Large-Scale Continuous Production of Carbon Nanotubes - A Review

L. Gowrisankar[1], G. Manivannan[2], S. Karthikeyan[3]*

[1]Department of Electronics and Communication Engineering, RVS College of Engineering & Technology, Coimbatore, TN, India
[2]Department of Chemistry, Erode Arts & Science College, Rangampalayam, Erode, TN, India
[3]Department of Chemistry, Chikkanna Government Arts College, Tiruppur, TN, India
Received: 10.10.2015   Accepted: 30.03.2016   Published: 30-03-2016
*environkarthi@gmail.com

ABSTRACT

This review represents the design, manufacturing and related process of carbon nanotubes by different routes. The synthesizing methods including continuous rotary reactor, high-presure carbon monoxide in plug flow reactor, cobaltmolybdenum fluidized bed catalytic reactor, the plasma-enhanced chemical vapor deposition (PECVD) and swirled floating catalyst chemical vapor deposition (SFCVD). Since the production process is continuous, the present technique can easily be scaled up for mass production carbon nanotubes for a wide variety of applications.

Keywords: Carbon nanotubes (CNT); Chemical vapor deposition (CVD); Fluidized bed.

1. INTRODUCTION

The first images of nanoscale, tubular carbon filaments were produced in the early 1950's by Russian scientists Radushkevich and Lykyanovich. but the tremendous potential impact of carbon nanotubes (CNTs) was not felt until the work of Iijima, 1991 and Bethune *et al.* 1993 Carbon nanotubes (CNTs) offer potential for significant improvement in thermal, electrical and mechanical properties over traditional materials used in electronics, composite materials, and interface layers that has attracted much attention in the past few years and intense research has been carried out to identify their remarkable properties and potential applications. The large-scale synthesis of nanotubes is the key point for their commercial application. Of the different techniques developed to synthesize carbon nanotubes, the CVD method appears to be the most promising for the processing of carbon nanotubes, due to its relatively low cost, controllability over precursor flow rate, composition, impurities and its potential high yield production. Nanotubes exhibit the highest Young's modulus and tensile strength among all materials. A single-walled nanotube can be either metallic, semiconducting, or semi-metallic depending on the helicity and diameter. By using a discontinuous reactor, only a small quantity of carbon nanotubes from 0.01 to 0.2 kg can be produced daily by the CVD process. It is for this reason that only a technology based on a continuous reactor can lead to the production of a large quantity of carbon nanotubes. There are various methods of production of carbon nano-tubes such as production of nanotubes by arc discharge, chemical vapor deposition, laser ablation, flame synthesis, high pressure carbon monoxide (HiPco), electrolysis, pyrolysis etc.

2. EXPERIMENTAL METHODS

2.1 Continuous Rotatory Reactor

The continuous reactor is schematically described in fig. 1. The reactor consists of a tubular inclined rotary kiln with a mobile bed, equipped with continuous systems for catalyst feeding and for the collection of gaseous and solid products, of a mass spectrometer for analyzing the output gas composition, and of a completely automated system of control and acquisition of data. The catalyst used for this study is a bimetallic catalyst supported on alumina, synthesized according to a method similar to that described by Tran et al. During the reaction, ethylene is used as the carbon source, balanced by nitrogen as the inert gas and/or by hydrogen, and is decomposed on the surface of the catalyst into solid carbon and gaseous hydrogen (Sophie et al. 2009) .

2.2 Plasma-enhanced Chemical Vapor Deposition

The plasma-enhanced CVD (PECVD) method can be used to synthesize carbon nanomaterials in large scale. An advantage of using the PECVD approach is that the as-synthesized products are almost totally deposited on the substrate and are easy to collect. At present, this is the only technique that allows size, alignment and orientation control of nanospecies. The plasmas used to

decompose and activate the reactants in the gas phase are usually generated by hot filaments (HF) or by electrical discharges at different frequencies (DC, RF, and MW). The schematic of a typical PECVD set-up is shown in fig. 2. In PECVD synthesis, the catalyst powder was generally loaded on a substrate by means of wet chemistry or sputtering, usually accompanied by either chemical etching or thermal annealing to induce the formation of catalyst particles on the substrate. During synthesis, the substrate was kept at temperatures in the range of 650–1500 °C, and reactant gas was introduced into the reactor with a pressure typically below 100 Torr. Moreover, the catalysis could be homogeneous in PECVD processes. For example, a metallorganic compound (e.g., ferrocene) was introduced into the reactor and decomposed by the plasma, directly providing metallic clusters in the gas phase.
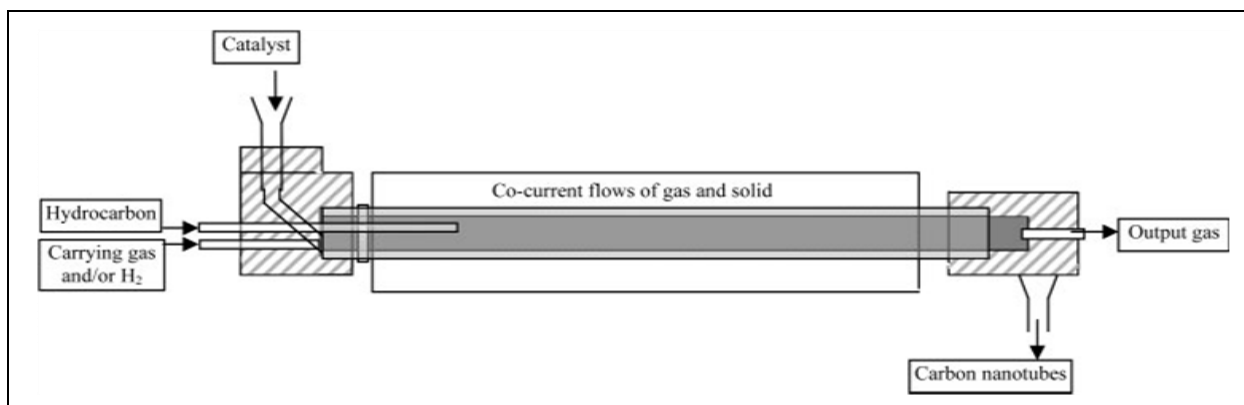

Fig. 1: Schematic experimental setup of catalytic chemical vapor deposition method
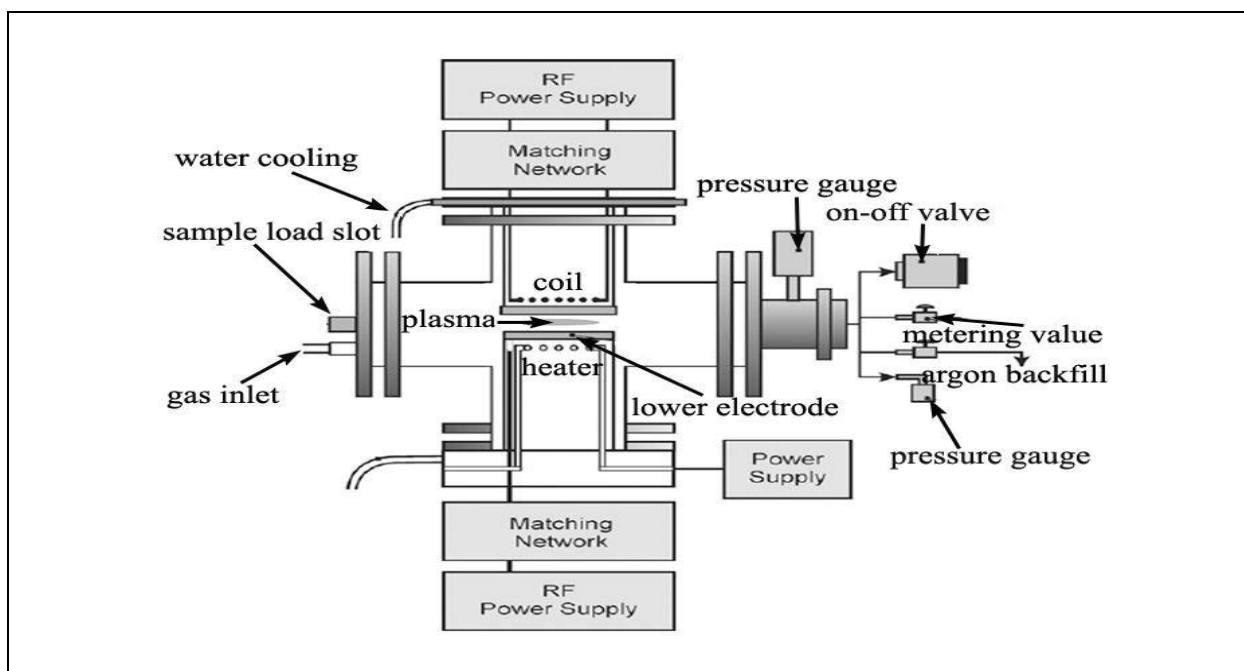

Fig. 2: Schematic of a typical plasma-enhanced chemical vapor deposition (PECVD)

2.3 Thermal Chemical Vapor Deposition

Nanomaterials can also be synthesized by means of thermal CVD. The method makes use of a flow reactor (quartz tube or stainless steel tube) placed inside a furnace for the pyrolysis of carbon-containing molecules. As reactants, carbon-rich gases mixed with argon or nitrogen flows are used, but sometimes the reactant can be in the form of liquid that is subsequently vaporized. If a catalyst is involved, the method is called catalytic CVD (CCVD). The catalyst can be either in powder form driven into the reactor together with the feed gases or previously coated or supported on a substrate. It is known that interesting and novel processes can occur under high-pressure conditions. Nevertheless,

atmospheric pressure is often adopted for easy management. Compared to the PECVD method, the CCVD method has higher scalability but poorer control in deposition area. It is known that large-scale generation of a material is a critical factor for commercialization. In fig. 3, the schematic of a typical thermal CVD apparatus is shown. By means of catalytic decomposition of hydrocarbons, magnetic materials can be encapsulated inside carbon nanomaterials.
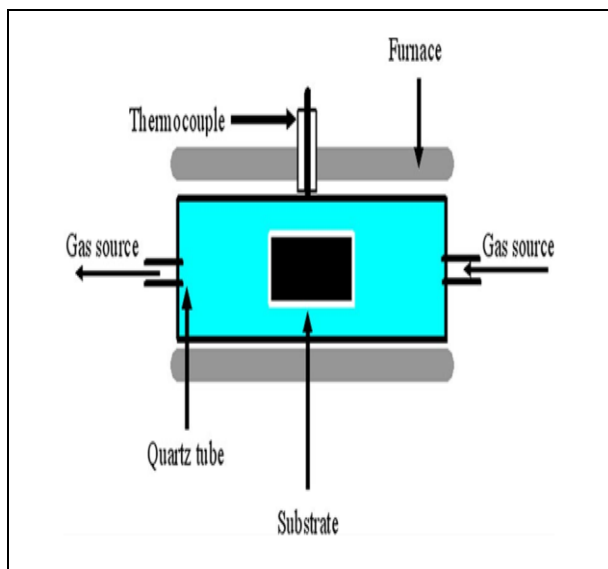

Fig. 3: Schematic of a typical thermal CVD apparatus

2.4 Swirled Floating Catalyst Chemical Vapor Deposition

Various modes of the CVD technique that exist include the microwave CVD, horizontal fixed bed catalytic CVD, and the rotary tube. Recently, we introduced the swirled floating catalyst chemical vapor deposition (SFCCVD) mode which was more successful than the microwave or the fixed bed catalytic CVD modes. In fig. 4 illustrates the setup of the SFCCVD. It is made of a vertical silica plug flow reactor inside a furnace. Gases flow into the reactor with the aid of a system of valves and rotameters through a swirled coiled mixer, which leads the catalyst from the vaporizer to the reactor. The upper part of the reactor is connected to a condenser, which leads to two delivery cyclones where the CNTs are collected. At the beginning, the reactor was vented consecutively with nitrogen and argon for 10 min each, while keeping all the other valves closed, to flush out contaminants and to ensure that there were no leakages. The temperature of the vaporizer was set at to vaporize the xylene-ferrocene mixture above their boiling points. Xylene was used as the solvent for the catalyst and also acted as the main carbon source.
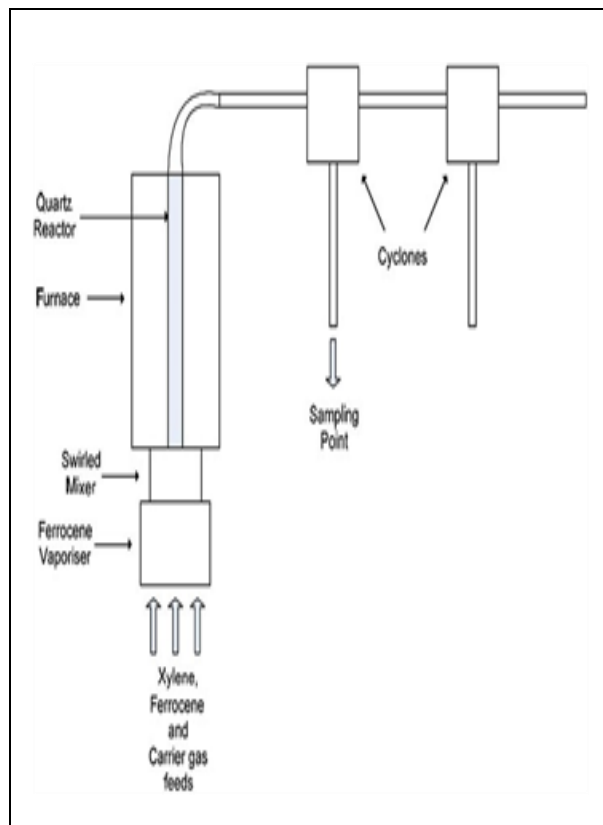

Fig. 4: Schematic of swirled floating catalyst chemical vapor deposition

2.5 Methane Chemical Vapor Deposition

Carbon nanotubes were synthesized by using the experimental setup shown in fig. 5. Typically, 0.1 g of the catalyst was placed into a quartz boat that was inserted into the center of a 1 in. diameter quartz tube mounted in an electric tube furnace. Ar was flown over the catalyst as it was heated from room temperature to 900 °C. The reaction began as Ar was replaced by CH_4 (flow rate 6000 cm3/min) for the desired reaction time (2-45 min). The flow was then switched to Ar and the furnace was cooled to room temperature. When producing large quantities of SWNTs, we typically used 5.0 g of catalyst and the CVD reaction time was 30 min (Cassell *et al.* 1999).

2.6 Arc Discharge

A simplified carbon-arc nanotube synthesis method that eliminates nearly all of the complex and expensive machinery associated with conventional nanotube growth techniques. In-deed, all that is required is an insulated bucket full of liquid nitrogen, graphite electrodes, and a dc power supply. The reaction can run in a continuous fashion and can be scaled up for industrial production levels. High-quality multi-walled carbon nanotubes are produced at high production rates. Fig. 6 shows a schematic of

the synthesis apparatus. To grow nanotubes, a graphite anode is dipped into an open container of liquid nitrogen containing a short non-consumable copper or graphite cathode. The electrodes are momentarily brought into contact and an arc is struck. Nanotubes formed in the arc-plasma region drop and collect on the bottom of the bucket. For continuous operation, the bottom of the bucket is funnel-shaped and sealed with a valve which opens automatically and periodically to flush nanotubes from the vessel (Ishigami *et al.* 1999).
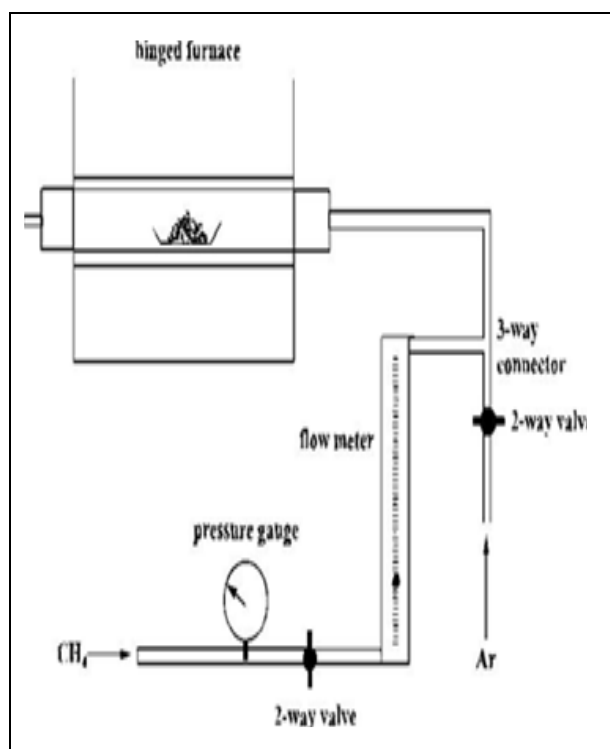

Fig. 5: Schematic experimental setup for methane CVD synthesis of SWNTs

2.7 DC Thermal Plasma Jet

The experiment were carried out in a dc plasma jet system using pure graphite rods 6 mm in diameter and homogeneous graphite rods doped with binary catalyst: 1.2 at. % Ni and 0.4 at.% Ce. The schematic diagram of the plasma tourch and graphite rod insertion port is shown in fig. 7. Graphite rods were fed into the reaction chamber perpendicular to plasma jet and close to the anode nozzle channel and diameter was 2 and 0.4 cm. The gap between the cathode and the anode was maintained at 0.6 cm. The carbon products condensed mostly in the bottom of the cooled reactor with in inner diameter and length 5.5 and 60 cm. The temperature was 1300 and 500K in the two mentioned reactor points in the case of Ar plasma jet.
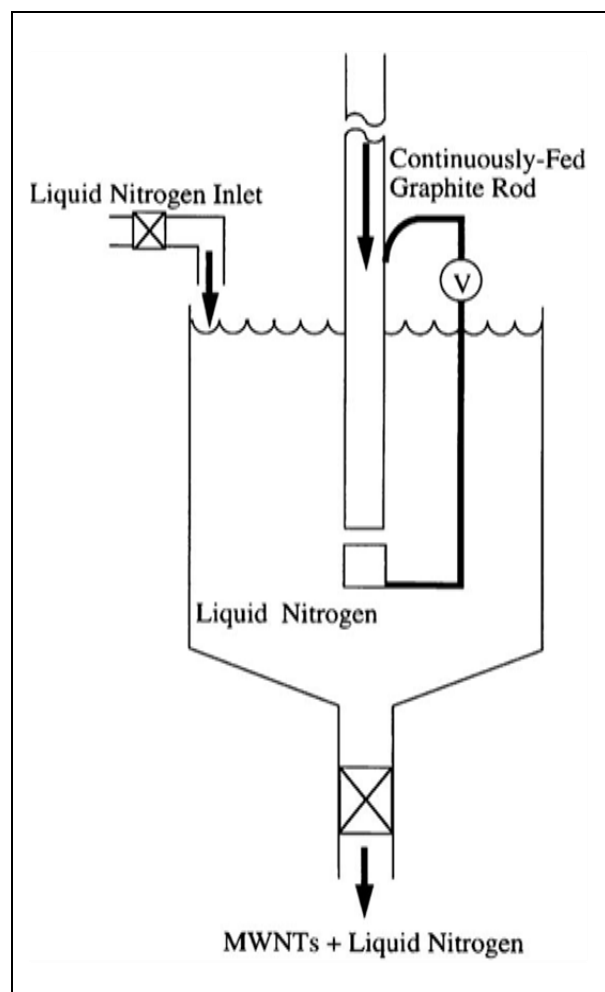

Fig. 6: Schematic of continuous production liquid-nitrogen reaction chamber for nanotube synthesis

2.8 Arc Discharge in Air

The synthesis process was done in direct current (DC) arc discharge apparatus. Fig. 8 shows the schematic of arc discharge apparatus used in this experiment .The are discharge system consists of a horizontal anode and vertical cathode assembly installed in a stainless steel cylindrical chamber. The pure graphite rod of 8 mm diameter and 150 cm length as anode is fixed to the helical rod holder in the transmission device. It is sent to the chamber by stepper motor. The cylindrical graphite of 80 mm diameter and 120 mm height as cathode fixed to a graphite disk of 160 mm diameter and 20 mm height is driven by motor with rotational speed of 3 r/min. The gap between the anode and cathode can be controlled by the stepper motor. The opposite side of the anode is composed of steel blade and a handle, which are used to scrape the film like MWCNT products that deposit on the surface of cylindrical cathode (Zhao *et al.* 2012).
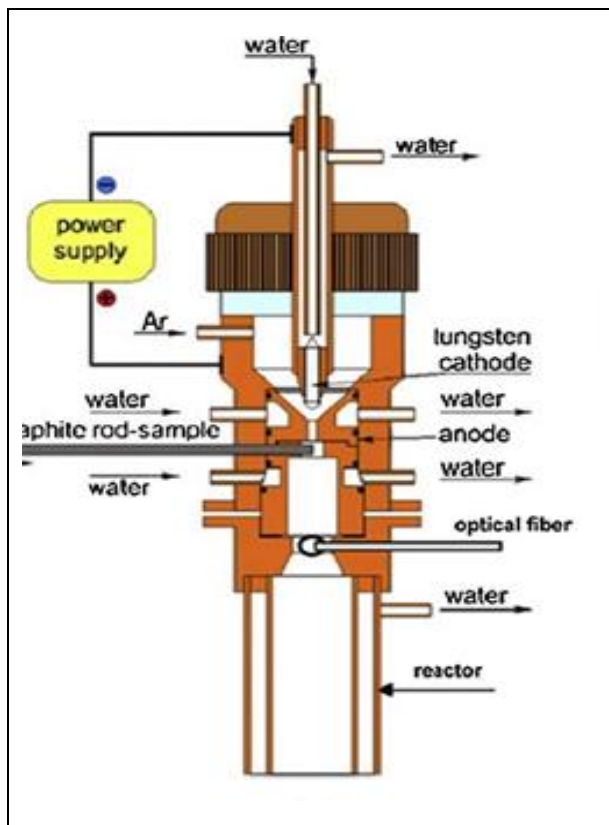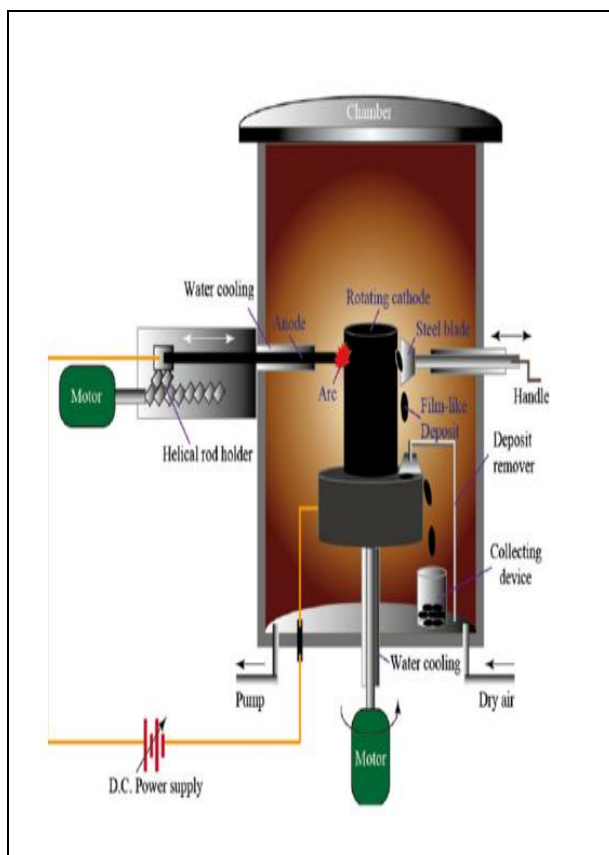
Fig. 7: Schematic of dc plasma jet system

Fig. 8: Schematic of arc discharge apparatus

2.9 Underwater AC Electric Arc

An AC electric arc is generated between two identical carbon rods of 6 mm in diameter, submerged in deionized water. No special shaping of the electrodes was used. Two computer controlled stepper motors, like shown in the schematic drawing in fig. 9, are used to regulate the distance between the electrodes. The current was varied between 85 and 45 A, at a voltage of 40 V. For all settings it was possible to ignite and maintain the arc. The production rates, weight losses of electrodes and the proportion of them as a percentage of the weight loss of the electrodes for each current value. Gas bubbles are continuously formed during the arc discharging process in the water (Biro *et al.* 2003).
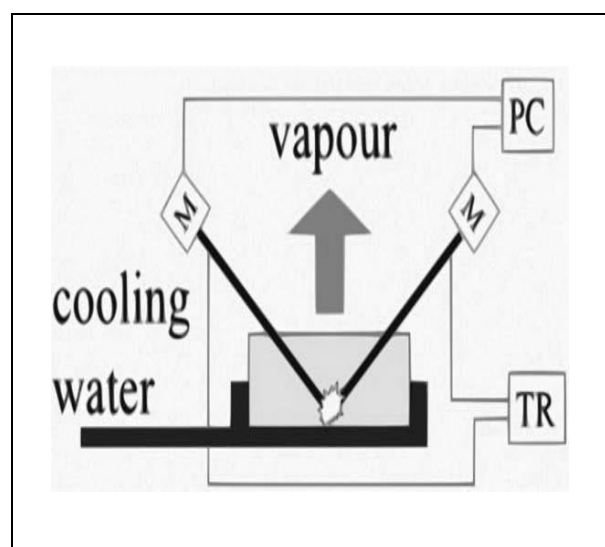

Fig. 9: Carbon nanotubes produced in an underwater AC electric arc

2.10 Thermal Plasma Jet

This method is based on the atomization of a gaseous mixture using a thermal plasma jet, which is used in the plasma spraying process, generated by arc discharge. Fig. 10 shows a schematic diagram of our system. A non-transferred thermal plasma system operated by a direct current (DC) has been laid out and manufactured to generate a thermal plasma jet. Thermal plasma of Ar (99.999%) was generated by applying a high volt-age of 3 kV between a zirconium-containing tungsten cathode and a copper anode. The created thermal plasma jet was stabilized by DC 100–300 A. This stabilized plasma jet with near sound velocity flowed into a Cu nozzle whose inner diameter was 6 mm. To enhance heat transfer between the plasma jet and reactants, hydrogen (99.99%) was used as an auxiliary gas. $Fe(CO)_5$ (Aldrich) catalyst, which was contained in a temperature-controlled bottle, was introduced into the reaction zone via bubbling with argon as a carrier gas. CO gas was used as a carbon

source. A triple calorimetric probe, which was made of Cu, was used to measure the temperature and velocity of the thermal plasma jet. The flow rates of the catalyst carrier gas and CO gas, which were controlled by mass flow controllers (DFC-4000, Flow Tech Co.), were in the range 10–50 sccm and 3–7 ksccm, respectively. A helical-type extension reactor, made of stainless steel, which had a long thin tube, was coiled on the inner surface of the chamber, and attached at the end of the plasma nozzle to increase the yield of CNTs. The soot produced was harvested through a collector as shown in fig. 10 (Hahn *et al.* 2004).
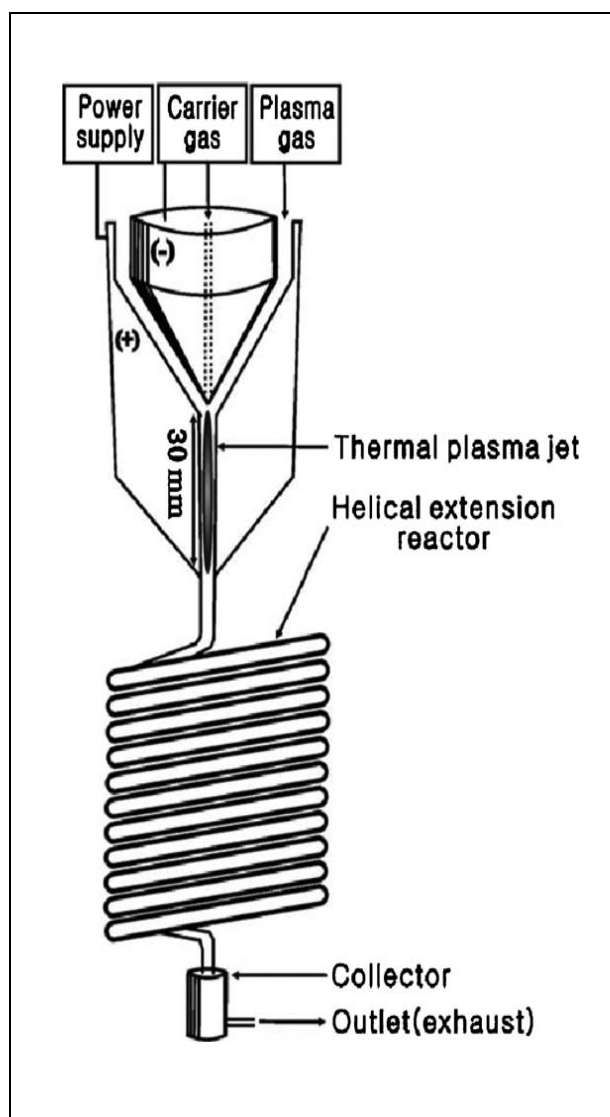

Fig. 10: A schematic of the thermal plasma system

2.11 Catalyst Vapor Deposition Method

Fig. 11 is a schematic diagram of the continuous mass production apparatus for carbon nanotubes. The carbon nanotube synthesizing system is a continuous mass synthesis system capable of achieving mass synthesis of carbon nanotubes, configured to include a number of reaction chambers in which separate synthesis steps for synthesizing carbon nanotubes are individually carried out; a heater moving around the reaction chambers while providing the temperature necessary for the synthesis reaction in the reaction chamber; and a drive motor to drive the heater along the section where the reaction chambers are arranged, such that the heater moves according to the reaction steps in the respective reaction chambers and matches the reaction temperature section to thereby continuously provide the correct reaction temperatures to the respective reaction chambers. To synthesize MWNTs, MgO/Fe/Mo mixed catalysts have been produced, using a mixture of ($Fe(NO_3)_2 \cdot 6H_2O$, purity:99%, Aldrich), Mo solution (Aldrich, ICP/DCP standard solution) and MgO powder. These catalytic materials were dissolved in alcohol for 1 hr and the Fe/Mo catalyst precursors embedded onto the MgO powder. After drying the catalysts containing solution, the mixed catalysts material was baked at 150 ºC for 10 h in a vacuum ambient and thenthe baked catalysts were ground into powder.
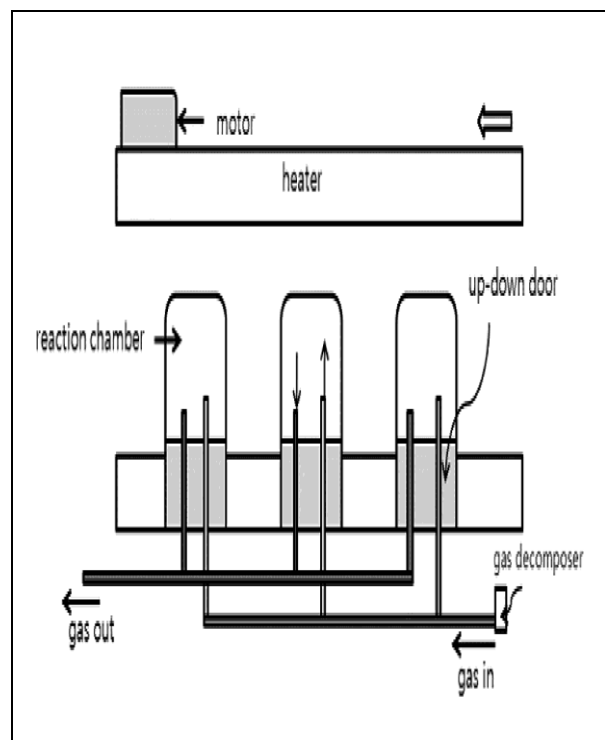

Fig. 11: Schematic showing the continuous mass production apparatus of a carbon nanotube synthesizing system

2.12 Catalytic Decomposition of a Ferrocene− xylene

Approximately 6.5 mol% of ferrocene was dissolved in xylene and was fed continuously into a two-stage tubular quartz reactor as shown in fig. 12.

Ferrocene has been shown to be a good precursor for producing Fe catalyst particles which can seed nanotube growth, and xylene was selected as the hydrocarbon source since it boils below the decomposition temperature of ferrocene Various parameters, such as the furnace temperature, ferrocene/xylene ratio and feed rate, total reaction time, and sweep gas flow rate were adjusted to determine the growth conditions for high purity aligned MWNTs (Andrews *et al.* 1999).

2.13 Spray Pyrolysis

SWCNTs were prepared by the experimental set-up shown in fig. 13. It only consisted of an electric furnace, a quartz tube (13 mm inner diameter), a sample collector and a quartz capillary used for spraying. Ferrocene was dissolved in ethanol at a given concentration. The concentration ranged from 1 g/100 ml to 1 g/800 ml. In a typical experiment, the quartz tube was flushed with Ar first in order to eliminate oxygen from the reaction chamber, and then heated to a temperature between 900 and 1150 °C.

After 15 min holding at the temperature, Ar flow was initiated at a rate of 80-120 l/hr, the alcohol solution dissolved with ferrocene was supplied by an electronic squirming pump.

2.14 Improved Floating Catalyst Method

An improved floating catalyst method was employed in which a vapor-phase catalyst was flowed into a horizontal reactor to achieve semicontinuous growth of SWNTs. The process diagram is given in fig. 14. Benzene was used as the carbon source, hydrogen as the carrier gas, and ferrocene as the catalyst precursor. To enhance the growth of SWNTs, a sulfur-containing additive (thiophene) was employed. During preparation, ferrocene was vaporized and carried into the reaction tube with a mixture of benzene and thiophene vapor, and hydrogen gas. The vaporized ferrocene was firstly reduced by hydrogen to form atomic iron, allowing atomic iron to agglomerate into iron clusters appropriate for the growth of SWNTs (Cheng *et al.* 1998).
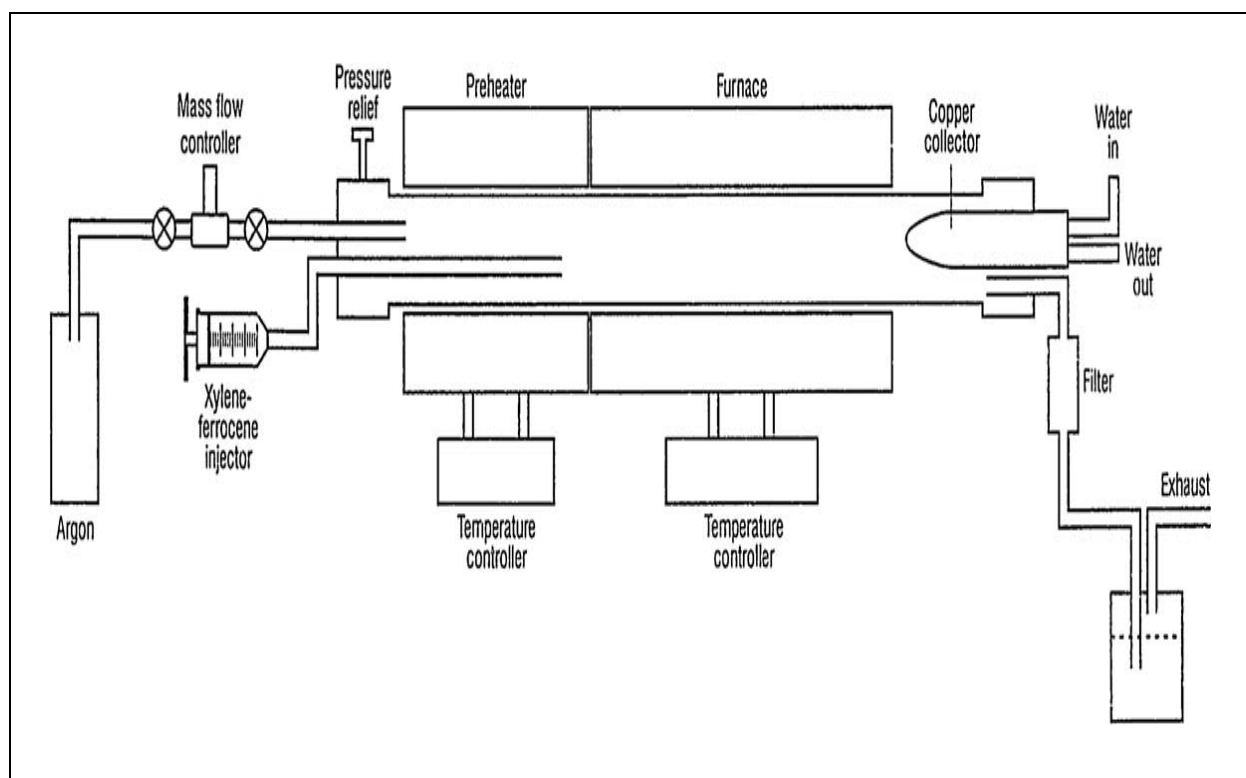

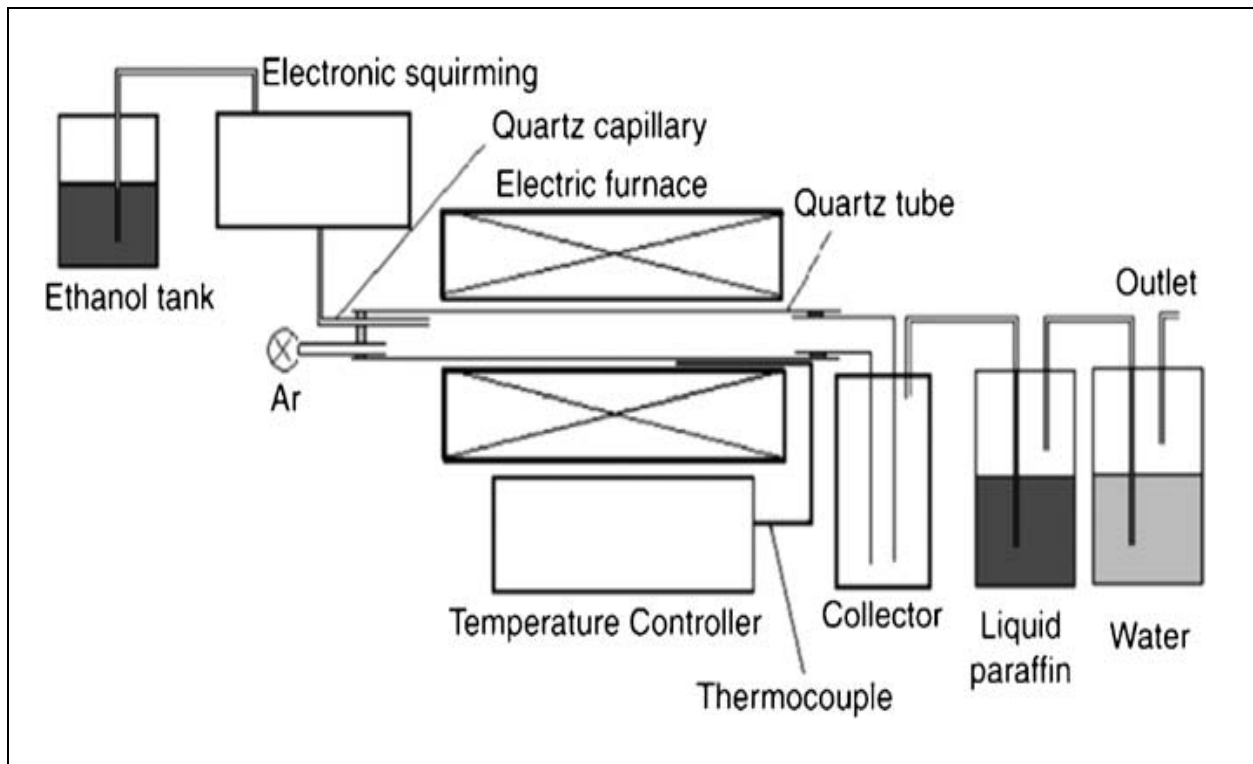**Fig. 12: Schematic of the reactor used for the nanotube synthesis**

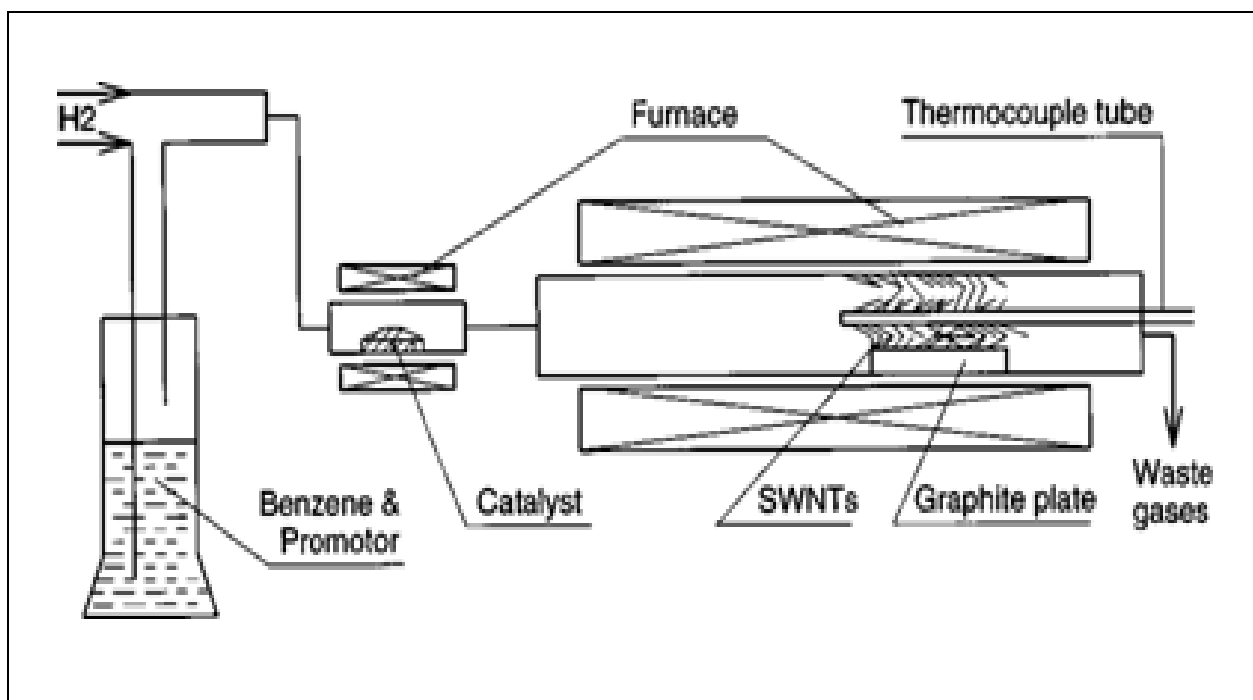**Fig. 13: Schematic illustration of the present experimental apparatus**

Fig. 14: Schematic diagram of the apparatus used for the synthesis of our SWNTs

Table 1. Comparison of the synthesis of carbon nantube from different techniques, carbon sources and catalyst

CNT type	Technique of synthesis	Carbon source	Catalyst	Reference
MWCNTs	SF CCVD	Acetylene	Ferrocene	Iyuke et al. 2009
SWCNTs	spray pyrolysis	alcohol	Ferrocene	Su et al. 2006
SWCNTs	improved floating catalyst	Benzene	Ferrocene & Thiophene	Cheng et al. 1998
MWCNTs	catalytic decomposition	xylene	Fe	Andrews et al. 1999
MWCNTs	Fixed bed CCVD	Acetylene	Co or $Fe/CaCO_3$	Couteau et al. 2003
MWCNTs	CVD	methane	$Fe/Mo/Al2O_3-SiO_2$	Cassell et al. 1999
MWCNTs	thermal plasma jet	graphite	$Fe(CO)_5$ and CO	Hahn et al. 2004
MWCNTs	water-assisted CVD	ethylene	Fe–Mo/MgO	Cheol et al. 2015
MWCNTs	Horizontal fixed bed CCVD	Ethane	Fe/Al_2O_3	Gulino et al. 2004
CNTs	fluidized bed CCVD	ethanol	$Fe-Co/Al_2O_3$	Firoozh et al. 2011
CNTs	Thermal Reduction Process	Ethanol (reductant as Mg)	-	Yitai et al. 2003
MWCNTs	Rotarytube CCVD	Acetylene	$Fe_2CO/CaCO3$	Mionic et al. 2008
MWCNTs	co-pyrolysis	Fe(CO)5 and pyridine	-	Vardhan et al. 2003
MWCNTs	AC arc in water	carbonelectrode	-	Biro et al.2003
MWCNTs	Microwave CVD	Acetylene	Co/SodiumYZeolite	Varadan et al. 2002

3. CURRENT ISSUES IN CONTINUOUS SYNTHESIS

It is obvious from the reviewed studies that catalysts are prepared separately and no purification step is taken into consideration, as the carbon products are simply collected in a collector, particularly in the case of the CVD method. The current issues of continuous synthesis reveal that bulk particle handling and its interaction with the reactor require much attention, at least for the CVD method. In the CVD method, bulk material handling is common for the process in which many problems encountered are attributed to the flow characteristic of the powders. The problem associated with this is the difficulty to differentiate CNTs from soot experimentally (Ying et al. 2011).

4. CONCLUSION

This review paper has mainly concentrated the possible routes to large scale synthesis of carbon tubes with high quality. To make sure CNTs are grown continuously, these authors have given priority to feeding and discharging mechanisms by supplying a carbon precursor, gases and a catalyst into the reaction zone. Among the catalysts, those based on Fe, Co, Ni and their alloys perform well. As carbon sources, acetylene, alcohols, methane, ethanol, ethylene, benzene and toluene are widely used. It is known that factors such as reactor design, preparation method of catalysts, catalyst category, support, catalyst additive, precursor reduction temperature, pyrolysis temperature, carbon source, additive to carbon source, and reaction time have impact on the growth of carbon nanomaterials. To achieving homogeneous carbon nanotubes, it is important that some of the basic knowledge is transferred to industry very soon so that more technologies appear commercially.

FUNDING

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

COPYRIGHT

REFERENCES

Andrews, R., Jacques, D., Rao, A. M., Derbyshire, F., Qian, D., Fan, X., Dickey, E. C. and Chen, J., Continuous production of aligned carbon nanotubes: A step closer to commercial realization, *Chem. Phys. Lett.,* 303(5-6), 467-474(1999).
https://doi.org/10.1016/S0009-2614(99)00282-1

Biro, L. P., Horvath, Z. E., Szalmas, L., Kertesz, K., Weber, F., Juhasz, G., Radnoxzi, G. and Gyulai, J., Continuous carbon nanotube production in underwater AC electric arc, *Chem. Phys. Lett*., 372(3-4), 399-402(2003).
https://doi.org/10.1155/2013/392126

Cassell, A. M., Raymakers, J. A., Kong, J., and Hongjie Dai, Large Scale CVD synthesis of single-Walled Carbon Nanotubes, *J. Phys. Chem. B*., 103(31), 6484-6492(1999).
https://doi.org/10.1021/Jp9900957s

Cheng, H. M., Li, F., Su, G., Pan, H. Y., He, L. L., Sun, X. and Dresselhaus, M. S., Large-scale and low-cost synthesis of single-walled carbon nanotubes by the catalytic pyrolysis of hydrocarbons, *Appl. Phys. Lett*., 72(25), 3282-3284(1998).
https://doi.org/10.1063/1.121624

Hahn, J., Han, J. H., Yoo, J. E., Jung, H. Y. and Suh, J. S., New continuous gas-phase synthesis of high purity carbon nanotubes by a thermal plasma jet, *Carbon*., 42(4), 877-883(2004).
https://doi.org/10.1016/J.Carbon.2004.01.073

Ishigami, M., Cumings, J., Zettl, A. and Chen, S., A simple method for the continuous production of carbon nanotubes, *Chem. Phys. Lett*., 319(5-6), 457-459(2000).
https://doi.org/S0009- 2614 00 00151-2

Sophie, L. P., Jean-Paul Pirard and Christophe Bossuot, Modeling of a continuous rotary reactor for carbon nanotube synthesis by catalytic chemical vapor deposition, *AIChE J.,* 55(3), 675-686(2009).
https://doi.org/10.1002/aic.11755

Su, L. F., Wang, J. N., Yu, F., Sheng, Z. M., Chang, H. and Pak, C., Continuous production of single-wall carbon nanotubes by spray pyrolysis of alcohol with dissolved ferrocene, *Chem. Phys. Lett.*, 420(4-6), 421- 425(2006).
https://doi.org/10.1016/j.cplett.2005.12.046

Zhao, J., Wei, L., Yang, Z. and Zhang, Y., Continuous and low-cost synthesis of high-quality multi-walled carbon nanotubes by arc discharge in air, Physica E Low Dimens. Syst. Nanostruct., 44(7-8), 1639-1634(2012).
https://doi.org/10.1016/j.physe.2012.04.010