In the Name of God

The Wondrous World of Carbon Nanotubes

‘a review of current carbon nanotube technologies’

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CNTs

- Multi Walled Nanotubes (MWNT) can be considered as a collection of concentric SWNTs with different diameters. The length and diameter of these structures differ a lot from those of SWNTs and, of course, their properties are also very different. (Figure 1-4)

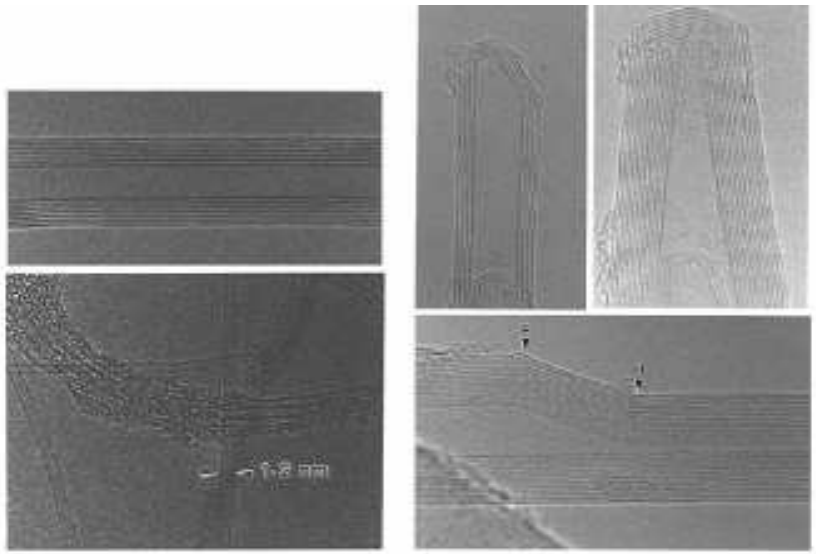
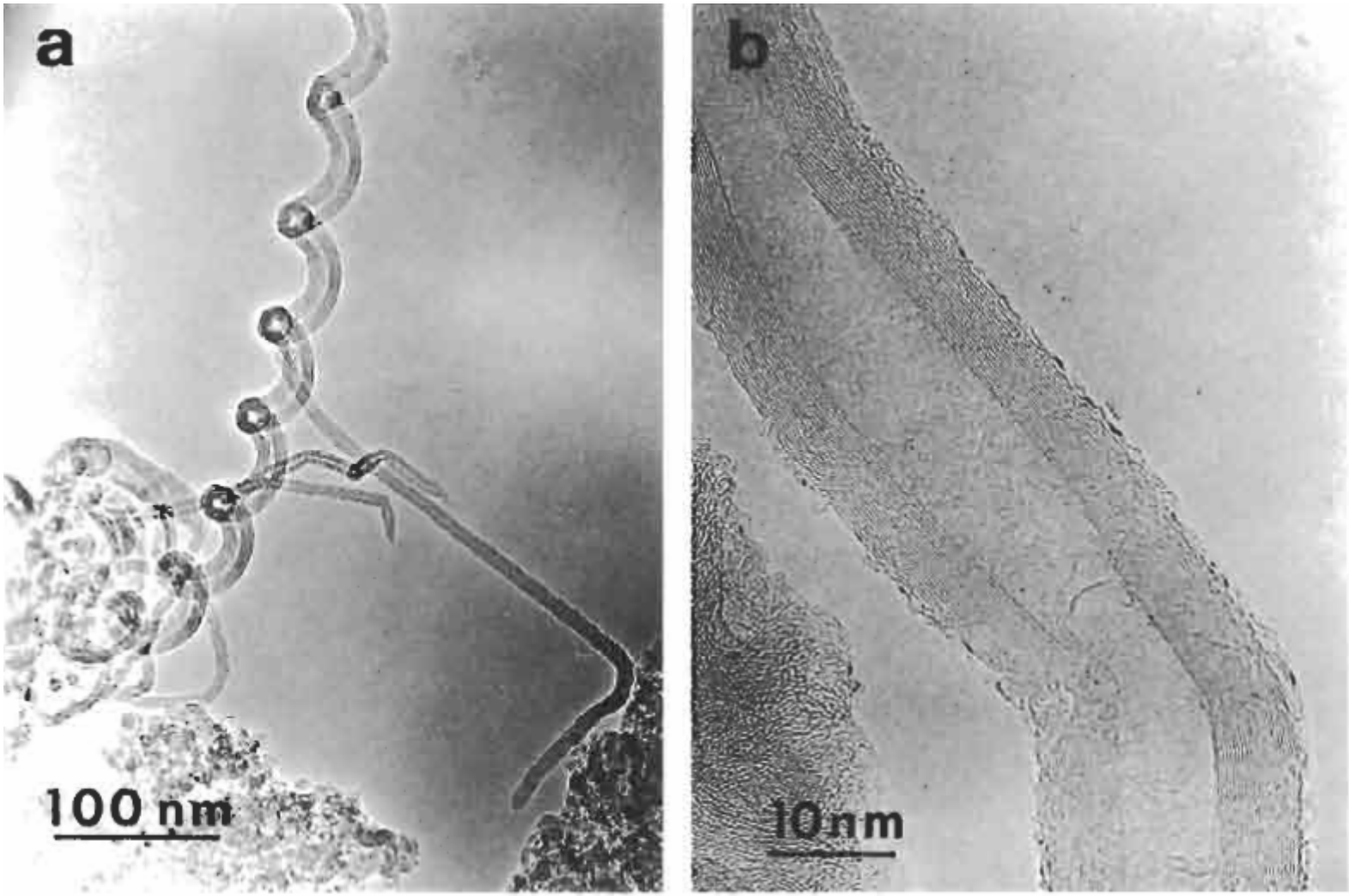
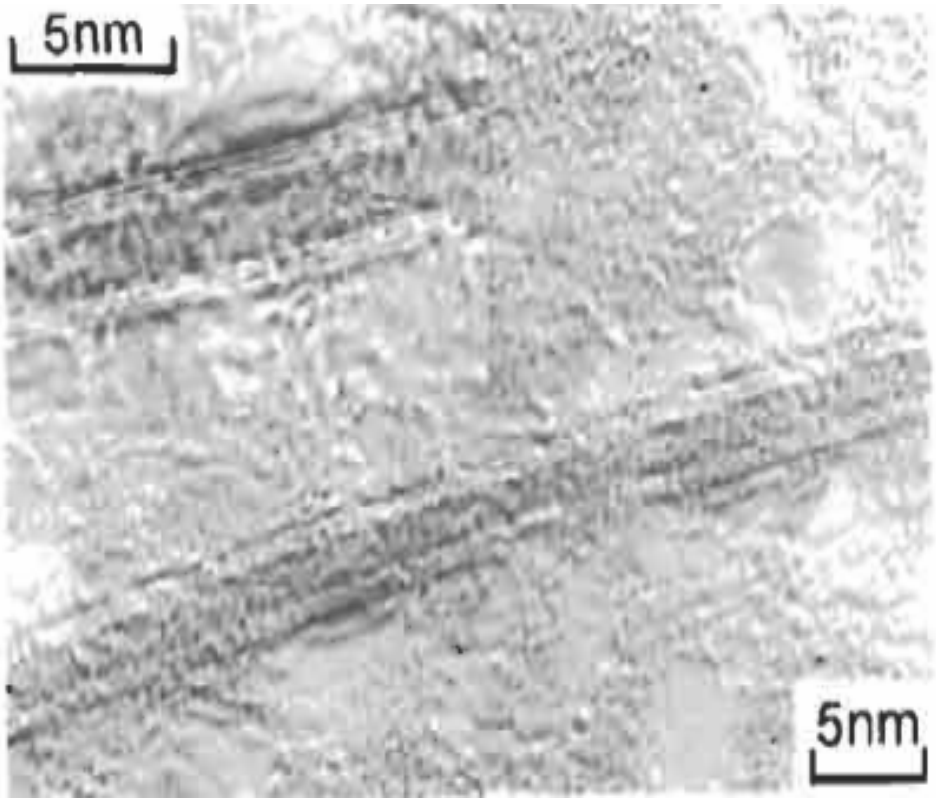
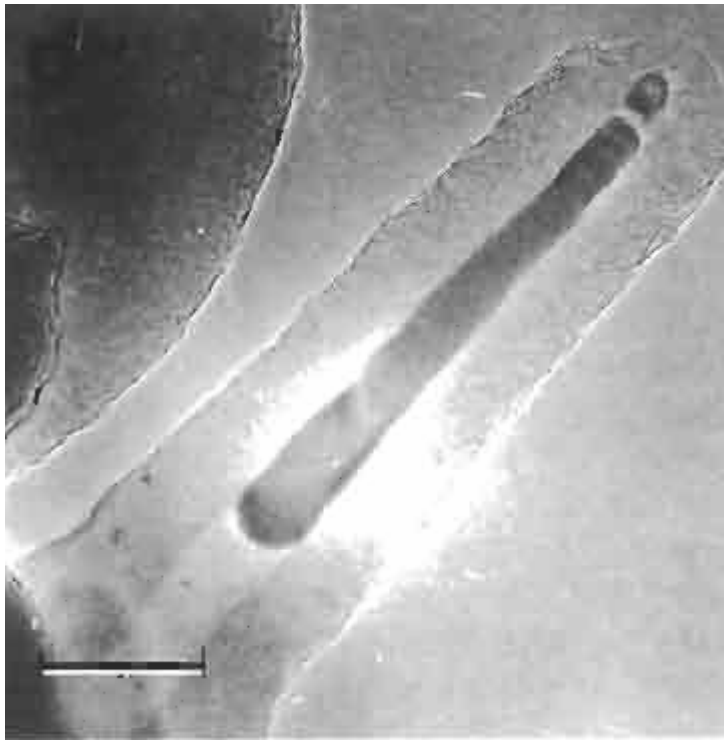


Figure 1-4: Different structures of MWNTs. Top-left: cross-section of a MWNT the different walls are obvious, they are separated by 0.34nm. Rotation around the symmetry axis gives us the MWNT. Top-right: Symmetrical or non-symmetrical cone shaped end caps of MWNTs. Bottom-left: A SWNT with a diameter of 1,2nm and a bundle of SWNTs covered with amorphous carbon. Bottom-right: A MWNT with defects. In point P a pentagon defect and in point H a heptagon defect.[6]


a
100 nm
b
10nm

CNTs





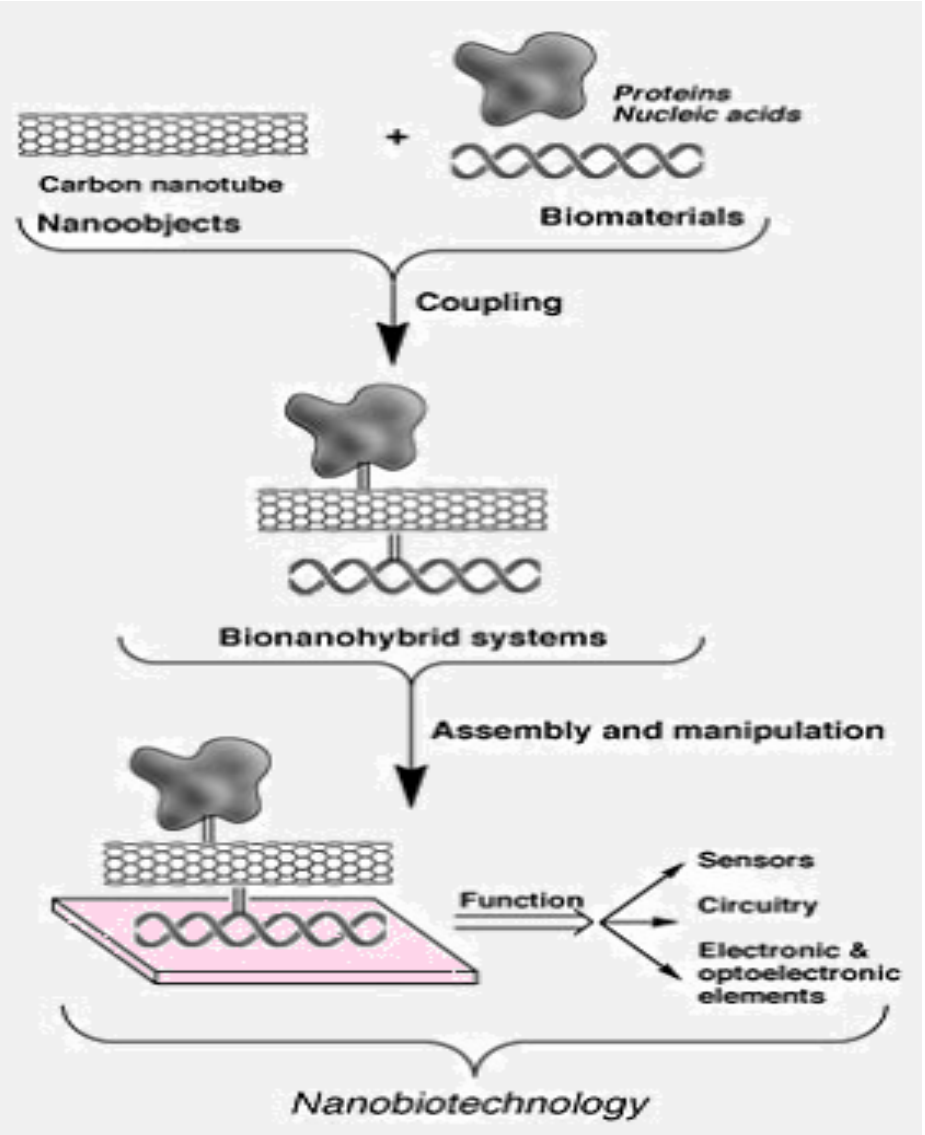
Special properties of carbon nanotubes

- **Chemical reactivity**: The chemical reactivity of a CNT is, compared with a graphene sheet, enhanced as a direct result of the curvature of the CNT surface.
- Carbon nanotube reactivity is directly related to the pi-orbital mismatch caused by an increased curvature. Therefore, a distinction must be made between the sidewall and the end caps of a nanotube. For the same reason, a smaller nanotube diameter results in increased reactivity.
- Covalent chemical modification of either sidewalls or end caps has shown to be possible. For example, the solubility of CNTs in different solvents can be controlled this way. Though, direct investigation of chemical modifications on nanotube behaviour is difficult as the crude nanotube samples are still not pure enough.

CNTs & nanobiotecnology

The integration of biomaterials (e.g. proteins/enzymes , antigens /antibodies or DNA) with CNTs provides new hybrid systems that combine the conductive or semiconductive properties of CNTs with the recognition or catalytic properties of the biomaterials.

This Bio hybrid system yield new bioelectronics systems (biosensors, field -effect-transistor) or template nanocircurity



CNTs and defects

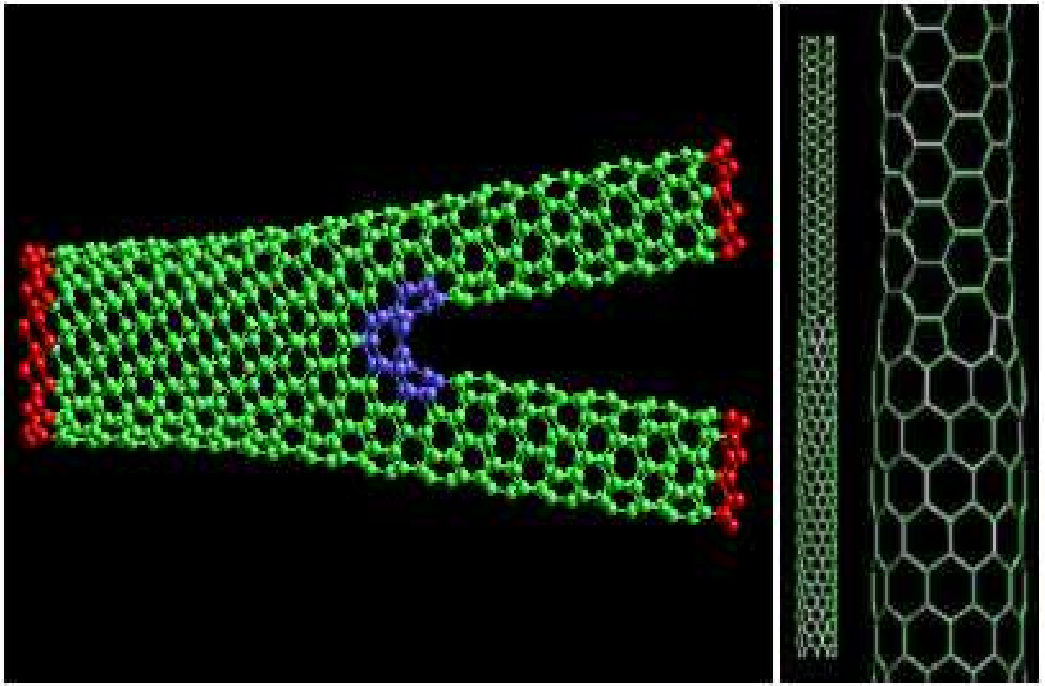


Figure 1-5: Left: A Y-branch, the defects are marked in blue. Right: A transition from a metallic to a semi-conducting SWNT. The change is made by insertion of pentagons and heptagons.

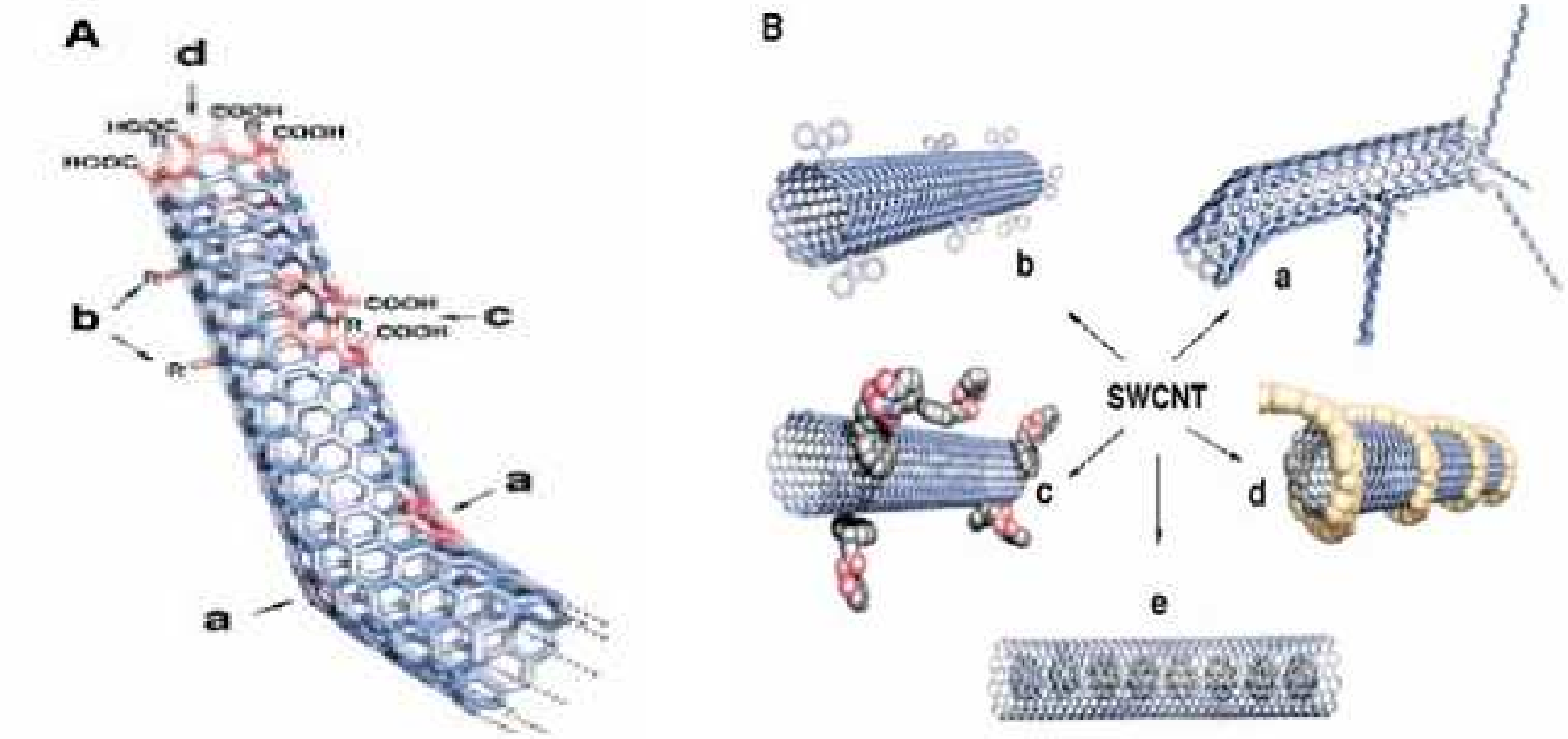
Carbon nanotubes modification

Current derivatization methods:

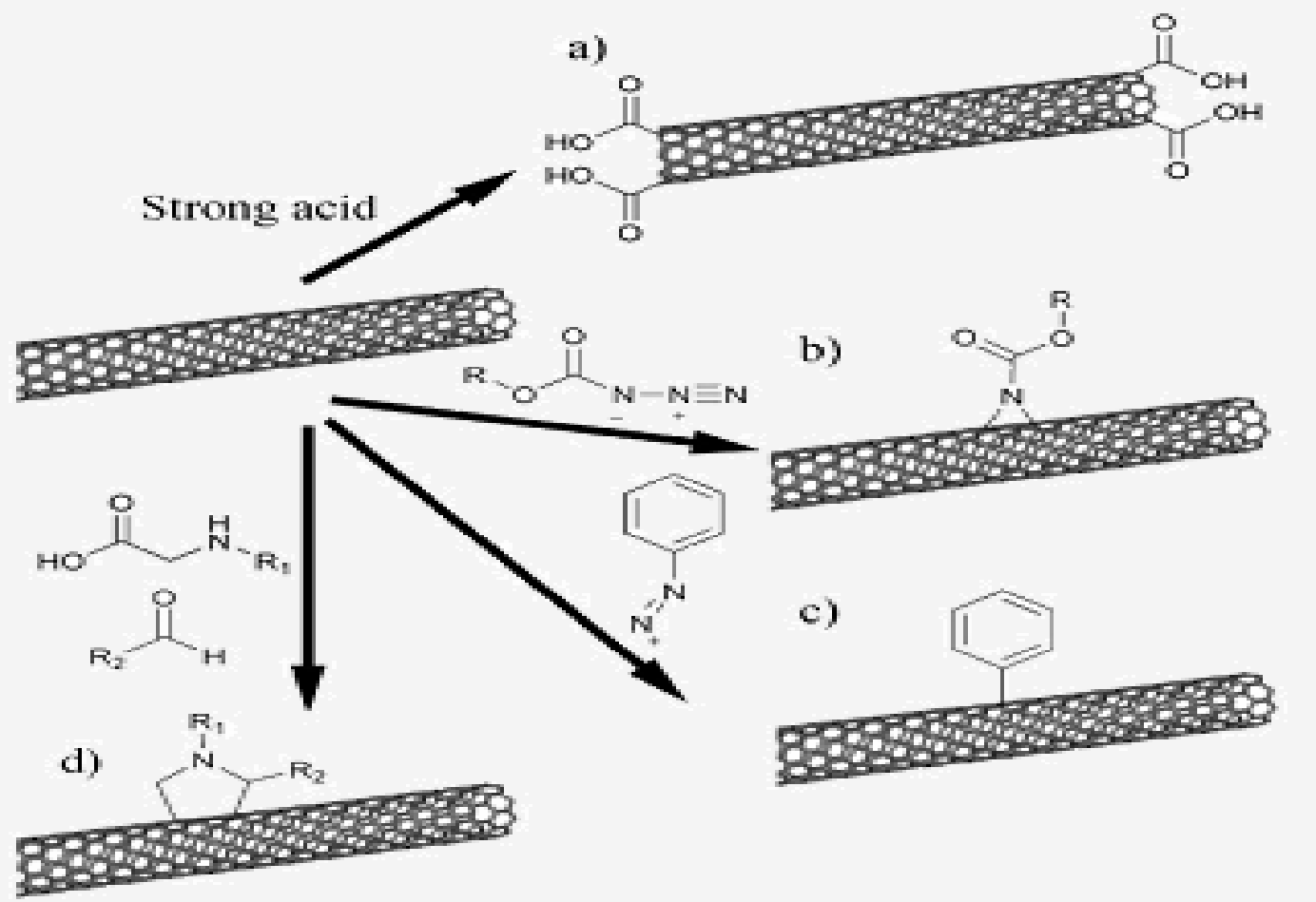
1-defect functionalized

2-sidewall fictionalization

3- noncovalent exo and endohedral fictionalization



Chemical modification of CNTs



Common methods for chemical functionalization of carbon nanotubes: (a) oxidation by strong acids, (b) nitrene cycloaddition, (c) arylation using diazonium salts, and (d) 1,3-dipolar cycloadditions.

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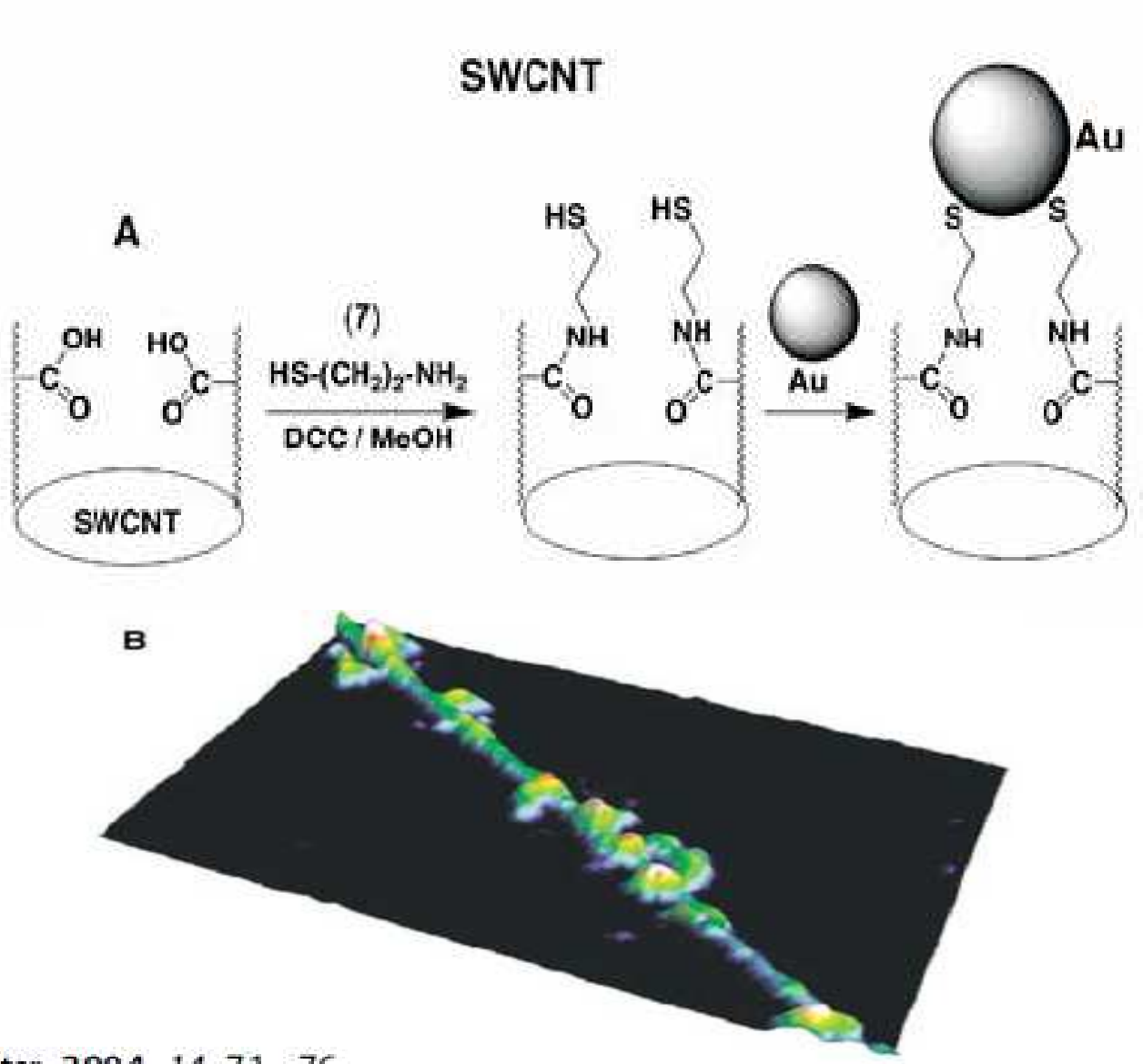
CNTs-Nanoparticle hybride system

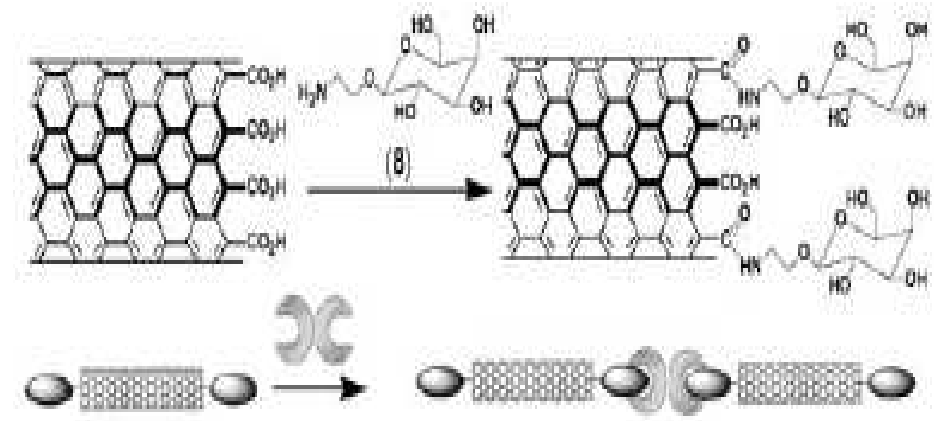


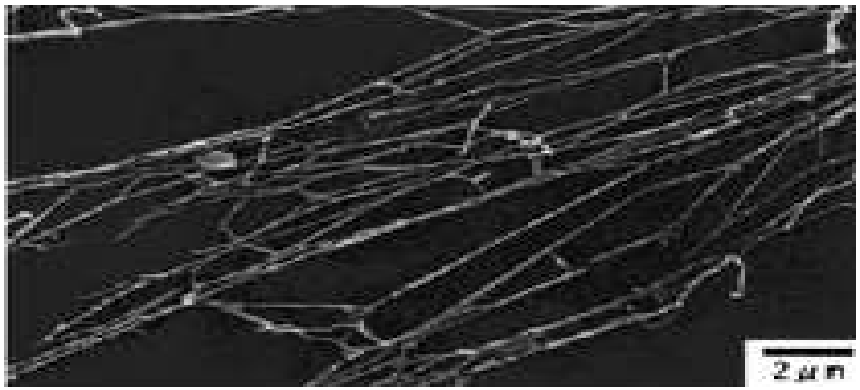
Adv. Funct. Mater. 2004, *14*, 71–76.

Using CNTs in nanocircuit fabrication

- By selectivity activated the end or sidwalls of CNT their elongation, specific placement on the solid support and, as a final goal the generation of nanocircurity can be achived.

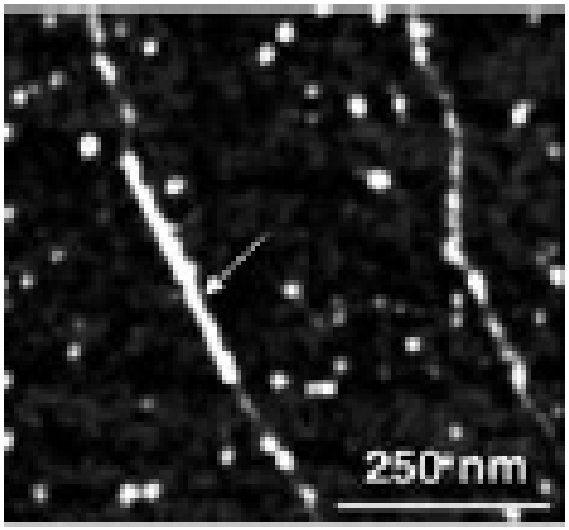
- CNTs have been elongated by the formation of biomolecule-junction that interconnect the ends of CNTs.

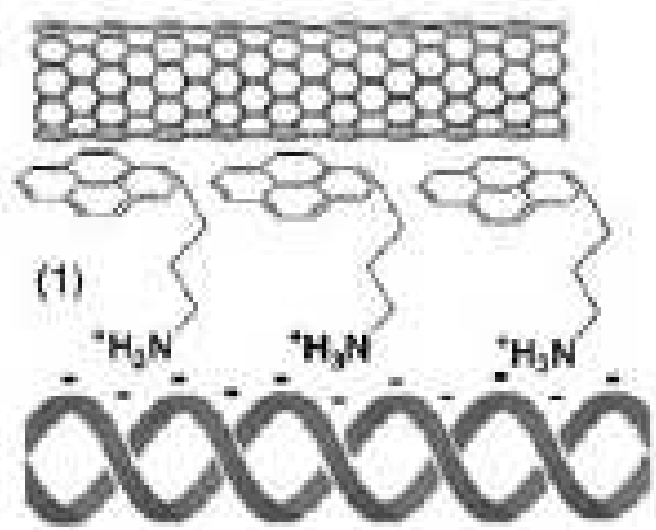




Chem. Lett. **2003**, *32*, 212–213.

A key issu in the use of CNTs in nanocircuit fabrication is the need for their controlled placement at well-defiend position on surfaces.
Anovel approach for directional placement of cnts on surface was developed with the use of DNA templates:
Double strand DNA was linearly aligned on the silicon surface





Electrical conductivity

- Electrical conductivity: Depending on their chiral vector, carbon nanotubes with a small diameter are either **semiconducting** or **metallic**. The differences in conducting properties are caused by the molecular structure that results in a different band structure and thus a different band gap. The differences in conductivity can easily be derived from the graphene sheet properties.

It was shown that a (n,m) nanotube is metallic as accounts that: n=m or (n-m) = 3i, where i is an integer and n and m are defining the nanotube.

The resistance to conduction is determined by quantum mechanical aspects and was proved to be independent of the nanotube length. For more, general information on electron conductivity is referred to a review by Ajayan and Ebbesen.

- Figure 5.15 is a plot of the energy gap of semiconducting chiral carbon nanotubes versus the reciprocal of the diameter, showing that as the diameter of the tube increases, the bandgap decreases.

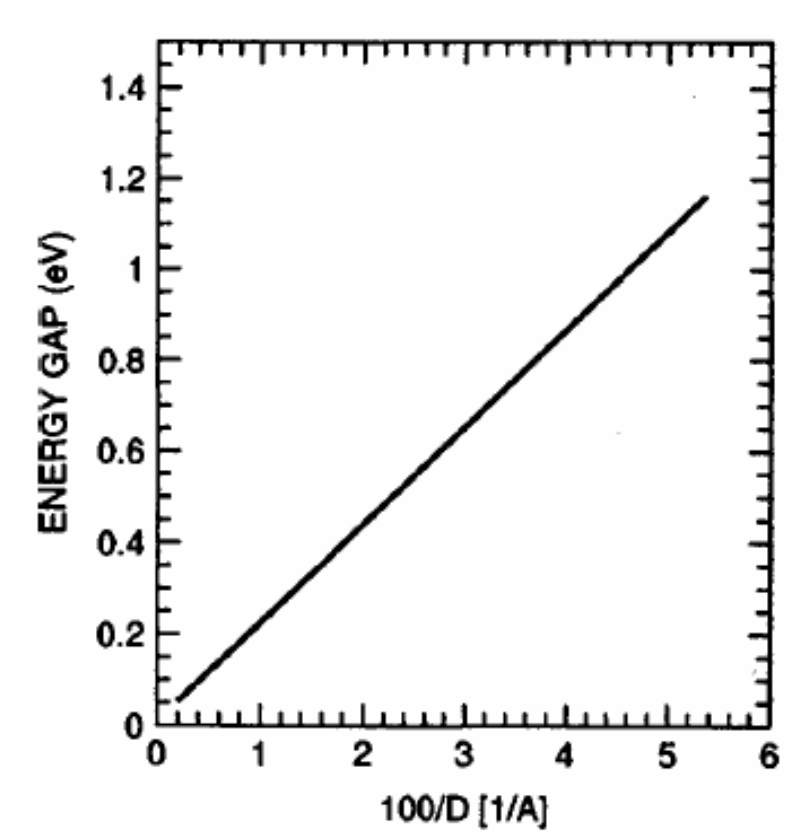
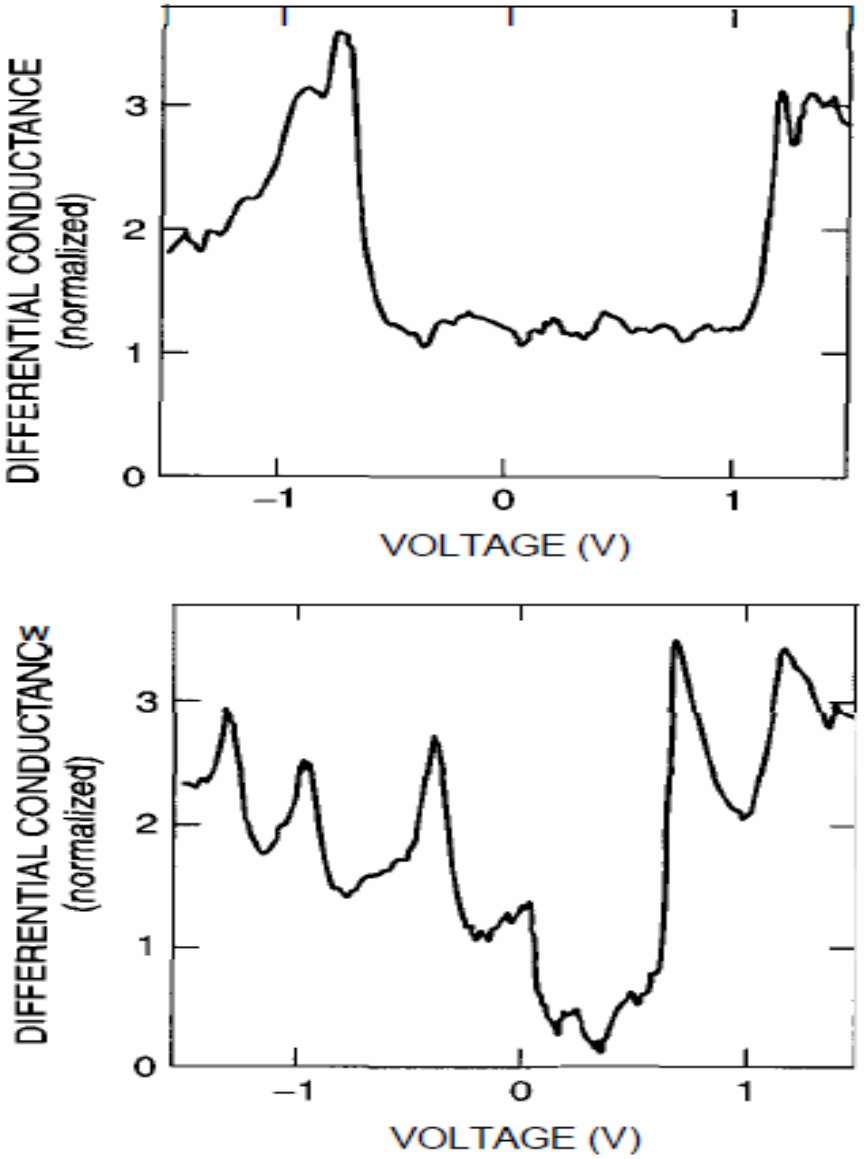


Figure 5.15. Plot of the magnitude of the energy band gap of a- semiconducting, chiral carbon nanotube versus the reciprocal of the diameter of the tube (10A= 1 nm). [Adapted from M. S.Dresselhaus et al., *Molec. Mater. 4, 27 (1994).*

- Scanning tunneling microscopy (STM), has been used to investigate the electronic structure of carbon nanotubes. In this measurement the position of the STM tip is fixed above the nanotube, and the voltage V between the tip and the sample is swept while the tunneling current Z is monitored. The measured conductance G = I/ V is a direct measure of the local electronic density of states. Figure 5.16 gives the STM data plotted as the differential conductance, which is (dI/dV)/(I/V) versus the applied voltage between the tip and carbon nanotube.

Figure 5.16. Plot of differential conductance *(d/ /dV) (/ /V) obtained from scanning tunneling* microscope measurements of the tunneling current of metallic (top figure) and semiconducting (bottom figure) nanotubes. [With permission from C. Dekker, *fhys. Today 22 (May 1999).]*



- As we have discussed earlier, electrons in the quantum theory can be viewed as waves.
- If the electron wavelength is not a multiple of the circumference of the tube, it will destructively interfere with itself, and therefore only electron wavelengths that are integer multiples of the circumference of the tubes are allowed. This severely limits the number of energy states available for conduction around the cylinder.
- The dominant remaining conduction path is along the axis of the tubes, making carbon nanotubes function as one-dimensional quantum wires.

- In the metallic state the conductivity of the nanotubes is very high.
- It is estimated that they can carry a billion amperes per square centimeter.
- Copper wire fails at one million amperes per square centimeter because resistive heating melts the wire. One reason for the high conductivity of the carbon tubes is that they have very few defects to scatter electrons, and thus a very low resistance.
- High currents do not heat the tubes in the same way that they heat copper wires. Nanotubes also have a very high thermal conductivity, almost a factor of 2 more than that of diamond. This means that they are also very good conductors of heat.

- **Magnetoresistance** is a phenomenon whereby the resistance of a material is changed by the application of a DC magnetic field.
- Carbon nanotubes display magnetoresistive effects at low temperature. Figure 5.18 shows a plot of the magnetic field dependence of the change in resistance AR of nanotubes at 2.3 and 0.35K compared to their resistance R in zero magnetic field.

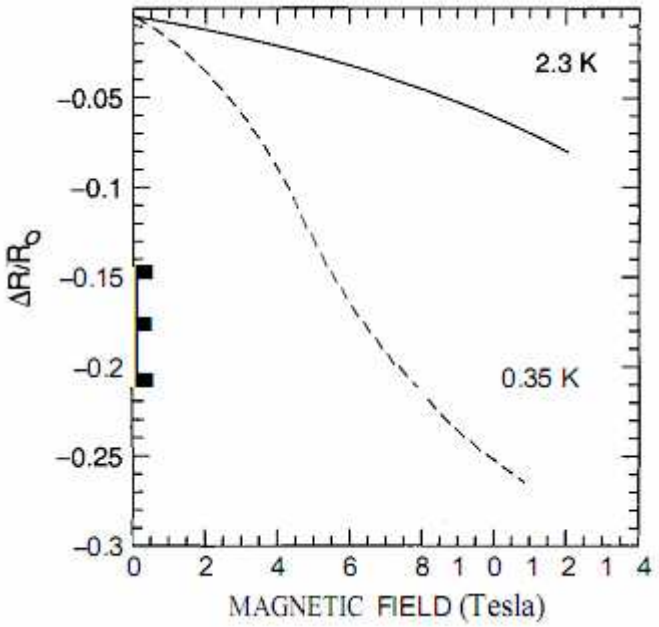


Figure 5.18. Effect of a DC magnetic field on the resistance of nanotubes at the temperatures of 0.35 and 2.3K. (Adapted from R. Saito, G. Dresselhaus, and M. S. Dresselhaus, Physical Properties of Nanotubes, Imperial College Press, 1998.)

- This is a negative magnetoresistance effect because the resistance decreases with increasing DC magnetic field, so its reciprocal, the conductance G = 1 /R, increases. This occurs because when a DC magnetic field is applied to the nanotubes, the conduction electrons acquire new energy levels associated with their spiraling motion about the field. It turns out that for nanotubes these levels, called Landau levels, lie very close to the topmost filled energy levels (the Fermi level). Thus there are more available states for the electrons to increase their energy, and the material is more conducting

Mechanical strength

- Carbon nanotubes have a very large Young modulus in their axial direction.
- The nanotube as a whole is very flexible because of the great length. Therefore, these compounds are potentially suitable for applications in composite materials that need anisotropic properties.
- Carbon nanotubes are very strong. If a weight W is attached to the end of a thin wire nailed to the roof of a room, the wire will stretch. The stress S on the wire is defined as the load, or the weight per unit cross-sectional area A of the wire:

$$S = \frac{W}{A}$$

- The strain e is defined as the amount of stretch AL of the wire per unit length L:

$$e = \frac{AL}{L}$$

L is the length of the wire before the weight is attached.

- Hooke's law says that the increase in the length of the wire is proportional to the weight at the end of the wire. More generally, we say stress S is proportional to strain e:

$$S = Ee$$

- The proportionality constant **E = LW/A AL** is Young's modulus, and it is a property of a given material. It characterizes the elastic flexibility of a material.

- Carbon nanotubes have Young's moduli ranging from 1.28 to 1.8TPa. One terapascal (TPa) is a pressure very close to 10^7 times atmospheric pressure. Young's modulus of steel is 0.21TPa, which means that Young's modulus of carbon nanotubes is almost 10 times that of steel. This would imply that carbon nanotubes are very stiff and hard to bend. However, this is not quite true because they are so thin.
- The deflection D of a cylindrical hollow beam of length L with a force F on the end and the inner and outer radii of r_i and r_0, has been shown to be

$$D = \frac{FL^3}{3EI}$$

where I is the areal moment of inertia given by $\Pi(r_o^4 - r_i^4)/4$,

Since the wall thickness of carbon nanotubes is about 0.34nm, $r_0^4 - r_i^4$ is very small, somewhat compensating for the large value of E.

- When carbon nanotubes are bent, they are very resilient. They buckle like straws but do not break, and can be straightened back without any damage.
- Most materials fracture on bending because of the presence of defects such as dislocations or grain boundaries. Because carbon nanotubes have so few defects in the structure of their walls, this does not occur. Another reason why they do not fracture is that as they are bent severely, the almost hexagonal carbon rings in the walls change in structure but do not break. This is a unique result of the fact that the carbon-carbon bonds are sp2 hybrids, and these sp2 bonds can rehybridize as they are bent. The degree of change and the amount of s-p admixture both depend on the degree of bending of the bonds.

- Strength is not the same as stiffness. Young's modulus is a measure of how stiff or flexible a material is.
- Tensile strength is a measure of the amount of stress needed to pull a material apart. The tensile strength of carbon nanotubes is about 45 billion pascals. High-strength steel alloys break at about 2 billion pascals. Thus carbon nanotubes are about 20 times stronger than steel. Nested nanotubes also have improved mechanical properties, but they are not as good as their single-walled counterparts. For example, multi-walled nanotubes of 200 nm diameter have a tensile strength of 0.007 TPa (i.e., 7 GPa) and a modulus of 0.6 TPa.

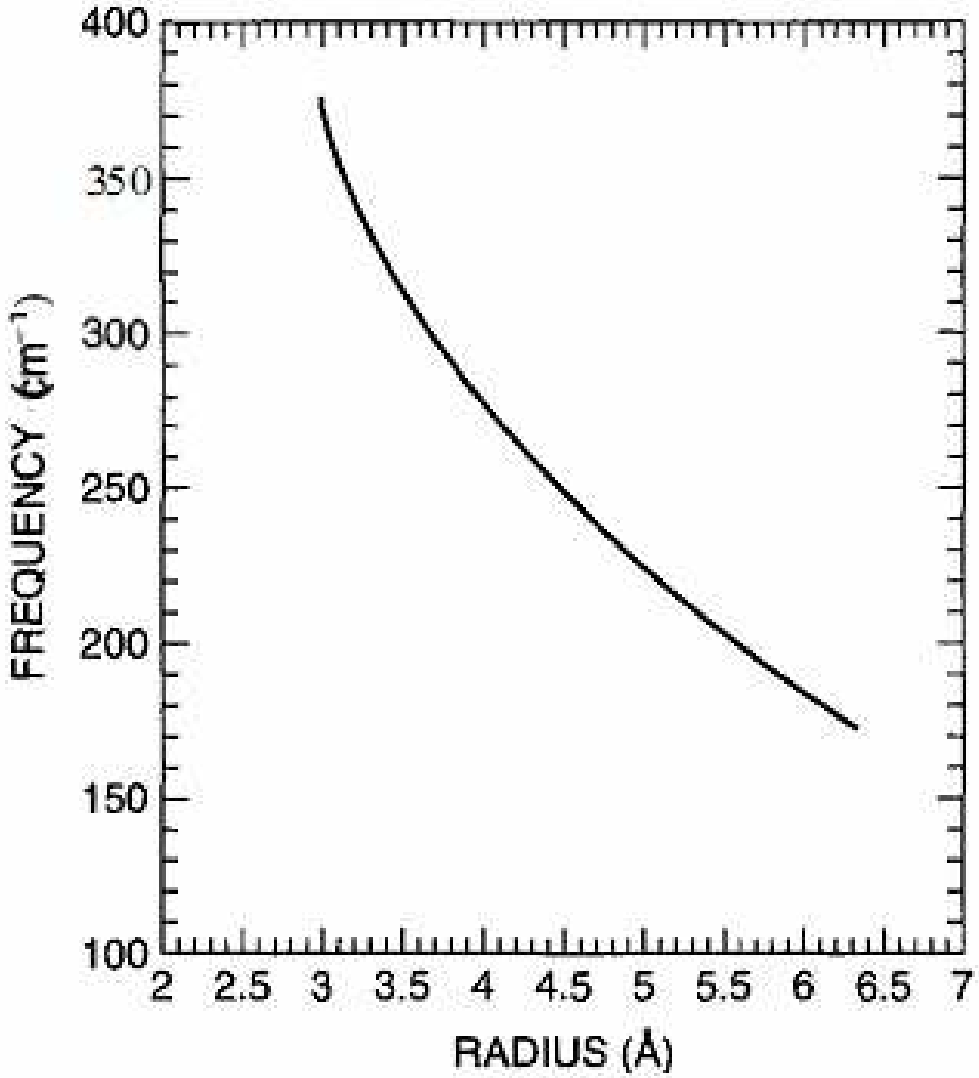
Vibrational Properties

- The atoms in a molecule or nanoparticle continually vibrate back and forth. Each molecule has a specific set of vibrational motions, called *normal modes of vibration*, which are determined by the symmetry of the molecule For example carbon dioxide CO_2, which has the structure O=C=O, is a bent molecule with three normal modes. One mode involves a bending of the molecule. Another, called the *symmetric stretch, consists of an in-phase elongation of the two C=O bonds.*

- The asymmetric stretch consists of out-of-phase stretches of the C=O bond length, where one bond length increases while the other decreases.

- Similarly carbon nanotubes also have normal modes of vibration. Figure 5.19 illustrates two of the normal modes of nanotubes. One mode, labeled *AIg involves an "in and out" oscillation of the* diameter of the tube. Another mode, the *E2, mode, involves a squashing of the tube* where it squeezes down in one direction and expands in the perpendicular direction essentially oscillating between a sphere and an ellipse.
- The frequencies of these two modes are Raman-active and depend on the radius of the tube. Figure *5.20 is a plot* of the frequency of the Alg mode as a function of this radius. The dependence of this frequency on the radius is now routinely used to measure the radius of nanotubes.

Figure 5.20.
Plot of the frequency of the Raman A,, vibrational normal mode versus the radius of the nanotube. (lOA= 1 nm). (Adapted from R. Saito, G. Dresselhaus, and M. S. Dresselhaus, Physical Properties of Nanotubes, Imperial College Press, 1998.)



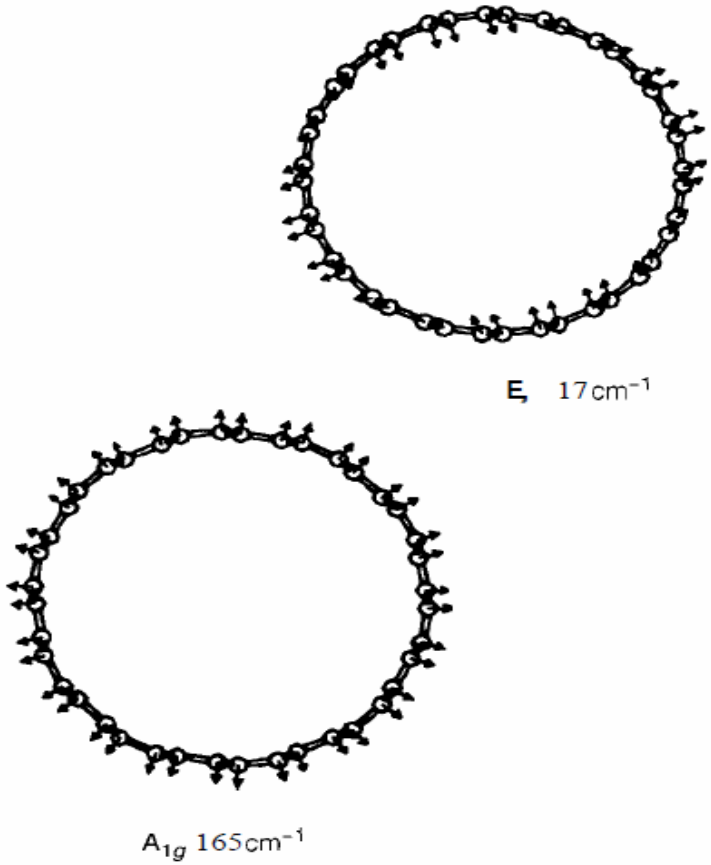


Figure 5.19. Illustration of two normal modes of vibration of carbon nanotubes

Carbon nanotube synthesis

- **Arc discharge** The carbon arc discharge method, initially used for producing C_{60} fullerenes, is the most common and perhaps easiest way to produce carbon nanotubes as it is rather simple to undertake.
- However, it is a technique that produces a mixture of components and requires separating nanotubes from the soot and the catalytic metals present in the crude product.
- Depending on the exact technique, it is possible to selectively grow SWNTs or MWNTs, which is shown in Figure 2-2. Two distinct methods of synthesis can be performed with the arc discharge apparatus.

- This method creates nanotubes through arc-vaporisation of two carbon rods placed end to end, separated by approximately 1mm, in an enclosure that is usually filled with inert gas (helium, argon) at low pressure (between 50 and 700 mbar).
- Recent investigations have shown that it is also possible to create nanotubes with the arc method in liquid nitrogen.
- A direct current of 50 to 100 A driven by approximately 20 V creates a high temperature discharge between the two electrodes. The discharge vaporises one of the carbon rods and forms a small rod shaped deposit on the other rod. Producing nanotubes in high yield depends on the uniformity of the plasma arc and the temperature of the deposit form on the carbon electrode.

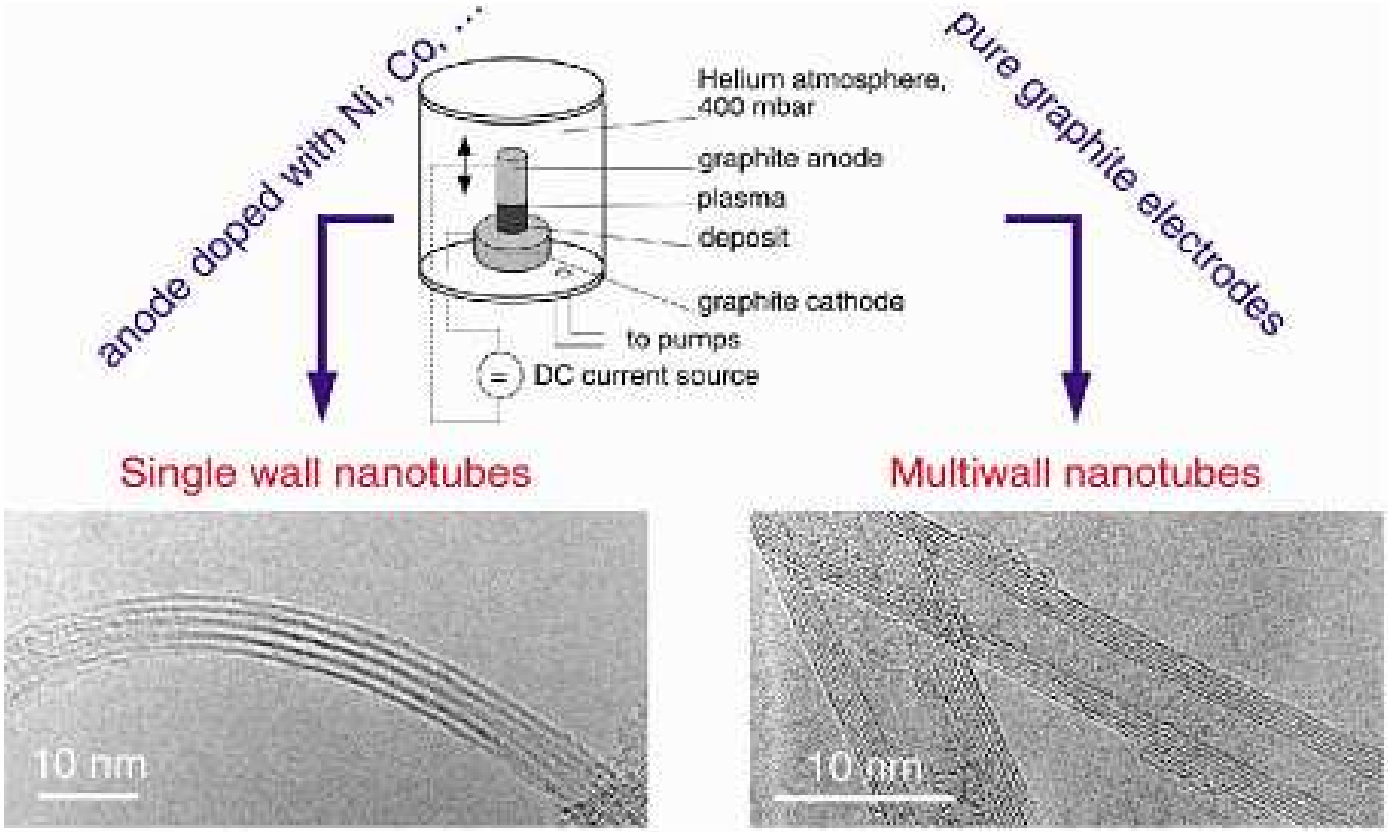


Figure 2-2:Experimental set-up of an arc discharge apparatus.

Synthesis of SWNT:

- If SWNTs are preferable, the anode has to be doped with metal catalyst, such as Fe, Co, Ni, Y or Mo.
- A lot of elements and mixtures of elements have been tested by various authors and it is noted that the results vary a lot, even though they use the same elements.
- The quantity and quality of the nanotubes obtained depend on various parameters such as the metal concentration, inert gas pressure, kind of gas, the current and system geometry. Usually the diameter is in the range of 1.2 to 1.4 nm.

Parameter affecting the process of arc discharge

- a) **Inert gas**: The most common problems with SWNT synthesis are that the product contains a lot of metal catalyst, SWNTs have defects and purification is hard to perform.
- On the other hand, an advantage is that the diameter can slightly be controlled by changing thermal transfer and diffusion, and hence condensation of atomic carbon and metals between the plasma and the vicinity of the cathode can control nanotube diameter in the arc process. This was shown in an experiment in which different mixtures of inert gases were used:

- It appeared that argon, with a lower thermal conductivity and diffusion coefficient, gave SWNTs with a smaller diameter of approximately 1.2 nm.
- A linear fit of the average nanotube diameter showed a 0.2 nm diameter decrease per 10 % increase in argon helium ratio, when nickel/yttrium was used (C/Ni/Y was 94.8:4.2:1) as catalyst.

Optical plasma control

- A second way of control is plasma control by changing the anode to cathode distance (ACD). The ACD is adjusted in order to obtain strong visible vortices around the cathode. This enhances anode vaporisation, which improves nanotubes formation. Combined with controlling the argon-helium mixture, one can simultaneously control the macroscopic and microscopic parameters of the nanotubes formed.
- With a nickel and yttrium catalyst (C/Ni/Y is 94.8:4.2:1) the optimum nanotube yield was found at a pressure of 660 mbar for pure helium and 100 mbar for pure argon. The nanotube diameter ranges from 1.27 to 1.37 nanometre.

Improvement of oxidation resistance

- There is also progress in developing methods to improve the oxidation resistance of the SWNTs, which is a consequence of the defects present in nanotubes. A strong oxidation resistance is needed for the nanotubes if they have to be used for applications such as field emission displays. Recent research has indicated that a modified arc-discharge method using a bowl-like cathode (see Figure 2-3), decreases the defects and gives cleaner nanotubes, and thus improves the oxidation resistance.
- The Raman spectrum of the newly synthesised nanotubes shows that the nanotubes formed are cleaner and less defective compared with those synthesised by conventional methods. The anode rod contained Ni and Y catalyst (C /Ni/Y is 94.8:4.2:1). No information is given about the diameter size.

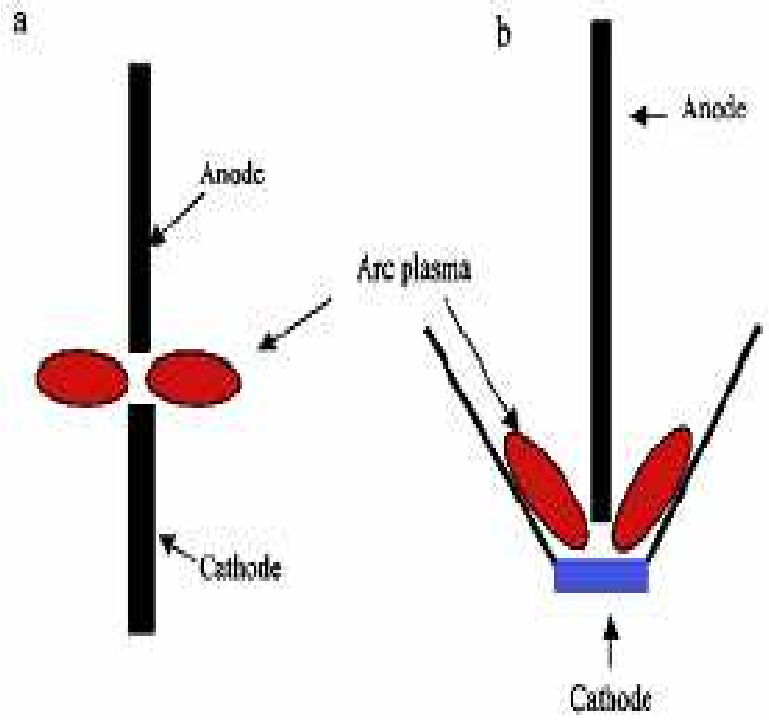


Figure 2-3: Schematic drawings of the electrode set-ups for (a) the conventional and (b) the new arc discharge electrodes.

Open air synthesis with welding arc torch

- Researchers discovered that it was possible to form CNTs in open air. A welding arc torch was operated in open air and the process was shielded with an argon gas flow. The anode and cathode were made of graphite containing Ni and Y (Ni/Y is 4.2:1 at. %).

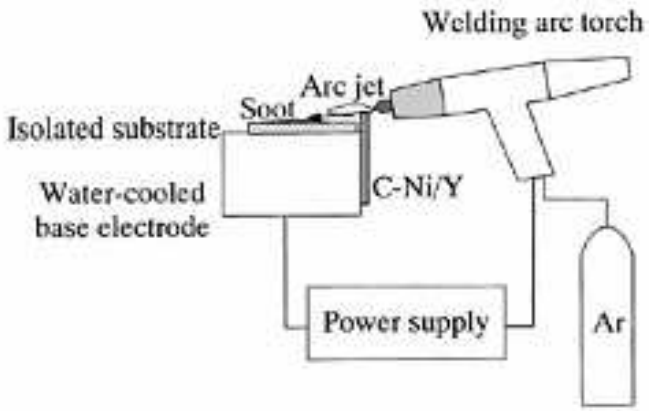


Figure 2-4: Experimental set-up of the torch arc method in open air.

- This method was modified for preparing SWNTs
- A plate target made of graphite containing metal catalyst Ni and Y (Ni/Y is 3.6:0.8 at. per cent), was fixed at the sidewall of a water–cooled, steel based electrode.
- The torch arc aimed at the edge of the target and the soot was deposited on the substrate behind the target (see Figure 2-4). The arc was operated at a direct current of 100 A. and shielding argon gas flowed through the torch, enhancing the arc jet formation beyond the target. In the soot, carbon nanohorns (CNHs) and bundles of SWNT with an average diameter of 1.32 nm were found.

- However, the yield was much lower than for the conventional low-pressure arc discharge method.
- There are two reasons for this fact. At first, because of the open air, the lighter soot will escape into the atmosphere. Secondly, the carbon vapour might be oxidised and emitted as carbon dioxide gas. In order to improve the yield in this method, contrivances for collecting soot and development of an appropriate target are required.