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SYNTHESIS, PROPERTIES, FUNCTIONALISATION AND APPLICATIONS OF CARBON NANOTUBES: A STATE OF THE ART REVIEW

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Abstract. The investigation of fullerenes and especially of carbon nanotubes (CNTs) has opened a new window for the development of polymer matrix composites with novel properties and applications. CNTs, which have a number of unexpected properties, both mechanical and electrical, seem to have a large potential as a filler, *i.e.* as a reinforcement in nanocomposites. With the discovery of carbon nanotubes, the research efforts have been initially concentrated on the better understanding of their processing conditions, modification, and properties.

Keywords: synthesis, carbon nanotube, filler, nanocomposite.

1. Carbon Allotropes

Carbon comes in several forms, which are known as three allotropes: graphite, diamond and fullerene (Fig.1.). Amorphic form of carbon is carbon black.
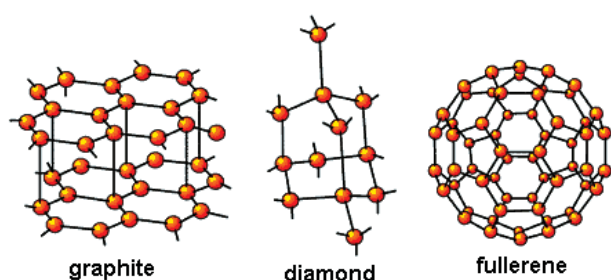

Fig. 1. The carbon allotropes

Carbon in those allotropes has differently hybridized orbitals: sp^2 (trigonal) – in graphitic structures, sp^3 (tetragonal) – in diamond or mixed – in carbon nanotubes [1-6].

The $1s^2 2s^2 2p^2$ configuration of the carbon atom does not account for the tetrahedral symmetry found in structures such as diamond or methane. In order to have an electron configuration that would account for this symmetry, the structure of the carbon atom must be altered to a state with four valence electrons instead of two, each in a separate orbital and each with its spin uncoupled from the other electrons. This alternation occurs as a result of the formation of hybrid atomic orbitals, in which the arrangement of the electrons of the L shell of the atom in the ground state is modified as one of the $2s$ electrons is promoted to the higher orbital $2p$ as shown in Fig. 2. These new orbitals are called hybrids since they combine the $2s$ and the $2p$ orbitals. They are labelled sp^3 since they are formed from one s orbital and three p orbitals.

The four hybrid sp^3 orbitals, known as tetragonal hybrids, have identical shape but different spatial orientation. Connecting the end points of these vectors (orientation of maximum probability) forms a regular tetrahedron with equal angles to each other of 109°28′. A graphic visualization of the formation of the sp^3 hybridization is shown in Fig. 3.
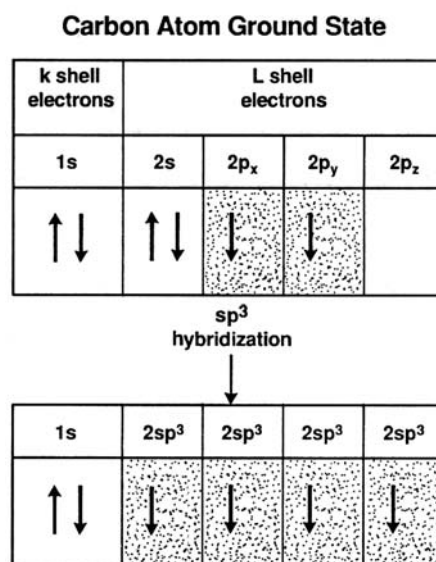

Fig. 2. The sp^3 hybridization of carbon orbitals. Shaded electrons are valence electrons (divalent for ground state, tetravalent for hybrid state)
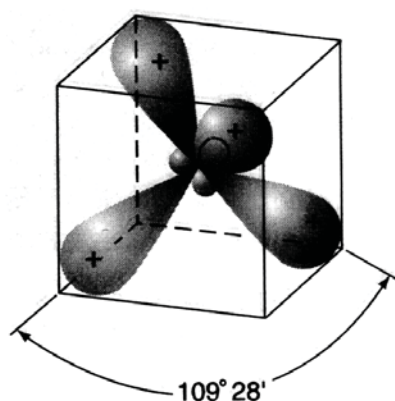
Fig. 3. Tetrahedral sp^3 orbitals

Carbon Atom Ground State

k shell electrons	L shell electrons			
1s	2s	$2p_x$	$2p_y$	$2p_z$
↑↓	↑↓	↓	↓	

sp^2
hybridization
↓

1s	$2sp^2$	$2sp^2$	$2sp^2$	2p
↑↓	↓	↓	↓	Free Delocalized Electron

Fig. 4. The sp^2 hybridization of carbon orbitals. Shaded electrons are valence electrons (divalent for ground state and tetravalent for hybrid state)
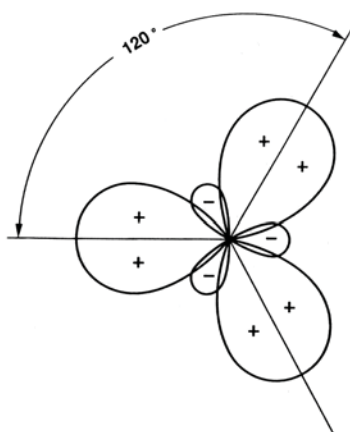

Fig. 5. Planar section of the sp^2 hybrid orbitals of the carbon atom

The other orbitals complete the series of electronic building blocks of all carbon allotropes and compounds: the sp^2 and the sp orbitals.

The sp^2 orbital is known as trigonal. The arrangement of the electrons of the L shell of the atom in the ground state is modified as one of the $2s$ electrons is promoted and combined with two of the $2p$ orbitals, to form three sp^2 orbitals and an unhybridized free (or delocalized) p orbital electron as shown in Fig.4.

Three identical sp^2 orbitals are in the same plane and their orientation of maximum probability forms a 120° angle from each other, as shown in Fig.5.

2. Fullerene and Carbon Nanotube

In the mid 1980s, Smalley and Kroto discovered fullerenes [7, 1]. Fullerenes are geometric cage-like structures of carbon atoms that are composed of hexagonal and pentagonal faces. The family of fullerene carbon molecules are considered another major allotropic form of carbon that combines both sp^2 and sp^3 bonds. These molecules are still in the early stages of investigation and some time will pass before their practical applications are found.

2.1. Carbon Nanotubes (CNTs)

A few years later, their discovery led to the synthesis of carbon nanotubes. Carbon nanotubes can be visualized as a sheet of graphite that has been rolled into a tube. Graphite is formed as a 2-D sheet of carbon atoms arranged in a hexagonal array so that each carbon atom has three nearest neighbors. "Rolling" a sheet of graphite into cylinders forms carbon nanotubes. The properties of nanotubes depend on atomic arrangement (how sheets of graphite are "rolled"), the diameter and length of the tubes, and morphology or nano-structure.

2.1.1. Structure of carbon nanotubes

Carbon nanotubes are formed from pure carbon bonds. Pure carbons only have two covalent bonds: sp^2 and sp^3, the former constitutes graphite and the latter constitutes diamond. The sp^2 is a strong bond within a plane but weak between planes, and is composed of one s orbital and two p orbitals. When more sp^2 bonds come together, they form six-fold structures like honeycomb pattern, which is the plane structure, the same structure as graphite. Graphite is stacked layer by layer so it is only stable in one single sheet. Viewing these layers perpendicularly shows the honeycomb patterns of graphite. Wrapping these patterns back on top of themselves, joining the edges, and closing one end while leaving one end open, we form a tube of graphite, which is a nanotube [8].

Carbon nanotubes are basically rolled up sheets of graphite that form tubes. The ends of a carbon nanotube

may be capped by a fullerene-like, or the tube end may be open. Typical tube diameters are in the nm range. Lengths up to a few hundreds of microns are found. There are two types of a basic nanotube: the single-wall nanotube and the multi-wall nanotube. Multi-wall carbon nanotubes (MWCNTs) are built from several coaxial layers of graphene cylinders (2–50 layers) with spacing between the layers close to that of the interlayer spacing of graphite (0.34 nm). Fig. 6 shows examples of carbon nanotubes structures.

Double-wall carbon nanotube (DWCNT) is the most basic member of the multi-walled carbon nanotube (MWCNT) family, which can be produced in significant quantities. These tubes consist of two concentric cylindrical graphene layers and their range of diameters is comparable to that of single-walled carbon nanotubes (SWCNTs). Several methods for producing DWCNT have been reported, such as catalytic chemical vapour deposition (CCVD), arc discharge or heating C_{60} molecules encapsulated in SWCNTs. Unfortunately, commercially viable methods such as CVD or arc discharge lead to products which contain catalyst particles and amorphous carbon. The products also contain some SWCNTs and MWCNTs along with DWCNTs. Of course, the diameter distribution and also the content of different tubes in the raw product vary between the different synthesis methods. There exists no single purification process which would remove all impurities and separate DWCNTs from other types of tubes [10].
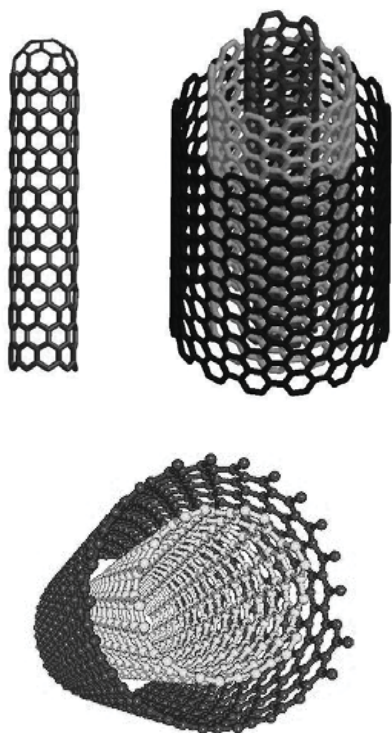

Fig. 6. Examples of carbon nanotubes structures. The nanotube can be capped as the SWCNT on the left. The MWCNT has been left uncapped to clarify the nested structure [9]
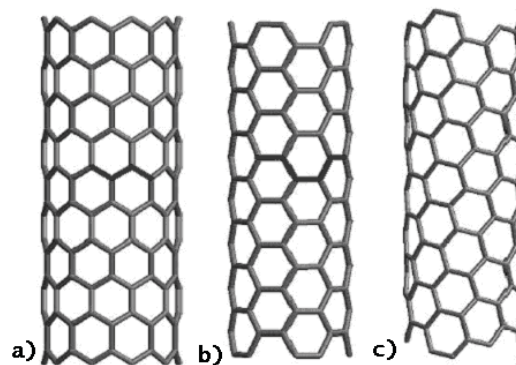

Fig. 7. Illustrations of the structure of a zig-zag (the q = 0^0 direction) (a), an armchair (the q = 30^0 direction) (b) and a chiral nanotube (a general direction $0< q < 30^0$) (c)

The properties of nanotubes depend on atomic arrangement (how the sheets of graphite are "rolled"), the diameter and length of the tubes and the morphology or nanostructure [11] (Fig. 7).

The structure of each nanotube is defined by the unit cell (smallest group of atoms that defines its structure) of the CNT. It is defined by the following equation:

$$c_n = na_1 + ma_2 \qquad (1)$$

where c_n – chiral vector; a_1, a_2 – unit vectors in the two-dimensional hexagonal lattice; n, m – integers.

2.1.2. Manufacturing of carbon nanotubes

The increased interest in many potential applications of carbon nanotubes and their future use strongly depend on the development of new techniques for large scale production. Carbon nanotubes are produced by three main techniques: arc discharge, laser ablation and chemical vapor deposition (CVD). The catalytic chemical vapor deposition (CCVD) is considered the only viable method offering lower energy consumption [12].

Arc-discharge method

The arc-discharge method [13] is the one by which CNTs were first produced and recognized. The schematic diagram of CNT production apparatus is shown in Fig. 8a. After evacuating the chamber with a vacuum pump, an appropriate ambient gas is introduced at the desired pressure, and then a dc arc voltage is applied between the two graphite rods. When pure graphite rods are used, the anode evaporates to form fullerenes, which are deposited in the form of soot in the chamber. However, a small part of the evaporated anode is deposited on the cathode, which includes CNTs. These CNTs, made of coaxial graphene sheets and called multi-walled carbon nanotubes (MWCNTs), are found not only on the top surface of the cathode deposit but also deep inside the deposit. Large-scale synthesis of MWCNTs by arc discharge has been achieved in He gas, and their thermal purification has also
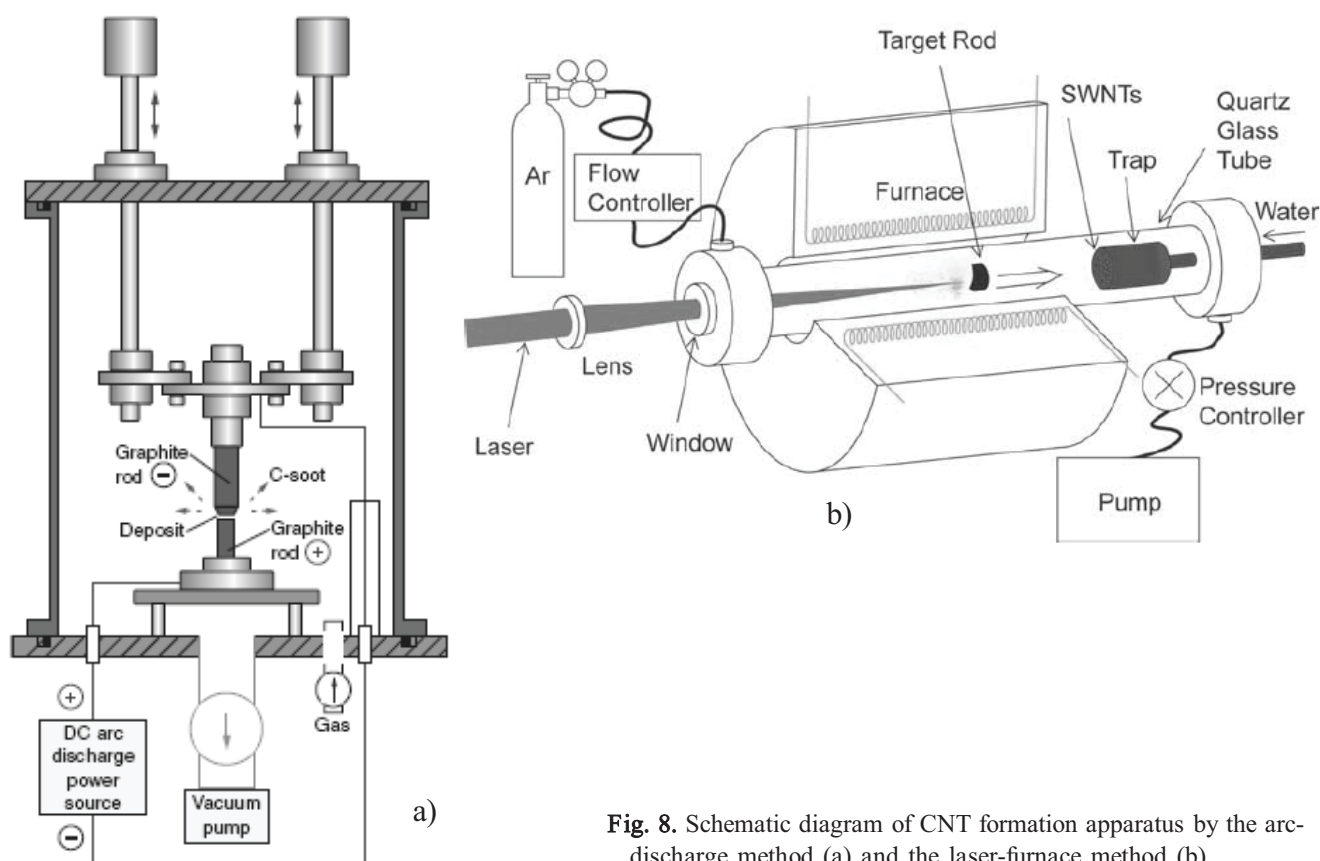
Fig. 8. Schematic diagram of CNT formation apparatus by the arc-discharge method (a) and the laser-furnace method (b)

been successful. When a graphite rod containing a metal catalyst (Fe, Co, *etc.*) is used as the anode with a pure graphite cathode, single-walled carbon nanotubes (SWCNTs) are generated in the form of soot.

Laser-furnace method

Fullerenes with a soccer ball structure are produced only at higher furnace temperatures, underlining the importance of annealing for nanostructures. These discoveries were applied to produce CNTs in 1996, especially SWCNTs. Fig. 8b shows the setup of the laser furnace, which consists of a furnace, a quartz tube with a window, a target carbon composite doped with catalytic metals, a water-cooled trap, and flow systems for the buffer gas to maintain constant pressures and flow rates. A laser beam (typically a YAG or CO_2 laser) is introduced through the window and focused onto the target located in the center of the furnace. The target is vaporized in high-temperature Ar buffer gas and forms SWCNTs. The Ar flow rate and pressure are typically 1 cm·s^{-1} and 500 torr, respectively. The SWCNTs produced are conveyed by the buffer gas to the trap, where they are collected. The vaporization surface is kept as fresh as possible by changing the focus point or moving the target.

The method has several advantages, such as high-quality SWCNT production, diameter control, investigation of growth dynamics, and the production of new materials. High-quality SWCNTs with minimal defects and contaminants, such as amorphous carbon and catalytic metals, have been produced using the laser-furnace method together with purification processes. The method provides high-quality DWCNTs and SWCNTs.

Chemical vapor deposition

CVD is another popular method for producing CNTs, in which a hydrocarbon vapor is thermally decomposed in the presence of a metal catalyst. The method is also known as thermal or catalytic CVD to distinguish it from the many other kinds of CVD used for various purposes. Compared with arc-discharge and laser methods, CVD is a simple and economic technique for synthesizing CNTs at low temperature and ambient pressure, at the cost of crystallinity. It is versatile as it harnesses a variety of hydrocarbons in any state (solid, liquid, or gas), enables the use of various substrates, and allows CNT growths in a variety of forms, such as powder, thin or thick films, aligned or entangled, straight or coiled, or even a desired architecture of nanotubes at predefined sites on a patterned substrate. It also offers better control over growth parameters. Fig. 9a shows a diagram of the setup used for CNT growth by CVD in its simplest form.

The process involves passing a hydrocarbon vapor (typically for 15–60 minutes) through a tube furnace in which a catalyst material is present at sufficiently high temperature (873.15–1473.15 K) to decompose the
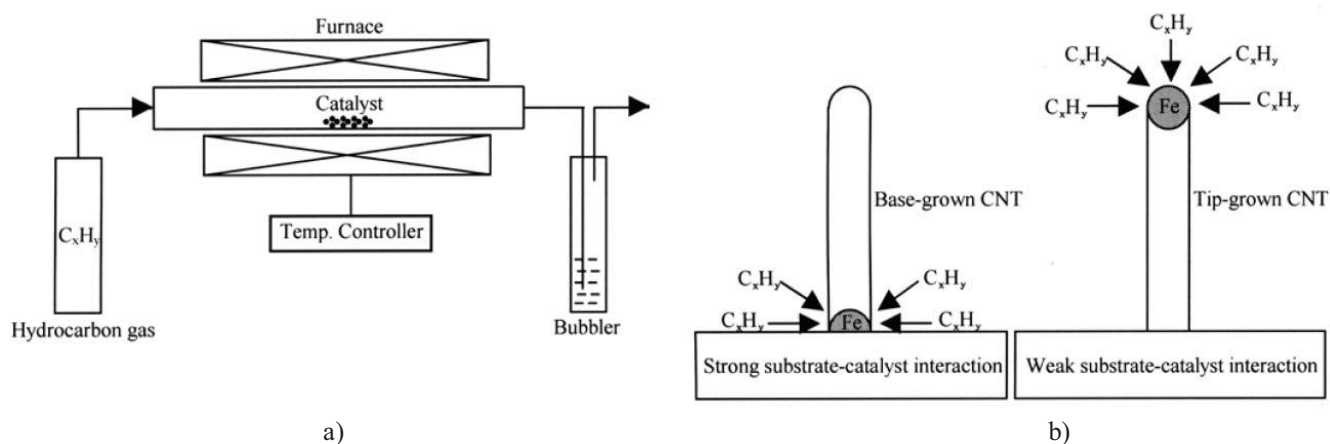
Fig. 9. Schematic diagram of a CVD setup (a) and probable models for CNT growth (b)

hydrocarbon. CNTs grow over the catalyst and are collected upon cooling the system to room temperature. In the case of a liquid hydrocarbon (benzene, alcohol, *etc*.), the liquid is heated in a flask and an inert gas purged through it to carry the vapor into the reaction furnace. The vaporization of a solid hydrocarbon (camphor, naphthalene, *etc*.) can be conveniently achieved in another furnace at low temperature before the main, high-temperature reaction furnace shown in Fig. 9a. The catalyst material may also be solid, liquid, or gaseous and can be placed inside the furnace or fed in from outside. Pyrolysis of the catalyst vapor at a suitable temperature liberates metal nanoparticles in situ (the process is known as the floating catalyst method). Alternatively, catalyst-plated substrates can be placed in the hot zone of the furnace to catalyze CNT growth. Catalytically decomposed carbon species of the hydrocarbon are assumed to dissolve in the metal nanoparticles and, after reaching supersaturation, precipitate out in the form of a fullerene dome extending into a carbon cylinder (like the inverted test tube shown in Fig. 9b with no dangling bonds and, hence, minimum energy. When the substrate-catalyst interaction is strong, a CNT grows up with the catalyst particle rooted at its base (known as the 'base growth model'). When the substrate-catalyst interaction is weak, the catalyst particle is lifted up by the growing CNT and continues to promote CNT growth at its tip (the "tip growth model").

The three main parameters for CNT growth in CVD are the hydrocarbon, catalyst, and growth temperature. General experience is that low-temperature CVD (873.15–1173.15 K) yields MWCNTs, whereas a higher temperature (1173.15–1473.15 K) reaction favors SWNT growth, indicating that SWCNTs have a higher energy of formation (presumably owing to their small diameters, which results in high curvature and high strain energy). Common efficient precursors of MWCNTs (*e.g.* acetylene, benzene, *etc*.) are unstable at higher temperatures and lead to the deposition of large amounts of carbonaceous compounds other than CNTs. Transition metals (Fe, Co, Ni) are the most commonly used catalysts for CNT growth, since the phase diagram of carbon and these metals suggests finite solubility of carbon in these transition metals at high temperatures.

Catalytic chemical vapor deposition (CCVD)

All kinds of carbon nanostructures (filaments) can be synthesized employing the CCVD method. In this case a tube furnace is loaded with a metal catalyst and fed with a carbon-containing gas or gas mixture. At moderate temperatures in the range of 773.15 to 1273.15 K (and different pressures) the carbon is deposited on the catalyst surfaces.

A short summary of the three most common techniques used nowadays is given in Table 1.

2.2. Properties of CNTs

One of the striking features of CNTs is the potential to use them in nanoscale devices. They have a very broad range of electronic, thermal, and structural properties that change depending on the different kinds of nanotubes (determined by its diameter, length, chirality, or twist).

2.2.1. Electronic properties

The electronic structure of carbon nanotubes is unique in materials science. A minor change in the structure can determine whether the tube is semiconducting or metallic. The conductivity of an SWNT is governed by its electronic structure which is determined by the index combination (n, m). A nanotube of type $(n;m)$ is metallic if $3/(n–m)$ and semiconducting if not. For MWCNTs the situation is more complex because the multiple layers contribute to the conductivity. Currently, most of the interest in the nanotube electronic transport focuses on individual tubes. Bulk transport may be interesting in conducting composites but the main interest is in devices based on

Summary of the major production methods and their efficiency [14]

Method	Arc discharge method	Chemical vapour deposition	Laser ablation (vaporization)
How	Connect two graphite rods to a power supply, place them a few millimeters apart, and throw the switch. At 100 amps, carbon vaporises and forms hot plasma.	Place substrate in oven, heat to 873,15 K, and slowly add a carbon-bearing gas such as methane. As gas decomposes it frees up carbon atoms, which recombine in the form of CNTs	Blast graphite with intense laser pulses; use the laser pulses rather than electricity to generate carbon gas from which the CNTs form; try various conditions until hit on one that produces prodigious amounts of SWCNTs
Typical yield	30 to 90 %	20 to 100 %	Up to 70 %
SWCNT	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.
MWCNT	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 MWCNT synthesis is possible.
Advantages	Can easily produce SWCNT, MWCNTs. SWCNTs have few structural defects; MWCNTs without catalyst, not too expensive, open air synthesis possible	Easiest to scale up to industrial production; long length, simple process, SWCNT diameter controllable, quite pure	Primarily SWCNTs, with good diameter control and few defects. The reaction product is quite pure.
Disadvantages	Tubes tend to be short with random sizes and directions; often needs a lot of purification	CNTs are usually MWCNTs and often riddled with defects	Costly technique, because it requires expensive lasers and high power requirement, but is improving

individual tubes. The tubes show both ballistic and diffusive transport character depending on the level of perfection of the tubes. SWCNTs are more typically ballistic while MWCNTs are diffusive because of a higher defect concentration [15].

2.2.2. Mechanical properties

The most important application of nanotubes based on their mechanical properties will be as reinforcements in composite materials [16-22]. The main results on tubes are:

- a very high Young's modulus of about 1 TPa (for SWCNT, there are many different results for this value, but all converge towards 1 TPa) and 1.28 TPa (for MWCNT) [23],
- a high tensile strength of around 50 GPa ([24]). The determination of the strength of CNTs is more difficult than that of the Young's modulus.

However, to date, their performance has been rather disappointing. The main problem is in creating a good interface between nanotubes and the polymer matrix and attaining good load transfer from the matrix to the nanotubes, during loading. This is because, firstly, SWCNTs are usually not dispersed in the matrix but distributed as bundles. Secondly, only small amounts of CNTs are dispersed in the host and, thirdly, there is insufficient bonding across the nanotube/host interface to transfer forces. So far, these composites tend to fail either by fracture at the nanotube/host interface or, for MWCNTs, by pull out of different shells of the MWCNTs. To maximize the advantage of nanotubes as reinforcing structures in high strength composites, the aggregates needs to be broken up and dispersed or cross-linked to prevent slippage. Stronger bonds between CNTs and host are needed, for example by creating covalent bonds by functionalisation along long tubes. Other way would be to use secondary bonds such as hydrogen bonds that, although only 5 % as strong as covalent bonds, could bond to more sites.

Nanotubes can have a very low defect density and many of their key properties, for example, the long electron scattering lengths and the ultra-low friction discussed above are based on this property. Despite this, as in any material, defects play an important role in nanotube properties. Defects act as scattering centers for charge carriers. They also make the tube less strong and thus defects are rarely desirable from the purely mechanical point of view. Defects are generated in the synthesizing process and can also be caused by, for example, ion or electron beam irradiation of the tube, or mechanical manipulation. The most typical structural defects are fivefold (pentagon) and sevenfold (heptagon) rings in the sixfold (hexagonal) lattice. Other types of typical defects are vacancies, interstitials and miscellaneous bonding configurations such as locally amorphous structure [11, 25]. Fig. 10 shows examples of defects in nanotubes and properties of carbon nanotubes have been summarized in Table 2.
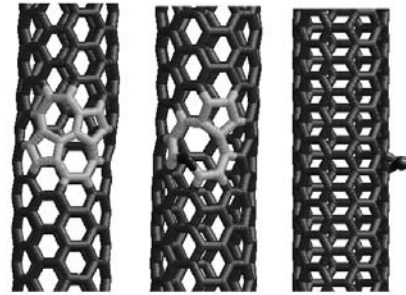

Fig. 10. Examples of defects in nanotubes. The leftmost image shows a Stone-Wales defect that has been given much consideration in nanotubes. It consists of a complex of two pentagons and two heptagons and is formed by a bond rotation from the hexagonal lattice. The center image shows a vacancy structure in which two of the dangling bonds in the vacancy have reconstructed to form a pentagon and the remaining dangling bond (blue) protrudes from the surface. The image on the right shows an ad-atom on the surface of a nanotube [9]

Table 2

Properties of carbon nanotubes [26-28]

Property	CNTs	
Average diameter	1.2–1.4 nm for SWCNT 30–50 nm for MWCNT	
Average length	A few hundred μm	
Carbon bond length	0.14 nm for SWCNT	
Distance from opposite carbon atoms	0.28 nm for SWCNT	
Parallel carbon bond separation	0.245 nm for SWCNT	
Density for SWCNT: (10.10) Armchair (17.0) Zigzag (12.6) Chiral	1.33 g/cm^3 1.34 g/cm^3 1.40 g/cm^3	
Young's Modulus	~1 TPa for SWCNT 10–60 GPa for MWCNT	
Strength	50–500 GPa for SWCNT 10–60 GPa for MWCNT	
Thermal conductivity	3000 Wm^{-1}K^{-1}	
Resistivity	5–50 μΩcm	
Large aspect ratio	>1000	

3. Purification and Functionalisation of Carbon Nanotubes

Functionalisation is a surface treatment which brings functional groups at the surface of nanofillers/nanoparticles. The filler functionalisation brings about favourable interactions between the functional groups and the polymer matrix. This is particularly important for fillers having strong tendency towards agglomeration as, for instance, carbon nanotubes. The enhanced filler-matrix interactions facilitate the dispersion of the filler in the polymer matrix and strengthen the interfacial bonding, leading to better reinforcement effects. The filler functionalisation often leads to restricted chain-mobility at the vicinity of the filler surface, and sometimes to enhanced glass-transition temperature.

The functionalisation might also accomplish changes in the chemical structure and physical properties of the

fillers. The electrical conductivity and the outstanding mechanical properties of carbon nanotubes can be mainly explained in terms of the graphite-like structure of the walls of these materials. The sp^2-hybridized carbon atoms in conjugated C=C bonds, in analogy to those described for graphite, enable the electron delocalization. Therefore, chemical reactions involving the cleavage of the C=C can lead to decreased electrical conductivity. Moreover, functionalisation method imputing higher amounts of energy, like milling in liquid ammonia, can cause the shortening of the carbon nanotubes.

The functionalisation methods can be classified in four main groups:

• *Strong oxidation.* The main goal of this procedure is the introduction of carboxylic acids and other carbonyl compounds at the surface of the carbon nanotubes. As a result the structural quality of the CNTs is worsened. This method is mostly suitable when an optimal reinforcement effect is primarily required [29-38].

• *Cycloaddition reactions.* In this method, the C=C bonds of the CNTs react with dienes, tetrazines or 1,3-dipoles, as illustrated in the Scheme 2. Although this procedure is not as drastic as the oxidation-based one, still C=C bonds are broken due to the chemical reactions, therefore changes in the electrical conductivity might take place [39-43].

• *Radical-based reactions.* Although milder than the other ones, this method is based on the cleavage of C=C by radical, which are generated *in-situ* during the functionalisation process [44-48].

• *Mild oxi-reduction reactions.* In these procedures, the C=C bonds are broken through reduction with metals followed by another functionalisation step. This method has high selectivity and the functionalised CNTs exhibit a remarkable dispersability. The main disadvantage of such methods is their complexity due to the use of air-sensitive and moisture-sensitive chemical, which is the most significant drawback for the breakthrough of this method [49, 50].

On the other hand, the use of surfactants, aromatic hydrocarbons (pyrenes) [51-54], conjugated polymers [54, 55], aromatic polyimides [56, 57], bio-macromolecules [53], cytosine [58], tiophene [59], as modifiers of carbon nanotubes has emerged as convenient
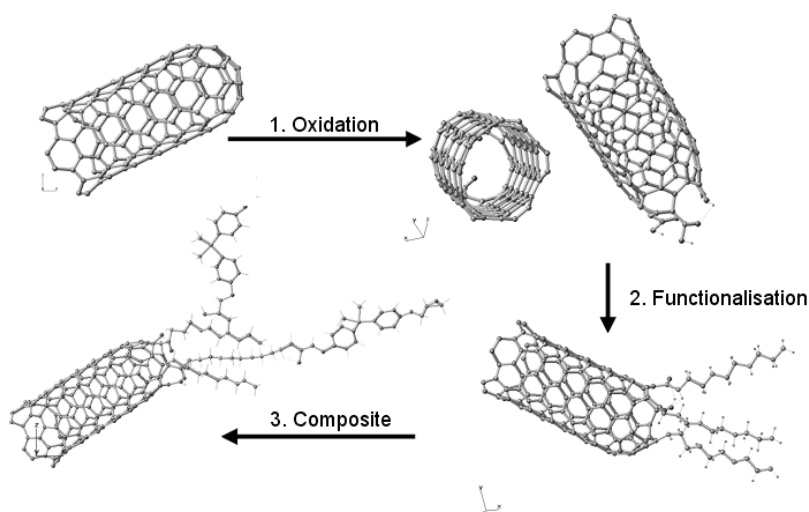

Fig. 11. Possible functionalisation process involving the oxidation with acids followed by reaction with amines
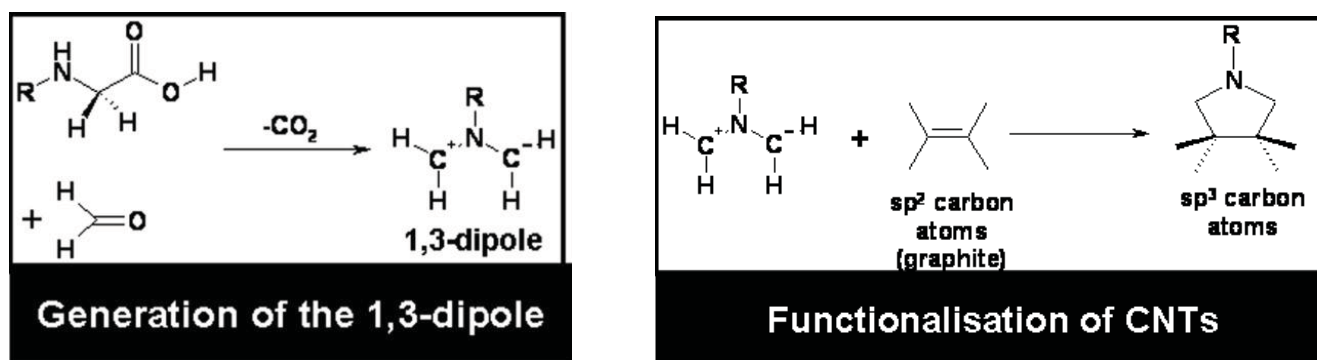

Fig. 12. Functionalisation of CNTs using 1,3-dipoles. These 1,3-dipoles are generated by the reaction of an functionalised amino-acid and formaldehyde. (R denotes any organic group attached to the nitrogen group of the amino-acid)

method for the surface modification of CNTs. This method is often reported as non-covalent functionalisation and often facilitates significantly the CNT dispersion in polymeric matrices and solvents. The main advantage of this methods is that no cleavage of C=C is necessary, so the electrical, thermal and mechanical properties of the CNTs are not necessarily affected.

Since the epoxy resin used in the present work has been an epoxy resin cured with an amine hardener, the chemical properties of the functionalised carbon nanotubes should be tailored for the chemical reactions involved during the curing process. Therefore the introduction of amine groups at the surface of the CNTs seems to be a plausible method for improving the epoxy dispersion in the epoxy as well as the filler adhesion to this polymer matrix.

4. Applications of CNTs

A key point for a new product to find a market is that it should have either a unique function not previously existing, or it should have a high (x10) performance advantage to displace an existing product in its market. We shall consider applications in four broad areas: composites, field emission, electronics, and electrochemistry.

4.1. Composites

The high aspect ratio (length to radius ratio) and high conductivity of CNTs makes them excellent for conducting composites. The first use of such composites was by Hyperion for electrostatically applying paint onto car components. Another use of nanotube composites is as antistatic shielding, on airplane wings and fuselages for example. This is a realistic application. The next application of conducting composites is as a transparent conductor. There is a huge market for transparent electronic conductors such as indium tin oxide (ITO) in displays. In this field, there is a drive towards flexible displays on plastic substrates.

The most important application of nanotubes based on their mechanical properties will be as reinforcements in composite materials [60-71]. Nanotube reinforcements will increase the toughness of the composites by absorbing energy during their highly flexible elastic behavior. This will be especially important for nanotube-based ceramic matrix composites. Other interesting applications of nanotube-filled polymer films will be in adhesives where a decoration of nanotubes on the surface of the polymer films could alter the characteristics of the polymer chains due to interactions between the nanotubes and the polymer chains.

4.2. Field Emission

High aspect ratio also makes CNTs ideal field-emission (FE) materials. FE is the emission of electrons from a solid under an intense electric field. CNTs have better FE performance than other forms of carbon such as diamond and diamond-like carbon. A clear application of FE from CNTs is as electron guns for next generation scanning electron microscopes (SEMs) and transmission electron microscopes (TEM). Present day microscopes use Schottky emitters of doped Si or metal FE tips. A single MWCNT FE source is found to have a factor of 30 times higher brightness than existing electron sources and a small energy width of 0.25 eV. The second use of CNTs is as FE cathodes in high power microwave amplifiers such as klystrons for base stations. The third possible application is as electron sources for miniature X-ray sources. In each of these applications, the CNTs should operate at the highest current density. A fourth application is in FE displays (FEDs).

4.3. Electrochemistry

The large surface area and low resistivity of CNTs makes them of great interest in electrochemistry. CNTs could be very useful for the storage of hydrogen, a key aspect of the clean energy economy. A storage capacity of 10 %, if readily cyclable, would be an extremely valuable property compared to other systems. However, it turns out that the hydrogen storage capacity of CNTs is less than 1 %. In order to allow access of hydrogen to the nanotube ends, the samples are subjected to intense ultrasonic treatment to break them up, but this deposits Ti from the sonic horn, and it is the Ti that is absorbing some hydrogen. Thus, the consensus is now that CNTs are not a useful hydrogen storage medium. This applies to all forms of nanostructured carbon.

4.4. Electronics

CNTs can carry the highest current density of any metal, 10^9–10^{10} A/cm^2, over 1000 times that for Cu, before failing as a result of electromigration (self-electrolysis). It is well known that feature sizes in Si integrated circuits are continually reducing. This forces the interconnects between each transistor to carry ever larger current densities.

CNTs have been made into field-effect transistors (FETs). The first examples were made by dispersing SWCNTs on SiO$_2$-covered Si wafers and then making contacts. The Si substrate is used as the bottom gate electrode. This is not suitable for a real device, as the gate would be common to all FETs on the wafer. Thus, CNT transistors have extremely good limiting performance over Si. However, this is somewhat misleading. The economics of Si devices is driven by the ability to place ever more transistors on a wafer – as transistors get smaller, so they get cheaper. A significant problem for electronic applications is that the band gap of a SWNT depends on its chirality.

The cohesive energy depends only weakly on diameter and very weakly on chirality, so that a mixture will contain both metallic and semiconducting nanotubes. This is a huge disadvantage in electronics. It is necessary to be able to grow a specific type of tube at a defined position in a defined direction with near 100 % yield.

5. Conclusions

Carbon nanotubes continue to attract considerable interest from academic and industrial researchers alike, but a lack of commercially available material of consistent quality and at an accessible price has prevented the development of industrially relevant performance data and consequently the market from expanding into commercial products and applications. Initially, the application of CNT as a filler material in matrix polymers in order to improve their properties has not been in the focus of research. However, the CNT potential of quite high mechanical properties and, especially, the fracture toughness of polymers can be improved. Low diameter of CNTs and their high aspect ratio make them an ideal material to improve the properties of the polymer matrix, compared to glass, carbon or aramid fibers.

References

[1] Laurie O., Cox D. E. and Wagner H.: Appl. Phys. Lett., 1998, **81**, 1638.

[2] Iijima S.: Nature, 1991, **354**, 56.

[3] Bundy F.: J. Geophys. Res., 1980, **85**, 6930.

[4] Wyckoff R.: Crystal Structures, 1963, 1.

[5] Dresselhaus M. and Steinbeck. J.: Tanso, 1988, **132**, 44.

[6] Kelly B.: Physics of Graphite. Applied Science. Englewood, NJ, London 1981.

[7] Kroto H., Heath J., O'Brien S. *et al.*: Nature, 1985, **318**, 162.

[8] http://www.seed.slb.com/en/scictr/watch/fullerenes/index.html

[9] Sammalkorpi M.: Helsinki University of Technology, Laboratory of Computational Engineering, Espoo REPORT B41, 2004 Online in PDF format: http://lib.hut.fi/Diss/2004/isbn9512273799/

[10] Osswald S., Flahaut E., Ye H. and Gogotsi Y.: Chem. Phys. Lett., 2005, **402**, 422.

[11] Dresselhaus M., Dresselhaus G. and Avouris P.: Topics Appl. Phys., 2001, **80**, 287.

[12] Lupu D., Biris A., Jianu A. *et al.*: Carbon, 2004, **42**, 503.

[13] Ando Y., Zhao X., Sugai T. and Kumar M.: Materials Today, 2004, **7**, 22.

[14] Daenen M., de Fouw R., Hamers B. *et al.*: The Wondrous World of Carbon Nanotubes, University of Technology, Eindhoven 2003.

[15] Ahlskog M., Laurent C., Baxendale M. and Huhtala M.: Encyclopedia of Nanoscience and Nanotechnology. American Scientific Publishers, NY 2004, **3**, 139.

[16] Fiedler B., Gojny F., Wichmann M. and Nolte M.: Composites Sci. Techn., 2006, **66**, 3115.

[17] Liu L. and Wagner H.: Composites Sci. Techn., 2005, **65**, 1861.

[18] Chen H., Jacobs O., Wu W. *et al.*: Polymer Testing, 2007, **26**, 351.

[19] Bal S. and Samal S.: Bull. Mater. Sci., 2007, **30**, 379.

[20] Giraldo L., Brostow W., Devaux E. *et al.*: J. Nanosci. Nanotechn., 2008, **8**, 8.

[21] Giraldo L., Lopez B. and Brostow W.: Polymer Eng.Sci., 2009, **49**, 898.

[22] Bottini M., Cerignoli F., Tautz L. *et al.*: J. Nanosci. Nanotechn., 2006, **6**, 3693.

[23] Xie X.-L., Maia Y.-W. and Zhoua X.-P.: Mat. Sci. Eng., 2005, **49**, 89.

[24] Huard B.: Appl. Physics, 1999, **69**, 255.

[25] Saito R., Dresselhaus G. and Dresselhaus M.: Physical Properties of Carbon Nanotubes. Imperial College Press 1992.

[26] Spires T. and Brown R.: Department of Botany. The University of Texas at Austin, Austin, Tx 1996.

[27] Gao G., Cagin T. and Goddard W.: Nanotechnology, 1998, **9**, 184.

[28] Kim K., Lim S., Lee I. *et al.*: Rev. Sci. Instrum., 2003, **74**, 4021.

[29] Hu Y., Wu L., Shen J. and Ye M.: J. Appl. Polym. Sci., 2008, **110**, 701.

[30] Lin S., Wei K., Lee T. *et al.*: Nanotechnology, 2006, **17**, 3197.

[31] Liu L. and Wagner H.: Composites Sci.Techn., 2005, **65**, 1861.

[32] Gojny F. and Schulte K.: Composites Sci. Techn., 2004, **64**, 2303.

[33] Chen H., Jacobs O., Wu W. *et al.*: Polymer Testing, 2007, **26**, 351.

[34] Ma P., Kim J. and Tang B.: Composites Sci. Techn., 2007, **67**, 2965.

[35] Velasco-Santos C., Martinez-Hernandez A., Lozada-Cassou M. *et al.*: Nanotechnology, 2002, **13**, 495.

[36] Marega R., Accorsi G., Meneghetti M. *et al.*: Carbon, 2009, **47**, 675.

[37] Verdejo R., Lamoriniere S., Cottam B., Bismarck A., Shaffer M.: Chemical Communication, 2007, 5, 513.

[38] Fiedler B., Gojny F., Wichmann M. *et al.*: Composites Sci. Techn., 2006, **66**, 3115.

[39] Fernandes M., Araujo R., Proenca M. *et al.*: J. Nanosci. Nanotechn., 2007, **7**, 3514.

[40] Hayden H., Gun'ko Y. and Perova T.: Chem. Phys. Lett., 2007, **435**, 84.

[41] Georgakilas V., Bourlinos A., Gournis D. *et al.*: J. Am. Chem. Soc., 2008, **130**, 8733.

[42] Araujo R., Proenca M., Silva C. and Paiva M.: Composites Sci. Techn., 2007, **67**, 806.

[43] Tagmatarchis N., Prato M.: Journal of Materials Chemistry, 2004, 14, 437.

[44] Yang D., Zhang X., Wang C. *et al.*: Progress in Natural Sci., 2009, **19**, 991.

[45] Liu P.: Eur. Polym. J., 2005, **41**, 2693.

[46] Ghislandi M., Prado L., Oyervides A. *et al.*: J. Polym. Sci. A, 2008, **46**, 3326.

[47] Wu H., Tong R., Qiu X. *et al.*: Carbon, 2007, **45**, 152.

[48] Liu J., Nie Z., Gao Y. *et al.*: J. Polym. Sci. A, 2008, **46**, 7187.

[49] Wunderlich D., Hauke F. and Hirsch A.: J. Mat. Chem., 2008, **18**, 1493.

[50] Balasubramanian K. and Burghard M.: *ibid*, 3071.

[51] Meuer S., Braun L., Schilling T. and Zentel R.: Polymer, 2009, **50**, 154.

[52] Ehli C., Guldi D., Herranz M. and Martin N.: J. Mat. Chem., 2008, **18**, 1498.

[53] Meuer S., Braun L. and Zentel R.: Chem. Commun., 2008, **27**, 3166.

[54] Wu X. and Shi G.: J. Mat. Chem., 2005, **15**, 1833.

[55] Balasubramanian K. and Burghard M.: J. Mat. Chem., 2008, **18**, 3071.

[56] Shigeta M., Komatsu M. and Nakashima N.: Chem. Phys. Lett., 2006, **418**, 115.

[57] Wise K., Park C., Siochi E. and Harrison J.: Chem. Phys. Lett., 2004, **391**, 207.

[58] Meng L., Fu C. and Lu Q.: Progress in Natural Sci., 2009, **19**, 801.

[59] Stepanian S., Karachevtsev M., Glamazda A. *et al.*: Chem. Phys. Lett., 2008, **459**, 153.

[60] Thostensen E., Ren Z. and Chou T.: Composites Sci. Techn., 2001, **61**, 1899.

[61] Gojny F., Wichmann M., Kopke U. *et al.*: Composites Sci. Techn., 2004, **64**, 2363.

[62] Li Q., Zaiser M. and Koutsos V.: Phys. Status. Solid. A., 2004, **201**, 89.

[63] Song Y. and Yuon J.: Carbon, 2005, **43**, 1378.

[64] Tang W., Santare M. and Advani S.: Carbon, 2003, **41**, 2779.

[65] Manchado L., Valentini L., Biagiotti J. and Kenny J.: Carbon, 2005, **43**, 1499.

[66] Potschke P. and Bhattacharyya A.: Polymer Preprint, 2003, **44**, 760.

[67] Giraldo L., Brostow W., Devaux E. *et al.*: J. Nanosci. Nanotechn., 2008, **8**, 3176.

[68] Giraldo L., Lopez B. and Brostow W.: Polymer Eng. Sci., 2009, **49**, 896.

[69] Kwiatkowska M., Broza G., Schulte K. and Roslaniec Z.: Rev. Adv. Mater. Sci., 2006, **12**, 154.

[70] Roslaniec Z., Broza G. and Schulte K.: Compos. Interfac., 2003, **10**, 95.

[71] Broza G.: Composites Sci. Techn., 2009, submitted.

СИНТЕЗ, ВЛАСТИВОСТІ, ФУНКЦІОНАЛІЗАЦІЯ ТА ЗАСТОСУВАННЯ ВУГЛЕЦЕВИХ НАНОТРУБОК: ОГЛЯД СУЧАСНОГО СТАНУ

Анотація. *Дослідження фулеренів і особливо вуглецевих нанотрубок (ВНТ) відкрило абсолютно нові перспективи для розвитку полімерних матричних композитів із новими властивостями і областями застосування. ВНТ, які проявляють непередбачувані властивості, як механічні, так і електричні, мають величезний потенціал як наповнювачі, тобто як підсилювачі в нанокомпозитах. З відкриттям ВНТ зусилля дослідників були спрямовані на виявлення умов їх отримання, модифікації та властивостях.*

Ключові слова: *синтез, вуглецева нанотрубка, наповнювач, нанокомпозит.*