CNTs have shown extremely smaller sizes, superior conductivity, greater mechanical strengths and elastic behavior, that is why these are used in other technological applications such as nanolithography, sensors, high resolution imaging and drug delivery systems also [17, 18].

Keeping in view the above-mentioned intriguing properties of CNTs, it is imperative to discuss the possible routes of their synthesis and the ways to



**Figure 1.** Schematic representation of SWCNT (A) and MWCNT(B) along with the transmission electron microscope (TEM) images of (C) SWCNT and (D) MWCNT respectively [3, 4].

enhance purity of CNTs, as it will pave the way towards improved technological device applications.

## 2. Structural analysis of MWCNTs and SWNTs

The type of bonding among carbon atoms plays crucial role in determining its different allotropes with distinct physical properties. When carbon constitutes  $SP^2$  hybridization, a layered structure is formed with weak van der Waal forces existing in out of plane carbon atoms, in contrast to stronger in-planes bonding among them. Ideal CNTs can be thought of nano-scaled graphene cylindrical shapes closing at each end via half fullerenes. In case of multi-walled carbon nanotubes, there exist at least two equicentered cylinders of graphene and theoretically, these numbers of cylinders can be infinitely large. It should be noticed that there must be regular spacing between any two concentric grapheme cylinders in MWCNTs. Previous studies have demonstrated a real spacing width of the order of 0.34 to 0.39 nm [19].

The real space analysis of multiwall nanotube images has shown a range of interlayer spacing (0.34 to 0.39 nm). It has been observed that the inner diameter of such nanotubes varies from 0.4 nm to roughly few nanometers, in comparison to its outer diameter ranging from 2 nm to 30 nm. MWCNTs are closed from both ends by pentagonal type of ring defect named as half-fullerenes, with significant axial size difference (1  $\mu$ m- few cm) between both ends [19].

Previous studies on SWNTs has documented their length  $10^9$  times greater than their diameters [20]. SWCNTs can be combined together in the form of ropes, to give hexagonal crystalline structure [21]. SWCNTs can assume three different types of structures such as armchair, chiral, and zigzag (**Figure 2B**) depending upon their wrapping in cylindrical form. The structure of SWCNTs is categorized by a pair of indices (n, m) that define chiral vector, which has prominent effect on the electrical properties of carbon nanotubes. Unit vectors along both directions in the crystal lattice is determined by the integers  $n$  and  $m$ . When

$m = 0$  ; nanotubes having zigzag structure.

$n = m$  ; nanotubes having armchair structure.

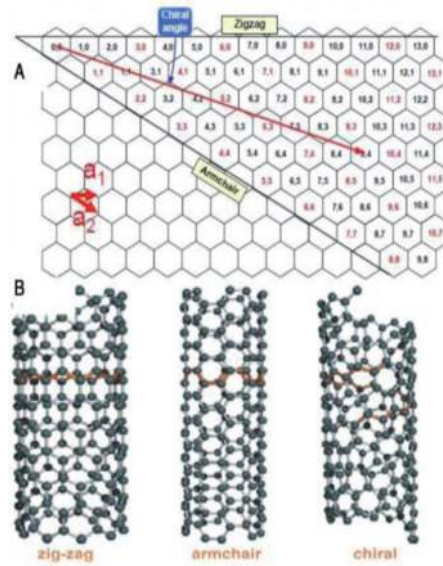
And other form is known as chiral structure.

The chiral vector can be defined as  $C = na_1 + ma_2$  and it is used to measure the nanotube's diameter, where as  $a_1$  and  $a_2$  vectors explicate the grapheme base cell vectors. It is further stated that the chirality vector demonstrates the direction in which grapheme sheets are wrapped. One can estimate the diameter of a carbon nanotube is calculated by

$$d = a\sqrt{m^2 + mn + n^2} / \pi \quad (1)$$

Where  $a = 1.43 \times \sqrt{3}$  shows lattice parameters of the grapheme sheet.

When  $m = 0$ , we get zigzag CNTs and if  $m = n$ , one ends up with armchair CNTs. For other values of  $m$ , chiral CNTs will be formed. If the difference of  $n-m$  is a number which is multiple of 3, then the nanotubes will show metallic behavior and will be of highly conducting nature, otherwise one will be dealing with semiconducting or semimetal types of nanotubes. Armchair type of SWCNTs are metallic in nature, while other structures can make the SWCNTs semiconductor also. The Russian model and Parchment model are two broadly used models to prepare the



**Figure 2.** Schematic of three different forms of SWNTs (A), where the chirality factor determines the diameter of carbon nanotubes and the (B) shows three different models of perfect SWCNT in atomic form [22].

MWCNTs. In the **Russian Doll model**, carbon nanotubes confine another nanotube inside and the diameter of the outer carbon nanotube is greater than the inner tube. When a single graphene sheet is rolled up many times just like the scroll of paper, it is known as **Parchment model**. The properties of SWCNTs are identical with MWCNTs. The outer layer in MWCNTs protects the inner CNTs against the chemical activity. It is considered as the main cause of higher tensile strength, which is absent in SWCNTs [23]. SWCNTs display  $sp^2$  bonding between two independent carbon atoms, and hence result in higher tensile strength even compared to steel, when used as composite material. This  $sp^2$  bonding is stronger than  $sp^3$  bonding, present in diamond. CNTs show elastic behavior upon the application of a strong force. It bends and twists without undergoing permanent deformation in carbon nanotubes. When external force is removed, it will come back to its original form. Its elasticity is measured by a quantity known as modulus of elasticity (**Table 1**).

SWCNTS	MWCNTs
These are twistable but more flexible	These nanotubes cannot be easily twisted.
Its evaluation and characterization is relatively simple and easy.	It has very complex structure and hence their evaluation is not easy.
There are more chances of defect while working with SWCNTs.	The chances of defects are less but once occurred, are difficult to be removed.
Purity of SWCNTs is poor	Purity of MWCNTs is high.
Synthesis of SWCNTs on large scale is comparatively tough as it requires proper control over growth conditions.	Bulk synthesis is easy
Single layers are present in SWCNTs.	Multiple layers are available in MWCNTs.
The use of catalyst is compulsory for their synthesis.	MWCNTs can be prepared without using catalyst.

**Table 1.** Difference between SWCNTs and MWCNTs [19].

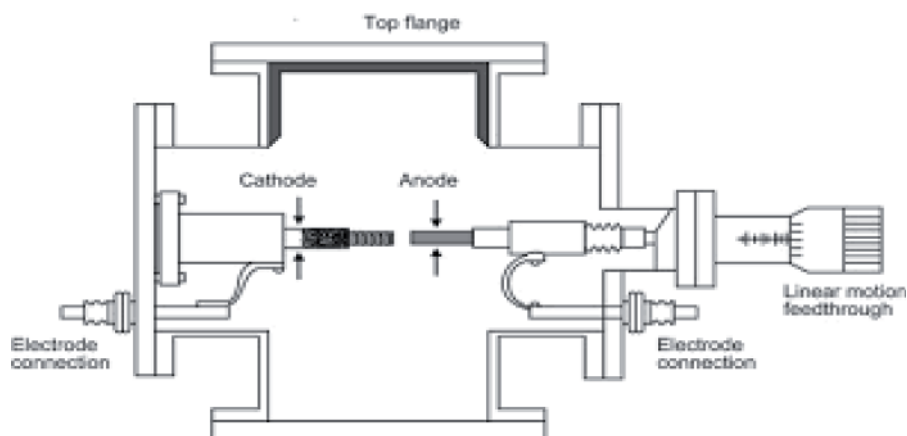
### 3. Synthesis

There are multiple methods to synthesis CNTs where gas phase processes are involved. These methods are mainly known as arc-discharge synthesis technique, laser-ablation method and Chemical Vapor Deposition (CVD). Laser ablation method involves the synthesis of CNTs under high temperatures, while in arc discharge technique, the synthesis of CNTs occurs at relatively low temperatures (<800°C). CVD method is currently in use, as it allows the control of nanotube's length, diameter, alignment, density and purity with maximum accuracy [24] during the synthesis.

#### 3.1 Synthesis of CNTs via arc discharge method

This method is implemented to synthesize the single and multi-walled carbon nanotubes (**Figure 3**) at a high temperature (above 1700°C).

The arc-discharge was initiated via applying a direct current of 200 A and a voltage of 20 V between the two electrodes. It was observed that the presence of iron, argon and methane was compulsory for the synthesis of SWNTs. The Arc discharge techniques is induced with the help of purest graphite electrodes having optical density of 6–10 mm and a diameter ranging from 6 to 12 mm. both of these electrodes were separated by 1–2 mm in a chamber containing helium gas at sub-atmospheric pressure. One can replace helium with hydrogen or methane gas. The working chamber consists of a graphitic anode and cathode, evaporated carbon [26] and minute amount of catalysts for example Ni, Co and Fe [27]. In arcing process is initiated by using direct current at pressure condition and the temperature of the chamber is raised up to 4000 K. In this procedure, half of the evaporated carbon is solidified on the tip of cathode. The rate at which evaporated carbon solidifies is set to be 1 mm/min and hence one gets “cigar like structure”. During this process, the anode is also consumed. A remaining carbon is now a hard-gray shell structure, which is deposited on the edges and further condensates in the ‘chamber soot’ in nearby vicinity of the chamber’s walls and ‘cathode soot’ on the negative graphite electrode (cathode). Furthermore, this inner material, anode soot and cathode soot (dark and soft materials) give rise to SWCNTs or MWCNTs along with nested graphene particles. Scanning electron microscopy (SEM) shows two different morphologies and surfaces are seen in the study of cathode deposited material. The



**Figure 3.**  
*The experimental set up of Arc discharge method [25].*

soft and dark inner core contains randomly oriented carbon nanotubes and the grey colored outer core is composed of grapheme layers.

In arc discharge synthesis technique, there are two different options to synthesize the carbon nanotubes; one with and other without using the catalyst precursors. Generally, the synthesis of MWCNTs is performed without using catalyst precursors. On the other hand, the synthesis of SWCNTs is subjected to the presence of different catalyst precursors. In order to expand the arc discharge, a complex anode [28], made of metal and graphite, is exploited. The metals used in complex anode range from Fe, Ni, Pt, Pd, Co-Pt, Ag, to a mixture of Ni-Ti Ni-Y, Co-Ni, Co-Cu. It is demonstrated to get highest yield (< 90%) of SWCNTs by using a complex anode, made up of a mixture of Ni-Y with an average diameter size of 1.4 nm [29] and this mixture is utilized worldwide to prepare SWCNTs on a large scale. This method is considered one of the most practiced method to synthesize SWCNTs in large quantities. But the main disadvantage of this method is least control over the chirality in the intended nanotubes.

### **3.2 Laser ablation technique in the synthesis of CNTs**

A graphite block is heated in quartz tube via high power lasers in a furnace at a temperature of 1200°C in argon atmosphere [30]. Here the laser vaporizes the graphite target within the quartz tube and SWCNTs are formed in the presence of metallic catalysts. The diameter of prepared carbon nanotubes is manipulated as a function of laser power such as the diameter of the tube decreases upon increasing the power of laser pulses and vice versa. Some other studies have dictated that the ultrafast sub-picosecond lasers have the ability to produce single walled carbon nanotubes on a large scale too [31]. It is further reported to manufacture carbon nanotubes up to 1.5 g/h via laser ablation method.

To harness CNTs with desired structural and chemical features, one should monitor the effect of different properties of lasers (peak power, frequency, oscillation wavelength, cw versus pulse), chamber pressure, distance between graphite target and substrate, ambient temperature and the flow and pressure of the buffer gas. By using this process, one can achieve high quality (purity) SWCNTs in large quantities. The mechanism and principles of laser ablation is identical with the arc-discharge method. Here the required energy is provided by a laser which strike with pure graphite pellet holding catalyst material i.e. cobalt and nickel (**Figure 4**).

The primary advantages of this method are the presence of the smaller amounts of metallic impurities and higher yield of CNTs. On the other hand, the carbon nanotubes produced via laser ablation method are not perfectly straight and uniform. This is an expensive method due to the requirement of high purity graphite rod and the availability of two laser beams to produce CNTs. By using this technique, the yield of nanotubes per day is relatively smaller than the arc discharge technique.

### **3.3 Chemical vapor deposition for CNTs synthesis**

One of the best techniques for the production of CNTs is chemical vapor deposition (CVD). There are different CVD techniques such as catalytic chemical vapor deposition either thermal [33] and water assisted [6], plasma enhanced oxygen assisted CVD [34–36] or hot filament CVD (HFCVD) [37]. But most extensively implemented CVD method for the production of CNTs is known as catalytic chemical vapor deposition. This route involves the Chemical breakdown of hydrocarbon on a specified substrate and helps expand the CNTs on different type of materials. Carbon atoms remain intact with the metallic catalytic particles, as was the case for arc discharge technique. After that carbon atoms are enabled to come in contact

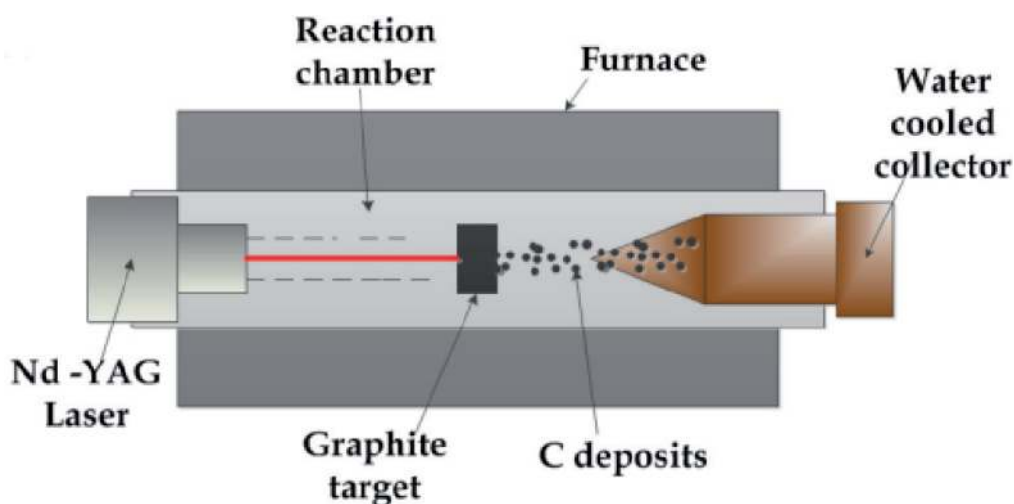


Figure 4.  
The laser ablation process [32].

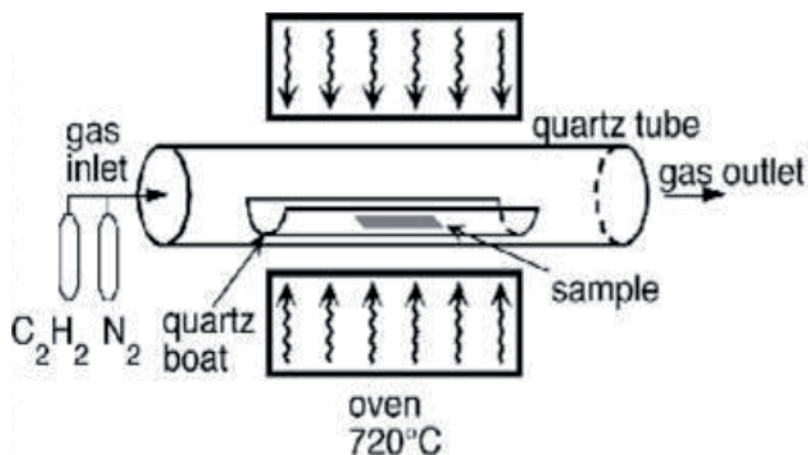


Figure 5.  
Chemical vapor deposition [38].

with metal particles and implanted with in the holes, initiating the production of carbon nanotubes (Figure 5).

This technique facilitates well aligned long carbon nanotubes and a layer of metallic catalyst particles are produced at 700°C. Most commonly catalyst metals are cobalt, nickel, iron and combination. The expansion of nanotubes carried out in fluidized bed reactor in the presence of a gas containing carbon such as ethylene, acetylene, methane, etc. and a process gas like H, Ne, or ammonia are used as well. The process gas reacts with the catalyst particles and disintegrates. Carbon atoms become prominent at the edges of nanoparticles where CNTs are created. CVD is very economical practical method for quite pure and large-scale production of carbon nanotubes as compare to laser ablation method. This method is easily controllable and give high purity of obtained materials, this is the main advantages of CVD [39].

#### 4. Purification of carbon nanotubes

Above mentioned as-synthesized methods of CNTs encounter certain impurities, such as smaller fullerenes, wrapped graphite sheets, metal catalyst particles,

and amorphous carbon contaminations. It is observed that the percentage of these impurities generally enhances as long as the diameter of CNTs increases. Therefore, it is important to get rid of these impurities to obtain homogeneously distributed CNTs in polymer or dispersion media due to their substantial effect on electro-mechanical properties of CNTs, interfering with the expected applications. It makes it unavoidable to apply certain purification techniques to get pure CNTs with better electrical and mechanical features [40, 41]. Due to the insoluble nature of CNTs, it is quite challenging to use liquid chromatography to get rid of these impurities. In addition, number of groups across the globe just characterize the commercially synthesized carbon nanotubes and do not have facilities to grow them. Due to the application of different analytical techniques such as Raman, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), even SWCNTs have shown doubled, triple and multi-walls of a single sample along with the presence of above-mentioned impurities. Hence, one cannot rely on the specification provided by different companies. Subjected to these various analytical characterization and impurities, researchers have applied various purification techniques, leading to significant loss of CNTs [42–44]. It is further observed that the use of acid treatment or surfactants might result in CNTs with activated surfaces, putting comprehensive changes in their desired properties [45].

Depending upon the nature of the structure (single-walled or multi-walled) in hands, growth process, and metal catalysts, various purification techniques such as mechanical, chemical and physical routes are to get dispersed carbon nanotubes with maximum possible exclusion of impurities [23]. The chemical methods allow the variation in surface energy by introducing functionalization of carbon nanotubes. It leads to better wettability and adhesion of CNTs to the polymer target media and hence the tendency of agglomeration decreases. But the use of acids might deteriorate the structural quality of CNTs, attributing un-desired physical properties.

The chemical route of purification produces highly pure CNTs but fragile to structural defects and product losses [46]. However, CNTs with higher purity can be achieved by removing the metal catalyst particles in controlled reaction. Physical methods are attractive due to the possibility of adsorption of variety of functional groups, leaving behind similar pi ( $\pi$ )- graphene structure and are implemented when higher weight fraction of CNTs is desired. Physical method separates the yield products on the bases of the size of CNTs [47]. Physical methods. These methods cause low damages and are more complex as well as less effective as compared to chemical methods. Here we will only explain the chemical methods for purification [48]. The most commonly used chemical purification method involves oxidation of synthesized CNTs in gas phase as well as in liquid phase. Most common purification methods with high success rates are

- Gas Phase
- Liquid Phase
- Intercalation Method

#### **4.1 Gas phase**

Purification can be done in dry gas oxidation. Carbon dioxide, hydrogen gas and dry/wet air are commonly used oxidation gases for this method [49–51].



#### 4.1.1 Air

Air oxidation is one of the gas phase oxidation methods to purify CNTs. The impurities in CNTs are removed by the thermal air oxidation at moderate temperatures. The walls of the CNTs and the binding between the entangled CNTs are affected by the presence of oxygen. It is also known as a strengthening process which starts at 480°C and amorphous carbon usually decayed between 480 and 500°C [52, 53]. The reactivity rate is greater for structure and amorphous carbon than cylindrical wall of CNTs when oxidation is done in air. Due to this selective oxidation, the amorphous carbon can be bare-off from the cross-linked CNT collections. If the temperature is raised to 750°C during the annealing process, the loss rate of CNTs enhances to about 90% and the structure of CNTs is destroyed significantly.

#### 4.1.2 Other gases

As in gas phase oxidation methods, controlled rate heating of CNTs is implemented for a longer period of time. Here the disordered amorphous carbon that is coming from the tip, destructs the purification on the base of oxidation by CO<sub>2</sub>. Mild oxidation carried out with CO<sub>2</sub> at 600°C [54].

The route of the reaction is shown:



Amorphous carbon and metal catalyst particles coated with carbon may be removed by hydrogen gas treatment at high temperatures. Amorphous carbon is converted into the carbon dioxide in air and then transformed again into methane in the presence of hydrogen. Ammonia (NH<sub>3</sub>) is used to remove residual carbon impurities and repair the damaged in sidewalls of CNTs, instead of using hydrogen gas. Ammonia has advantages over hydrogen in terms of ease in handling. Only a small number of defects are observed in the CNTs when they were exposed to NH<sub>3</sub> gas at high temperatures during purification process. In addition, strong van der Waals forces are induced between CNTs after NH<sub>3</sub> treatment, leading to a damage recovery of sidewall [52, 55] of CNTs.

#### 4.1.3 Effect of gas phase oxidation

Oxidation of amorphous carbon in gas phase is easy to control as compared to liquid phase oxidation techniques. Higher activation energies are required in gas phase oxidation processes. Gas phase oxidation can better oxidize the CNTs than the liquid phase oxidation without introducing defects. This yield purified nanotubes, arranged in tight bundles without forming clusters. Moreover, there is no need to use complicated/sophisticated equipment, filtration and separation processes required after the purification [56, 57].

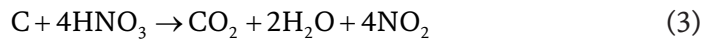
### 4.2 Liquid phase

Despite the fact that the advantages of gas phase oxidation are clear, it has some limitations. Metal particles cannot be eliminated straightaway, and further treatment is compulsory. In order to overcome this drawback, liquid phase purification treatments are developed to eliminate the amorphous carbon and metal catalysts [57, 58].

The oxidant and mineral acid, in the form of solution can uniformly react with the network of the raw CNTs samples. Therefore, processing with selective oxidizing agent with precise control can yield high-purity CNTs. The scientific community mostly uses HNO<sub>3</sub>, NaOH and H<sub>2</sub>O<sub>2</sub> as an oxidizing agent for liquid phase oxidation.

#### 4.2.1 Nitric acid oxidation

Nitric acid is commonly used for purification of CNTs due to its capability of removing metal catalysts, nontoxicity and economy. It can remove the amorphous carbon selectively because of its mild oxidizing ability. A concentrated nitric acid is used to produce SWCNTs through laser ablation in a single step. The synthesized SWCNTs were sonicated in concentrated nitric acid for a few minutes, following the refluxing for 4 h under magnetic stirring process carried at 120–130°C. The product reached 30–50 wt. % of its raw samples and the metal defects were reduced up to app. 1@ wt. %. The purity of SWCNTs and its production totally depends upon the concentration of nitric acid and reflux time in nitric acid treatment. The elimination of metallic impurities can be confirmed via XRD analysis of CNTs. During the purification, the nitric acid reacts with the defected parts and intercalate into the CNTs to unzip the tube walls by further oxidative etching, which in turn causes an increase in nanotubes inter-layer spacing. Normally, the reactive carbons were eliminated through the following chemical reaction:



Most of the catalyst particles are removed in nitric acid's treatment at high temperatures for 24 h. The unwanted impurities are removed and melted effectively from CNTs, and some oxidative defects in the sidewall of CNTs are also induced in this process. The intensity of the D-band spectrum produced by the defects and carbon particles in the sample after acid treatment, can be used to determine the disorder degree of the sample [57, 59].

#### 4.2.2 Sodium hydroxide treatment

It has been observed clearly from Scanning electron microscope (SEM) that silica and alumina support can be eliminated significantly after NaOH treatment. Based on the reaction between NaOH and carbon, a single-step method for simultaneous purification and opening of multi-walled carbon nanotubes has been formulated [48, 60]. The redox reactions between carbon and NaOH followed through the highly reactive sites of the material. As a result, NaOH only interacts with the carbon impurities and defects of the carbon nanotubes, that is with the tip while the uniform graphite layers of the nanotubes walls remain intact. This is because metallic sodium cannot be inserted into well-organized materials, and can only be carried out by highly disordered carbon impurities [61]. Therefore, in addition to the opening of tubes, NaOH treatment removed the catalytic support, amorphous carbon, and the catalyst metal particles. Its mild conditions removed the metal impurities without damaging the sidewalls of CNTs.

#### 4.2.3 Hydrogen peroxide oxidation

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) attacks on the carbon surface and cannot eliminate metal particles due to its mild oxidization capability. It is inexpensive and green

oxidizing agent and is commonly used with HCl. Generally, H<sub>2</sub>O<sub>2</sub> can be transformed into a toxic salt. H<sub>2</sub>O<sub>2</sub> with HCl has been examined to eliminate the metallic particles during purification of CNTs. Macro-scale purification consists of two parts such as refluxing treatment in H<sub>2</sub>O<sub>2</sub> solution following the cleaning process performed with HCl. Particle size of Fe has a significant effect on the oxidation of amorphous carbon. The oxidation and removal of metal particles in this process is performed in a single container to make it simple. The purity and yield of the product in this treatment are better than NH<sub>3</sub> treatment. Carbon coated iron impurities were liquified in an aqueous solution of H<sub>2</sub>O<sub>2</sub> and HCl at 40-70°C for 4–8 h. The production of CNTs increased to approximately 50 wt. % and the purity raised up to 96 wt. % with this treatment [62].

### 4.3 Intercalation method

Halogen may be intercalated into carbon nanotubes for selective oxidation of carbonaceous impurities. Brominating is one of the effective procedures in CNTs purification process. Graphite intercalation compounds are formed by the attachment of atomic or molecular layers of a different chemical species between layers in graphite host materials. The intercalation of bromine (Br<sub>2</sub>) in CNTs is confirmed by using HR-TEM [48]. The mixing of raw CNTs with pure liquid bromine under nitrogen atmosphere yielded Br. Under these conditions, charge transfer between Br and carbon occurred, enabling the formation of complex C-Br<sub>2</sub> on CNT surface and at deformed sites. It was observed that the orientation of Br on CNT surface is like a rod of a wheel, which is perpendicular to the curve of graphitic layers on CNTs. Intercalation of Br usually, happens on the surface of CNTs, where large numbers of defected sites are available. Br will be more reactive to those regions where different types of defects (amorphous carbon and other disorder carbonaceous materials) exist. When brominated, CNTs were passed through the air combustion at 550°C, and it was observed that the layers of the graphite were damaged along the line in which Br collected, showing the effect on the reactivity of the tubes toward oxygen upon adding Br. The amorphous carbon can be effectively oxidized due to the oxidation difference between brominated regions and CNTs. The catalyst particles, which was bounded, were opened and removed at the same time. Due to the tube action, Br diffused into the tubular CNTs and caused in the breakage of inner graphite layers during oxidation [63–65].

## 5. Conclusion

A detailed overview of synthesis and purification of carbon nanotubes is presented in this chapter. Synthesis techniques (i.e., arc discharge synthesis, laser ablation of graphite/laser vaporization synthesis method, chemical vapor deposition (CVD), high pressure carbon monoxide synthesis and flame synthesis) have been described in detail to highlight their importance as well as drawbacks. Arc discharge synthesis method is one of the most used technique for carbon nanotubes in large quantities. Its main drawback is the lack of control over the chirality in the nanotubes. Laser ablation method has the ability to produce CNTs in large quantities having small impurities. However, it is an expensive method as compare to arc discharge method for the synthesis of CNTs. A high purity CNTs can be obtained by using Chemical vapor deposition method. It is most suitable for large-scale manufacturing of CNTs at economical cost than laser ablation method. Chemical-based purification methods (i.e., gas phase, liquid phase and intercalation method) for CNTs are discussed comprehensively. These methods can efficiently eliminate

amorphous carbon, polyhedral carbon and metal impurities at the cost of decreasing a significant amount of CNTs or damaging structure of CNTs. Gas phase purification is considered for purifying CNTs because it does not significantly grow sidewall defects in CNTs. However, it has limitation that it does not remove metal particles straightforwardly. Liquid phase oxidation produces defects on CNTs sidewall and may break-down CNTs into shorter ones with different lengths. The intercalation is best suitable for purifying CNTs without destroying their alignment. These features of synthesis and purification methods of CNTs will help researchers to select between these different methods according to their requirements.

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