Carbon Nanotubes: A Review

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***Abstract*— Since the first discovery of the carbon nano tubes in 1991 , in the consecutive years several techniques have been developed for their preparation . These techniques have improved a lot and they produce carbon nanotubes of required characteristics. The review here describes the major techniques used such as laser ablation, arc discharge, chemical vapour deposition(CVD) and gives an idea on which technique may be useful for the production the CNTs having particular characteristics.**

***Keywords*—carbon nanotubes, laser ablation, arc discharge, chemical vapour deposition (CVD), purification**

I. INTRODUCTION

Iijima discovered the carbon nano tubes in 1991, using an electron microscope while studying cathodic material deposition through vaporizing carbon graphite in an electric arc-evaporation reactor under an inert atmosphere during the synthesis of fullerenes. They appeared to be made of a perfect network of hexagonal graphite rolled up to form a hollow tube. The nano tube diameter range is from one to several meters and is much smaller as compared to its length.

Over the years, the fabrication techniques have been improved and other techniques have been discovered that can be characterised based on the parameters of the carbon nanotubes such as shape, size, type and also its quantity.

II. PROPERTIES OF CARBON NANOTUBES

Carbon nanotubes exhibit unusual photochemical, electronic, thermal and mechanical properties. The SCWNTs are found to behave like metals, semi-metals or semi-conductive one dimensional objects. They have very high tensile strength (~150GPa nearly 100 times that of steel), high modulus (~1TPa), low density (1100-1300 kg/m^{3}) thermal conductivity (~3000 W/mK) and high electrical conductivity (comparable to copper).

III. TYPES OF CNTS

Carbon nano tubes or CNTs are cylindrical in shape with diameter ranging from 1-100 nm and having the length extended up to few micrometers in scale. The two basic forms of the CNTs are:

A. Single Walled Nano tubes

SWNTs consist of a single tube of graphene. [2] They can be considered as a graphene layer (single layer of graphite) rolled into single sheet.

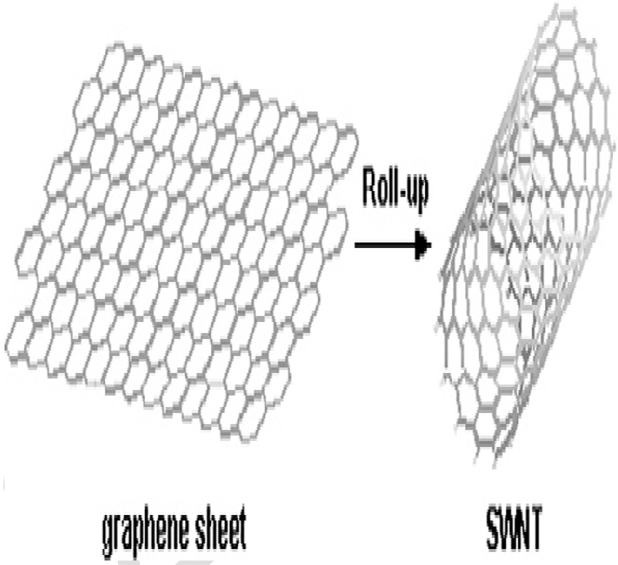

Fig.1 Graphene sheet rolled to a CNT-schematic representation [3]

They have a length to diameter ratio equal to 1000 or more. They have diameters close to 1nm.It consists of two separate regions- the sidewall of the tube and the end cap of the tube, having different physical and chemical properties. They are very good electric conductors and exhibit certain electrical properties that are not exhibited by the MWNTs.

B. Multi Walled Nano tubes

MWNTs are composed of several concentric tubes of graphene fitted one inside the other. The length, diameter and the properties are different as compared to the single walled nanotubes. The inter-layer distance of the graphene layers in the MWNTs is close to 3.3A.

The Double Walled Nano tubes and the SWNTs have nearly the same properties. They are a special case of the MWNTs. The double walled carbon nano tubes were first synthesized by the chemical vapour deposition method on a gram scale in 2003.

IV. SYNTHESIS

The major methods for the synthesis of the carbon nano tubes are:

A. Arc-Discharge

B. Chemical Vapour Deposition

C. Laser Ablation

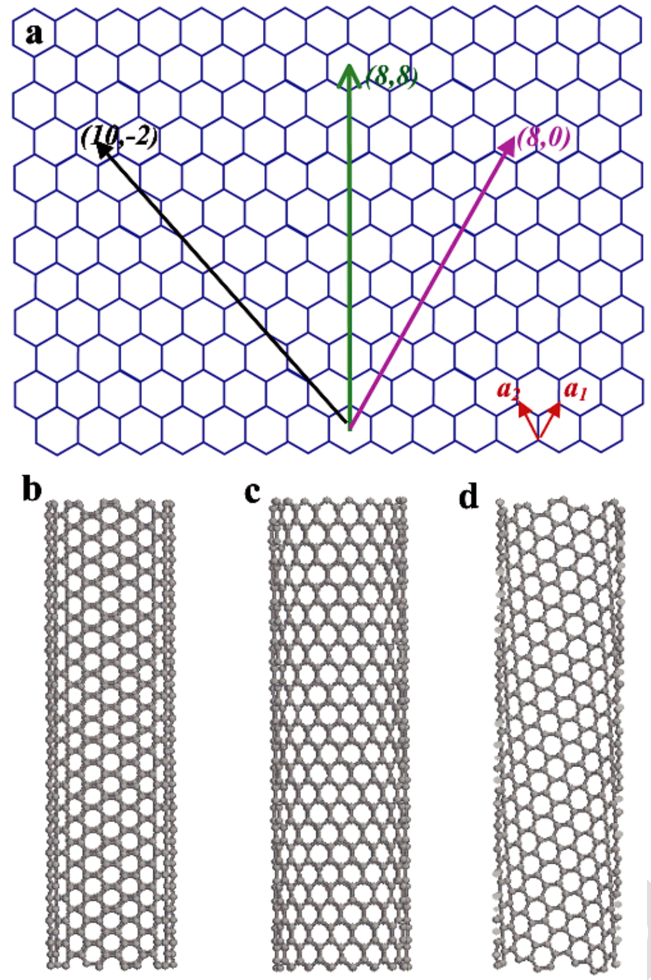

Fig. 2 (a) Schematic honeycomb structure of a graphene sheet. Single-walled carbon nano tubes can be formed by folding the sheet along lattice vectors. The two basis vectors **a**1 and **a**2 are shown. Folding of the (8, 8), (8, 0), and (10,−2) vectors lead to armchair (b), zigzag (c), and chiral (d) tubes, respectively.

A. *Arc Discharge Method*

In the laboratory scale production, the two carbon electrodes are separated by a 4mm wide gap and are placed in a water cooled chamber. The DC voltage is provided in the arc between the two electrodes under the helium atmosphere at sub-atmospheric pressure.Ni/Y and Co/Ni catalysts are used in production of the SWNTs using this method. [5]

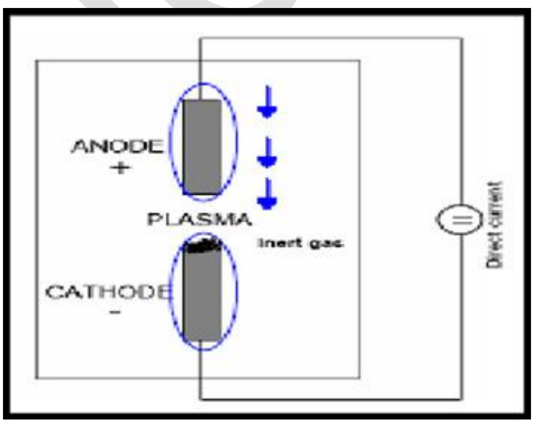

Fig. 3 Arc Discharge Method

B. *Laser Ablation Method*

In 1995, Guo synthesised the CNTs using this method for the first time. [6]The principles and the mechanisms of this method are similar to that of the Arc discharge method but the laser is used as the energy source instead of DC current. SWNTs with high quality and high purity are prepared using this method. Carbon nano tubes are nowadays prepared using different types of lasers. The original method developed by researchers at Rice University used a "double-pulse laser oven" process. There are several researchers who have used variations of the lasers to include one-laser pulse (green or infrared), different pulse widths (ns to micros as well as continuous wave), and different laser wavelengths (e.g., CO_2, or free electron lasers in the near to far infrared).[7]

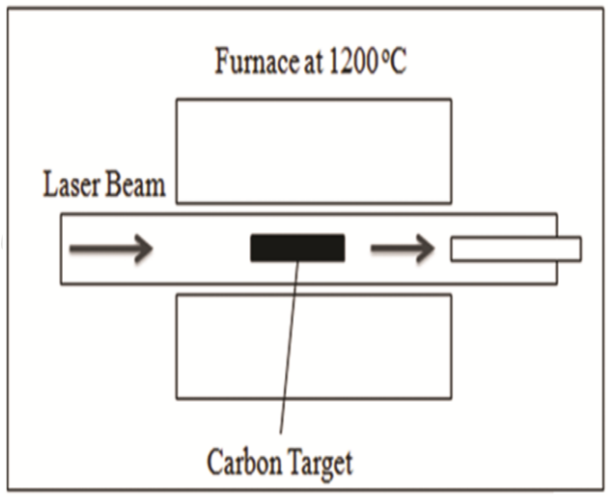

Fig. 4 Laser Ablation Method [9]

C. *Chemical Vapour Deposition Method*

The Chemical Vapour Deposition Technique requires low temperature (<800°C) and has replaced the arc discharge and the laser ablation techniques.

A number of methods under the CVD (Chemical Vapour Deposition) methods are hot filament, water assisted, and oxygen assisted, microwave plasma, radiofrequency, thermal and plasma enhanced methods. Mostly the CVD methods are thermal or plasma enhanced .The high temperature is required to decompose the carbon source. The process is catalyst based and the most commonly used metal catalysts are Fe, Co and Ni. The most preferred hydrocarbon sources are methane, ethane, acetylene, ethylene, carbon monoxide .The carbon sample is allowed to cool down in an inert gas environment to avoid the etching away of CNTs by reaction with oxygen. Higher temperature is required for the synthesis of SWNTs as compared to that of MWCNTs. If SWNTs are to be synthesised, the anode has to be doped with a metal catalyst such as Fe, Co, Ni, Y or Mo. If the two electrodes are graphite electrodes, than the major product will be the MWNTs. DWNTs have been prepared using acetylene as the carbon source over well-dispersed metal nano-particles-Co/Fe Binary System embedded in heat resistant zeolites at temperature above

900⁰C. Using Plasma Enhanced CVD methods, the nano tubes can be prepared at a comparatively lower temperature. The disadvantage is mixture of SWCNTs and MWCNTs are produced together during the CVD. [2], [3], [13]

1) PECVD :

CNTs were produced by (Lasorsa et al. 2010) for use in the manufacture of nano sensors and (Perez et al. 2010). They were manufactured by Plasma Enhanced Chemical Vapor Deposition method. These sensors require specific structure of the carbon nanotubes only as any change in them will lead to change in the properties of the bio-sensors in which they are used.

The PECVD reactor used had a radiofrequency source of 13.56 MHz and output power of 1200 watts. The figure below shows it.

The glass tube is made of pyrex glass and is closed by bronze plates with the manholes corresponding to the entry of gases. The sample holder was constructed with a steel tube and was heated by resistive cartridge. The ultrapure methane used was controlled with a mass flow controller.

The sample holders of Cu impregnated with a solution of ferric nitrate in isopropyl alcohol were placed on the heated central electrode of reactor and were subjected to 900 °C temperature and pressure of 400 torr.The conditions remained constant throughout the process.

The CNTs were found inside the hollows of sample holder and the zones impregnated with ferric nitrate solution. The multiple walls CNT obtained had average dimensions: length 5 nm and average diameter 7nm.

Thus, a large number of CNTs of desired structure can be produced.

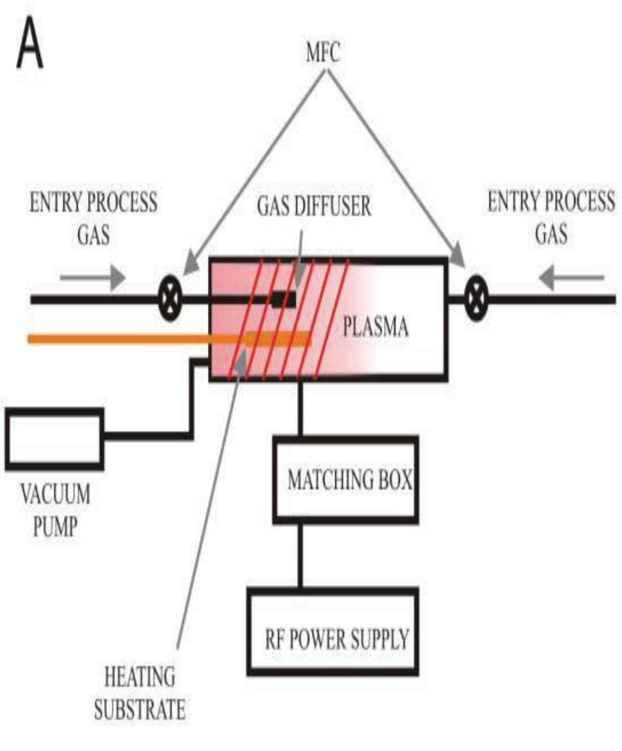

Fig. 5 Plasma Enhanced Chemical Vapor Deposition [10]

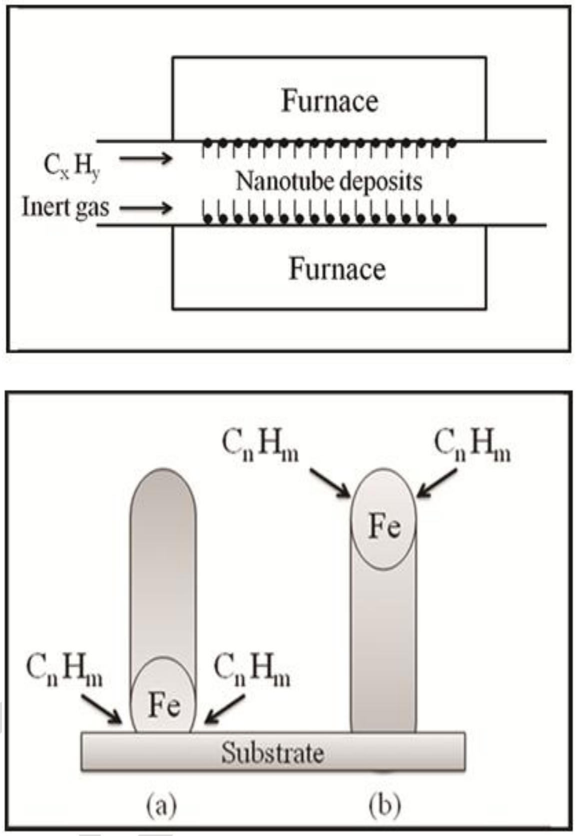

Fig. 6 Chemical Vapour Deposition Method [9]

2) MPECVD & PECVD :

Bower et al. Showed that the highly aligned CNTs can be grown by microwave plasma enhanced chemical vapour deposition method. The alignment resulted from the self-bias and they were grown normal to the surface of optical glass fibres. The upper alignment in the plasma region is straight while the base shows random curled structure associated with thermal CVD. The growth rate was 40 times faster than thermal CVD.

Using the conventional thermal CVD techniques, such carbon nanotubes that are highly aligned and curled from the bottom can be produced in larger quantities and lower costs but we will have less control over size, diameter and length. [11]

The thermal CVD is a single step process while the PE CVD is a double – step process.

The double-step methods involve coating the active catalystonto a substrate, this has the advantage of controlling the morphology and distribution of the catalyst particle. Also, the CNT growth location can be controlled and thus higher-purity ACNTs are produced by double-step methods compared with single-step methods. [12]

3) Radio Frequency Plasma Process :

Radio frequency (RF) plasma processes have been developed and seem to be one the most promising methods for the large-scale synthesis CNTs from various solid carbon feed. The RF plasma torches generate plasma jets with large hot volumes and low speeds in comparison to DC plasma torches that extend the interaction time between plasma and the feed or the CNTs produced.

Although, the RF plasma synthesis by Kim et al. reported high quality SCWNTs at a large scale from solid carbons and a good scalability the purity of the samples was low i.e. 20-30 wt %. This showed that the RF induction plasma process seems to be mainly attributable to the incomplete treatment of solid feedstock in the plasma jet and to the formation of amorphous carbon as a by-product.

They are also the typical drawbacks of vaporisation methods. Up to 40% purity had been achieved in the work above but to achieve higher purity, liquid stock was employed rather than solid stock.

The liquid stocks consisted of liquid hydrocarbons and metallic catalysts and are fed to the RF induction plasma torch through an atomizer. [14]

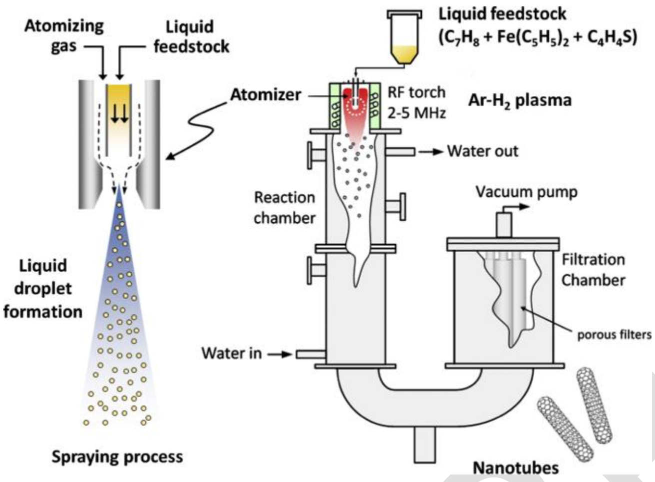

Fig. 6 A schematic diagram of an RF induction thermal plasma process developed for the large-scale synthesis of high quality SWCNTs from liquid feedstock.[14]

D. Vapor solid – solid (VSS) growth mechanism

This mechanism consists of four steps that were explained by Jourdain V. et al. (2002)

In the first step, nano sized metallic particles are formed on the substrate by either laser ablation or by annealing a very thin metallic film.

The second step is the decomposition of hydro carbon gas over the surface of metal catalyst nano particles to release the hydrogen and carbon, which dissolve in them.

The third step is the diffusion of carbon through the metal particle and precipitation.

The final step consists of over coating and deactivation of the catalyst and termination of nanotube growth.

E. Vapor liquid solid (VLS) method growth mechanism

It consists of three main stages i.e. Nucleation, precipitation and deposition. Initially, at higher temperature the metal is evaporated with carbon at high temperature by arc discharge method and a metal- carbon alloy particles are formed.

Initially, in the liquid state (due to decrease in melting point of the alloy); due to high temperature the carbon content is more than solubility limit in a solid state. Therefore, with decrease in temperature of cathode, liquid alloy particles begin to segregate excess carbon on their surfaces. [15]

V. PURIFICATION

The carbon nano tubes obtained by any method needs to be purified for their specific applications as they contain impurities like carbon particles, catalyst particles that tend to disrupt the properties of the carbon nano tubes. They can be purified by various methods such as oxidation, acid treatment, annealing and thermal treatment, ultrasonication, magnetic purification, microfiltration and cutting. [3]

VI. CONCLUSION

From the literature review, the CVD techniques and its variants are better techniques as they give higher yield (20-100%), produce CNTs on a large scale with controllable diameter and length. It is found as cost effective as compared to other methods. Further, it is also seen that the laser ablation method is the costliest as it requires expensive lasers and high power equipments. Production with the arc-discharge methods may not be too costly but the product obtained has low purity and often requires expensive purification techniques to be performed.

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