In the Name of God

The Wondrous World of Carbon Nanotubes

‘a review of current carbon nanotube technologies’

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Synthesis using arc discharge method

- Synthesis of MWNT using arc discharge:
- If both electrodes are graphite, the main product will be MWNTs. But next to MWNTs a lot of side products are formed such as fullerenes, amorphous carbon, and some graphite sheets.
- Purifying the MWNTs, means loss of structure and disorders the walls. However scientist are developing ways to gain pure MWNTs in a large-scale process without purification.
- Typical sizes for MWNTs are an inner diameter of 1-3 nm and an outer diameter of approximately 10 nm.
- Because no catalyst is involved in this process, there is no need for a heavy acidic purification step. This means, the MWNT, can be synthesised with a low amount of defects.

Synthesis in liquid nitrogen

- A first, possibly economical route to highly crystalline MWNTs is the arc-discharge method in liquid nitrogen, with this route mass production is also possible. For this option low pressures and expensive inert gasses are not needed.

The content of the MWNTs can be as high as 70 % of the reaction product. Analysis with Auger-spectroscopy revealed that no nitrogen was incorporated in the MWNTs. There is a strong possibility that SWNTs can be produced with the same apparatus under different conditions.

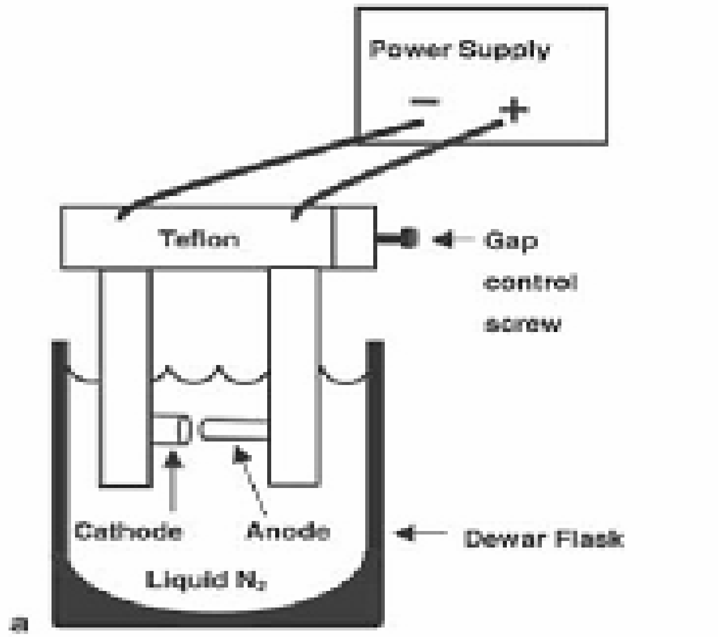

Figure 2-5: Schematic drawings of the arc discharge apparatus in liquid nitrogen.

Magnetic field synthesis

- Synthesis of MWNTs in a magnetic field gives defect-free and high purity MWNTs that can be applied as nanosized electric wires for device fabrication. In this case, the arc discharge synthesis was controlled by a magnetic field around the arc plasma.
- Extremely pure graphite rods (purity > 99.999 %) were used as electrodes. Highly pure MWNTs (purity > 95 %) were obtained without further purification, which disorders walls of MWNTs.

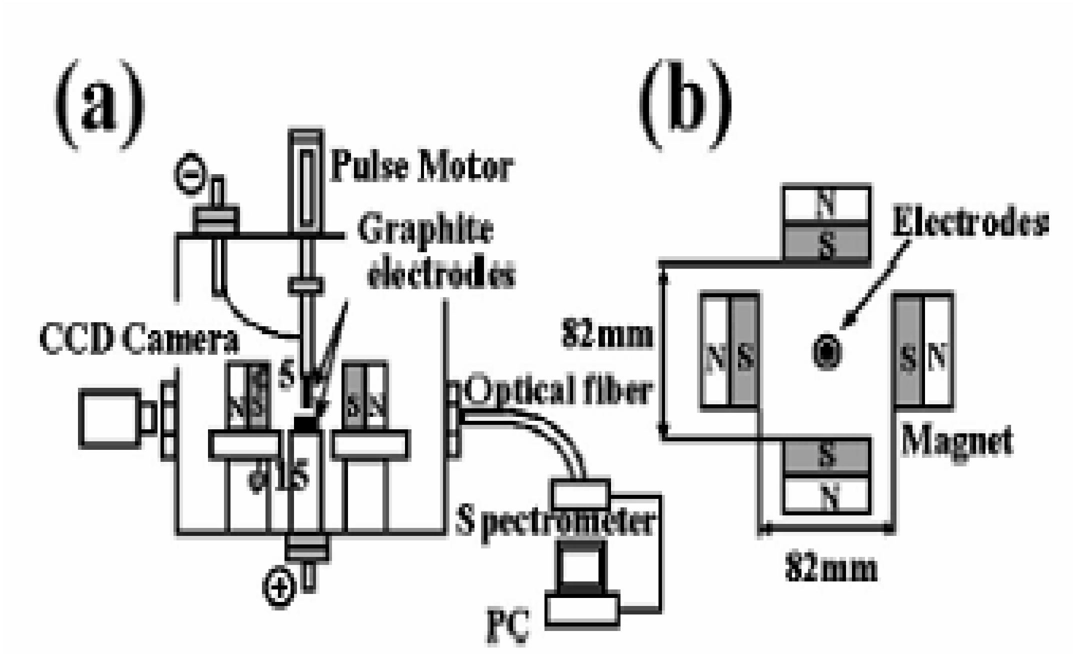

Figure 2-6: Schematic diagram of the synthesis system for MWNTs in a magnetic field.

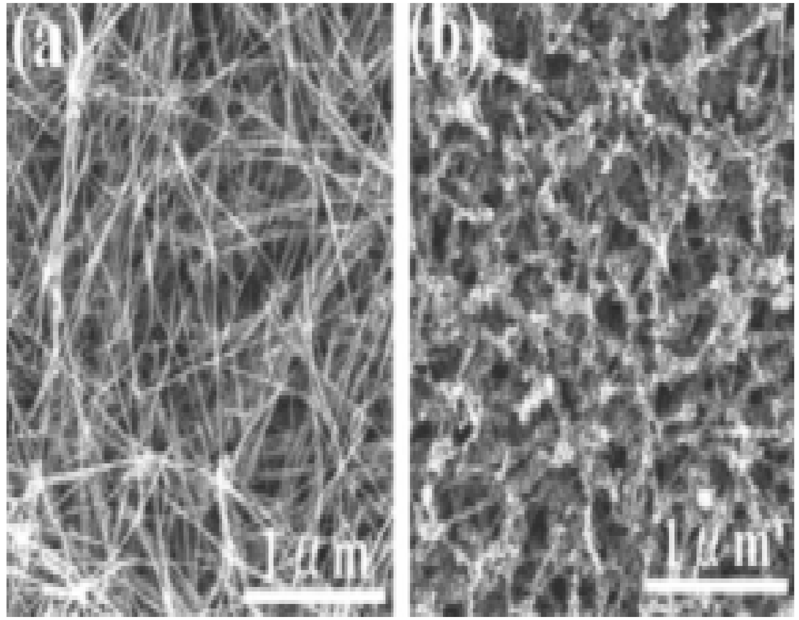

Figure 2-7: SEM images of MWNTs synthesised with (a) and without (b) the magnetic field.

Plasma rotating arc discharge

- A second possibly economical route to mass production of MWNTs is synthesis by plasma rotating arc discharge technique.
- The centrifugal force caused by the rotation generates turbulence and accelerates the carbon vapour perpendicular to the anode. In addition, the rotation distributes the micro discharges uniformly and generates a stable plasma. Consequently, it increases the plasma volume and raises the plasma temperature.

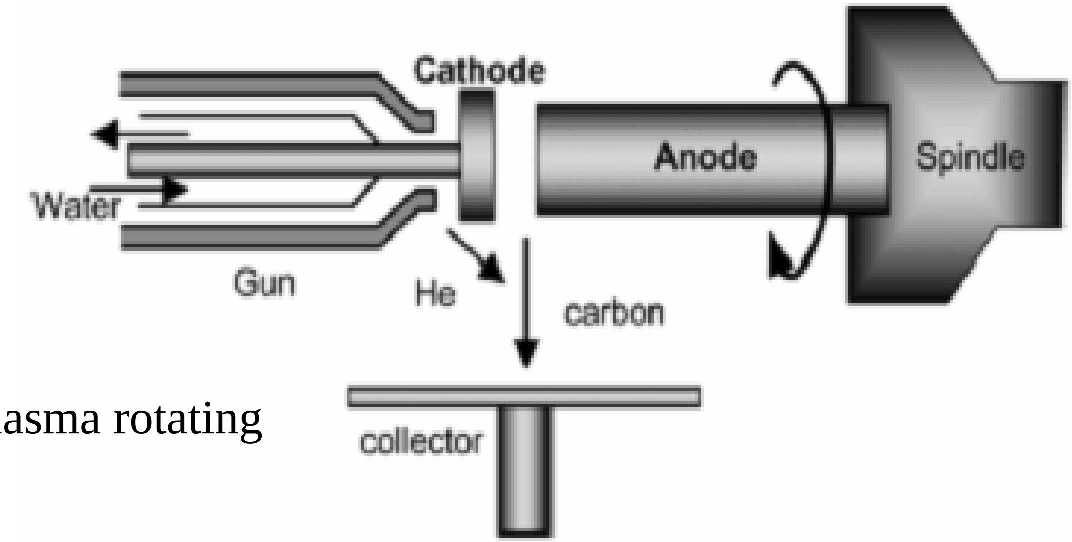

Figure 2-8: Schematic diagram of plasma rotating electrode system.

- At a rotation speed of 5000 rpm a yield of 60 % was found at a formation temperature of 1025 °C without the use of a catalyst.
- The yield increases up to 90% after purification if the rotation speed is increased and the temperature is enlarged to 1150 °C. The diameter size was not mentioned in this publication.

Laser ablation

- In 1995, Smalley' s group at Rice University reported the synthesis of carbon nanotubes by laser vaporisation.
- The laser vaporisation apparatus used by Smalley' s group is shown in Figure 2-9.
- A pulsed, or continuous laser is used to vaporise a graphite target in an oven at 1200 °C.
- The main difference between continuous and pulsed laser, is that the pulsed laser demands a much higher light intensity (100 kW/cm^2) compared with 12 kW/cm^2.
- The oven is filled with helium or argon gas in order to keep the pressure at 500 Torr.
- A very hot vapour plume forms, then expands and cools rapidly. As the vaporised species cool, small carbon molecules and atoms quickly condense to form larger clusters, possibly including fullerenes.

- The catalysts also begin to condense, but more slowly at first, and attach to carbon clusters and prevent their closing into cage structures. Catalysts may even open cage structures when they attach to them.
- From these initial clusters, tubular molecules grow into single-wall carbon nanotubes until the catalyst particles become too large, or until conditions have cooled sufficiently that carbon no longer can diffuse through or over the surface of the catalyst particles. It is also possible that the particles become that much coated with a carbon layer that they cannot absorb more and the nanotube stops growing. The SWNTs formed in this case are bundled together by van der Waals forces

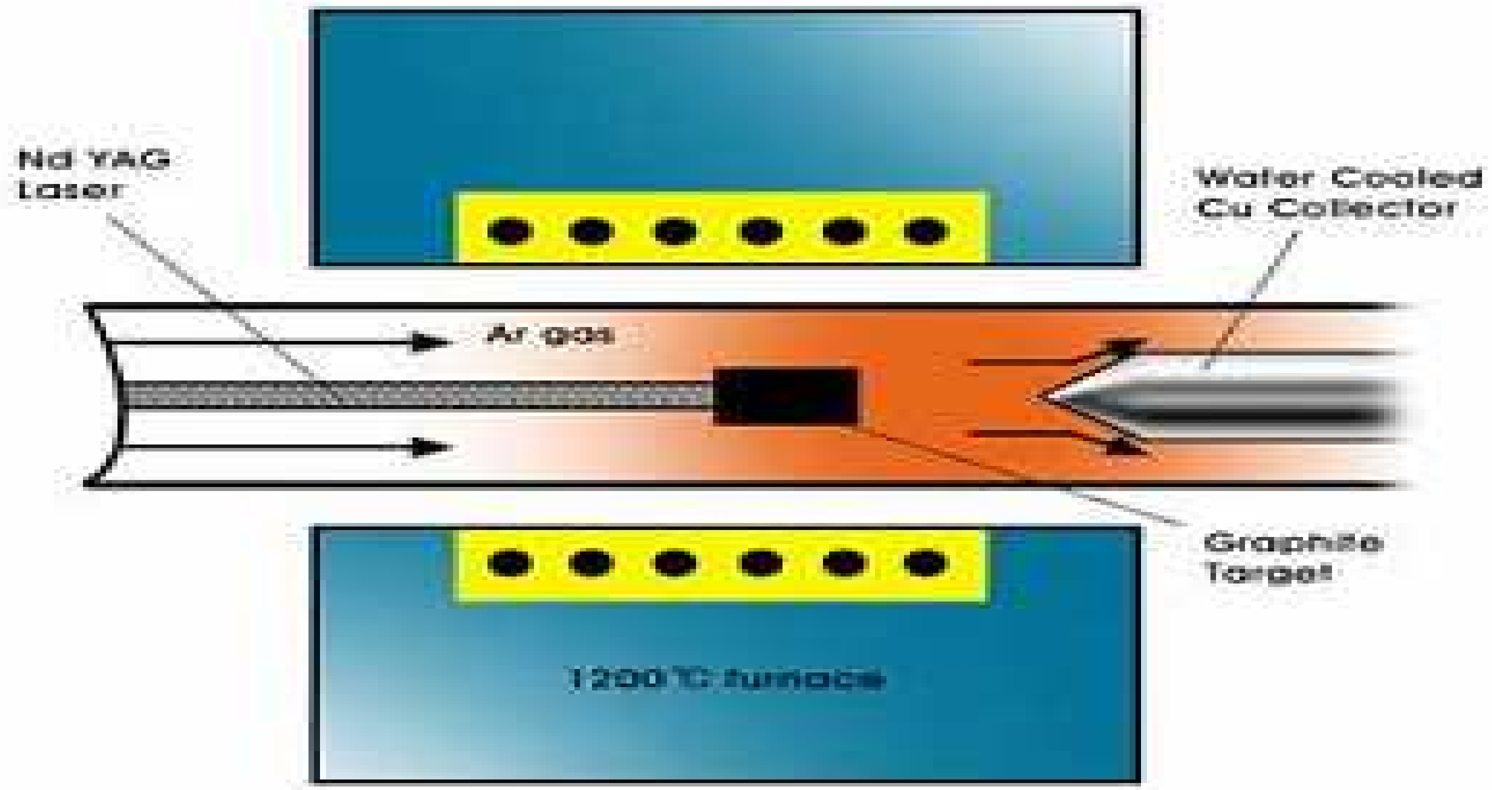

Figure 2-9: Schematic drawings of a laser ablation apparatus.

- This suggests that fullerenes are also produced by laser ablation of catalyst-filled graphite, as is the case when no catalysts are included in the target. However, subsequent laser pulses excite fullerenes to emit C2 that adsorbs on catalyst particles and feeds SWNT growth. However, there is insufficient evidence to conclude this with certainty
- Laser ablation is almost similar to arc discharge, since the optimum background gas and catalyst mix is the same as in the arc discharge process. This might be due to very similar reaction conditions needed, and the reactions probably occur with the same mechanism.

SWNT versus MWNT in laser ablation

- The condensates obtained by laser ablation are contaminated with carbon nanotubes and carbon nanoparticles.
- In the case of pure graphite electrodes, MWNTs would be synthesised, but uniform SWNTs could be synthesised if a mixture of graphite with Co, Ni, Fe or Y was used instead of pure graphite.
- SWNTs synthesised this way exist as ' ropes' , see Figure 2-10. Laser vaporisation results in a higher yield for SWNT synthesis and the nanotubes have better properties and a narrower size distribution than SWNTs produced by arc-discharge.
- Nanotubes produced by laser ablation are purer (up to about 90 % purity) than those produced in the arc discharge process. The Ni/Y mixture catalyst (Ni/Y is 4.2/1) gave the best yield.

- The size of the SWNTs ranges from 1-2 nm, for example the Ni/Co catalyst with a pulsed laser at 1470 °C gives SWNTs with a diameter of 1.3-1.4 nm. In case of a continuous laser at 1200 °C and Ni/Y catalyst (Ni/Y is 2:0.5 at. %), SWNTs with an average diameter of 1.4 nm were formed with 20-30 % yield, see Figure 2-10.

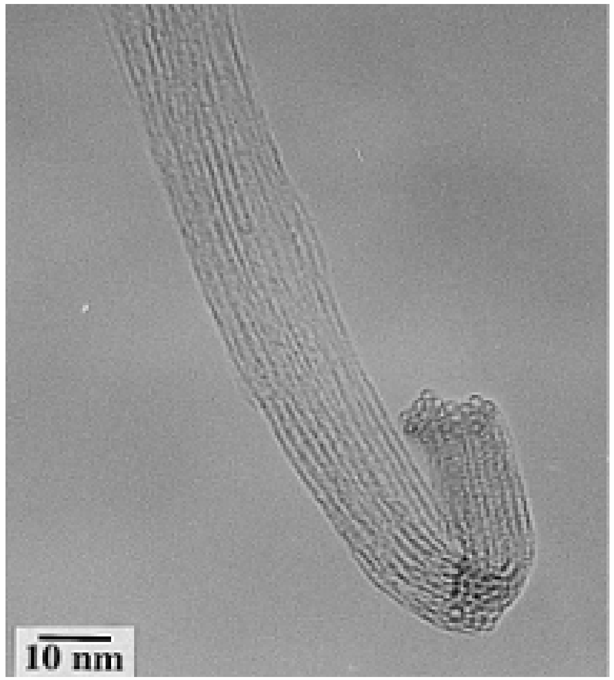

Figure 2-10: TEM images of a bundle of SWNTs catalysed by Ni/Y (2:0.5 at. %) mixture, produced with a continuous laser.

Large scale synthesis of SWNT

- Because of the good quality of nanotubes produced by this method, scientists are trying to scale up laser ablation. However the results are not yet as good as for the arc-discharge method, but they are still promising. In the next two sections, two of the newest developments on large-scale synthesis of SWNTs will be discussed. The first is the 'ultra fast Pulses from a free electron laser method, the second is 'continuous wave laser-powder' method. Scaling up is possible, but the technique is rather expensive due to the laser and the large amount of power required.

Ultra fast Pulses from a free electron laser (FEL) method

- Usually the pulses in an Nd:YAG system have width of approximately 10 ns, in this FEL system the pulse width is ~ 400 fs. The repetition rate of the pulse is enormously increased from 10 Hz to 75 MHz. To give the beam the same amount of energy as the pulse in an Nd:YAG system, the pulse has to be focused. The intensity of the laser bundle behind the lens reaches ~5 x 10^{11} W/cm^2, which is about 1000 times greater than in Nd:YAG systems.

- A jet of preheated (1000 °C) argon through a nozzle tip is situated close to the rotating graphite target, which contains the catalyst.
- The argon gas deflects the ablation plume approximately 90° away from the incident FEL beam direction, clearing away the carbon vapour from the region in front of the target.
- The produced SWNT soot, is collected in a cold finger. This process can be seen in Figure 2-11. The yield at this moment is 1.5 g/h, which is at 20 % of the maximum power of the not yet upgraded FEL. If the FEL is upgraded to full power and is working at 100 % power, a yield of 45 g/h could be reached since the yield was not limited by the laser power.

With this method the maximum achievable yield with the current lasers is 45 g/h, with a NiCo or NiY catalyst, in argon atmosphere at 1000 °C and a wavelength of ~3000 nm.

The SWNTs produced in bundles of 8-200 nm and a length of 5-20 microns has a diameter range 1-1.4 nm.

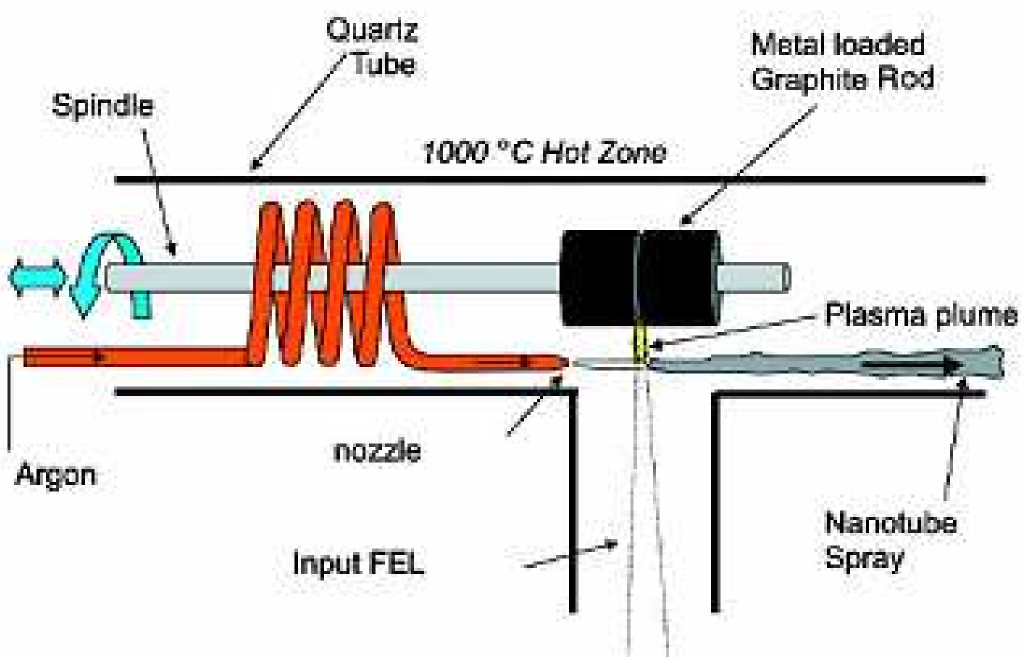

Figure 2-11: Schematic drawings of the ultra fast-pulsed laser ablation apparatus.

Continuous wave laser-powder method

- This method is a novel continuous, highly productive laser-powder method of SWNT synthesis based on the laser ablation of mixed graphite and metallic catalyst powders by a 2-kW continuous wave CO_2 laser in an argon or nitrogen stream. Because of the introduction of micron-size particle powders, thermal conductivity losses are significantly decreased compared with laser heating of the bulk solid targets in known laser techniques. As a result, more effective utilisation of the absorbed laser power for material evaporation was achieved. The set-up of the laser apparatus is shown in Figure 2-12.
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The established yield of this technique was 5 g/h. A Ni/Co mixture (Ni/Co is 1:1) was used as catalyst, the temperature was 1100 °C. In the soot a SWNT abundance of 20-40% w. as found with a mean diameter of 1.2-1.3 nm. An HRTEM-picture of this sample is shown in Figure 2-12.

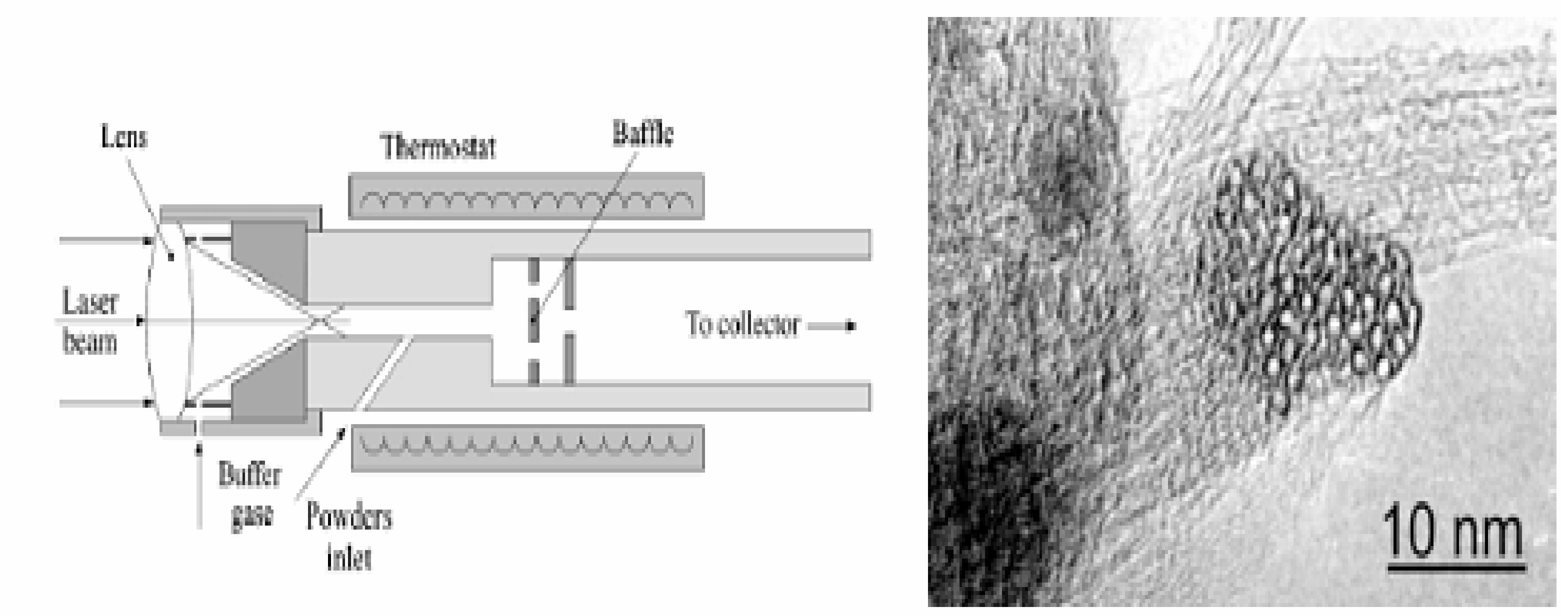

Figure 2-12: (Left) The principle scheme of the set-up for carbon SWNT production by continuous wave laser-powder method (Right) HRTEM of a SWNT-bundle cross-section.