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Review Article

CARBON NANOTUBES: A REVIEW ON PREPARATION TECHNIQUES AND APPLICATIONS IN VARIOUS FIELDS

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ABSTRACT
Carbon nanotubes (CNTs) are allotropes of carbon with a nanostructure that can have a length-to-diameter ratio greater than 1,000,000. Different types of carbon nanotubes can be produced by different methods: Arc discharge, laser ablation, chemical vapour deposition and flame synthesis. Purification of the tubes can be divided into a couple of main techniques: oxidation, acid treatment, annealing, sonication, filtering and functionalisation techniques. Economically feasible large-scale production and purification techniques still have to be developed. Fundamental and practical nanotube researches have shown possible applications in the fields of energy storage, molecular electronics, nanomechanic devices, composite materials and immobilization of enzymes. Various immobilization methods have been developed, and in particular, specific attachment of enzymes on carbon nanotubes has been an important focus of attention. With the growing attention paid to cascade enzymatic reaction, it is possible that multi enzyme co-immobilization would be one of the next goals in the future. In this paper, we focus on preparation techniques, various applications of CNTs and enzyme immobilization on carbon nanotubes.

Key words: Carbon nanotubes, Chemical vapour deposition, Immobilization, oxidation and Allotropes

INTRODUCTION

Fullerenes are large, closed-cage, carbon clusters and have several special properties that were not found in any other compound before. Therefore, fullerenes in general form an interesting class of compounds that surely will be used in future technologies and applications. Before the first synthesis and detection of the smaller fullerenes C_{60} and C_{70}, it was generally accepted that these large spherical molecules were unstable. However, some Russian scientists[1,2] already had calculated that C_{60} in the gas phase was stable and had a relatively large band gap.

As is the case with numerous, important scientific discoveries, fullerenes were accidentally discovered. In 1985, Kroto and Smalley[3] found strange results in mass spectra of evaporated carbon samples. Herewith, fullerenes were discovered and their stability in the gas phase was proven. The search for other fullerenes had started.

Diamond and graphite are considered as two natural crystalline forms of pure carbon. In diamond, carbon atoms exhibit hybridization, in which four bonds are directed towards the corners of a regular tetrahedron. The resulting three-dimensional network (diamond) is extremely rigid, which is one reason for its hardness. In graphite, hybridization occurs, in which each atom is connected evenly to three carbons (120°) in the plane, and a weak bond is present in the axis. The set forms the hexagonal (honeycomb) lattice typical of a sheet of graphite[5].

A new form of carbon, Buckminster fullerene (), was discovered in 1985 by a team headed by Korto and coworkers[6].

Besides diamond, graphite, and fullerene (), quasi-one-dimensional nanotube is another form of carbon first reported by Ijima in 1991 when he discovered multiwalled carbon nanotubes (MWCNTs) in carbon soot made by an arc-discharge method[7]. Carbon nanotubes (CNTs) are allotropes of carbon. CNTs are tubular in shape, made of graphite. The tubes contained at least two layers, often many more, and ranged in outer diameter from about 3 nm to 30 nm. About two years later, he made the observation of single-walled carbon nanotubes (SWCNTs) [8]. At about the same time, Dresselhaus et al. synthesized single-walled carbon nanotubes by the same route of producing MWCNTs but adding some transition metal particles to the carbon electrodes[9].

The single-walled nanotubes are generally narrower than the multi walled tubes, with diameters typically in the range 1-2 nm, and tend to be curved rather than straight (FIGURE 1). A significant amount of work has been done in the past decade to reveal the unique structural, electrical, mechanical, electromechanical, and chemical properties of CNTs. Recent research has focused on improving the quality of catalytically-produced nanotubes[10,11].

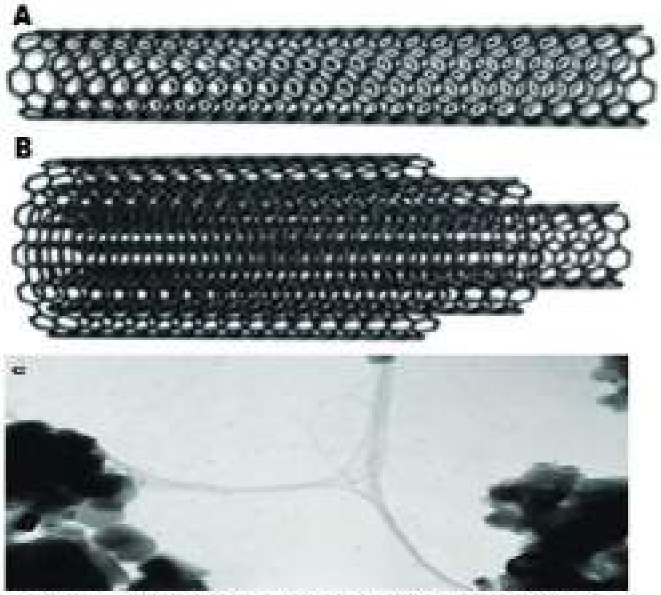

FIGURE 1: REPRESENTATIONS OF SWCNT (A) AND MWCNT (B) WITH TYPICAL TRANSMISSION ELECTRON MICROGRAPHS (C)[12]

ADVANTAGES OF CARBON NANOTUBES (CNT)

- Improves conductive, mechanical, and flame barrier properties of plastics and composites

- Optimizes processing fabrication, and reduces shipping costs
- Enables eco-friendly anti-fouling paints, and other new applications
- Enables clean, bulk micromachining and assembly of electronic components
- Improves the true total cost of formulation, processing, and manufacturing
- Extremely small and lightweight, making them excellent replacements for metallic wires.
- Resources required to produce them are plentiful, and many can be made with only a small amount of material.
- Are resistant to temperature changes, meaning they function almost just as well in extreme cold as they do in extreme heat.
- Have been in the R&D phase for a long time now, meaning most of the kinks have been worked out.
- As a new technology, investors have been piling into these R&D companies, which will boost the economy.

DISADVANTAGES

- Despite all the research, scientists still don't understand exactly how they work
- Extremely small, so are difficult to work with this technology
- Currently, the process is relatively expensive to produce the nanotubes
- Would be expensive to implement this new technology in and replace the older technology in all the places.
- At the rate our technology has been becoming obsolete; it may be a gamble to bet on this technology.

TYPES OF CARBON NANOTUBES

Carbon nanotubes are two types:
i) SWCNTs—Single-walled carbon nanotubes and
ii) MWCNTs—Multiple-walled carbon nanotubes.

Comparison between SWCNT and MWCNT is as presented in Table 1 [13,14,15]

TABLE 1: COMPARISON BETWEEN SWCNT AND MWCNT[15]

SWCNT	MWCNT
Single layer of graphene.	Multiple layer of graphene
Catalyst is required for synthesis.	Can be profuced without catalyst.
Bulk synthesis is difficult as it requires proper control over growth and atmospheric condition	Bulk synthesis is easy.
Not fully dispersed, and form bundled structures	Homogeneously dispersed with no apparent bundled formation
Resistivity usually in the range of 10^{-4}–10^{-3} Ω m.	Resistivity usually in the range of 1.8×10^{-5}–6.1×10^{-5} Ω m
Purity is poor	Purity is high
TypicalSWCNTcontent in as-prepared samples by chemical vapour deposition (CVD) method is about 30–50 wt%. However high purity up to 80% has been reported by using arc discharge synthesis method.	Typical MWCNT content in as-prepared samples by CVD method is about 35–90 wt%.
A chance of defect is more during functionalisation.	A chance of defect is less especially when synthesized by arc-discharged method.
Characterization and evaluation is easy	It has very complex structure
It can be easily twisted and are more pliable.	It cannot be easily twisted.

STRUCTURE AND MORPHOLOGY OF CNT

Comprised entirely of carbon, the structure of pure SWCNT can be visualized as rolled-up tubular shell of graphene sheet which is made up of benzene type hexagonal rings of carbon atoms (Figure 2(a)). Graphene sheets are seamless cylinders derived from a honeycomb lattice, representing a single atomic layer of crystalline graphite. A MWCNT is a stack of graphene sheets rolled up into concentric cylinders. Each nanotube is a single molecule composed of millions of atoms and the length of this molecule can be tens of micrometers long with diameters as small as 0.7 nm[17]. The SWCNTs usually contain only 10 atoms around the circumference and the thickness of the tube is only one-atom thick. Nanotubes generally have a large length-to-diameter ratio (aspect ratio) of about 1000, so they can be considered as nearly one-dimensional structures[18]. MWCNTs are larger and consist of many single-walled tubes stacked one inside the other. The name MWCNT is restricted to nanostructures with outer diameter of less than 15 nm, above which the structures are called carbon nanofibers. CNTs are distinct from carbon fibers, which are not single molecules but strands of layered-graphite sheets[19,20]

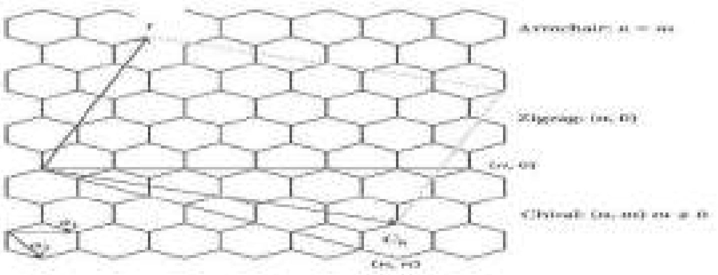

FIGURE 2: SCHEMATIC REPRESENTATION OF FORMATION OF SINGLE-WALLED CARBON NANOTUBES BY ROLLING OF A GRAPHENE SHEET ALONG LATTICE VECTORS WHICH LEADS TO ARMCHAIR, ZIGZAG, AND CHIRAL TUBES[20].

In addition to the two different basic structures, there are three different possible types of carbon nanotubes. These three types of CNTs are armchair carbon nanotubes, zigzag carbon nanotubes, and chiral carbon nanotubes. The difference in these types of carbon nanotubes are created depending on how the graphite is "rolled up" during its creation process. The choice of rolling axis relative to the hexagonal network of the grapheme sheet and the radius of the closing cylinder allows for different types of SWCNTs.

CARBON NANOTUBES SYNTHESIS TECHNIQES

A variety of techniques have been developed to produce CNTs and MWNTs with different structure and morphology in laboratory quantities. There are three methods commonly used to synthesize CNT: arc discharge[21,22], laser ablation [23], and chemical vapor deposition (CVD)[24-27]. The basic elements for the formation of nanotubes are catalyst, a source of carbon, and sufficient energy. The common feature of these methods is addition of energy to a carbon source to produce fragments (groups or single C atoms) that can recombine to generate CNT. The energy source may be electricity from an arc discharge, heat from a furnace (~900°C) for CVD, or the high-intensity light from a laser (laser ablation).

A) ARC DISCHARGE AND LASER VAPOURIZATION

Arc discharge and laser ablation were the first methods that allowed synthesis of SWCNTs in relatively large (gram) amount.[28] For the growth of single-wall tubes, a metal catalyst is needed in the arc-discharge system[29]. The growth of high-quality SWCNTs at the 1–10 g scale was also produced using a laser-ablation (laser oven) method and a typical industrial continuous wave -laser system also can use for production of SWCNTs[30]. With the arc and laser methods, only powdered samples with nanotubes tangled into bundles can be produced. The common feature of arc discharge and laser ablation methods is the need for high amount of energy to induce the reorganization of carbon atoms into CNTs. The temperature used is even higher than 3000°C, which is beneficial for good crystallization of the CNTs, thus, the products are always produced with good graphite alignment. However, the basic requirements of these systems, including vacuum conditions and continuous graphite target replacement, pose difficulties to the large-scale production of CNTs.

B) CHEMICAL VAPOUR DEPOSITION (CVD)

The CVD method involves the decomposition of a gaseous or volatile compound of carbon, catalyzed by metallic nanoparticles, which also serve as nucleation sites for the initiation of carbon-nanotube growth. In contrast the previous two methods, CVD has been proven to be a preferred route for large-scale production of carbon nanotubes[28,31]. Here the carbon is deposited from a hydrocarbon (or other carbon bearing source) in the presence of a catalyst at temperatures lower than 1200°C. The CNT structure, such as its wall number, diameter, length, and alignment, can be well controlled during the CVD process. Thus, the CVD method has the advantages of mild operation, low cost, and controllable process. Over the last twelve years, several methods have been developed that have the potential for industrial-scale preparation of nanotubes. All of them are based on CVD methods. The following are the different CVD methods

i) PLASMA ENHANCED CVD

The plasma enhanced CVD method generates a glow discharge in a chamber or a reaction furnace by a high frequency voltage applied to both electrodes. A substrate is placed on the grounded electrode. In order to form a uniform film, the reaction gas is supplied from the opposite plate. Catalytic metal, such as Fe, Ni and Co are used on for example a Si, SiO2, or glass substrate using thermal CVD or sputtering. After nanoscopic fine metal particles are formed, carbon nanotubes will be grown on the metal particles on the substrate by glow discharge generated from high frequency power. A carbon containing reaction gas, such as C2H2, CH4, C2H4, C2H6, CO is supplied to the chamber during the discharge [32]

The catalyst has a strong effect on the nanotube diameter, growth rate, wall thickness, morphology and microstructure. Ni seems to be the most suitable pure-metal catalyst for the growth of aligned multiwalled carbon nanotubes (MWNTs)[33]. The diameter of the MWNTs is approximately 15 nm. The highest yield of carbon nanotubes achieved was about 50% and was obtained at relatively low temperatures (below 330 ° C) [32]

ii) 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 nanometer-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 ° 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 3 shows a schematic diagram of thermal CVD apparatus in the synthesis of carbon nanotubes.

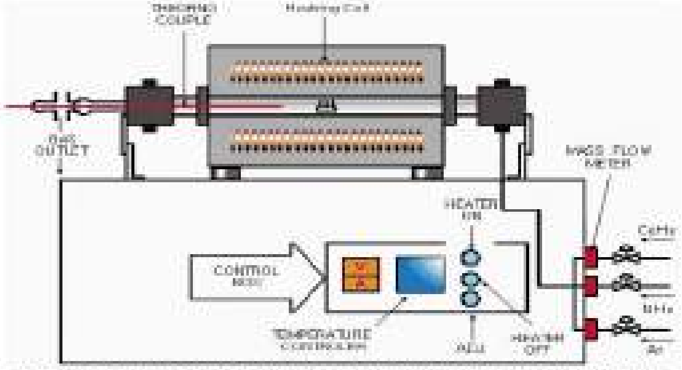

FIGURE 3: SCHEMATIC DIAGRAM OF THERMAL CVD APPARATUS.

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 [34]

iii) ALCOHOL CATALYTIC CVD

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 utilized over iron and cobalt catalytic metal particles supported with zeolite. Generation is possible is possible at a relatively low minimum temperature of about 550 ° 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 .

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[35]

iv) VAPOUR PHASE GROUTH

Vapour phase growth is a synthesis method of carbon nanotubes, directly supplying reaction gas and catalytic metal in the chamber without a substrate [36] Two furnaces are placed in the reaction chamber. Ferrocene is used as catalyst. In the first furnace, vaporization 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 synthesized as carbon nanotubes. The diameter of the carbon nanotubes by using vapour phase growth are in the range of 2 – 4 nm for SWNTs [37] and between 70 and 100 nm for MWNTs.[38]

v) AERO GEL-SUPPORTED CVD

In this method SWNTs are synthesized 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 [38]. 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 de nanotubes is between 1,0 nm and 1,5 nm. The optimal reaction temperature is approximately 860 ° C

vi) LASER-ASSISTED THERMAL CVD

In laser-assisted thermal CVD (LCVD) a medium power, continuous wave CO2 laser, which was perpendicularly directed onto a substrate, pyrolyses sensitized mixtures of Fe(CO)5 vapour and acetylene in a flow reactor. The carbon nanotubes are formed by the catalyzing action of the very small iron particles. Figure 4 shows the experimental set-up for laser-assisted CVD [39]

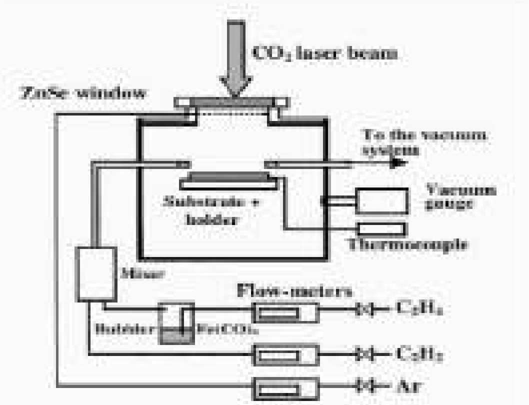

FIGURE 4: EXPERIMENTAL SET-UP FOR LASER-ASSISTED CVD

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.

TABLE 2: A SUMMARY OF THE MAJOR PRODUCTION METHODS AND THEIR EFFICIENCY.

Method	Arc discharge	Laser ablation	Chemical vapour deposition
Process	Connect two graphite rods to a power supply, place them a few millimetres apart. At 100 amps, carbon vaporizes and forms hot plasma.	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 SWNTs.	Place substrate in oven, heat to high temperature, 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.
Condition	Low-pressure inert gas (Helium).	Argon or Nitrogen gas at 500 Torr.	High temperatures within 500 to 1000°C at atmospheric pressure.
Typical yield	30–90%	Up to 70%	20–100%
SWCNT	Short tubes with diameters of 0.6–1.4 nm.	Long bundles of tubes (5–20 microns), with individual diameter from 1-2 nm.	Long tubes with diameters ranging from 0.6 to 4 nm.
MWCNT	Short tubes with inner diameter of 1–3 nm and outer diameter of approximately 10 nm	Not very much interest in this technique, as it is too expensive, but MWNT synthesis is possible.	Long tubes with diameter ranging from 10 to 240 nm
Carbon source	Pure graphite	Graphite	Fossil-based hydrocarbon and botanical hydrocarbon
Cost	High	High	Low
Advantage	Can easily produce SWNT, MWNTs. SWNTs have few structural defects; MWNTs without catalyst, not too expensive, open air synthesis possible.	Good quality, higher yield, and narrower distribution of SWNT than arc-discharge.	Easiest to scale up to industrial production; long length, simple process, SWNT diameter controllable, and quite pure.
Disadvantage	Tubes tend to be short with random sizes and directions; often needs a lot of purification.	Costly technique, because it requires expensive lasers and high-power requirement.	Often riddled with defects.

PURIFICATION AND DISPERSION OF CARBON NANOTUBES

As-synthesized CNTs prepared by the above methods inevitably contain carbonaceous impurities and metal catalyst particles, and the amount of the impurities commonly increases with the decrease of CNT diameter. The fundamental problems that still exist are how to remove impurities, such as amorphous carbons and metallic catalysts, and obtain uniform dispersions of the carbon nanotubes in dispersing media or polymer solutions. The impurities in unpurified carbon nanotubes severely reduce the mechanical or electrical properties[40,41]

The following methods are mainly used for purification of CNTs

GAS PHASE OXIDATION

(i) In general, chemical oxidation includes gas phase oxidation (using air, O_2, Cl_2, H_2O, etc.), liquid phase oxidation (acid treatment and refluxing, etc.), and electrochemical oxidation.

(ii) Tubes are heated at a controlled rate either in wet air or vacuum or other oxidizing agents for an extended time at about 330°C.

(ii) This is a good way to remove carbonaceous impurities.

(iii) The disadvantages of this method are that it often opens the end of CNTs, cuts CNTs, damages surface structure and introduces oxygenated functional groups (–OH, –C=O, and –COOH) on CNTs. Metal particles cannot be directly removed, and further acid treatment is needed.[42-55]

LIQUID PHASE OXIDATION

i) Usually, the acid treatment will remove the metal catalyst and some fullerenes.

(ii) Reflux in HNO3, HCl, or other acid for period of time ranging from 4 to 48 hours.

(iii) HNO3 is the only acid that does not cause degradation to tubes (unless left in HNO3 for extended time frames, usually >16 hrs).

(iv) The metal catalyst is solvated while the CNTs remain in suspended form.[43,48,52-55]

ELECTROCHEMICAL OXIDATION

(i) CNTs with fewer defects show higher electrochemical oxidation resistance than CNTs with more defects. Suitable for purifying CNT arrays without destroying their alignment.

(ii) The CNTs electrode is immersed in 0.2 M HNO3 solution or 0.2 M HCl (purging with N2 for 20 min prior to use) and the potential was cycled between +1.00 and +2.00 V at a scan rate of 50 mV s−1.

(iii) Increases the specific area of nanotubes by cutting off the nanotube tips and by converting the surface property of nanotubes from the hydrophobic state to the hydrophilic state.[56,57]

CENTRIFUGATION

(i) Centrifuge at 7,000 g or more for 30 min to 3 hours. Often supernatant is removed after one run and centrifuged again.

(ii) This removes nanospheres, metal nanoparticles, other carbon particles, but some methods produce a low yield of nanotubes, especially when centrifugation is repeated many times[58-60]

FILTRATION

(i) This technique is often used in conjunction with oxidation. The acid decomposition products are highly soluble in basic solution and CNTs are not and are separated using a basic solution of pH 11 and filtered using 3–5 µm filter, often under vacuum.

(ii) This removes nanospheres, metal nanoparticles, polyatomic carbons, and fullerenes, without any noted negative effects.[61]

MAGNETIC

(i) CNTs is suspended in soap or toluene and nanoparticle powder (ZrO2, NHCl4, CaCo3, diamond) is added. This particles will attach to the CNTs and make them magnetic.

(ii) The slurry is sonicated for 2 hr and subsequently the magnetic particles are trapped using permanent magnetic poles.

(iii) This is then followed by chemical treatment.

(iv) This removes catalyst materials and small inorganic particles. Few to no known negative effects[62-64]

MICROWAVE PURIFICATION

(i) CNTs are sonicated, then diluted in HNO_3 (or other acid).

(ii)Micro waved at 100–200 W, and microwave is ramped up to ~200°C over 30 min.

(iii)Microwave is then held at temperature 200°C for 30–90 minutes. This removes amorphous carbon, metals, and other nanoparticles, with no known negative effects[65-67].

ULTRASONICATION

(i) CNTs are suspended in distilled water, toluene, or acid solution and sonicated for 5–30 minutes.

(ii) This separates tubes from attached particles, creating dispersion of nanotubes and other particles for better centrifugation.

(iii) 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.[68-70]

APPLICATIONS OF CNTs

1. ENERGY STORAGE

Graphite, carbonaceous materials and carbon fibre electrodes are commonly used in fuel cells,

batteries and other electrochemical applications/. Advantages of considering nanotubes for energy storage are their small dimensions, smooth surface topology and perfect surface specificity. The efficiency of fuel cells is determined by the electron transfer rate at the carbon electrodes, which is the fastest on nanotubes following ideal Nernstian behaviour.[10] Electrochemical energy storage and gas phase intercalation will be described more thoroughly in the following chapters of the report.

a) HYDROGEN STORAGE

The advantage of hydrogen as energy source is that its combustion product is water. In addition, hydrogen can be easily regenerated. For this reason, a suitable hydrogen storage system is necessary, satisfying a combination of both volume and weight limitations. The two commonly used means to store hydrogen are gas phase and electrochemical adsorption. Because of their cylindrical and hollow geometry, and nanometre-scale diameters, it has been predicted that carbon nanotubes can store a liquid or a gas in the inner cores through a capillary effect.

As a threshold for economical storage, the Department of Energy has set storage requirements of 6.5% by weight as the minimum level for hydrogen fuel cells. It is reported that SWNTs were able to meet and sometimes exceed this level by using gas phase adsorption (physisorption). Yet, most experimental reports of high storage capacities are rather controversial so that it is difficult to assess the applications potential.

Another possibility for hydrogen storage is electrochemical storage. In this case not a hydrogen molecule but an H atom is adsorbed. This is called chemisorption. Lithium intercalation The basic principle of rechargeable lithium batteries is electrochemical intercalation and deintercalation of lithium in both electrodes. An ideal battery has a high-energy capacity, fast charging time and a long cycle time. The capacity is determined by the lithium saturation concentration of the electrode materials. For Li, this is the highest in nanotubes if all the interstitial sites (inter-shell van der Waals spaces, inter-tube channels and inner cores) are accessible for Li intercalation.

b) ELECTROCHEMICAL SUPERCAPACITORS

Supercapacitors have a high capacitance and potentially applicable in electronic devices. Typically, they are comprised two electrodes separated by an insulating material that is ionically conducting in electrochemical devices. The capacity of an electrochemical super cap inversely depends on the separation between the charge on the electrode and the counter charge in the electrolyte. Because this separation is about a nanometre for nanotubes in electrodes, very large capacities result from the high nanotube surface area accessible to the electrolyte. In this way, a large amount of charge injection occurs if only a small voltage is applied. This charge injection is used for energy storage in nanotubes supercapacitors.[72]

Generally speaking, there is most interest in the double-layer supercapacitors and redox supercapacitors with different charge-storage modes.

2. MOLECULAR ELECTRONICS WITH CNTs

a) FIELD EMMITING DEVICES

If a solid is subjected to a sufficiently high electric field, electrons near the Fermi level can be extracted from the solid by tunneling through the surface potential barrier. This emission current depends on the strength of the local electric field at the emission surface and its work function (which denotes the energy necessary to extract an electron from its highest bounded state into the vacuum level). The applied electric field must be very high in order to extract an electron. This condition is fulfilled for carbon nanotubes, because their elongated shape ensures a very large field amplification. [71]

For technological applications, the emissive material should have a low threshold emission field and large stability at high current density. Furthermore, an ideal emitter is required to have a nanometer size diameter, a structural integrity, a high electrical conductivity, a small energy spread and a large chemical stability. Carbon nanotubes possess all these properties. However, a bottleneck in the use of nanotubes for applications is the dependence of the conductivity and emission stability of the nanotubes on the fabrication process and synthesis conditions.

Examples of potential applications for nanotubes as field emitting devices are flat panel displays, gasdischarge tubes in telecom networks, electron guns for electron microscopes, AFM tips and

microwave amplifiers.

b) TRANSISTORS

The field-effect transistor – a three-terminal switching device – can be constructed of only one semiconducting SWNT. By applying a voltage to a gate electrode, the nanotube can be switched from a conducting to an insulating state. Such carbon nanotube transistors can be coupled together, working as a logical switch, which is the basic component of computers.[73]

3. NANOPROBES AND SENSORS

Because of their flexibility, nanotubes can also be used in scanning probe instruments. Since MWNT tips are conducting, they can be used in STM and AFM instruments (Figure 5). Advantages are the improved resolution in comparison with conventional Si or metal tips and the tips do not suffer from crashes with the surfaces because of their high elasticity. However, nanotube vibration, due to their large length, will remain an important issue until shorter nanotubes can be grown controllably.

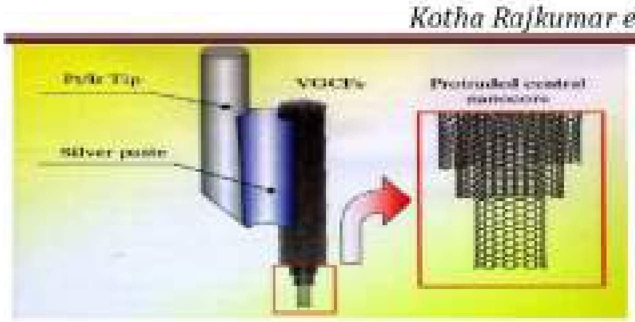

FIGURE 5: USE OF A MWNT AS AFM TIP. VGCF STANDS FOR VAPOUR GROWN CARBON FIBRE. AT THE CENTRE OF THIS FIBRE THE MWNT FORMS THE TIP[71]

Nanotube tips can be modified chemically by attachment of functional groups. Because of this, nanotubes can be used as molecular probes, with potential applications in chemistry and biology.

Other applications are the following:

- A pair of nanotubes can be used as tweezers to move nanoscale structures on surfaces. [72]
- Sheets of SWNTs can be used as electromechanical actuators, mimicking the actuator mechanism present in natural muscles.
- SWNTs may be used as miniaturised chemical sensors. On exposure to environments, which contain NO2, NH3 or O2, the electrical resistance changes.

4. COMPOSITE MATERIALS[71]

Because of the stiffness of carbon nanotubes, they are ideal candidates for structural applications. For example, they may be used as reinforcements in high strength, low weight, and high performance composites.

One of the most important applications of nanotubes based on their properties will be as reinforcements in composite materials. However, there have not been many successful experiments that show that nanotubes are better fillers than the traditionally used carbon fibres. The main problem is to create a good interface between nanotubes and the polymer matrix, as nanotubes are very smooth and have a small diameter, which is nearly the same as that of a polymer chain. Secondly, nanotubes aggregates, which are very common, behave different to loads than individual nanotubes do. Limiting factors for good load transfer could be sliding of cylinders in MWNTs and shearing of tubes in SWNT ropes. To solve this problem the aggregates need to be broken up and dispersed or cross-linked to prevent slippage.

A main advantage of using nanotubes for structural polymer composites is that nanotubes reinforcements will increase the toughness of the composites by absorbing energy during their highly flexible elastic behaviour. Other advantages are the low density of the nanotubes, an increased electrical conduction and better performance during compressive load.

5. IMMOBILIZATION OF PROTEINS AND ENZYMES

Practical use of enzymes has been realized in various industrial processes, and is being expanded in new fields, such as fine-chemical synthesis, pharmaceuticals, biosensors, and biofuel cells[74]. To improve enzyme stability, enzymes have generally been studied with the enzymes immobilized on a solid support[73]. Nanomaterials can serve as excellent supporting materials for enzyme immobilization, because they offer the ideal characteristics for balancing the key factors that determine the efficiency of biocatalysts, including surface area, minimized mass transfer resistance, and effective enzyme loading[75-77]. Carbon nanotubes are receiving a great deal of attention as alternative matrices for enzyme immobilization. CNTs are better support material for enzyme immobilization compared to common support like zirconia, silica, and epoxy. They are more stable under harsh condition, provide higher loading of enzyme, and enhanced catalytic activity of enzyme up to 2-fold greater than flat support and up to 10 times higher than native enzyme[78]. The CNTs, besides exhibiting extraordinary mechanical, electrical, and thermal properties, also provide high surface area for higher enzyme loading, reduced diffusion limitations, and a biocompatible microenvironment that helps enzymes to retain its catalytic properties[79,80]. Apart from proteins, other biological molecules can also be immobilized on CNTs such as nucleic acids, antigens, peptides, and drugs. The type of biomolecule immobilized on the CNTs lead to different applications which renders these biomolecule conjugates great versatility. Table 3 shows the application of some selected protein-CNTs conjugates in various areas.

TABLE 3: APPLICATIONS OF CARBON NANOTUBE-PROTEIN BI-CONJUGATES

Protein	Carbon nanotube Nanomaterials	Application	Reference
β-Glucosidase	MWCNT-COOH	Biocatalysis	81
Candida rugosa Lipase	MWCNTs or MWCNTs-COOH	Biocatalysis	82
Horseradish	SWCNT/chitosan modified glassy carbon electrode (GCE)	Bioelectrochemical sensor	83
Trametes hirsuta Laccase	MWCNT modified GCE	Biofuel cells	84
Horseradish peroxidase, Myoglobin, Cytochrome c	SWNT/ionic liquid modified GCE	Biofuel cells, biosensors	85
Cerrena unicolor Laccase	CNT modified boron-doped diamond electrode	Biofuel cells, biosensors	86
Alcohol dehydrogenase	SWCNT/poly (dimethyldiallylammonium chloride) (PDDA) modified GCE	Ethanol biosensor	87
Glucose oxidase	SWCNT/silica modified GCE	Glucose biosensor	88
Glucose oxidase, Horseradish peroxidase	MWCNT-toluidine blue/nafion modified GCE	Glucose biosensor	89
Cytochrome c	MWCNT/chitosan/ionic liquid modified GCE	H_2O_2 detector	90
Horseradish peroxidase	MWCNT/chitosan/sol-gel modified GCE	H_2O_2 detector	91
Cytochrome c	MWCNT/poly(amidoamine)/chitosan modified GCE	Nitrite biosensor	92
Trametes versicolor Hemoglobin	MWCNT/chitosan	Oxygen biosensor, Biofuel cells	93

CONCLUSION

Different modified synthesis techniques have been developed in order to produce CNTs in large scale for commercial application. At the moment, CVD method is the most promising method to produce large quantity of CNTs since the cost is relatively low compared to other methods. Commercial applications of CNTs have been rather slow to develop, however, primarily because of the high production costs of the best quality nanotubes. The chemistry of CNTs has made enormous stride. Fictionalization of CNTs, and particularly CNTs of defined length, diameter, and chirality, will lead to the better control of CNT-based materials and devices at the molecular level. The present paper shows that their immense potential for biotechnology and biomedicine are only just starting to be realized. Various biomolecules (proteins, enzymes, or DNA/RNA) can interact and be immobilized on the CNTs, leading to a wide field of application.

ABBREVIATIONS: Carbon nanotubes (CNTs)

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