In the name of God

The Wondrous World of Carbon Nanotubes

‘a review of current carbon nanotube technologies’

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Thermal chemical vapour deposition

- In this method Fe, Ni, Co or an alloy of the three catalytic metals is initially deposited on a substrate. After the substrate is etched in a diluted HF solution with distilled water, the specimen is placed in a quartz boat.
- The boat is positioned in a CVD reaction furnace, and nanometre-sized catalytic metal particles are formed after an additional etching of the catalytic metal film using NH3 gas at a temperature of 750 to 1050^{o} C.
- As carbon nanotubes are grown on these fine catalytic metal particles in CVD synthesis, forming these fine catalytic metal particles is the most important process.
- Figure 2-14 shows a schematic diagram of thermal CVD apparatus in the synthesis of carbon nanotubes.

Thermal chemical vapour deposition

When growing carbon nanotubes on a Fe catalytic film by thermal CVD, the diameter range of the carbon nanotubes depends on the thickness of the catalytic film.
By using a thickness of 13 nm, the diameter distribution lies between 30 and 40 nm.
When a thickness of 27 nm is used, the diameter range is between 100 and 200 nm.
The carbon nanotubes formed are multiwalled

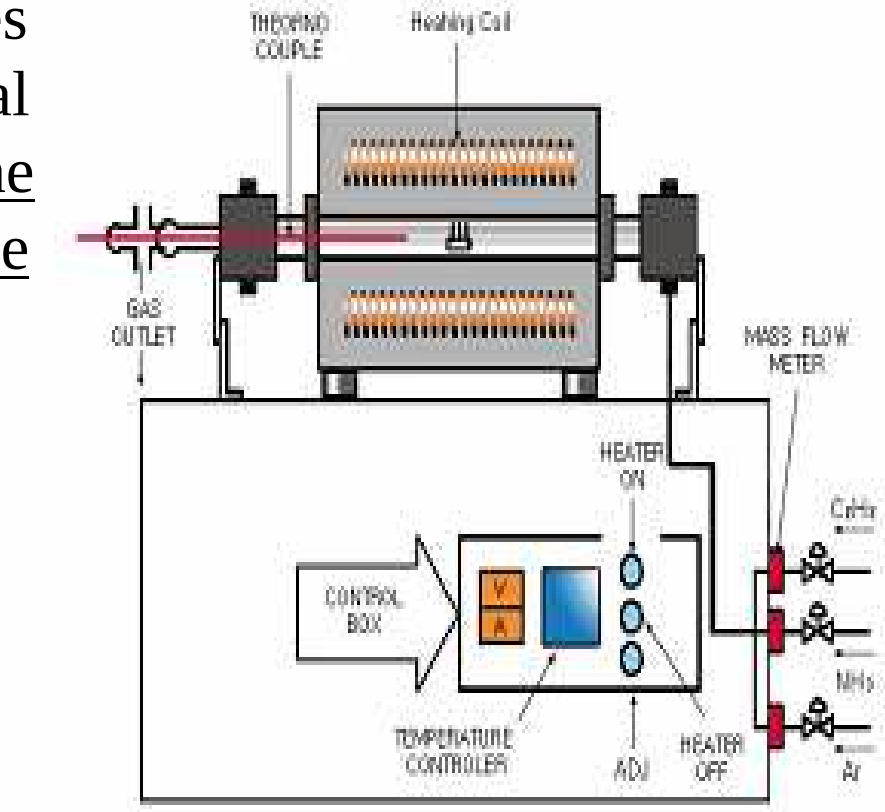

Figure 2-14: Schematic diagram of thermal CVD apparatus.

Alcohol catalytic chemical vapour deposition

- Alcohol catalytic CVD (ACCVD) is a technique that is being intensively developed for the possibility of large-scale production of high quality single wall nanotubes SWNTs at low cost.
- In this technique, evaporated alcohols, methanol and ethanol, are being utilised over iron and cobalt catalytic metal particles supported with zeolite.
- Generation is possible at a relatively low minimum temperature of about 550 ^{o} C.
- It seems that hydroxyl radicals, who come from reacting alcohol on catalytic metal particles, remove carbon atoms with dangling bonds, which are obstacles in creating high-purity SWNTs.
- The diameter of the SWNTs is about 1 nm.
- Figure 2-15 shows the ACCVD experimental apparatus.

Alcohol catalytic chemical vapour deposition

The lower reaction temperature and the high-purity features of this ACCVD technique guarantee an easy possibility to scale production up at low cost. Furthermore, the reaction temperature, which is lower than 600 °C, ensures that this technique is easily applicable for the direct growth of SWNTs on semiconductor devices already patterned with aluminium

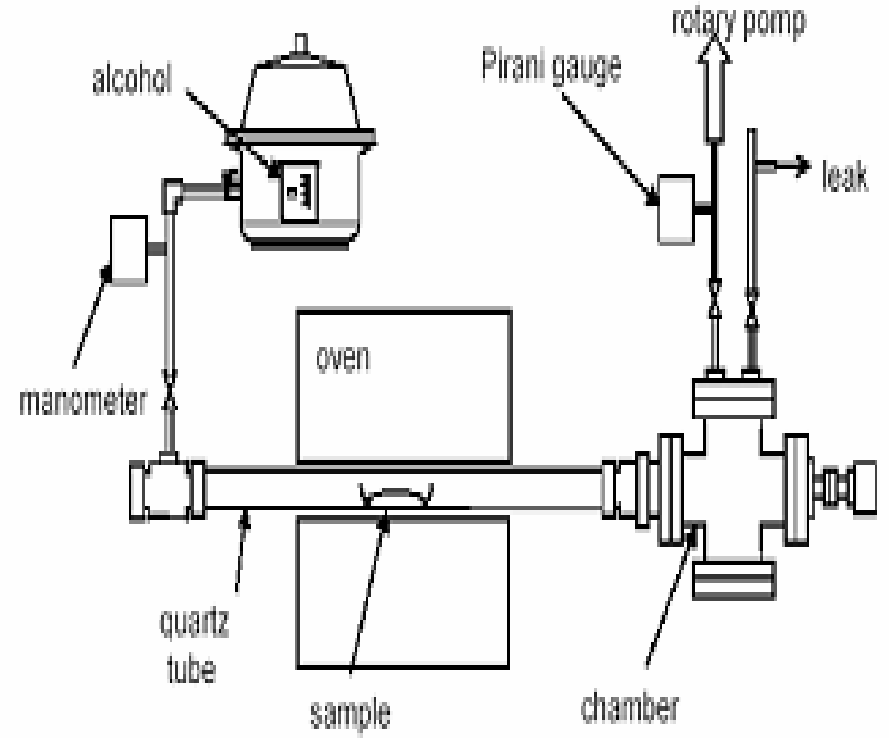

Figure 2-15: ACCVD experimental apparatus

Vapour phase growth

- Vapour phase growth is a synthesis method of carbon nanotubes, directly supplying reaction gas and catalytic metal in the chamber without a substrate.
- Figure 2-16 shows a schematic diagram of a vapour phase growth apparatus.
- Two furnaces are placed in the reaction chamber.
- Ferrocene is used as catalyst.
- In the first furnace, vaporisation of catalytic carbon is maintained at a relatively low temperature. Fine catalytic particles are formed and when they reach the second furnace, decomposed carbons are absorbed and diffused to the catalytic metal particles. Here, they are synthesised as carbon nanotubes.
- The diameter of the carbon nanotubes by using vapour phase growth are in the range of 2 – 4 nm for SWNTs and 40 and between 70 and 100 nm for MWNTs.

Vapour phase growth

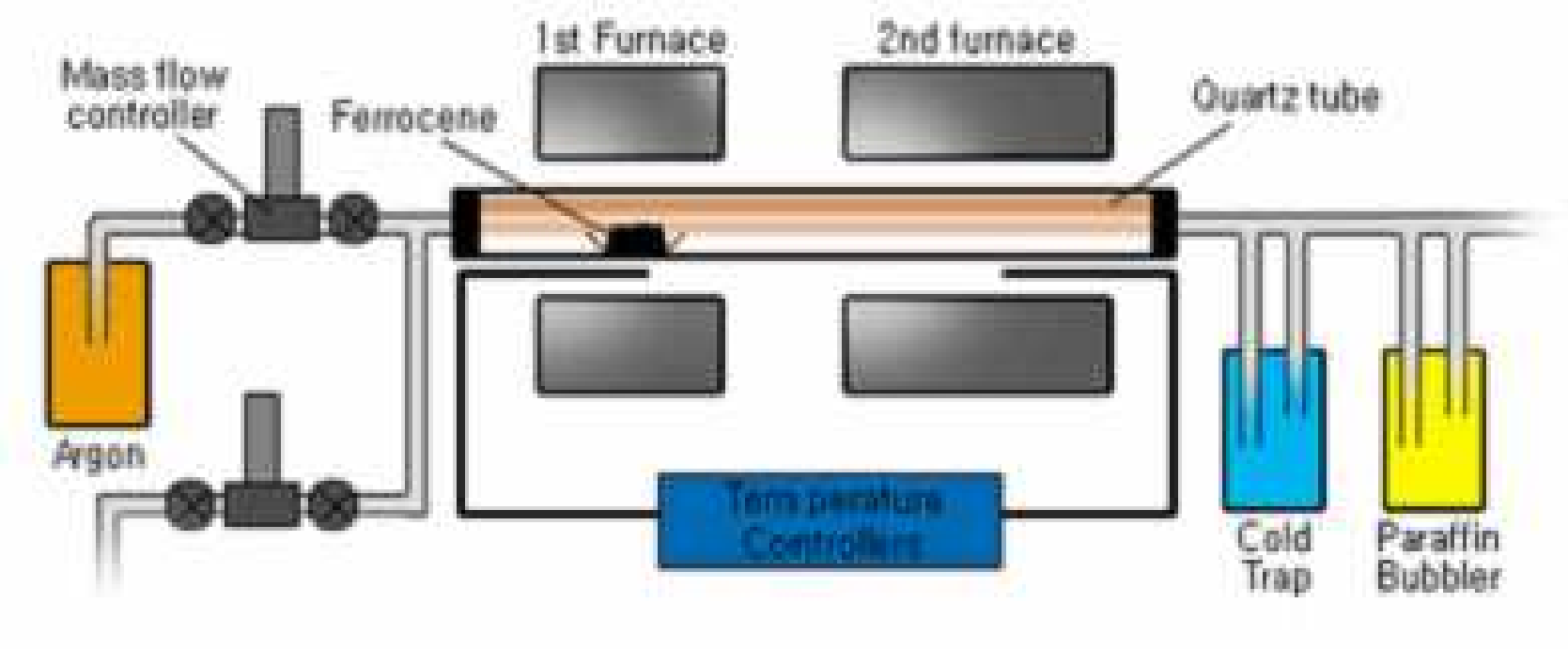

Figure 2-16: Schematic diagram of a vapour phase growth apparatus.

Aero gel-supported chemical vapour deposition

- In this method SWNTs are synthesised by disintegration of carbon monoxide on an aero gel-supported Fe/Mo catalyst.
- There are many important factors that affect the yield and quality of SWNTs, including the surface area of the supporting material, reaction temperature and feeding gas. Because of the high surface area, the porosity and ultra-light density of the aero gels, the productivity of the catalyst is much higher than in other methods. After a simple acidic treatment and a oxidation process high purity (>99%) SWNTs can be obtained. When using CO as feeding gas the yield of the nanotubes is lower but the overall purity of the materials is very good. The diameter distribution of the nanotubes is between 1.0 nm and 1.5 nm. The optimal reaction temperature is approximately 860 ^{o}C.

Laser-assisted thermal chemical vapour deposition

- In laser-assisted thermal CVD (LCVD) a medium power, continuous wave CO_2 laser, which was perpendicularly directed onto a substrate, pyrolyses synsitised mixtures of $Fe(CO)_5$ vapour and acetylene in a flow reactor.
- The carbon nanotubes are formed by the catalysing action of the very small iron particles. Figure 2-17 shows the experimental set-up for laser-assisted CVD.
- By using a reactant gas mixture of iron pentacarbonyl vapour, ethylene and acetylene both single- and multi-walled carbon nanotubes are produced. Silica is used as substrate.
- The diameters of the SWNTs range from 0.7 to 2.5 nm. The diameter range of the MWNTs is 30 to 80 nm.

Laser-assisted thermal chemical vapour deposition

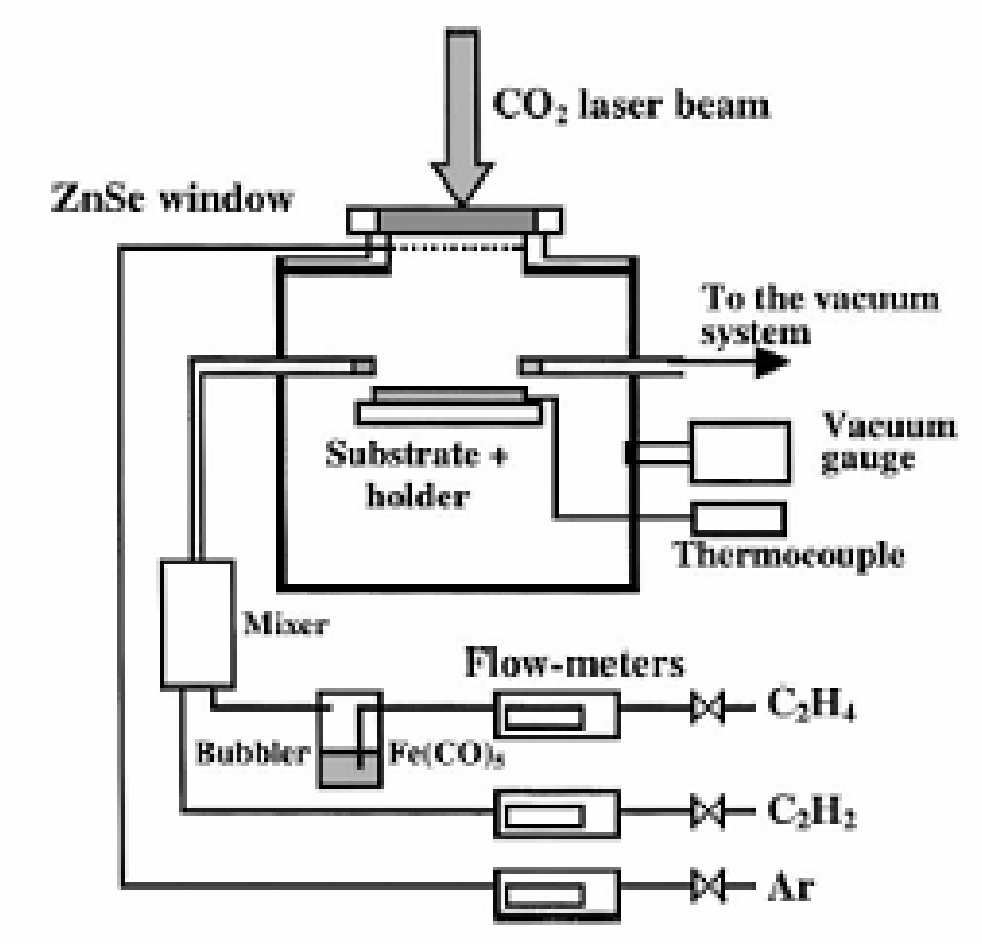

Figure 2-17: Experimental set-up for laser-assisted CVD

CoMoCat process

- In this method, SWNTs are grown by CO disproportionation at 700 – 950 ^{o}C. The technique is based on a unique Co-Mo catalyst formulation that inhibits the sintering of Co particles and therefore inhibits the formation of undesired forms of carbon that lower the selectivity.
- During the SWNT reaction, cobalt is progressively reduced from the oxidic state to the metallic form. Simultaneously Molybdenum is converted to the carbidic form (Mo_2C). Co acts as the active species in the activation of CO, while the role of the Mo is possibly dual. It would stabilise Co as a well-dispersed Co2+ avoiding its reduction and would act as a carbon sink to moderate the growth of carbon inhibiting the formation of undesirable forms of carbon. It is found that one of the critical conditions for an effective reactor operation is that the space velocity has to be high enough to keep the CO conversion as low as possible.

CoMoCat process

- Figure 2-18 shows a fluidised bed reactor for a CoMoCat process. The most important advantage of fluidised bed reactors is that they permit continuous addition and removal of solid particles from the reactor, without stopping the operation.

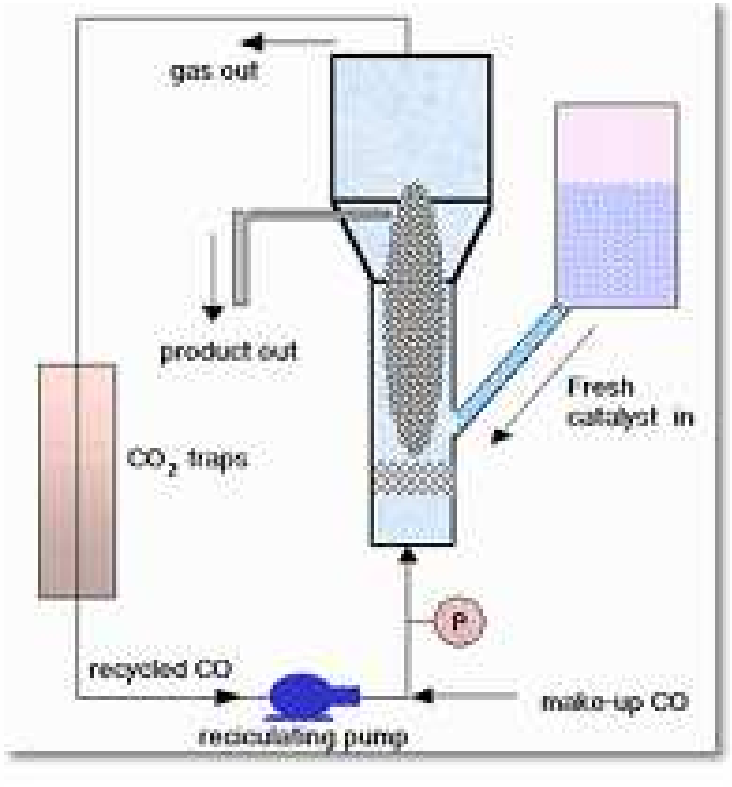

Figure 2-18: Schematic diagram of a CoMoCat apparatus

CoMoCat process

- This method can be scaled-up without losses in SWNT quality. By varying the operation conditions, SWNTs can be produced with different diameter ranges. In Table 2-1 several diameter ranges at different temperatures are given.
- The CoMoCat catalyst has a high selectivity towards SWNTs, namely 80 – 90 %.

Table 2-1: Diameter range versus temperature

Temperature (°C)	*Diameter range*
750	0.9 ± 0.05
850	0.9 – 1.25
950	1.00 – 1.40

High pressure CO disproportionation process

- The High pressure CO disproportionation process (HiPco) is a technique for catalytic production of SWNTs in a continuous-flow gas phase using CO as the carbon feedstock and $Fe(CO)_5$ as the iron-containing catalyst precursor.
- SWNTs are produced by flowing CO, mixed with a small amount of $Fe(CO)_5$ through a heated reactor.
- Figure 2-19 shows the layout of CO flow-tube reactor.
- Size and diameter distribution of the nanotubes can be roughly selected by controlling the pressure of CO. This process is promising for bulk production of carbon nanotubes.

High pressure CO disproportionation process

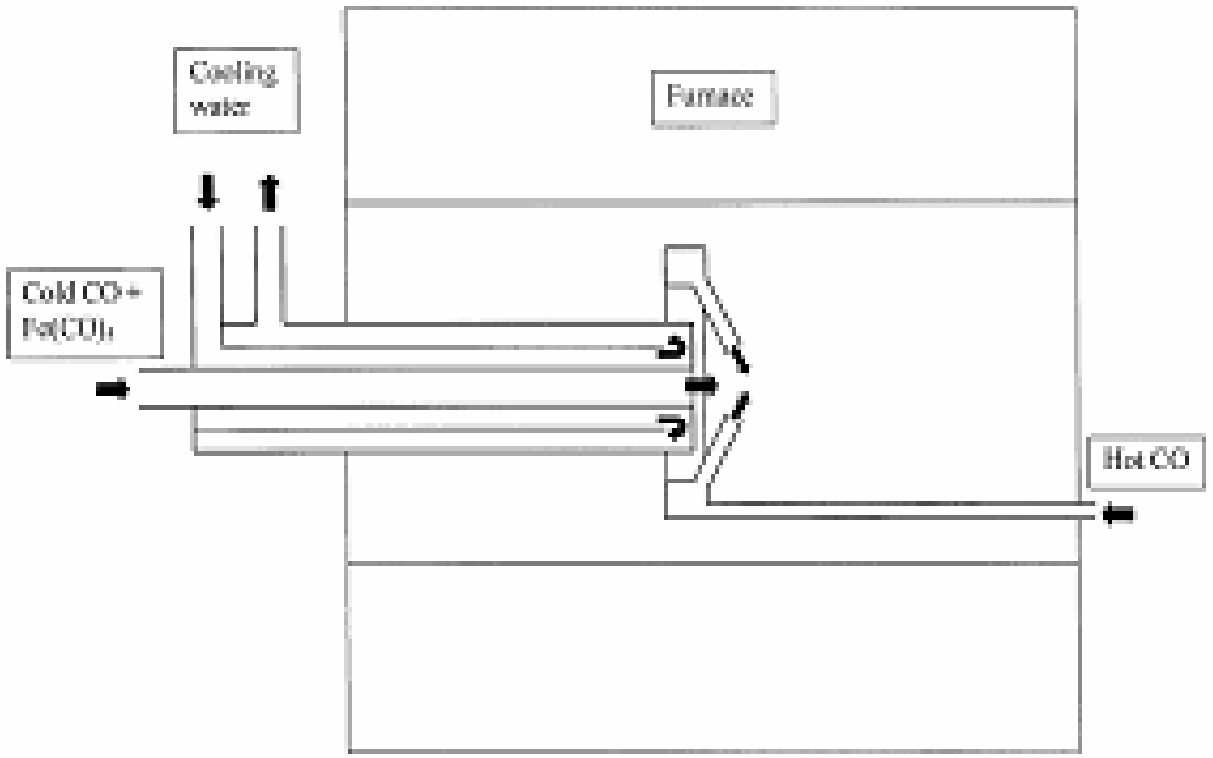

Figure 2-19: Layout of CO flow-tube reactor

High pressure CO disproportionation process

- Nanotubes as small as 0.7 nm in diameter, which are expected to be the smallest achievable chemically stable SWNTs, have been produced by this method.
- The average diameter of HiPco SWNTs is approximately 1.1 nm.
- The yield that could be achieved is approximately 70%. The highest yields and narrowest tubes can be produced at the highest accessible temperature and pressure SWNT material with 97% purity can be produced at rates of up to 450 mg/h with this process.

Flame synthesis

- This method is based on the synthesis of SWNTs in a controlled flame environment, that produces the temperature, forms the carbon atoms from the inexpensive hydrocarbon fuels and forms small aerosol metal catalyst islands. SWNTs are grown on these metal islands in the same manner as in laser ablation and arc discharge.

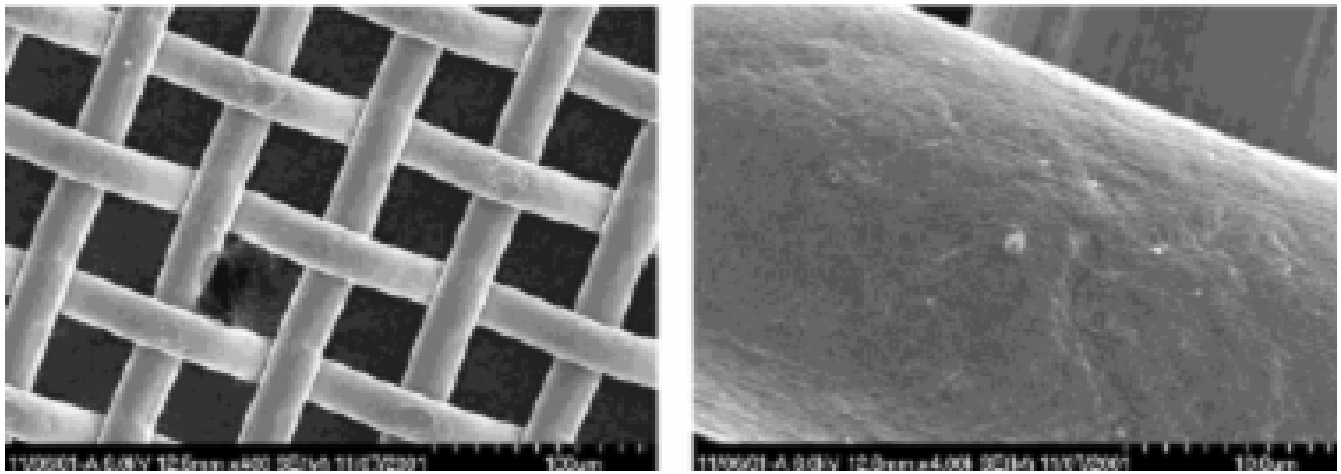

Figure 1.1 Meshes on which the metal catalyst is coated, used in flame synthesis

Flame synthesis

- These metal catalyst islands can be made in three ways. The metal catalyst (cobalt) can either be coated on a mesh, on which metal islands resembling droplets were formed by physical vapour deposition. These small islands become aerosol after exposure to a flame.
- The second way, is to create aerosol small metal particles by burning a filter paper that is rinsed with a metal-ion (e.g. iron nitrate) solution.
- The third way, is the thermal evaporating technique in which metal powder (e.g. Fe or Ni) is inserted in a trough and heated.
- In a controlled way a fuel gas is partially burned to gain the right temperature of ~800 °C and the carbon atoms for SWNT production. On the small metal particles the SWNTs are than formed.
- As optimisation parameters the fuel gas composition, catalyst, catalyst carrier surface and temperature can be controlled. In the literature found, the yield, typical length and diameters are not stated.

Summary

Method	Arc discharge method	Chemical vapour deposition	Laser ablation (vaporization)
Who	Ebbesen and Ajayan, NEC, Japan 1992 [15]	Endo, Shinshu University, Nagano, Japan [53]	Smalley, Rice, 1995 [14]
How	Connect two graphite rods to a power supply, place them a few millimetres apart, and throw the switch. At 100 amps, carbon vaporises and forms a hot plasma.	Place substrate in oven, heat to 600 °C, and slowly add a carbon-bearing gas such as methane. As gas decomposes it frees up carbon atoms, which recombine in the form of NTs	Blast graphite with intense laser pulses; use the laser pulses rather than electricity to generate carbon gas from which the NTs form; try various conditions until hit on one that produces prodigious amounts of SWNTs
Typical yield	30 to 90%	20 to 100 %	Up to 70%
SWNT	Short tubes with diameters of 0.6 - 1.4 nm	Long tubes with diameters ranging from 0.6-4 nm	Long bundles of tubes (5-20 microns), with individual diameter from 1-2 nm.
MWNT	Short tubes with inner diameter of 1-3 nm and outer diameter of approximately 10 nm	Long tubes with diameter ranging from 10-240 nm	Not very much interest in this technique, as it is too expensive, but MWNT synthesis is possible.
Pro	Can easily produce SWNT, MWNTs. SWNTs have few structural defects; MWNTs without catalyst, not too expensive, open air synthesis possible	Easiest to scale up to industrial production; long length, simple process, SWNT diameter controllable, quite pure	Primarily SWNTs, with good diameter control and few defects. The reaction product is quite pure.
Con	Tubes tend to be short with random sizes and directions; often needs a lot of purification	NTs are usually MWNTs and often riddled with defects	Costly technique, because it requires expensive lasers and high power requirement, but is improving

Table 2-2: A summary of the major production methods and their efficiency

Purification of Carbon nanotubes

- A large problem with nanotube application is next to large scale synthesis also the purification.
- The as-produced SWNT soot contains a lot of impurities. The main impurities in the soot are graphite (wrapped up) sheets, amorphous carbon, metal catalyst and the smaller fullerenes. These impurities will interfere with most of the desired properties of the SWNTs. Also in the fundamental research, it is preferred to obtain SWNTs or the impurities, as pure as possible without changing them.
- In order to understand the measurements better, the SWNT samples also have to be as homogeneous as possible.
- The common industrial techniques use strong oxidation and acid refluxing techniques, which have an effect on the structure of the tubes.

Purification Techniques

1-Oxidation:

- Oxidative treatment of the SWNTs is a good way to remove carbonaceous impurities or to clear the metal surface.
- The main disadvantages of oxidation are that not only the impurities are oxidised, but also the SWNTs.
- The damage to SWNTs is less than the damage to the impurities. These impurities have relatively more defects or a more open structure. Another reason why impurity oxidation is preferred, is that these impurities are most commonly attached to the metal catalyst, which also acts as oxidising catalyst.

- Altogether, the efficiency and the yield of the procedure are highly dependable on a lot of factors, such as metal content, oxidation time, environment, oxidising agent and temperature.
- The fact that metal acts as oxidising catalyst, the metal content should certainly be taken into consideration, when looking at the oxidising time.
- For example, when the temperature is raised above 600°C, SWNTs will also oxidise, even without catalyst. This is the case with thermal, fixed air and pure oxygen oxidations. These can easily oxidise all the components, so the temperature and the time should be in good control.

2-Acid treatment

- In general the acid treatment will remove the metal catalyst. First of all, the surface of the metal must be exposed by oxidation or sonication. The metal catalyst is then exposed to acid and solvated. The SWNTs remain in suspended form.
- When using a treatment in HNO_3, the acid only has an effect on the metal catalyst. It has no effect on the SWNTs and other carbon particles .
- If a treatment in HCl is used, the acid has also a little effect on the SWNTs and other carbon particles.
- The mild acid treatment (4 M HCl reflux) is basically the same as the HNO_3 reflux, but here the metal has to be totally exposed to the acid to solvate it.

3- Annealing

- Due to high temperatures (873 – 1873 K) the nanotubes will be rearranged and defects will be consumed .
- The high temperature also causes the graphitic carbon and the short fullerenes to pyrolyse. When using high temperature vacuum treatment (1873 K) the metal will be melted and can also be removed.

- **4- Ultrasonication**:
- In this technique particles are separated due to ultrasonic vibrations. Agglomerates of different nanoparticles will be forced to vibrate and will become more dispersed.
- The separation of the particles is highly dependable on the surfactant, solvent and reagent used.
- The solvent influences the stability of the dispersed tubes in the system. In poor solvents the SWNTs are more stable if they are still attached to the metal. But in some solvents, such as alcohols, mono dispersed particles are relatively stable.
- When an acid is used, the purity of the SWNTs depends on the exposure time. When the tubes are exposed to the acid for a short time, only the metal solvates, but for a longer exposure time, the tubes will also be chemically cut.

5- Magnetic Purification

- In this method ferromagnetic (catalytic) particles are mechanically removed from their graphitic shells. The SWNTs suspension is mixed with inorganic nanoparticles (mainly ZrO_2 or $CaCO_3$) in an ultrasonic bath to remove the ferromagnetic particles. Then, the particles are trapped with permanent magnetic poles. After a subsequent chemical treatment, a high purity SWNT material will be obtained. Figure 3-1 shows a schematic diagram of the apparatus for magnetic purification.

This process does not require large equipment and enables the production of laboratory-sized quantities of SWNTs containing no magnetic impurities.

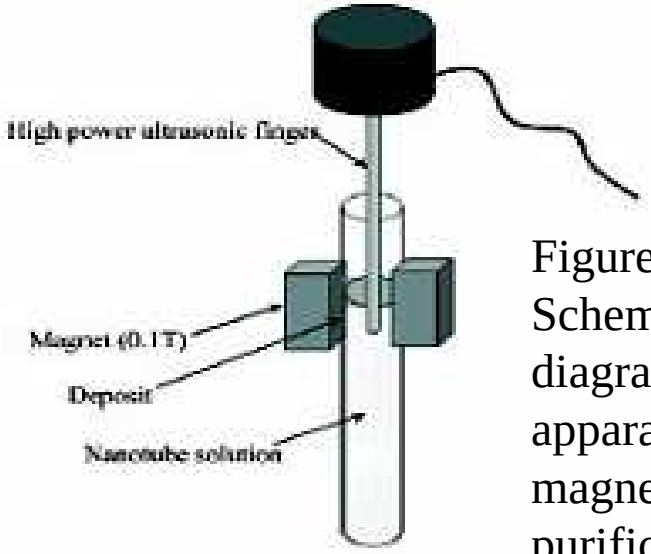

Figure 3-1: Schematic diagram of the apparatus for magnetic purification

- **6- Micro filtration:**
- Micro filtration is based on size or particle separation.
- SWNTs and a small amount of carbon nanoparticles are trapped in a filter. The other nanoparticles (catalyst metal, fullerenes and carbon nanoparticles) are passing through the filter.
- Figure 3-2 shows a schematic diagram of a micro filtration cell.
- One way of separating fullerenes from the SWNTs by micro filtration is to soak the as-produced SWNTs first in a CS_2 solution. The CS2 insolubles are then trapped in a filter. The fullerenes which are solvated in the CS_2, pass through the filter.

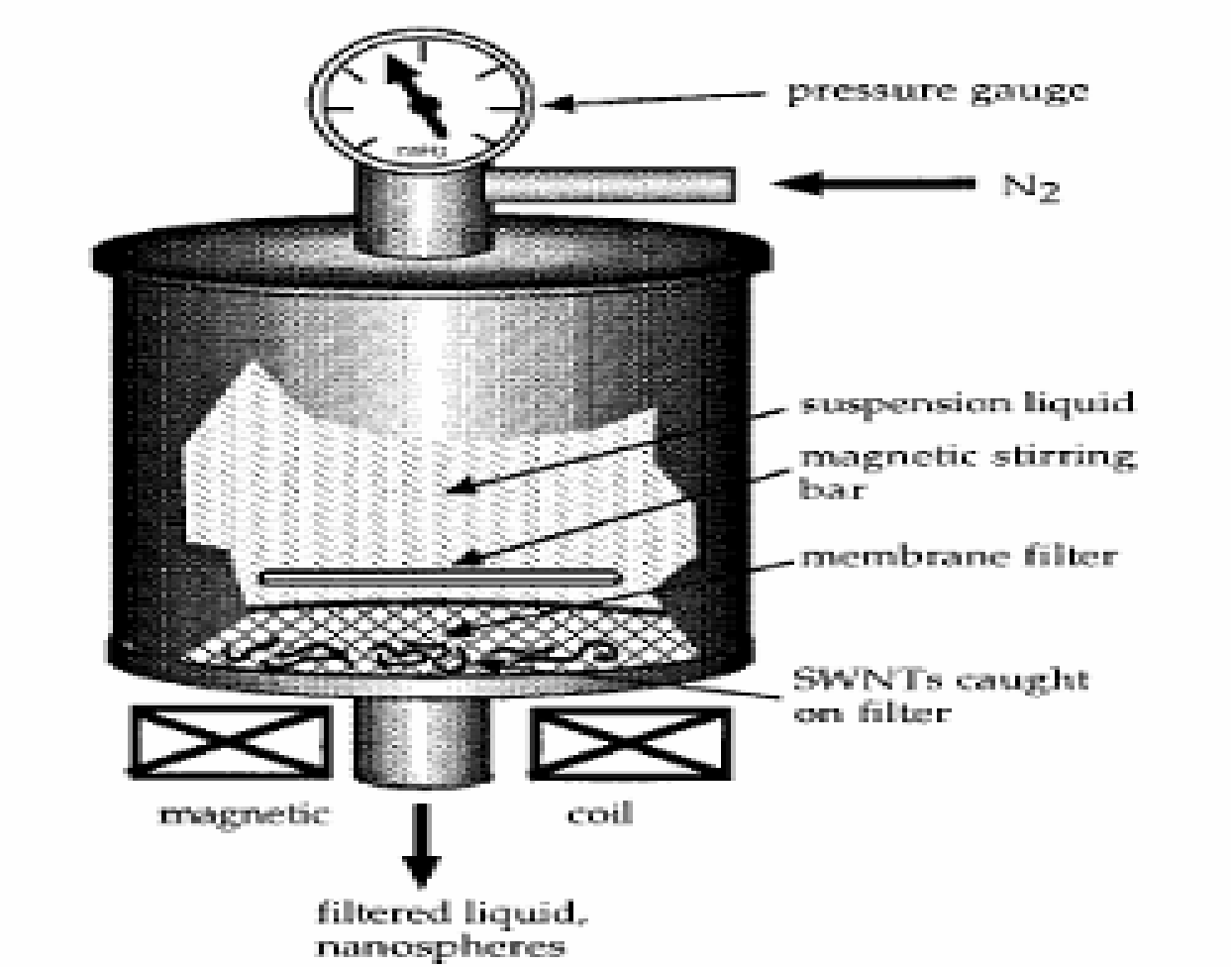

Figure 3-2: Schematic diagram of a micro filtration cell

- **9- Chromatography**
- This technique is mainly used to separate small quantities of SWNTs into fractions with small length and diameter distribution.
- The SWNTs are run over a column with a porous material, through which the SWNTs will flow. The columns used are GPC (Gel Permeation Chromatography) and HPLC-SEC (High Performance Liquid Chromatography - Size Exclusion Chromatography) columns. The number of pores the SWNTs will flow through, depends on their size.
- This means that, the smaller the molecule, the longer the pathway to the end of the column will be and that the larger molecules will come off first.
- The pore size will control what size distribution can be separated. However, a problem is that the SWNTs have to be either dispersed or solvated. This can be done by ultrasonicationor functionalisation with soluble groups.