Synthesis of Carbon Nanotubes

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This handout briefly summarizes the production methods of carbon nanotubes.

1. Introduction

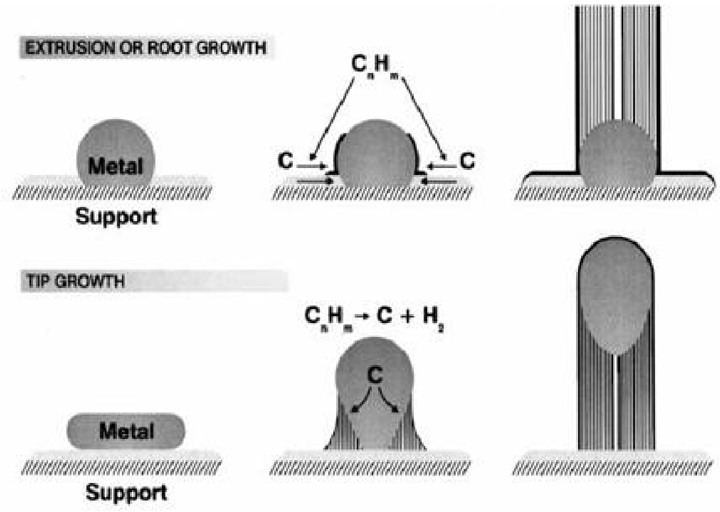
Carbon nanostructures like fullerenes, graphene and nanotubes are of great interest for the current research as well as for future industrial applications. The reason for this is that the band gap of single-walled carbon nanotubes (SWNTs) can vary from zero to about 2 eV and hence their electrical conductivity can be the one of a metal or the semiconductor. Moreover, the carbon nanotubes market is steadily growing and thus effective and cheap solutions for the production of high quality carbon nanotubes are needed. To the best of my knowledge, the main focus in the current research lays on exploring the effective production methods for single-walled carbon nanotubes (SWNTs) because of their unique physical and chemical properties and hence their potential electronic application.

This handout presents different synthesis methods like arc discharge (AD), laser ablation, chemical vapour deposition (CVD) as well as some of the more recent methods working with high pressure of the carbon monoxide or some unique catalytic mixture. The production methods are explained and their advantages and disadvantages examined. The actual production of carbon nanotubes contains the following steps: synthesis, purification, inspection and packaging. Although this handout concentrates on the synthesis, the other factors should not be completely neglected as they contribute significantly to the production costs.

2. Growth Mechanism

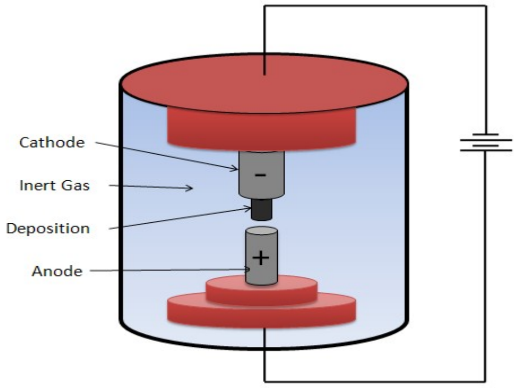
To begin with, I shortly explain the general growth mechanism of carbon nanotubes that is basically common for different growth methods.

First of all, the exact way in which nanotubes are formed is not completely understood. One distinguishes between extrusion or tip-growth, and base-growth, which are both a three-step process. As schematically sketched in Fig.1, first, a round or pear-shaped precursor for the formation of nanotubes is formed on the surface of the metal catalyst. Second, the carbon diffuses on the sides of the precursor leaving, however, the top of it free – that is the reason for the hollow core of the

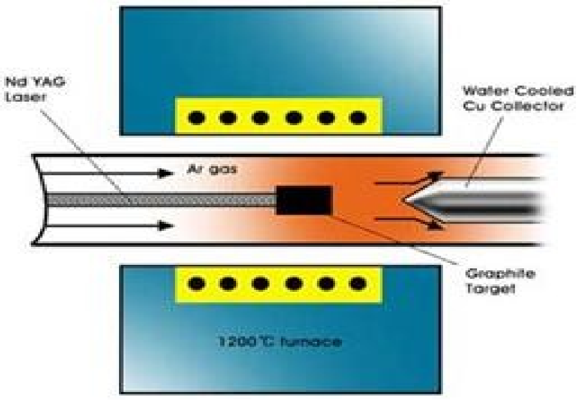


[Fig.1: http://students.chem.tue.nl/ifp03/synthesis.html] nanotube. Out of this a rod-like carbon structure is formed. By the base growth (extrusion) the nanotube grows upwards from the metal particle that remains attached to the substrate. By the tip growth the particle detaches and stays on the top of the growing nanotube. Depending on the size of the catalyst particles, single-walled or multi-walled nanotubes are grown.

3. Arc Discharge and Laser Ablation



[Fig.2: http://students.chem.tue.nl/ifp03/synthesis.html]



[Fig.3:http://students.chem.tue.nl/ifp03/synthesis.html]

The two methods that are schematically sketched in Fig.2 and Fig.3 share some similarities both in their working principle and in the pros and cons of the production.

During the arc discharge, that for the carbon nanotubes was firstly used by Sumio Iijima in 1991 [1], two graphite rods are placed in an enclosure that is filled with some inert gas (like helium or argon) at low pressure (between 50 and 700 mbar). The carbon rods act as electrodes which are kept at different potentials. The anode is moved close to the cathode until an arc appears and the electrodes are kept at the distance of 1 mm for the whole duration of the process that takes about one minute. After the de-pressurisation and cooling of the chamber the nanotubes together with the by-products, can be collected. Most nanotubes deposit on the cathode.

The synthesis product yield which represents the amount of carbon nanotubes expected in the converted carbon is 60% [2].

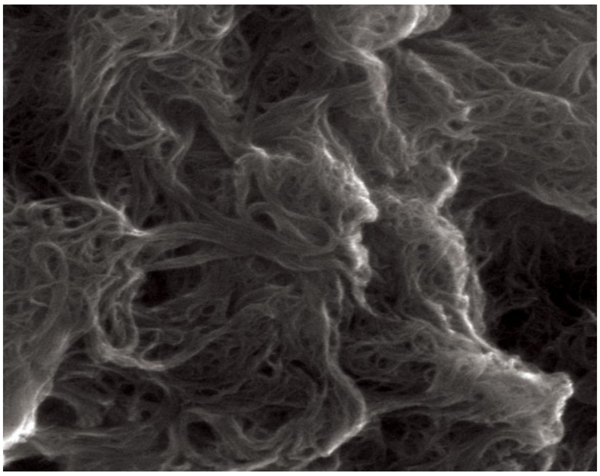
In 1995 Richard E. Smalley and his group used for the first time laser ablation to grow high quality nanotubes. Intense laser pulses ablate a carbon target which is placed in a tube-furnace (see Fig. 3) heated to 1200°C [3]. During the process some inert gas like helium or argon flows through the chamber to carry the grown nanotubes to the copper collector. After the cooling of the chamber the nanotubes and the by-products, like fullerenes and amorphous carbon over-coating on the sidewalls of nanotubes can be collected.

The use of pure carbon leads for both methods to the synthesis of multi-walled nanotubes and the addition of a catalyst like iron, yttrium, sulphur, nickel and molybdenum leads to the formation of the single-walled carbon nanotubes [4].

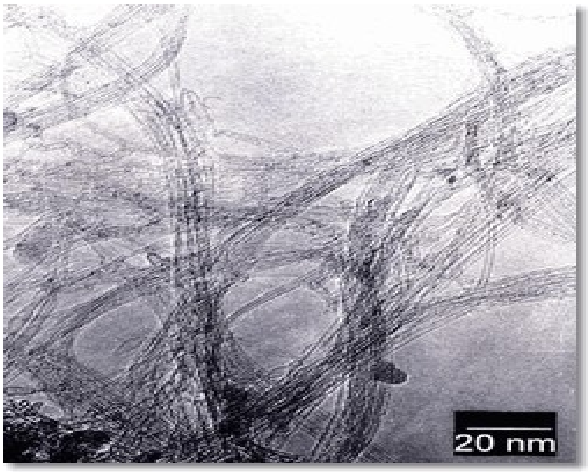
As the temperatures involved in these methods are very high, e.g. up to 4000°C for the arc discharge [5], approximately 28% of the carbon anode evaporates [2].

Nowadays these methods are almost not used any more for the synthesis. The reasons for it are: the very high temperatures involved, the consequent evaporation of the carbon source, the highly tangled, and disordered nanotubes resulting. Moreover, no structure, pattering or substrate growth is possible; due to the short process times only synthesis of the short nanotubes is possible. In addition to that, the amount of the purification needed is very high. In order to address this issues other methods were developed.

4. HiPco and CoMoCat



[Fig.4: http://www.nanointegris.com/en/hipco]



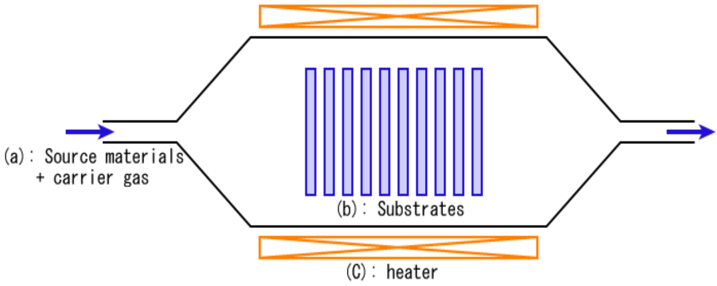
http://www.ou.edu/engineering/nanotube/comocat.htm

In 1999 Richard E. Smalley and his co-workers developed a high pressure carbon monoxide method called HiPco for the synthesis of carbon nanotubes [6]. In this process in the continuous-flow gas phase carbon monoxide acts as a feedstock and iron carbon monoxide Fe(CO)5 as a catalyst. With the HiPco method the thinnest single-walled carbon nanotubes of very high quality, few structural defects, and high intrinsic selectivity were achieved [7].
The purity of the created product or the synthesis product yield is as high as 97% and the purification yield is 90% [2]. HiPco process runs continuously and allows the reuse of carbon monoxide [2]. It produces continuously single-walled carbon nanotubes at a rate of 0.45 g/h [6].

In 2000 Kitiyanan proposed another method named after the unique catalyst mixture of cobalt and molybdenum used, CoMoCat [8]. During this process carbon monoxide decomposes under the temperatures between 700°C and 950°C into simple carbon and carbon dioxide. The special strong point of this method is that it inhibits the formation of the by-products that appear quite numerous in the arc discharge and laser ablation methods.

5. Chemical Vapour Deposition

The catalytic chemical vapour deposition of carbon was reported already in 1959 [9] , but only in 1993 carbon nanotubes were formed in this way [10]. During CVD, a substrate covered with metal catalysts, like nickel, cobalt, iron, or a combination is heated to approximately 700°C [11]. The growth starts after two gases are passed through the chamber, a carrier gas like nitrogen, hydrogen or argon, and some hydrocarbon gas like acetylene (C2H2) or methane (CH4). The synthesis production yield, which indicates the amount of carbon nanotubes in the converted carbon, reaches 90% [2]. CVD is commonly used for the industrial purposes because the method is already well investigated and offers acceptable results on the industrial-scale.



http://en.wikipedia.org/wiki/Chemical_vapor_deposition

6. New Direction in the Chemical Vapour Deposition

As for the fact that CVD is such a promising method for the production of carbon nanotubes, there is an ongoing research in this field. Some new methods were developed and some of them will be briefly presented in this chapter.

CVD-method allows the pretreatment of the substrate surface which can lead to impressive, controlled multi-walled and single-walled nanotubes architectures [12]. Multi-walled nanotubes self-assemble into aligned structures because of the Van der Waals interaction between the single tubes. The substrates are catalytically patterned by the photolitography which enables selective deposition of the catalyst and consequently selective and controlled growth of carbon nanotubes. During CVD growth, the outer walls of the tubes interact with their neighbours via van der Waals forces, forming a rigid bundle which grows perpendicularly to the substrate [13, 14].

In 2004 Sumio Iijima introduced another modification, the super-growth CVD or water-assisted CVD [15]. Here, the activity and lifetime of the catalyst are enhanced by addition of water into the CVD reactor. With this method dense, well-aligned "forests", perpendicular to the substrate with heights up to 2.5 mm can be produced [11].

With the low temperature CVD that was firstly reported in 2006 tungsten filament increases the decomposition of the precursor gases. Single-walled nanotubes were observed at temperatures as low as 350°C [15].

In 2007 a high-efficiency CVD-method based on hydrocarbon gas camphor (C10H16O) [16] was demonstrated. This technique promises to be especially environment-friendly.

7. Conclusion

This handout presented different production methods of carbon nanotubes. Nowadays mostly used on industrial-scale techniques are chemical vapour deposition with its various modifications as well as HiPco-process that can continuously produce tiny, high-quality nanotubes. The nanotubes produced with CoMoCat and HiPco method are mostly used for scientific purposes. In June 2009 calculated manufacturing costs from cost models gives total manufacturing costs for arc, CVD and HiPco of $1,906/g, $1,706/g, and $485/g, respectively [2]. Prices per gram on the open market vary strongly not only by different fabrication methods, but also by the purification percentage. These prices (September 2008) vary from about $30/g for CVD with about 60% purity to $7000/g with more than 99% purity [2].

8. Bibliography

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