

Review Article

Carbon Nanotubes: A Review on Structure and Their Interaction with Proteins

N. Saifuddin, A. Z. Raziah, and A. R. Junizah

Department of Science, Mathematics, and Computing, College of Foundation and General Studies, Universiti Tenaga Nasional, Jalan IKRAM-UNITEN, Selangor, 43000 Kajang, Malaysia

Correspondence should be addressed to N. Saifuddin; saifuddin@uniten.edu.my

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Carbon nanotubes (CNTs) are allotropes of carbon with a nanostructure that can have a length-to-diameter ratio greater than 1,000,000. Techniques have been developed to produce nanotubes in sizeable quantities, including arc discharge, laser ablation, and chemical vapor deposition. Developments in the past few years have illustrated the potentially revolutionizing impact of nanomaterials, especially in biomedical imaging, drug delivery, biosensing, and the design of functional nanocomposites. Methods to effectively interface proteins with nanomaterials for realizing these applications continue to evolve. The high surface-to-volume ratio offered by nanoparticles resulted in the concentration of the immobilized entity being considerably higher than that afforded by other materials. There has also been an increasing interest in understanding the influence of nanomaterials on the structure and function of proteins. 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 multienzyme coimmobilization would be one of the next goals in the future. In this paper, we focus on advances in methodology for enzyme immobilization on carbon nanotubes.

1. Introduction

Diamond and graphite are considered as two natural crystalline forms of pure carbon. In diamond, carbon atoms exhibit sp^3 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, sp^2 hybridization occurs, in which each atom is connected evenly to three carbons (120°) in the xy plane, and a weak π bond is present in the z axis. The sp^2 set forms the hexagonal (honeycomb) lattice typical of a sheet of graphite [1]. A new form of carbon, Buckminster fullerene (C_{60}), was discovered in 1985 by a team headed by Korto and coworkers [2]. Besides diamond, graphite, and fullerene (C_{60}), 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 [3]. 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) [4]. 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 [5]. The single-walled nanotubes are generally narrower than the multiwalled 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 [6, 7].

2. Classification of Carbon Nanotubes

Carbon nanotubes are classified in following two types: SWCNTs—Single-walled carbon nanotubes and

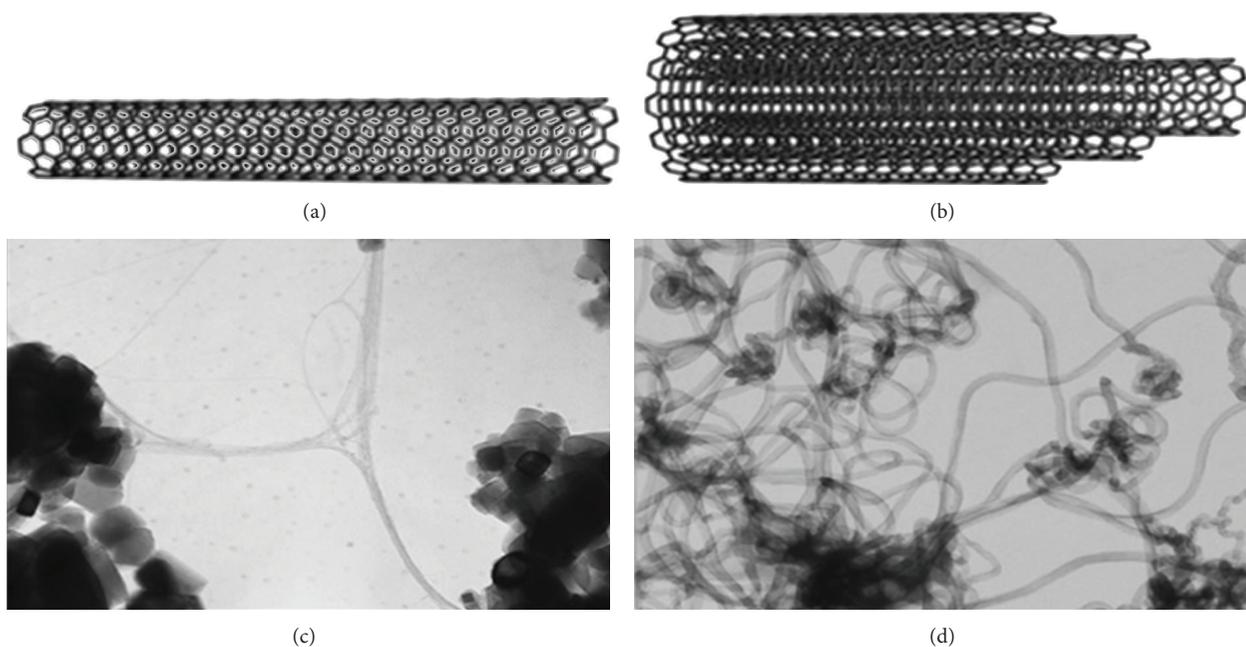


FIGURE 1: Molecular representations of SWCNT (top left) and MWCNT (top right) with typical transmission electron micrographs (below) [8].

TABLE 1: Comparison between SWCNT and MWCNT.

| SWCNT | MWCNT |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|
| Single layer of graphene. | Multiple layer of graphene |
| Catalyst is required for synthesis. | Can be produced 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. Typical SWCNT content 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. | Purity is high. Typical MWCNT content in as-prepared samples by CVD method is about 35–90 wt%. |
| A chance of defect is more during functionalization. | 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. |

MWCNTs—Multiple-walled carbon nanotubes. Comparison between SWCNT and MWCNT is as presented in Table 1 [9–11].

3. Structure and Morphology

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 [11]. 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 [12]. 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 [13, 14].

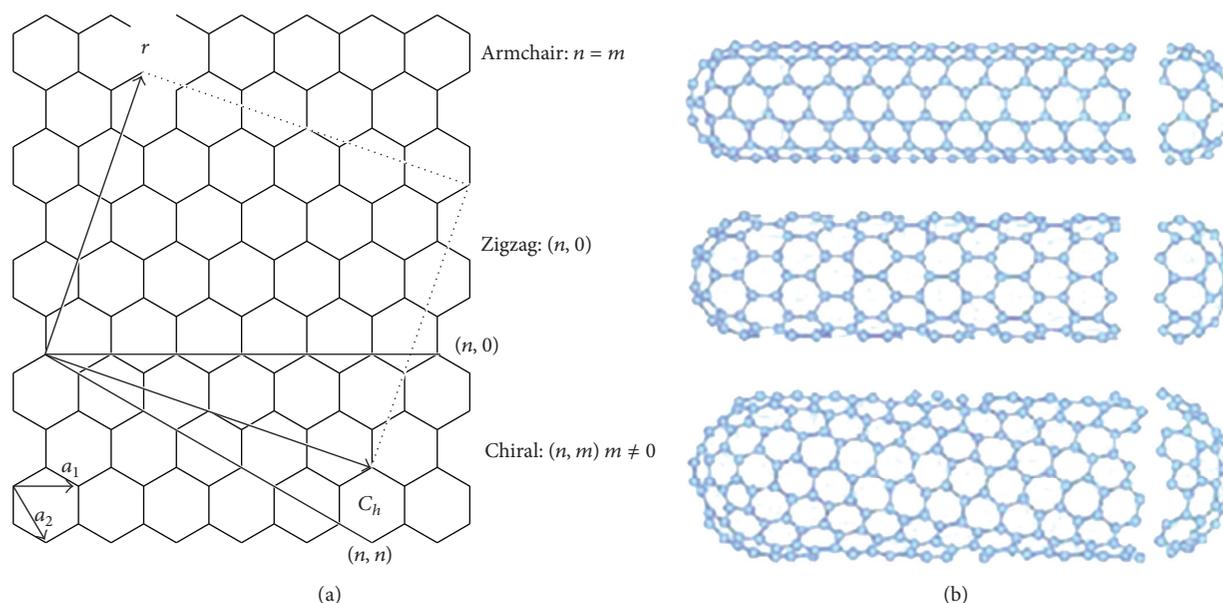


FIGURE 2: Schematic representation of (a) formation of single-walled carbon nanotubes by rolling of a graphene sheet along lattice vectors which leads to armchair, zigzag, and chiral tubes and (b) the three types of carbon nanotubes [14].

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.

The chiral vector is represented by a pair of indices, n and m , where these two integers correspond to the number of unit vectors along the two directions in the honeycomb crystal lattice of grapheme. When $m = 0$ the nanotube is called “zigzag”, when $n = m$ the nanotube is called “armchair”, and all other configuration are designated as chiral. Figure 2 shows the three different types of SWCNTs: armchair, zigzag, and chiral. Further details of the structure can be found in reviews by [12, 15, 16].

4. Properties

The strength of the sp^2 carbon-carbon bonds gives carbon nanotubes amazing mechanical properties. No previous material has displayed the combination of superlative mechanical, thermal, and electronic properties attributed to them. Their densities can be as low as 1.3 g/cm^3 (one-sixth of that of stainless steel). CNTs Young’s moduli (measure of material stiffness) are superior to all carbon fibres with values greater than 1 TPa which is approximately 5x higher than steel [17]. However, their strength is what really sets them apart. Carbon nanotubes are the strongest materials ever discovered by mankind. The highest measured tensile strength or breaking strain for a carbon nanotube was

up to 63 GPa which is around 50 times higher than steel [17]. Even the weakest types of carbon nanotubes have strengths of several GPa [18]. Besides that, CNTs have good chemical and environmental stability and high thermal conductivity ($\sim 3000 \text{ W/m/K}$, comparable to diamond). These properties, coupled with the lightness of carbon nanotubes, give them great potential in applications such as aerospace.

The electronic properties of carbon nanotubes are also extraordinary. It has high electrical conductivity (comparable to copper). Especially notable is the fact that nanotubes can be metallic or semiconducting. The rolling action breaks the symmetry of the planar system and imposes a distinct direction with respect to the hexagonal lattice and the axial direction. Depending on the relationship between this axial direction and the unit vectors describing the hexagonal lattice, the nanotubes may behave electrically as either a metal or a semiconductor. Semiconducting nanotubes have bandgaps that scale inversely with diameter, ranging from approximately 1.8 eV for very small diameter tubes to 0.18 eV for the widest possible stable SWCNT [19]. Thus, some nanotubes have conductivities higher than that of copper, while others behave more like silicon. There is great interest in the possibility of constructing nanoscale electronic devices from nanotubes. There are several areas of technology where carbon nanotubes are already being used. These include flat-panel displays, scanning probe microscopes, sensing devices, and fuel cell.

5. Carbon Nanotubes Synthesis Techniques

High-quality nanotube materials are desired for both fundamental and technological applications. High quality refers to the absence of structural and chemical defects over a

significant length scale (e.g., 1–10 microns) along the tube axes. The number of patents and publication on the synthesis of carbon nanotube is increasing rapidly. However there are many challenges remaining that must be resolved regarding synthesis of CNT. Currently, there are four main challenges in the field of nanotube synthesis. (a) Mass production, that is, the development of low-cost, large-scale processes for the synthesis of high-quality nanotubes, including SWCNTs. (b) Selective production, that is, control over the structure and electronic properties of the produced nanotubes. (c) Organization, that is, control over the location and orientation of the produced nanotubes on a flat substrate. (d) Mechanism, that is, the development of a thorough understanding of the processes of nanotube growth. The growth mechanism is still a subject of controversy, and more than one mechanism might be operative during the formation of CNTs.

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 [20, 21], laser ablation [22], and chemical vapor deposition (CVD) [23–26]. 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 ($\sim 900^\circ\text{C}$) for CVD, or the high-intensity light from a laser (laser ablation).

6. Arc Discharge and Laser Vaporization

Arc discharge and laser ablation were the first methods that allowed synthesis of SWCNTs in relatively large (gram) amounts. Both methods involve the condensation of hot gaseous carbon atoms generated from the evaporation of solid carbon [27]. For the growth of single-wall tubes, a metal catalyst is needed in the arc-discharge system [28]. The growth of high-quality SWCNTs at the 1–10 g scale was also produced using a laser-ablation (laser oven) method [22]. Besides the laser-oven method, there are reports regarding usage of a typical industrial continuous wave CO_2 -laser system for production of SWCNTs [29]. Nevertheless, the equipment requirements and the large amount of energy consumed by these methods make them less favorable for nanotube production. 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.

7. Chemical Vapor 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 [27, 30]. 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. Among these methods, five different approaches have been shown to be the most promising:

- (i) Methane CVD- It was first reported in 1998, where bulk amount of SWCNTs were synthesized by CVD from methane at 900°C [23, 31]. Su et al. [26] significantly improved the yield of this method using Al_2O_3 aerogels impregnated with Fe/Mo nanoparticles as a catalyst.
- (ii) HiPCO, which stands for high-pressure catalytic decomposition of carbon monoxide, uses high-pressure CO as the carbon source for the preparation of SWCNTs [32]. The catalysts used in a HiPCO process are in the gas phase produced from a volatile organometallic catalyst precursor.
- (iii) CO CVD uses CO as a feed gas. Compared with samples made using the same catalyst and methane, the amount of amorphous carbon can be reduced. An important advance in the CO CVD method is the development of the Co-Mo catalyst [33]. In that process Co-Mo bimetallic catalysts and a fluidized-bed CVD reactor was used to produce a large quantity of SWCNTs. The most important advantage of fluidized-bed reactors is that they permit continuous addition and removal of solid particles from the reactor, without stopping the operation.
- (iv) Alcohol CVD, was reported in 2002 by Maruyama et al. [34], which produce high-purity SWCNTs without any amorphous carbon coating using alcohols such as methanol and ethanol as a carbon source. It was proposed that the OH radical formed at high temperature from alcohols can remove the amorphous carbon efficiently during nanotube growth, leaving only pure SWCNTs as a product.
- (v) Plasma-enhanced CVD (PECVD) methods have also been widely used for making carbon materials including MWCNTs and SWCNTs recently [35–39]. The reactive species in the plasma system could affect the growth of very small diameter tubes, with implications to both diameter control and selective etching of metallic SWCNTs.

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, but is improving. | Often riddled with defects. |

In Table 2, a short summary of the three most common techniques used is given [40].

8. Catalyst

Catalysts play a crucial role in the CVD synthesis of CNTs and therefore improving the desired characteristics of catalyst will enhance the obtained CNTs quality as well as the process yield. Carbon nanostructures are commonly synthesized using transition metal nanoparticles as catalysts [22]. The structure of CNTs has been found to be determined by the size and chemical composition of the metal catalysts. However, at present, the diameter, length, and chirality of CNTs have not been controlled sufficiently in a single process due to incomplete understanding of the role of the catalyst in nanotube nucleation and growth [41]. It is accepted that CNT growth by CVD involves surface and/or bulk diffusion of carbon at a metal catalyst particle. CNT-CNT or CNT-substrate interactions in addition to the arrangement and activity of the catalytic sites determine if CNTs grow in an isolated, tangled, or aligned configuration. At all stages of CNT growth, chemical and mechanical interactions are highly coupled, and these interactions must be further understood for efficient synthesis of CNTs [42].

Transition metals in the form of nanoparticles are considered as the most effective catalysts. The peculiar ability of transition metals to promote CNT growth is strongly related

to these factors: (a) catalytic activity for decomposition of volatile carbon compounds, (b) ability of metastable carbides formation, and (c) diffusion of carbon through and over the metallic particles [43–45]. The catalytic CVD process for CNTs growth utilizes heterogeneous catalysts, which are the catalytically active metal particles, typically with a diameter of 1–10 nm, anchored on a high surface inert area. The Transition metals used to date as catalysts include Fe, Ni, Co, and Mo. More recent studies however, have shown that other metals such as In, Cu, Ag, Pd, Mn, Mo, Cr, Al, and Au can also be used for SWCNT formation [46, 47]. Since SWCNT nucleation requires a catalyst particle, a great deal of attention has been paid to the catalysts role in forming the embryonic stage of SWCNT. However, their full role has yet to be determined and this is in part due to conflicting results, which may indicate that several mechanisms exist.

In order to obtain CNTs, the catalyst must be prepared as a nanoparticle catalyst [48]. The absorption of carbon in catalyst particles and the precipitation rates of CNTs from the catalyst particles both show great dependence on the size of the catalyst particles. Under a given CVD there is an optimal particle size diameter to nucleate SWCNTs with a fixed feeding rate of carbon. Smaller catalyst nanoparticles are easily poisoned by excess feeding, and larger catalyst particles are inactive due to under feeding [49].

So far, the published results concerning catalysts have mainly focused on the synthesis of monodispersed CNTs,

but there have been very few detailed experimental studies of the reaction pathways. Furthermore, the interaction between catalysts and the surface of substrates need to be further investigated and characterized. Efforts in future will be geared towards finding optimal CVD conditions to discover the detailed mechanism of catalysis, and facilitating control over the growth of CNTs for future fabrication of nanotube-based devices.

8.1. Carbon Sources. One of the major barrier to the industrial application of CNTs, lies on the cost of their carbonaceous precursors. Various carbon sources have been used to produce CNTs since its first discovery by Iijima in 1991. Different methods in producing the CNTs show different usage of carbon source. The arc discharge was the first technique used for the production of carbon nanotubes. The CNTs produced by this method were grown on the negative end of graphite electrode under inert atmosphere of helium or argon with a very high temperature needed in order to evaporate the pure graphite or coevaporate the graphite and metal [50–53]. Similar to arc discharge method, graphite is used in the laser ablation method. Graphite is vaporized by laser irradiation under an inert atmosphere with the presence of metal catalyst to produce the carbon nanotubes [22, 51, 54, 55].

There are two main carbon sources for the synthesis of CNTs-using CVD method: fossil-based hydrocarbon and plant based hydrocarbon. Hydrocarbon was long and widely used as the conventional carbon source in the field of CNTs research. Natural gas becomes the most preferable carbon source to many researchers. Because its stability at high temperature against self-decomposition, methane catalytic decomposition by transition metal catalyst particles is the dominant process in carbon nanotubes growth. Besides methane several other carbon species such as acetylene, benzene, xylene, toluene, and so forth, have been used as a carbon feedstock to synthesize CNTs [56–60]. These carbon precursors are related to fossil fuels and in view of the insufficient available in near future and its environmental effects, it is necessary to consider developing carbonaceous materials from the natural resource. Efforts are now directed to the use of nonpetroleum products. Syntheses of CNTs from natural precursors are rare, however, over the past several years natural renewable resources have become more attractive because of their environmental benefits and lower cost [61]. One such appreciable effort is to use nondegradable polymers for synthesis of CNTs [62]. There have been reports on the use of natural precursor such as: camphor ($C_{10}H_{16}O$), turpentine oil ($C_{10}H_{16}$), eucalyptus oil ($C_{10}H_{18}O$), castor oil ($C_{54}H_{100}O_7$), coconut oil ($C_{39}H_{74}O_6$), and palm oil ($C_{67}H_{127}O_8$) for synthesis of CNTs [63–70]. Published data show that, some researchers have used waste cooking palm oil as the biocarbon precursor in their studies [71]. Waste cooking oil, which is much less expensive than virgin vegetable oil, is a promising alternative to vegetable oil for CNT production. Suriani and coworkers [71] reported the use of waste cooking palm oil for the synthesis of vertically aligned carbon nanotubes (VACNT). The result showed that the

complex composition of the waste oil (leaching of fats and other hydrocarbons from the fried objects) did not affect the synthesis process.

9. 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 (1) remove impurities, such as amorphous carbons and metallic catalysts, and (2) 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. The as-produced CNTs soot contains a lot of impurities. Up to now, all currently known production methods generate CNTs with impurities. Purification has been an important synthetic effort since the discovery of carbon nanotubes. In general, the main impurities in the soot are graphite (wrapped up) sheets, amorphous carbon, metal catalyst, and the smaller fullerenes. Also, structural defects, such as dangling bonds, are often found in most types of CNTs. These impurities will interfere with most of the desired properties of the CNTs. Purification difficulties are considerable because CNTs are insoluble and, hence, liquid chromatography is limited. Thus, extensive research has been dedicated to the purification of carbon nanotubes in order to remove foreign nanoparticles that modify the physicochemical properties of carbon nanotubes. Here, we just intend to give a brief overview of the principles with a few examples. Good review articles on the purification of nanotubes are available in the recent literature [72, 73]. Much effort has therefore been expended in the development of purification techniques; the resulting approaches are summarized in Table 3. These methods utilize either one or a combination of several elemental techniques.

Obtaining pure monodisperse SWCNTs of specific structures in large quantities is a problem. SWCNTs have attractive electronic properties, since they become metallic or semiconductive depending on chiral indices (n, m). However, their strong tendency to form bundles (or ropes) due to strong van der Waals interactions prevents their utilization as the ultimate nanomaterial. Successful dispersion of SWNTs could lead to the diameter and/or chirality-selective separation of individual SWNTs. Disaggregation and uniform dispersion are critical challenges that must be met, since carbon nanotubes tend to self-associate into microscale aggregates. Hence, the thermodynamic drive toward aggregation must be overcome. There are two distinct approaches for dispersing carbon nanotubes: the mechanical method and methods that are designed to alter the surface energy of the solids, either physically (noncovalent treatment) or chemically (covalent treatment) [74, 75]. Chemical methods use surface functionalization of CNT to improve their chemical compatibility with the target medium (solvent or polymer solution/melt), that is, to enhance wetting or adhesion characteristics and

TABLE 3: Characteristic of various processes for purification of CNTs.

| Process | Description | References |
|-----------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------|
| Gas phase oxidation | (i) In general, chemical oxidation includes gas phase oxidation (using air, O ₂ , Cl ₂ , H ₂ O, 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. (iii) This is a good way to remove carbonaceous impurities. (iv) 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. | [134–145] |
| Liquid phase oxidation (acid treatment) | (i) Usually, the acid treatment will remove the metal catalyst and some fullerenes. (ii) Reflux in HNO ₃ , HCl, or other acid for period of time ranging from 4 to 48 hours. (iii) HNO ₃ is the only acid that does not cause degradation to tubes (unless left in HNO ₃ for extended time frames, usually >16 hrs). (iv) The metal catalyst is solvated while the CNTs remain in suspended form. | [135, 140, 144–147] |
| 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 HNO ₃ solution or 0.2 M HCl (purging with N ₂ 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. | [148, 149] |
| 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. | [150–152] |
| 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. | [153] |
| 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. | [143, 145, 150, 154–156] |
| Magnetic | (i) CNTs is suspended in soap or toluene and nanoparticle powder (ZrO ₂ , NHCl ₄ , CaCO ₃ , 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. | [157–159] |
| Microwave purification | (i) CNTs are sonicated, then diluted in HNO ₃ (or other acid). (ii) Microwaved 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. | [160–162] |

reduce their tendency to agglomerate. However, aggressive chemical functionalization, such as the use of neat acids at high temperatures, might introduce structural defects resulting in inferior properties for the tubes. Noncovalent treatment is particularly attractive because of the possibility of adsorbing various groups on CNT surface without disturbing the π system of the graphene sheets. The noncovalent surface treatment by surfactants or polymers has been widely used in the preparation of both aqueous and organic solutions

to obtain high weight fraction of individually dispersed nanotubes. Many dispersion reagents have been reported, among them to name a few are surfactants [76, 77], polycyclic aromatic hydrocarbons [78], DNA [79], and peptide [80].

10. Biomolecular-Nanoparticle Interaction

10.1. Modification of Carbon Nanotubes. The chemical inertness of CNTs hampers their processability and this has

impeded the full realization of their potential. Chemical functionalization of CNTs has been shown to impart solubility in a variety of solvents, to modify their electronic properties, and to cause significant debundling. Problems of solubility of CNTs due to the formation of bundles, make them hardly soluble in common solvents. The solubility of carbon nanotubes in water is limited and proper amounts of stabilizers are required to avoid flocculation and phase separation. One disadvantage of the CNTs concerning their use in biochemistry and biomedical applications is that they are highly hydrophobic and generally form insoluble aggregates. Due to the less solubility of CNTs in any of the solvents, it is also very difficult to isolate one carbon nanotube from the other. Like graphite, CNTs are relatively nonreactive, except at the nanotube caps which are more reactive due to the presence of the dangling bonds. The reactivity of the sidewalls of the carbon nanotube π -system can be influenced by the tube curvature or chirality. The hydrophobic surfaces of carbon nanotubes adsorb a wide class of substances by π - π and/or van der Waals interactions [81–83]. Therefore, proper stabilization of CNTs dispersions is a prerequisite for technological applications.

Loung et al. [84] reported that when CNTs were sonicated in organic solvents, they produce dangling bonds that will undergo further chemical reactions. Many efforts in recent years have led the development of versatile chemical modification methodologies in order to solve the insolubility problem. The recent expansion in methods to chemically modify and functionalize carbon nanotubes has made it possible to solubilize and disperse carbon nanotubes in water, thus opening the path for their facile manipulation and processing in physiological environments. The surface functionalization of CNTs by chemically attaching an organic functional groups will aid the carbon nanotube materials in becoming biocompatible, improving their solubility in physiological solutions and selective binding to biotargets. Two main paths are usually followed for the functionalization of CNTs: attachment of organic moieties either to carboxylic groups that are formed by oxidation of CNTs with strong acids or direct bonding to the surface double bonds [85]. Important early reports by Georgakilas et al. (2002) have shown method to functionalize CNTs using organic compounds. Approximately one organic group per 100 carbon atoms of the nanotube is introduced to yield remarkably soluble bundles of nanotubes [86]. The solubilization of the nanotubes generates a novel, interesting class of materials, which combines the properties of the nanotubes and the organic moiety, thus offering new opportunities for applications in materials science, including the preparation of nanocomposites. Fluorination, addition of carbenes and nitrenes, electrophiles, or peroxy radicals were found to be successful reactions for sidewall covalent functionalization of CNTs [85, 86].

In recent years, efforts have been devoted to explore the potential biological applications of CNTs, motivated by their interesting size, shape, and structure, as well as attractive optical and electrical properties. First, with all atoms exposed on the surface, SWNTs have ultrahigh surface area (theoretically $1300 \text{ m}^2/\text{g}$) that permits efficient loading of

multiple molecules along the length of the nanotube sidewall. Second, supramolecular binding of aromatic molecules can be easily achieved by π - π stacking of those molecules onto the polyaromatic surface of nanotubes [87, 88]. It has been demonstrated that biological and bioactive species such as proteins, carbohydrates, and nucleic acids can be conjugated with carbon nanotubes [89–91]. Both noncovalent and covalent strategies have been explored to engineer the interface between biological molecules and CNTs with the goal of preserving the functional properties of the biomolecules. The biomolecule immobilization on the sidewall of the CNTs, and more interestingly inside the CNTs has been reported in both computational and experimental fields [92–97]. Based on these exciting observations and potential applications, the conformational changes of biomolecules in these confined environments tend to be of great significance mainly because these conformational changes affected by the biomolecules-CNT interactions could directly impact their biological functions. However, the atomic details of the interactions at the molecular level, and the dynamic mechanisms of the biomolecules-CNT systems are still challenging due to the complexity of the biomacromolecules. The interaction between nanostructured materials and living systems is of fundamental and practical interest and will determine the biocompatibility, potential utilities, and applications of novel nanomaterials in biotechnological processes. However, the studies on the CNT-organic nanoparticle hybrid architectures are poorly developed comparatively. For example, there are not enough studies on the influence that the nanomaterial properties (such as composition, morphology, and surface chemistry) have on the structure and function of conjugated proteins. The most important parameter in all such studies is the type of carbon nanotubes used, which is determined by (i) the preparation and manufacturing process followed; (ii) the structural characteristics of the CNTs; (iii) the surface characteristics of the CNTs and the characteristics of the functional groups at the surface of CNTs. Interactions with cells have to be performed using biocompatible CNTs, achieved by either covalent or noncovalent surface functionalization to produce water-soluble CNTs [98].

10.2. 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 [99]. To improve enzyme stability, enzymes have generally been studied with the enzymes immobilized on a solid support [100]. 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 [100–102]. 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

TABLE 4: Applications of carbon nanotube-protein biconjugates.

| Protein | Carbon nanotube nanomaterials | Application | Reference |
|-------------------------------------------------|------------------------------------------------------------------|----------------------------------------|-----------|
| β -Glucosidase | MWCNT-COOH | Biocatalysis | [163] |
| <i>Candida rugosa</i> Lipase | MWCNTs or MWCNTs-COOH | Biocatalysis | [164] |
| Horseradish peroxidase | SWCNT/chitosan modified glassy carbon electrode (GCE) | Bioelectrochemical sensor | [165] |
| <i>Trametes hirsuta</i> Laccase | MWCNT modified GCE | Biofuel cells | [166] |
| Horseradish peroxidase, Myoglobin, Cytochrome c | SWNT/ionic liquid modified GCE | Biofuel cells, biosensors | [167] |
| <i>Cerrena unicolor</i> Laccase | CNT modified boron-doped diamond electrode | Biofuel cells, biosensors | [168] |
| Alcohol dehydrogenase | SWCNT/poly(dimethyldiallylammonium chloride) (PDDA) modified GCE | Ethanol biosensor | [169] |
| Glucose oxidase | SWCNT/silica modified GCE | Glucose biosensor | [170] |
| Glucose oxidase, Horseradish peroxidase | MWCNT-toluidine blue/naftion modified GCE | Glucose biosensor | [171] |
| Cytochrome c | MWCNT/chitosan/ionic liquid modified GCE | H ₂ O ₂ detector | [172] |
| Horseradish peroxidase | MWCNT/chitosan/sol-gel modified GCE | H ₂ O ₂ detector | [173] |
| Cytochrome c | MWCNT/poly(amidoamine)/chitosan modified GCE | Nitrite biosensor | [174] |
| <i>Trametes versicolor</i> Hemoglobin | MWCNT/chitosan | Oxygen biosensor, Biofuel cells | [175] |

enzyme up to 2-fold greater than flat support and up to 10 times higher than native enzyme [103]. 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 [104, 105]. 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 4 shows the application of some selected protein-CNTs conjugates in various areas.

11. Immobilization Approaches

Enzyme immobilization is central to bioreactor and biosensor technologies. An immobilized molecule is one whose movement in space has been restricted either completely or to a small limited region by attachment to a solid structure. Expensive enzymes are not favoured to be used in industries in the free state as they are difficult to be separated from the products and consequently are lost after the first use. Alternatively, enzymes can be immobilized on solid supports so that they can be easily separated from the products by simple filtration. The main advantage for enzyme immobilization is the easy separation of the enzyme from the reaction mixture (substrates and products) and its reusability for tens of time, which reduces the enzyme and the enzymatic products cost tremendously. Beside this splendid advantage, the immobilization process imparts many other advantages to the enzyme such as (a) the ability to stop the reaction rapidly by removing the enzyme from the reaction solution (or vice versa), (b) product is not contaminated with the enzyme, and (c) enhancement of enzyme stability against pH,

temperature, solvents, contaminants, and impurities. There are five principal methods for immobilization of enzymes and cells (adsorption, covalent, entrapment, encapsulation, and crosslinking) and no one method is perfect for all molecules or purposes.

It was reported that small proteins such as metallothionein, cytochrome C, and β -lactamase were able to adsorb on the internal as well as outer walls of CNTs after the ends were opened by treatment with concentrated nitric acid [106, 107]. Since then, both multiwalled (MWCNT) and single-walled CNTs (SWCNT), have been demonstrated to have the ability to adsorb many types of proteins. The adsorbed proteins form a coat on the CNT surface when visualized by atomic force microscopy (AFM) or electron microscopy. To fully explore the potential of the enzyme-CNT complex, it is essential to find optimal methods for enzyme immobilization. For enzyme immobilization, SWNTs are attractive for their higher surface area for enzyme interaction, but MWNTs are desirable for their easier dispersibility and lower cost. Proteins can interact with nanotubes with multiple types of interactions. Noncovalent (physioadsorption) and covalent (chemical bond formation) conjugations have been reported for the immobilization of various enzymes [108]. Noncovalent attachment preserves the unique properties of both enzymes and CNTs, but the immobilized protein can be gradually lost during the use of the CNT-enzyme complex [108]. Covalent conjugation provides durable attachment, but the enzyme structure may be more disrupted. Functionalization of CNTs with organic, polymeric, and biological molecules can provide biocompatible nanotube composites with specific groups on their surface. No matter what method is used, the main challenge is promoting the stable attachment of enzymes while maintaining their activity and function as closely as possible to their native state [109]. The performance CNT-enzyme complexes are affected by a

combination of the nanotube chemistry and immobilization method.

11.1. The NonCovalent Immobilization. The noncovalent approach is considered to be a more promising technique, because there is less distortion of the conformational structure of the immobilized enzymes [110, 111]. In most cases the interaction between the protein and the CNTs involves the physically adsorbed of the protein onto the CNTs. The adsorption of protein onto the CNTs involves both hydrophobic and electrostatic interaction [96, 112, 113]. Pristine CNTs being highly hydrophobic will contribute to hydrophobic interaction through interaction of the side chains of hydrophobic amino acids of the proteins with the sidewall of CNTs. As for the electrostatic interaction, the π electrons on the surface of the CNTs will interact with the π electrons of the aromatic ring of amino acids (e.g., phenylalanine and tryptophan). Apart from electrostatic and hydrophobic interaction, hydrogen bonds, and nonspecific adsorption can also play a role for enzyme adsorption onto CNTs [110]. The adsorption typically involves bathing the CNTs in a solution of the enzyme and shaking the sample to allow time for the physical adsorption onto the surface to occur and then rinsing away enzyme that is not adsorbed. This technique can be carried out by direct physical adsorption onto CNTs (direct physical adsorption) or adsorption with the assistance of substances such as polymers, surfactants, and linking molecules (specific adsorption). As CNTs have a natural affinity for diverse proteins, the adsorption is spontaneous when proteins come in contact with CNTs in a solution and follows a pseudosaturation behavior.

The hydrophobic, nanoscale environment of a CNT can influence protein or enzyme structure and function. Using techniques such as FT-IR and AFM, the conformation of the adsorbed protein was observed to be distorted or partially unfolded due to the strong interaction with the CNTs [96]. Studies have revealed that enzymes have structural changes upon adsorption, and some enzymes have significant loss of alpha-helix content. The nature of the enzyme or protein influences the extent of its denaturation upon adsorption. Molecular dynamics simulations have shown that, in the organic solvent heptane, the hydrogen bonds at the active site of the lipase can be better preserved when the enzyme is immobilized on the surface of the CNT [114]. Even though the denaturation of enzymes or proteins occurs, CNTs can stabilize enzymes at elevated temperatures and in organic solvents to a greater extent than conventional flat supports [112, 113]. It has been hypothesized that the highly curved surfaces of CNTs are unfavorable for enzyme denaturation in harsh conditions and suppress lateral interactions between adjacent adsorbed enzymes. The increased curvature of CNTs could probably contribute to a reduction of detrimental interactions between immobilized protein molecules, this in turn leads to increased enzyme stability on CNTs compared to that on flat surfaces.

For the direct physical adsorption method, the interacting force between the protein or enzyme and CNTs is predominantly a hydrophobic interaction [108]. The amounts

of enzymes adsorbed on CNTs are affected by various factors, such as the nature of the enzyme, the surface chemistry of the CNT, and operation variables. Table 5 shows examples of proteins or enzymes that have been immobilized by direct physical adsorption and the types of interaction forces that involved.

Besides the direct noncovalent immobilization, indirect immobilization via polymers, and biomolecules attached to the CNTs facilitates the immobilization of enzymes or proteins. Polymers and biomolecules have been used to functionalize CNTs. The functionalized CNTs have good aqueous dispersibility, and the formation of the enzyme-CNT complex is achieved via the anchor molecule. Polymers coated on CNTs can provide negatively and positively charged functional groups on the surface of CNT-polymer complexes. The binding specificity for enzymes or proteins are due to the combination of many molecular properties such as hydrophobicity, electrostatic interactions, hydrogen bonding, and steric properties [115, 116]. Table 6 shows examples of proteins or enzymes that have been immobilized by indirect specific adsorption and the types of interaction forces that involved.

The benefits of noncovalent attachment methods for the immobilization of enzymes among others are improved preservation of protein structures and CNT properties. However, the immobilized protein is in equilibrium in a solution and can therefore be gradually lost through leaching during the usage. On the other hand, covalent conjugation provides durable attachment, but the harsh oxidation step (e.g., with strong acids) disrupts the π -networks on the CNT surfaces and may diminish their mechanical and electronic properties [117]. Hence covalent attachment of enzymes can result in high reusability. Covalent attachment of proteins on carboxylated CNTs using the popular cross-linker 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) was first reported by Huang et al. [118] and Jiang et al. [119].

11.2. The Covalent Immobilization

11.2.1. Direct Covalent Linking Proteins onto CNTs. To prevent leaching of proteins or enzymes, covalent bonds have been used to attach the protein or enzyme molecules to CNTs. The covalent functionalization of CNTs can generally be achieved by two main approaches: (i) esterification or amidation of oxidized tubes and (ii) sidewall covalent attachment of functional groups [85, 86]. An efficient one-step method for covalent attachment of alkyl groups terminated with a carboxylic acid to the sidewalls of carbon nanotubes have been performed [120]. Further functionalization of the carboxyl groups on the nanotube side chains with terminal amines and diamines impart improved solubility and processing to the nanotubes, which may allow their attachment into polymer composite materials through chemical bonding via terminal functional groups on the nanotubes. These functional groups also provide sites for covalent attachment of biologically active moieties, for example, amino acids, peptides proteins, and oligonucleotides [120]. Covalent immobilization of enzymes on CNTs has also been performed

TABLE 5: Noncovalent immobilization by direct physical adsorption.

| Protein or enzyme immobilized | Types of interaction | References |
|--------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| Lysozyme-CNT complex | (i) Hydrophobic regions on exterior of protein interact with the wall of CNTs through hydrophobic interactions. (ii) The π - π stacking interaction between the sidewalls of CNTs and the aromatic rings (both these hydrophobic and π - π interactions have been widely used to explain the driving force of the direct adsorption of many enzyme on CNTs). (iii) Electrostatic interaction. In addition to hydrophobic and π - π interactions, lysozyme interacts with the nanotubes through protonated amino moieties with defect sites of the CNTs at pH values lower than the isoelectric point. At pH levels higher than the isoelectric point, they interact via amine adsorption. | [110, 111] |
| Glucose oxidase; 2,5-dihydroxy benzaldehyde; bovine serum albumin. | (i) Hydrogen bonding interactions between the carboxylated CNTs and proteins supports the adhesion of the enzyme complex onto CNTs. | [176] |

TABLE 6: Noncovalent immobilization of protein and enzymes by indirect specific adsorption.

| Protein or Enzyme immobilized | Types of interaction | References |
|-------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------|
| Glucose oxidase | (i) Surface of CNTs was positively charged by coating poly (sodium 4-styrenesulfonate) combined with ionic liquids. (ii) The enzyme was adsorbed onto nanotube composites through electrostatic interactions. | [177, 178] |
| Alcohol dehydrogenase | (i) Chitosan-encapsulated CNTs have a positively charged surface; enzymes were immobilized through electrostatic interaction. | [179] |
| Glucose oxidase and Alcohol dehydrogenase | (i) single stranded DNA was wrapped on CNTs, and enzymes were immobilized onto DNA-wrapped CNTs. (ii) The binding of DNA onto CNTs appears to be primarily due to π - π stacking interaction, with the plane of the aromatic-nucleotide bases oriented parallel to the surface of the nanotube. | [178, 180–182] |
| DNAzyme; Glucose oxidase | (i) Streptavidin and flavin adenine dinucleotide have also been used as the linking molecules between enzymes and CNTs. (ii) DNAzyme immobilized onto CNTs attached with streptavidin via stable amide linkages. (iii) Glucose oxidase has been immobilized onto CNTs functionalized with the flavin adenine dinucleotide via amide linkages. | [183, 184] |
| Horseradish peroxidase; Cytochrome c | (i) Enzymes were adsorbed onto CNTs which were coated with surfactants such as Triton X-100, sodium dodecyl sulfate, and cetyltrimethylammonium bromide. (ii) Enzymes and surfactants are coassembled onto the CNTs. The CNTs are sonicated in the solution of a surfactant. When enzyme is mixed with the suspension, it binds to the CNTs more strongly than the surfactant and displaces the surfactant to gain access to the CNT surface. | [104, 185, 186] |

TABLE 7: Structural studies of protein immobilized onto carbon nanotubes.

| Protein | Nanomaterial | Spectroscopic techniques | Results | Reference |
|------------------------|----------------------------------------------------|-------------------------------------|-----------------------------------------------------------------------------------------------------------------------------|-----------|
| Albumin Lysozyme | SWCNTs | Circular dichroism Vis-Near IR | The protein are partially unfolded upon immobilization | [110] |
| Cytochrome c | MWCNT/poly (amidoamine)/chitosan | UV-Vis | No structural changes upon immobilization | [174] |
| Amyloglucosidase | SWCNTs, MWCNTs (in combination of coupling agents) | Circular dichroism | Enzyme retains its structure when physically adsorbed. However, covalent attachment leads to significant loss of structure. | [187] |
| Horseradish peroxidase | SWCNTs | Circular dichroism and fluorescence | Enzyme retain high percentage of their native structure when immobilized. | [113] |

by allowing the reaction of the free amine groups (on the protein surface) with carboxylic acid groups that are generated by sidewall oxidation of CNTs, which is facilitated by 1-ethyl-3-(3dimethylaminopropyl) carbodiimide [112, 113, 118, 119]. The method has been widely applied to the covalent immobilization of proteins on carboxylated CNTs [108]. For some enzymes, the enzyme-loadings are higher than 1000 μg enzyme per mg of CNTs [121, 122]. The conjugates are stable at high temperatures, providing a combination of useful attributes such as low mass transfer resistance, high activity and stability, and reusability. It has been reported that the uncovered surface of CNTs may promote the accessibility of substrate to the enzyme and the CNTs can facilitate heat transfer [122]. Ji et al. [121] have showed that covalently attached lipase on CNTs has advantages over free lipase in catalysis in organic solvent. The immobilized lipase greatly improves the conversion of the substrate compared to the native lipase. It has been demonstrated that enzymes on SWCNTs have much higher activity than those conjugated to MWCNTs [109].

11.2.2. Covalent Attachment of Proteins onto CNTs with Linking Molecules. Linking molecules which act as “bridge” between the material and protein are frequently used for covalent immobilization of protein and enzymes onto CNTs. They bind to CNTs through hydrophobic and π - π interactions [123, 124] and also covalently bind the enzyme through, for example, an amide bond [125, 126]. These linking molecules present advantages in the immobilization of enzymes. In the immobilization of horseradish peroxidase, the highly reactive succinimidyl ester groups were covered on CNTs, using 1-pyrenebutanoic acid succinimidyl ester as the linking molecule [123]. Pang et al. [124] have reported that with aminopyrene, the amino functional groups were introduced uniformly on the CNT surface and the immobilized-laccase enzyme showed higher electrocatalytic activity and better stability than the laccase immobilized on the pristine CNTs. Linking molecules can provide specific sites for CNTs to immobilize enzymes [102, 127]. Figure 3 summarizes the three main method of biomolecule immobilization on CNTs.

12. Structure and Catalytic Behavior of Immobilized Enzymes

The premise of using nanoscale structures for immobilization is to reduce diffusion limitations and maximize the functional surface area to increase enzyme loading [128]. In addition, the physical characteristics of nanoparticles such as enhanced diffusion and particle mobility can impact inherent catalytic activity of attached enzymes [101]. Immobilization of enzymes is advantageous for commercial application due to convenience in handling, ease of separation of enzymes from the reaction mixture and reuse, and a possible increase in thermal and pH stability [129, 130]. Poor biocatalytic efficiency of immobilized enzymes, however, is a main drawback that hinders the large-scale application. Noncovalent techniques, which employs simple physical adsorption and usually do not require the harsh processing conditions are

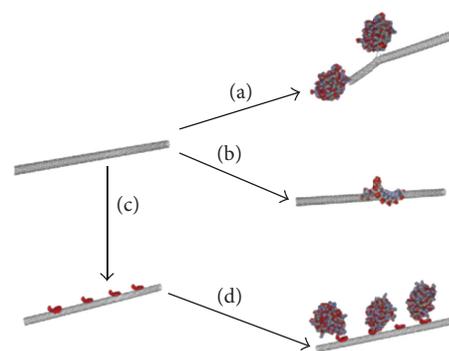


FIGURE 3: The three main approaches for modifying carbon nanotubes with biomolecules: the covalent approach (step a), noncovalent approach (step b), and hybrid approach where a small molecule “anchor” is first noncovalently absorbed to the carbon nanotube (step c), followed by a chemical reaction between the anchor and the biomolecules of interest (step d). (Adapted from Yang et al. [133])

simpler in practice, however leads to lower amounts of loading than more involved methods as reported by a study by Zhang and Henthorn [131]. The authors found that the amount of enzyme loading was significantly less for the direct adsorption method (66 micrograms of enzyme per milligram of dry carbon nanotubes) than for the linker molecule method (140 $\mu\text{g}/\text{mg}$). Over the past 6 years or so some research groups have investigated the activity-structure relationship of the immobilized enzymes. A study of retained enzyme activity was then conducted and they found that only 27% of the enzyme activity remained when the conjugation was produced using direct adsorption, while 57% of the enzyme activity was retained using the linker molecule [131]. Karajanagi et al. [96] had reported that direct physical adsorption cause a significant change in the secondary structure of the protein [132], used circular dichroism spectroscopy and fluorescence to analyze the structural changes that occurred upon protein adsorption. In many cases, the higher stability is attributed in a more rigid structure that the enzyme adopts.

Several spectroscopic techniques have been used in order to monitor possible structural changes upon immobilization. Table 7 shows the results of some recent works in this area. The type of the enzyme and the nanotubes, the functional groups on the surface of the CNTs, and immobilization techniques are crucial factors which affect the structure of the enzyme upon immobilization [116].

13. Conclusion

Various 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 strides, and it is clear that this subject will drive the applications of carbon nanotubes. Functionalization 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. However, there is not a universal enzyme support and the best method of immobilization might differ from enzyme to enzyme, from application to application, and from carrier to carrier. In the future, information derived from protein sequences, 3D-structures, and reaction mechanism should be further combined with the fascinating properties of CNTs and physical/chemical methods in order to produce the immobilized enzyme with even more stability and higher catalytic activity. Using noncovalent approaches, enzymes can be less denatured upon immobilization and the intrinsic electronic structure and properties of CNTs are preserved.

It is also necessary to study how the linking molecules interact with enzymes and affect the enzyme structure and the arrangement of enzymes on CNTs. The mobility, confining effects, solution behaviors, and interfacial properties of nanoscale materials can introduce unique properties to biocatalyst systems, making it possible to develop a revolutionary class of biocatalyst that differs from traditional immobilized enzymes in terms of preparation, catalytic efficiency, and application potential. In the future, new mechanisms and phenomena may continue to appear. Interest in this field is rapidly growing and is likely to fuel more exciting developments in the near future.

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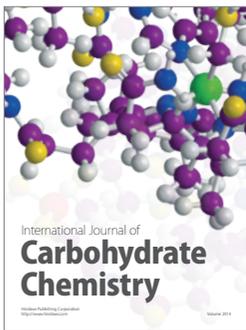
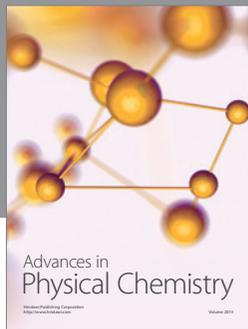
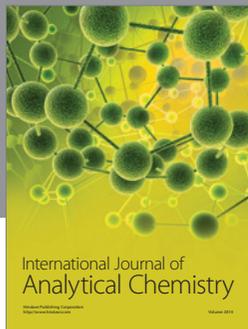
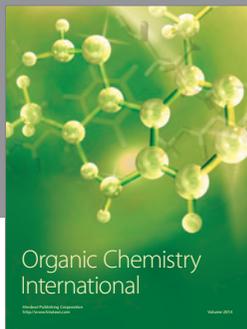
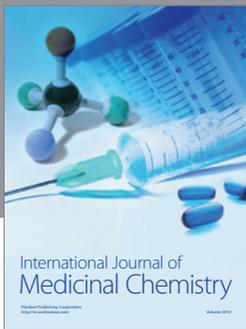
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