Review of Carbon Nanotubes Growth and Synthesis

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Carbon nanotubes are tubular nanostructures derived from rolled graphene planes. Carbon nanotubes are fullerenes related structures but a fullerenes's carbon form a sphere; while a nanotubes are cylindrical. The growth mechanism of carbon nanotubes depend on the synthesis method. Carbon nanotubes were synthesized through either physical or chemical method . Physical methods discussed were arc discharge and laser ablation method. Arc method is the primary technique used to synthesize carbon nanotubes. Laser ablation is improved development of arc method leading to production of highly pure products of carbon nanotubes at lower energy consumption. However, due to high operating cost as well as low production rate has made large scale production o nanotubes using these methods difficult. Therefore, chemical method, i.e., decomposition of hydrocarbon method is believed to appear as a promising method for scalling up the production of uniform size carbon nanotubes at a relatively low cost.

Keywords: Carbon nanotubes, growth method, synthesis, methane decomposition.

1.0 INTRODUCTION

Carbon nanotubes, the hollow cylinders of graphite sheets, are named according their physical dimension which is in the range of nano scale (*nm* in diameter and *μm* length). Properties of carbon nanotubes differ by the way of rolling up the sheet of graphite into cylinders, resulting different diameter and microscopic structures of the tubes. Therefore, carbon nanotubes are valued by the chiral angle, angle of the sp^2 configuration around the tube axis, diameter of the tubes and morphology of the carbon nanotubes (Endo, et. al., 1997).

The physics of carbon nanotubes has rapidly evolved into a research field since their discovery by Iijima in multi wall form in 1991 and as single wall tubes two years later (Iijima, et.al., 1993). Since then the theoretical and experimental studies in different fields, such as electronics, optical, electronic transport, elasticity, vibration properties were studied (Saito, et. al., 1998). Besides the fundamental physical properties, studies of potential applications of carbon nanotubes have showed substantial progress in this decade (Baughman, 2003; Hoenlein, et. al., 2003). Thus, their potential as substitution material to current technologies emerged to be feasible in near future.

Comparing defect free carbon nanotubes properties to other material, their properties are really amazing that enable their applications in many advance technologies that attracted numerous researchers' interest. Carbon nanotubes density is approximately half the density of aluminium. Their tensile strength is thousand times higher than the strength of steel alloys. Also, carbon nanotubes can carry current up to thousand times capacity of copper wires. Although pure diamond is well known as good heat transmission, carbon nanotubes are predicted doubled the ability of diamond in heat transmission. Additionally, carbon nanotubes are stable up to higher temperature than metal wires in microchips (Collins, et. al., 2000, Dekker, 1999, Dresselhaus, et. al., 2000).

Believing on the carbon tubes bringing new revolution to current technologies, carbon nanotubes synthesis methodology are studied and developed over the past decade; either using physical methods such as arc discharge and laser ablation method; or chemical methods, such as hydrocarbon catalytic decomposition method or more known as chemical vapor deposition.

2.0 GROWTH MECHNISM OF CARBON NANOTUBES

The growth mechanism for cylindrical fullerene nanotubes is especially interesting. There are several proposed ideas of the growth of these amazing properties nanotubes. Firstly, carbon nanotubes are always capped and the growth mechanism involves carbon absorption process which finished by the pentagon defects on the caps. Second idea in which carbon nanotubes are always open ended during growing process by hexagon continuation on the tube side.

From Fig 1, it is clear that either carbon dimers or trimers absorbed will give hexagonal configuration which extends the open end growth of carbon nanotubes. The absorption of carbon molecules result the chirality's and physical properties of the tubes. Sequential absorption of carbon dimers gives continuous growth of chiral nanotubes. If carbon atom was added out of sequence, then addition of carbon dimers would result in the addition of pentagon, which could lead to capping of nanotubes. On the other hand, absorption of carbon trimers out of sequence merely adds a hexagon which allows continuous growth of the tubes (Dresselhaus, et. al., 2000). The chirality's of different tubes whether is an armchair or zig zag edge of the tubes depends on the initiation of growth which provides necessary edge site to complete absorption and self assembled of carbon molecule in sequence. However, the growth model for carbon nanotubes remains incomplete on the proposed fundamental physic science.

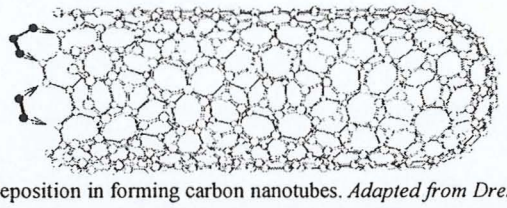

Fig 1: Carbon atom deposition in forming carbon nanotubes. *Adapted from Dresselhaus et. al. 2000.*

Researchers predicted that large scale production of single wall carbon nanotubes through the power of catalysis has no doubt in practical apprentice; but need further improvement. In this point of view, researchers believed that carbon nanotubes in situ formation is due to carbon atoms generated by dissociative chemisorption of hydrocarbon on particular edges of the metal particle diffuse to the opposite planes and crystallize there as continuous graphite-like structure as shown in Fig 2 (Ebbesen, 1997). The bonding of carbon molecules before crystallization is explained using the science of physic aforementioned which resulted in three chirality's of carbon nanotubes, namely planar, armchair and zig zag.

In short, the configuration of carbon molecules bonding in carbon nanotubes formation could be explained with the same science of physic regardless whether the carbon nanotubes is synthesized using physical methods (i.e., arc discharge and laser ablation) or chemical method (i.e., hydrocarbon catalytic decomposition). At this point, the initiation and growth mechanism of carbon nanotubes were not discussed.

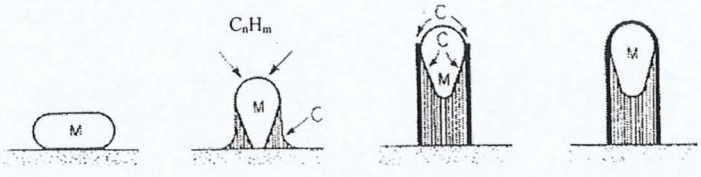

Fig 2: Carbon nanotube growth mechanism with catalyst present. *Adapted from Ebbesen, 1997*

3.0 SYNTHESIS OF CARBON NANOTUBES

Carbon nanotubes seemed to be combination of carbon fibers and fullerenes (Inagaki, et. al., 2004). Due to this reason, carbon nanotubes has such unique properties is the graphitic hexagonal network that well aligned in long axis. Several methods were developed to synthesize this material, generally with carbon source and with presence of catalysts.

3.1 PHYSICAL METHOD

3.1.1 Arc Discharge

Arc discharge method(F ig 3a) was long used to synthesize a variety of carbon materials such as carbon whiskers, soot and fullerenes. It is developed to synthesize carbon nanotubes since the last decade. The critical parameters that determine the products forming are the type and pressure of gas surrounding the arc (Dresselhaus, et. al., 2000).

In arc method, carbon atoms are evaporated by plasma of helium gas, which has high ionization potential; then ignited by high currents passed through opposing carbon anode and cathode. Good yield are obtained for pressure around 500 torr of gas helium pressure. Higher or lower pressure might change the quality of carbon nanotubes or apparently no carbon nanotubes produced. The main advantage of this method is that the macroscopic structure and the microscopic structure of the deposit are well aligned with each other corresponding to the flow of current. Because of this reason, arc method was also claimed to be the best method in synthesizing single wall carbon nanotubes with well controlled quality, i.e., length and diameter. Bethune and coworkers uses carbon anode containing a small percentage of cobalt catalyst to synthesize abundance of single wall carbon nanotubes in soot material (Bethune et. al., 1993).

However, this method operates at high temperature, which approaches 3700°C. Also, the shape and structure of the deposit depend on many factors, including cooling of the electrode, current flowing, pressure of the surrounding gas and distance of both the electrodes. In addition, besides nanotubes and nanoparticles, there are always lots of sheet like carbonaceous materials in the deposit. Yield of carbon nanotubes from arc method is another challenge before this method could be practical method in synthesizing well tailored carbon nanotubes.

3.1.2 Laser Ablation

Smalley and coworkers modified arc method and developed laser ablation method (Thess, et. al., 1996). This method utilized intense laser pulses to ablate a carbon target containing catalyst under high temperature. Similar to arc method, carbon target was surrounded by inert gas (Fig 3b). Differs from arc method is that this inert gas does not affect the structure of carbon nanotubes synthesized, but act as a carrier of the carbon deposit synthesized to the effluent stream. Also, temperature needed in laser ablation is lower than arc method, i.e., 1200°C. However, in both arc discharge and laser ablation, single wall nanotubes growth parallel with fullerenes, graphitic polyhedrons and amorphous carbon in the form of particles or on the sidewalls of nanotubes (Dresselhaus, et. al., 2000).

There is another method which is seldom mentioned in literature, i.e., carbon vapor method. This method was used to produce carbon whiskers developed by Cuomo and Harper. In this method, carbon was vaporized in vacuum using electron beam or by heating. After crystallization, various structure of carbon was observed, including carbon nanotubes. However, intensive study is needed in order to investigate suitability of this simple method to synthesize bulk quantity of well graphitized carbon nanotubes.

In short, all these methods involve condensation of carbon atoms generated from evaporation of solid carbon sources; and the temperatures involved in these methods are close to the melting temperature of graphite, 3000 – 4000 °C (Dresselhaus, et. al., 2000). Thus, high production cost and low production rate has made large scale production of carbon nanotubes difficult through these physical methods.

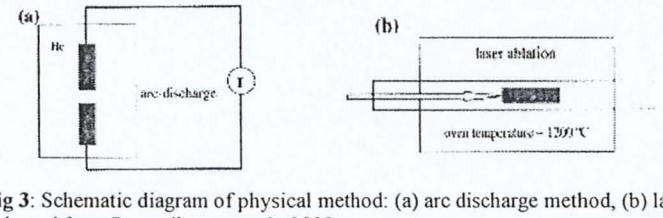

Fig 3: Schematic diagram of physical method: (a) arc discharge method, (b) laser ablation method. *Adapted from Dresselhaus, et. al., 2000.*

3.2 CHEMICAL METHOD

The general description of chemical method (Fig 4) is dissociation of gaseous hydrocarbon molecules catalyzed by transition metal, and dissolution and saturation of carbon atoms on metal nanoparticles in sp^2 of hexagonal axis that the length increases with time of reaction and forms carbon nanotubes and also gaseous by-product (Ebbesen, et. al., 1997).

3.2.1 Catalytic Decomposition of Hydrocarbon

Catalytic decomposition of hydrocarbon can be defined as chemical reaction that breaks larger molecules into smaller molecules with the assistance of catalyst. It consists of reaction using several carbon feed stocks such as methane, benzene, acetylene, carbon monoxide, ethylene to produce simpler molecules.

Hydrocarbon decomposition or more known as chemical vapor deposition method which is the first developed chemical method to synthesize carbon nanotubes employ gaseous and liquid phase hydrocarbon such as methane, ethylene, acetylene, benzene, etc., as carbon feedstock and reaction temperature is in the range 550 to 950°C with presence of catalyst such as iron, nickel or cobalt metal precursor. In chemical vapor deposition, carbon feedstock is vaporized into gaseous phase if it was in liquid phase at room temperature. Gaseous feedstock than passed through gaseous metal precursor, decomposed and forms carbon nanotubes and gaseous by-product at effluent stream.Transition metal, such as iron, nickel and cobalt were used, similar to arc discharge and laser ablation methods in synthesizing single wall carbon nanotubes. This simply showed that both physical and chemical method share the common single wall carbon nanotubes growth mechanism, although very different approach to provide carbon feedstock were used.

In chemical vapor deposition, carbon feedstock and metal precursor were evaporated in gaseous phase during reaction. Therefore, it is possible to synthesize nanotubes at uniform diameter because by evaporation of metal precursor, reaction was catalyzed by metal precursor nanoparticles at the uniform atomic size. Moreover, the temperature needed in vapor deposition method is much lower than physical methods. However, chemical vapor deposition does not provide vaporized carbon feedstock sufficient thermal energy and support to anneal nanotubes into crystalline structure like in physical methods. Thus, it was not easy task to control the growth of carbon nanotubes. However, Rice University in Houston has developed scalable production techniques, which yield highly aligned, continuous macroscopic fibers, composed solely of single-wall carbon nanotubes using chemical method and projected to yield kilograms of carbon nanotubes in 2005 (Houston, et. al., 2004).

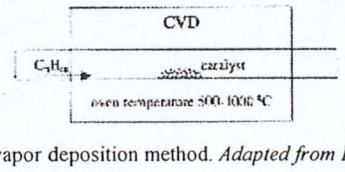

Fig 4: Schematic diagram of vapor deposition method. *Adapted from Dresselhaus et. al. 2000.*

As a conclusion, carbon nanotubes synthesized can be categorized into two main groups (Inagaki, et. al., 2004):

a. Carbons produced by vaporization of carbon clusters or fragments.
b. Carbons produced by catalytic effects of nano-sized metallic particles.

4.0 METHANE DECOMPOSITION

In our work, natural gas which is abundance in Malaysia was selected as the carbon source. Natural gas contains up to 90% of methane, which is the most stable hydrocarbon at high temperature against self decomposition was alternative in synthesizing carbon nanotubes today (Zein, et. al., 2004_a). Therefore, researcher believed catalytic decomposition of methane by transition metal catalyst particles can be dominant process

in carbon nanotubes growth. The choice of hydrocarbon feedstock is thus one of the key elements to the growth of high quality single wall carbon nanotubes containing no amorphous and soot particle (Qian, et. al., 2004). Methane, the simplest hydrocarbon form, react with present of transition metal nanoparticle gives carbon nanotubes and also pure hydrogen as by-product (Piao, et. al., 2002, Zein, et. al., 2004_b).

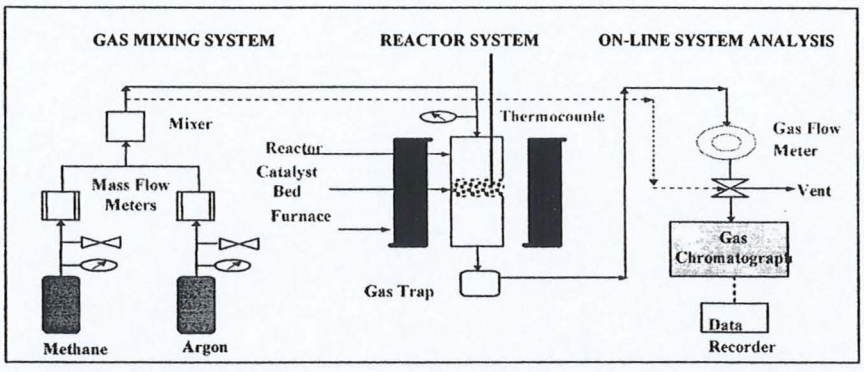

Fig. 5: Schematic diagram of methane decomposition fixed bed reactor system. *Adapted from Zein, et. al., 2004_b.*

In general, methane decomposition happen in fixed bed reactor where methane was passed through fixed bed of transition metal catalyst at temperature higher than 550°C (Qian, et. al., 2003). At the effluent stream, high purity hydrogen gas was analyzed (Zein, 2003; Takaneka, et. al., 2003); whereas, carbon nanotubes deposited on catalyst bed. For safety reason, inert gas at defined ratio of methane fed into reactor. Fig 5 shows a typical fixed bed reactor system for methane decomposition at laboratory scale.

Methane decomposition process is promising for enabling scale up of defect free nanotubes material to kilogram level. With designed supported catalyst of Titanate supported Nickel nanoparticles (Fig 6), well graphitized carbon nanotubes were produced without amorphous and soot material (Fig 7). Catalyst design is important in methane decomposition reaction in controlling the diameter of carbon nanotubes produced. Whereas, type of transition metal and supportive material used in catalyst synthesis are important in obtaining higher yield of carbon nanotubes from single step reaction of methane decomposition (Ermakova, et. al., 2001; Takaneka, et. al., 2003;).

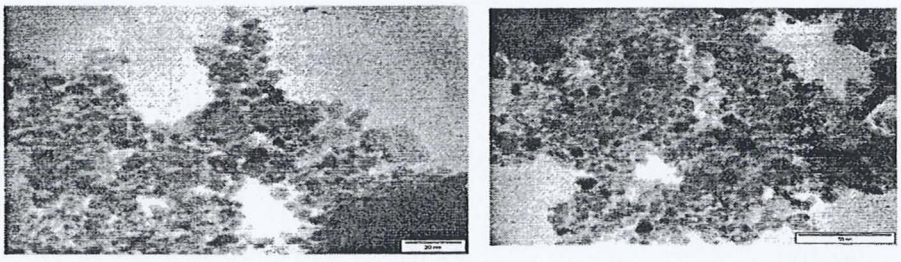

Fig 6: TEM images of Titanate supported Nickel nanoparticles (size ranged from 25 -40 nm) were used to synthesize carbon nanotubes in methane decomposition.

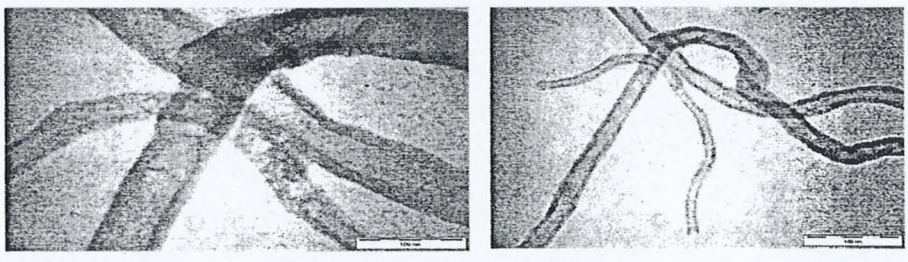

Fig 7: TEM images of carbon nanotubes (diameter ranged from 30-50 nm) synthesized using Ni/TiO_2 nanoparticles shown in Fig 6.

5.0 CONCLUDING REMARKS

The challenge in carbon nanotubes synthesis development remains. An efficient growth approach to structurally perfect nanotubes at large scales is still lacking. Besides, growing defect-free carbon nanotubes continuously to macroscopic lengths has been difficult. In addition, control over carbon nanotubes growth on surfaces should be gained. Lastly, it is a formidable task of controlling the chirality of single wall carbon nanotubes by any existing growth methods. With these achieved, it can be vision that in future, controlled growth carbon nanotubes will allow carbon nanotubes be used as key components in electronic, mechanical, chemical, biochemical and electromagnetic devices upon the next revolution of its technology.

With the application of carbon nanotubes in batteries and flat panel by Samsung Advance Institute of Technology today, it is practical to project that progress in carbon nanotubes synthesis has been built upon the success in materials synthesis. It is an ultimate goal to gain control over the carbon nanotubes growth in diameter and be able to direct the growth at any desire length. Such control need detail studies on the controlling parameters, and once successful, is going to contribute toward the technology in carbon nanotubes synthesis.

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