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STUDY ON SYNTHESIS OF CARBON NANOTUBES

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ABSTRACT

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. These cylindrical carbon molecules have unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology. Owing to the material's exceptional strength and stiffness, nanotubes have been constructed with length-to-diameter ratio of up to 132,000,000:1, significantly larger than for any other material. In this paper we study about the different methods of synthesis of carbon nanotubes.

Keywords: Carbon Nanotubes, Synthesis, Nanostructure.

I INTRODUCTION

There have been numerous reviews on the synthesis of carbon nanotubes, which are members of the fullerene family.[1–4] Since their discovery, carbon nanotubes have been of great interest, both for the elucidation of fundamental one-dimensional science and for a wide variety of potential applications. Though Iijima was credited for recognizing carbon nanotubes in 1991,[5] the first nanotubes were produced much earlier, possibly as a result of Roger Bacon's work studying carbon whiskers in 1960[6]. Nanotubes were probably first observed directly by Endo in the 1970s via high-resolution transmission electron microscopy (HRTEM) when he was exploring the production of carbon fibers by pyrolysis of benzene and ferrocene at 1000˚C,[7,8] and Tibbetts also imaged some nanotube-like material in 1984[9]. However, Iijima was first to recognize that nanotubes were made up of concentric rolled graphene sheets with a large number of potential helicities and chiralities, rather than a graphene sheet rolled up like a scroll, as originally proposed by Bacon. Some common methods of synthesis are:

1. Arc Discharge
2. Laser Ablation
3. Thermal
4. Plasma Enhanced

1.0 Methods of Synthesis

1.1 Arc Discharge

Arc discharge was the first recognized method for producing both SWCNTs and MWCNTs, and has been optimized to be able to produce gram quantities of either. Arc discharge synthesis uses a low-voltage (~12 to 25

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V), high-current (50 to 120 amps) power supply (an arc welder can be used). An arc is produced across a 1-mm gap between two graphite electrodes 5 to 20 mm in diameter. An inert gas such as He or Ar is used as the atmosphere for the reaction, at a pressure of 100 to 1000 torr. Iijima produced the first MWCNTs by this method.5 He found that nanotubes formed on the cathode, along with soot and fullerenes. Iijima and Ichihashi and Bethune et al. were the first to report on the production of SWCNTs.[10,11] Both Iijima and Bethune found that SWCNTs could only form by adding metal catalyst to the anode; specifically, Iijima used an Fe:C anode in a methane:argon environment, while Bethune utilized a Co:C anode with a He environment. There are several variations one can make to tailor the arc discharge process. Currently, most growth is carried out in an Ar:He gas mixture. By tailoring the Ar:He gas ratio, the diameter of the SWCNTs formed can be controlled, with greater Ar yielding smaller diameters.[12]

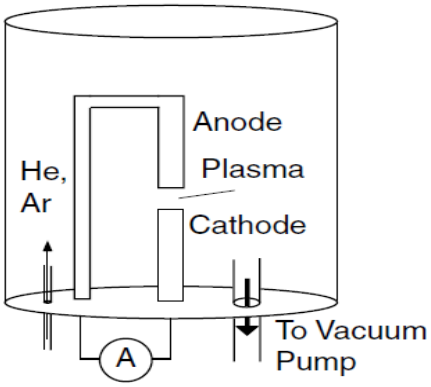

Figure 1 Schematic of an Arc Discharge Chamber

1.2 Laser Ablation

The laser ablation technique uses a 1.2 at. % of cobalt/nickel with 98.8 at.% of graphite composite target that is placed in a 1200˚C quartz tube furnace with an inert atmosphere of ~500 Torr of Ar or He and vaporized with a laser pulse. A pulsed- or continuous-wave laser can be used. Nanometer-size metal catalyst particles are formed in the plume of vaporized graphite. The metal particles catalyze the growth of SWCNTs in the plasma plume, but many by-products are formed at the same time. The nanotubes and by-products are collected via condensation on a cold finger downstream from the target. The by-products of this synthesis are graphitic and amorphous carbon, "bucky onions" (concentric fulleriod spheres) surrounding metal catalyst particles and small fullerenes (C60, C70, etc.).

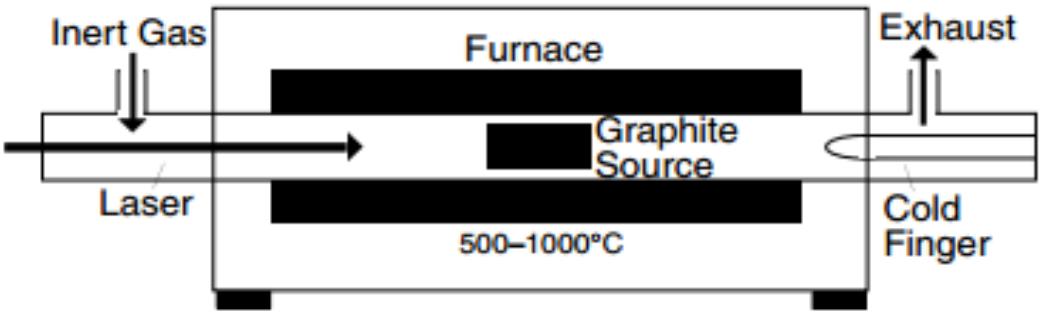

Figure 2 Schematic of a Laser Ablation Furnace

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1.3 Thermal Synthesis

Thermal synthesis is considered a "medium temperature" method, since the hot zone of the reaction never reaches above 1200˚C. Fundamentally different from plasma-based synthesis, thermal synthesis relies on only thermal energy and, in almost all cases, on active catalytic species such as Fe, Ni, and Co to break down carbon feedstock and produce CNTs. Depending on the carbon feedstock, Mo and Ru are sometimes added as promoters to render the feedstock more active for the formation of CNTs. CVD, HiPco, and flame synthesis are considered thermal CNT synthesis methods.

1.3.1 Chemical vapor deposition

The CVD process encompasses a wide range of synthesis techniques, from the gram-quantity bulk formation of nanotube material to the formation of individual aligned SWCNTs on SiO_2 substrates for use in electronics. CVD can also produce aligned vertical MWCNTs for use as high-performance field emitters.[13] Additionally, CVD in its various forms produces SWCNT material of higher atomic quality and higher percent yield than the other methods currently available and, as such, represents a significant advance in SWCNT production. The majority of SWCNT production methods developed lately have been direct descendents of basic CVD. Simply put, gaseous carbon feedstock is flowed over transition metal nanoparticles at medium to high temperature (550 to 1200˚C) and reacts with the nanoparticles to produce SWCNTs.

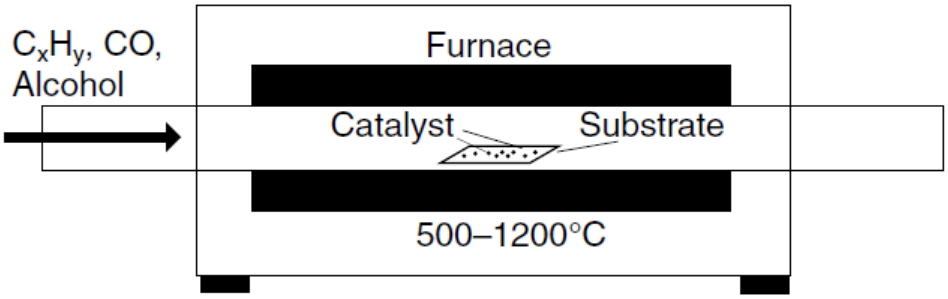

Figure 3 Schematic of a CVD Furnace.

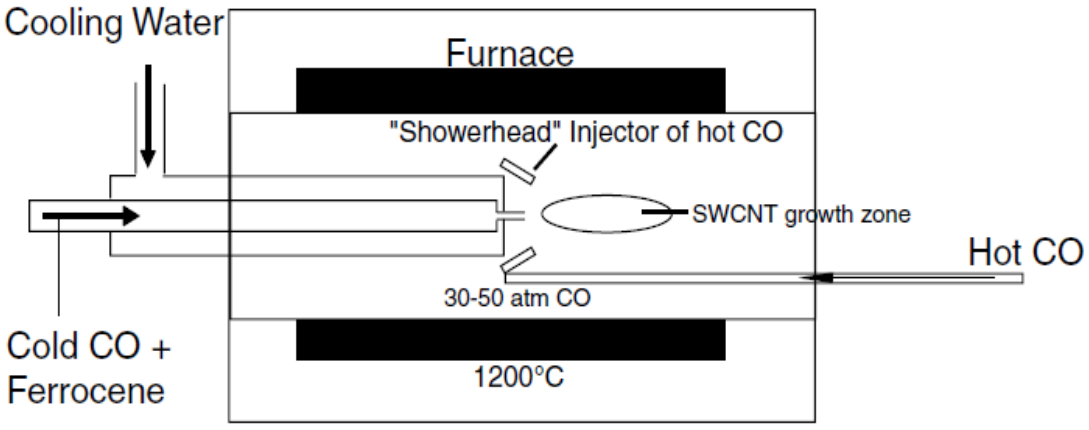

Figure 4 Schematic of a HiPco furnace

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The CO gas + catalyst precursor is injected cold into the hot zone of the furnace, while excess CO gas is "showered" on it from all sides. Empirically this leads to the highest yield and longest individual nanotubes formed by this process.

1.3.2 High-pressure carbon monoxide synthesis

Though related to CVD synthesis, HiPco deserves a separate mention, since in recent years it has become a source of high-quality, narrow-diameter distribution SWCNTs around the world. The metal catalyst is formed in situ when $Fe(CO)_5$ or $Ni(CO)_4$ is injected into the reactor along with a stream of carbon monoxide (CO) gas at 900 to 1100˚C and at a pressure of 30 to 50 atm. The reaction to make SWCNTs is the disproportionation of CO by nanometer-size metal catalyst particles. Yields of SWCNT material are claimed to be up to 97% atomic purity. The SWCNTs made by this process have diameters between 0.7 and 1.1 nm. By tuning the pressure in the reactor and the catalyst composition, it is possible to tune the diameter range of the nanotubes produced.[14]

1.3.3 Flame synthesis

Though still not a viable method for the production of high-quality SWCNTs, so-called flame synthesis has the potential to become an extremely cheap and simple way to produce nanotubes. Flames have been shown to produce MWCNTs since the early 1990s.[15] The current yields are low, but it is extremely attractive and potentially very cheap to be able to produce nanotubes with technology no more complicated than fire.

1.4 PECVD synthesis

Plasma-enhanced chemical vapor deposition (PECVD) systems have been used to produce both SWCNTs and MWCNTs. PECVD is a general term, encompassing several differing synthesis methods. Direct PECVD systems can be used for the production of MWCNT field emitter towers [16] and some SWCNTs [17]. A remote PECVD can also be used to produce both MWCNTs and SWCNTs [18]. For SWCNT synthesis in the direct PECVD system, the researchers heated the substrate up to 550 to 850˚C, utilized a CH4/H2 gas mixture at 500 mT, and applied 900 W of plasma power as well as an externally applied magnetic field. The remote PECVD system utilized by Li et al. used CH4/Ar held at 500 mT, with only 50 to 75 W of plasma power.[18] To grow

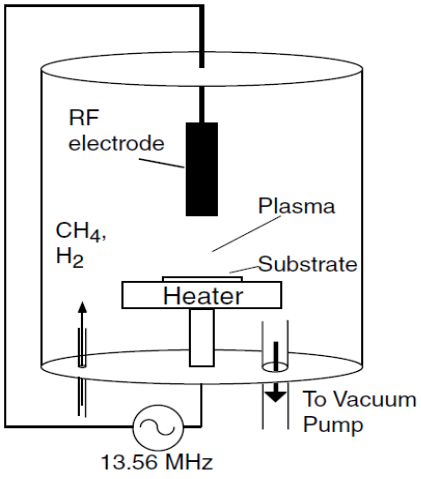

Figure 5 Schematic of a direct radiofrequency PECVD system.

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SWCNT by hot-wire CVD (HWCVD), hydrocarbons with dissolved Fe-containing molecules are passed over an extremely hot filament near the furnace entrance to facilitate a plasma-induced breakdown of hydrocarbons and nucleation of nanotube growth. By initiating growth in the vapor phase, a substrate can be placed downstream in a cooler area of the furnace (~450˚C) so that the nanotubes can deposit from the vapor phase onto the substrate.[19] This is useful because by lowering the substrate temperature, the variety of substrates on which SWCNTs can be synthesized is widened.

II CONCLUSION

Although the growth mechanism of CNTs is not exactly known, new synthesis methods for higher yield, higher purity and low defects of produced CNTs are main points of investigation which are pushed forward by the prospering fields of nanotechnology and nanoscience that have many ideas of possible applications.In this paper, We have presented the different synthesis methods for CNTs preparation including arc discharge, laser ablation and CVD and some new approaches of synthesis regarding the various CNTs types, namely MWNTs, SWNTs and DWNTs. . We anticipate that synthesizing method will produce cheap CNTs and as a result allow industrial applications based on CNTs to flourish

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