CHAPTER II

THEORY AND LITERATURE REVIEW

'*There's plenty of room at the bottom*', was the title of Richard Feynman's talk, when he gave a lecture at American Physical Society Meeting at Caltech in 1959 [1]. This valuable phrase has been the mainspring of scientific inspiration for scientists around the world to initiate the scientific movement of tiny level which is nowadays called "Nanoscience and Nanotechnology". Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at larger scale while nanotechnology is the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale [2].

Nanotechnology deals with materials and systems having the following key properties [3];

- They have at least one dimension smaller than 100 nm.
- They are designed through processes that exhibit fundamental control over the physical and chemical characteristics of molecular scale structure.
- They can be combined into larger structures.

A wide group of nanomaterials enables access to the new ranges of electronic, magnetic, mechanical and optical properties. One of interesting nanomaterials which has attracted the attention of many researchers since the last decade is "Carbon Nanotubes" (CNTs) [4]. There are many allotropes of carbon structures which have been well known in nowadays such as diamond, graphite, fullerene (C_{60}) and carbon nanotube. The major allotropes of carbon; diamond and graphite, should be considered and compared with carbon nanotube in term of their structure as shown in Figure 2.1. The chemical bonding of carbon nanotubes is composed entirely of sp^2 bonds, similar to graphite. This bonding structure, which is stronger than the sp^3 bonds found in diamonds, provides the molecules with their unique strength. Nanotubes naturally align themselves into "ropes" held together by van der Waals forces [5]. In diamond, each carbon atom is bonded to four others in a three dimensional lattice while in graphite, each carbon atoms is attached to three others in a same plane and form a hexagonal lattice. The remaining bond in graphite structure is used to hold the other planes above and below. However, the bonds in the plane of graphite are stronger than in diamond but the interplanar bonds are relatively weak and enable the planes to slide [6].

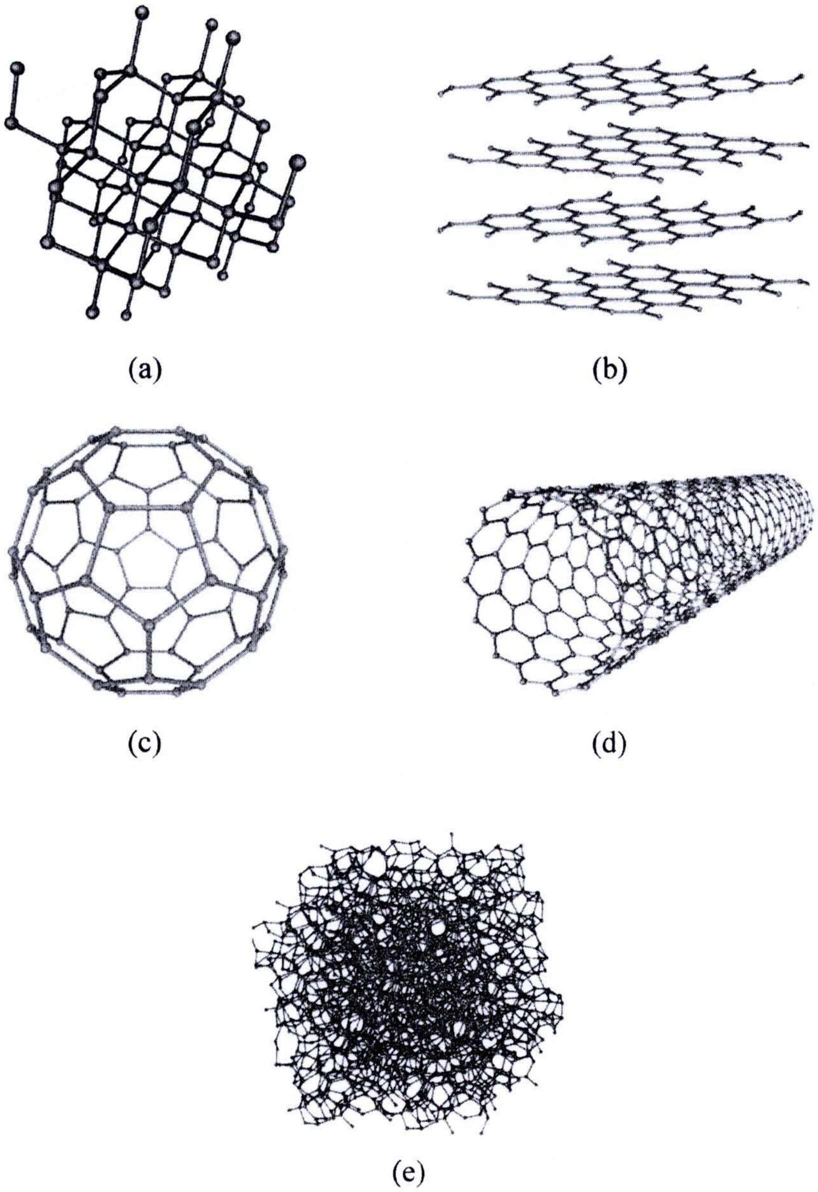


Figure 2.1 Carbon Allotropes; (a) Diamond, (b) Graphite, (c) Fullerene (C_{60}), (d) Single Walled Carbon Nanotube and (e) Amorphous Carbon.

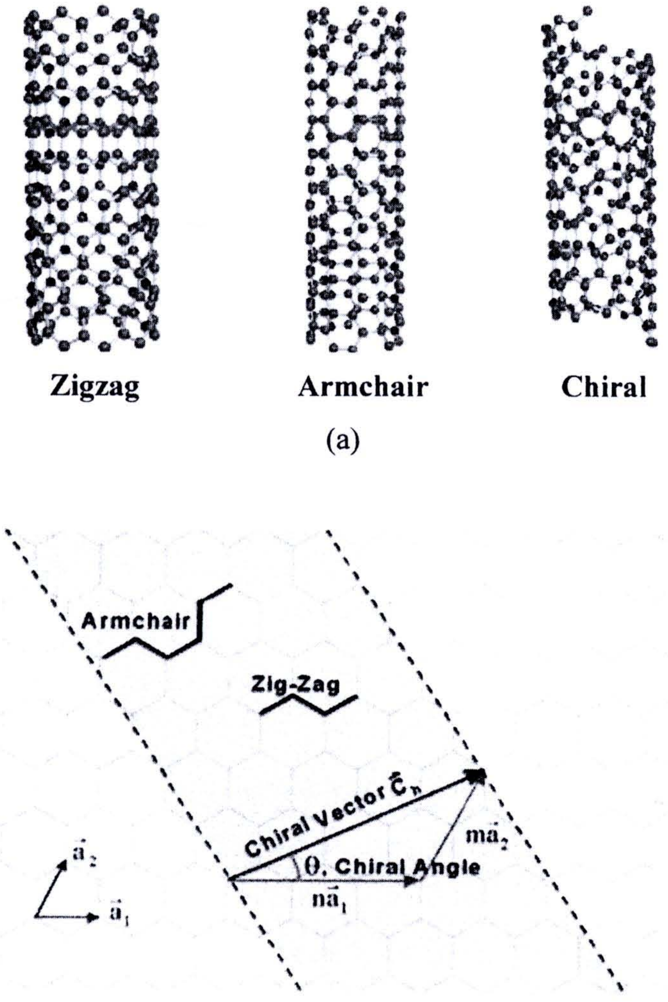
2.1 Introduction to Carbon Nanotubes

Since the discovery of multiwalled carbon nanotubes in 1991 by Iijima [7] and singlewalled carbon nanotubes in 1993 by Iijima's team from NEC, Japan [8] and Bethune's team from IBM, California, U.S.A. [9], the breakthrough of carbon nanotubes in last decade has been illustrated by a great number of scientific publications in multidisciplinary field. Among their remarkable properties; high tensile strength, high stability in thermal and chemical, high electrical conductivity and biocompatibility, all of these properties become important reason that carbon nanotubes to be integrated in wide variety of applications. Carbon nanotubes are nanoscale graphene cylinder covered their edge by a half of fullerene. There are two main types of carbon nanotubes which are singlewall carbon nanotubes and multiwall carbon nanotubes. Singlewall carbon nanotubes (SWCNTs) are a roll of monolayered graphene sheet while multiwall carbon nanotubes (MWCNTs) are several graphitic concentric layers. The diameter varies from 0.4 to 2 nm for SWCNT and from 1.4 to 100 nm for MWCNT, while their length can be reached in several micrometers [10].

Three crystallographic configurations of carbon nanotubes; zigzag, armchair, and chiral of CNTs (Figure 2.2(a)) depend on how the graphene sheet is rolled up. These groups are determined by the chiral vector which received by the equation (1)

$$Ch = n\hat{a}_1 + m\hat{a}_2 \quad \dots\dots\dots\dots\dots\dots\dots (1)$$

Where $\hat{a}_1$ and $\hat{a}_2$ are unit vectors in the two dimensional hexagonal lattice, and n and m are integers. Another important factor is the chiral angle (Figure 2.2(b)), which is the angle between Ch and $\hat{a}_1$. When $n = m$ and the chiral angle is 30 degrees, it is known as an armchair type. When n or m is zero and the chiral angle is equal to zero, the nanotube is known as zigzag. Chiral nanotubes are formed when the chiral angles are ranged between 0° and 30°.



(a)

(b)

Figure 2.2 (a) Crystallographic configurations of CNTs [11], (b) Direction of rolled hexagonal sheet of graphite to form a CNT [12].

In addition, radius of carbon nanotube can be calculated follow equation (2)

$$R = \frac{Ch}{2\pi} \quad \ldots\ldots\ldots(2)$$

R = radius of carbon nanotube, Ch = Chiral vector

Diameter of carbon nanotube can be calculated follow equation (3)

$$D = \frac{c}{\pi} \quad \text{..........(3)}$$

D = diameter of carbon nanotube, c = circumference

Length of chiral vector can be calculated follow equation (4)

$$C = |Ch| = a\sqrt{\left(n^2 + nm + m^2\right)} \quad \text{............(4)}$$

C = Length of chiral vector, a = length of unit vector, n, m = integer

Length of unit vector can be calculated follow equation (5)

$$a = |\hat{a}_1| = |\hat{a}_2| = a_{cc}\sqrt{3} \quad \text{.................(5)}$$

a_{cc} = 0.1421 nm (bond length of C-C)

a = 0.1421x1.732 = 0.2411nm

Chiral angle which is the angle between Ch harvest zigzag C-C bond can be calculated follow equation (6)

$$\theta = \tan^{-1}\left(\frac{m\sqrt{3}}{m + 2n}\right) \quad \text{..........................(6)}$$

n, m = integer

The unique electrical property of carbon nanotubes which is an important parameter should also be considered that which the crystallographic configuration of carbon nanotubes was provided metallic carbon nanotube and semiconductor carbon nanotube. It's depend on the difference of integer of unit vector as follow,

$|n\text{-}m| = 3q$ metallic - armchair

$|n\text{-}m| = 3q \pm 1$ semiconductor – zigzag

q = integer 0,1,2,3...

Intershell spacing of multiwall carbon nanotubes can be calculated (7).

$$D = 0.344 + 0.1\exp\left(\frac{-c}{4\pi}\right) \quad \text{..............(7)}$$

D = intershell spacing of MWCNTs, c = circumference

2.2 Carbon nanotubes synthesis

2.2.1 Electric Arc Discharge technique

The most widely used technique to produce nanotubes is the electric arc discharge (Figure 2.3). The synthesis is performed in a water-cooled reaction chamber first evacuated and then filled with an inert gas atmosphere (helium or argon, 660 mbar). Two graphite rods are used as electrodes: one is fixed while another one can be moved by a translation mechanism. The mobile electrode (the anode) is moved towards the cathode until the distance between them is less than 1 mm that a current (100 A) passes through the electrodes and plasma is created between them. The average temperature in the inter-electrode plasma region is extremely high (of the order of 4000 K) and therefore the carbon is sublimated and the positive electrode is consumed. In order to maintain the arc between the electrodes, the anode has to be continuously translated to keep a constant distance between the rods.

The deposit consists of a hard grey outer shell and a soft fibrous black core. The outer hard shell is formed of nanoparticles and MWCNTs fused together whereas the core contains about one-thirds polyhedral graphitic nanoparticles and two-thirds MWCNTs. To synthesize SWCNTs, the electrodes are doped with a small amount of metallic catalyst particles. Among the two methods, the arc discharge has the advantage of being much cheaper than the laser ablation method [13, 14].

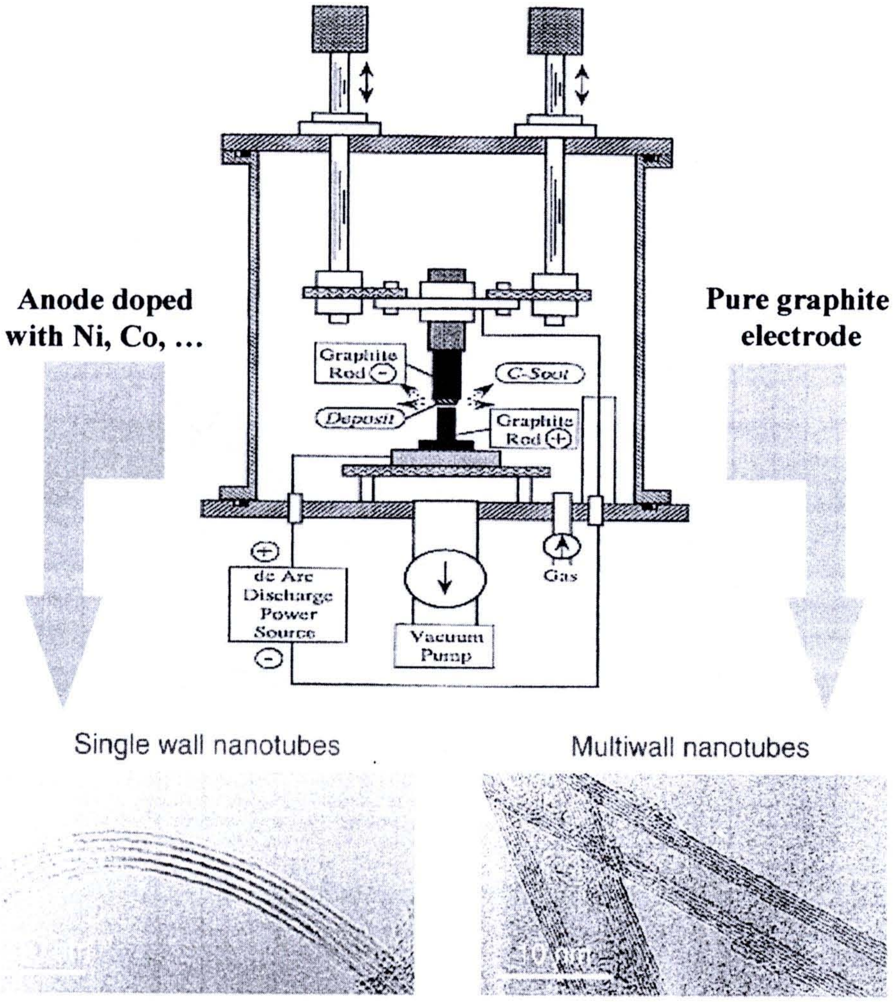


Figure 2.3 Arc discharge apparatus produced the first carbon nanotubes[15,16]

2.2.2 Laser Ablation Technique

The laser ablation technique (Figure 2.4) operates at similar conditions to arc discharge. Both methods use the condensation of carbon atoms generated from the vaporization of graphite targets. Also, SWCNTs are formed when graphite targets containing catalyst. Such as Ni, Co, Pt, are vaporized by a laser. The graphite target is placed in a quartz tube surrounded by a furnace (at 1,200 °C).

A constant gas flow (Ar or He) is passed through the tube in order to transfer the soot generated to a water-cooled Cu collector. The SWCNTs usually condense as ropes or bundles consisting of several individual SWCNTs. By products such as amorphous carbon or encapsulated metal catalyst particles are also present. When just a pure graphite target is used, MWCNTs are found only. These nanotubes are formed with 4 to 24 graphitic layers and their length can reach 300 nm. The laser ablation technique favors the growth of SWCNTs, while MWCNTs are usually not generated with this method. A disadvantage of this method is that it requires expensive lasers [13, 14].

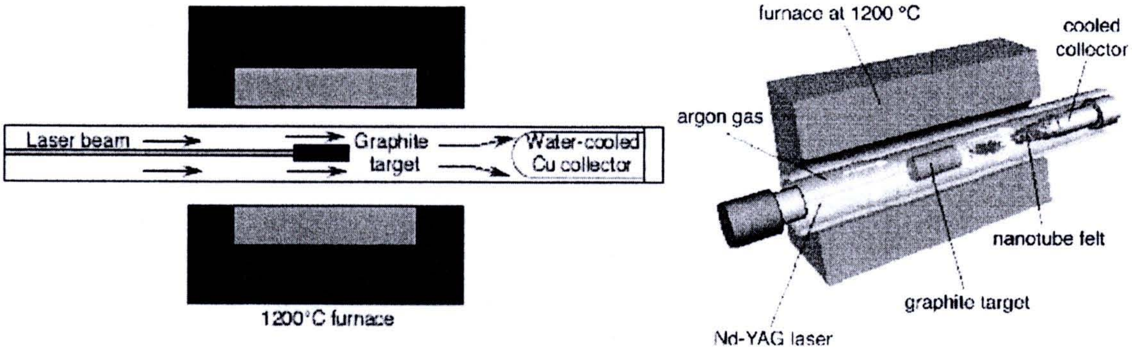


Figure 2.4 Laser ablation apparatus for producing carbon nanotubes[13,17].

2.2.3 Chemical Vapor Deposition Technique

Most of chemical vapor deposition (CVD) method uses methane, carbon monoxide, ethylene, or acetylene as the carbon feedstock, and the growth temperature is typically in the range of 823-1023 K. Iron, Nickel, or Cobalt nanoparticles are often used as the catalysts. In the CVD process growth as shown in Figure 2.5 involves heating a catalyst material to high temperature in a tube furnace using a hydrocarbon gas pass through the tube reactor over a period of time. The basic mechanism in this process is the dissociation of hydrocarbon molecules catalyzed by the transition metal and saturation of carbon atoms in the metal nanoparticle. Precipitation of carbon from the metal particle leads to the formation of tubular carbon solid.

This process has two main advantages: the nanotubes are obtained at much lower temperature, although this is at the cost of lower quality, and the catalyst can be deposited on a substrate, which allows for the formation of novel structures [12-14].

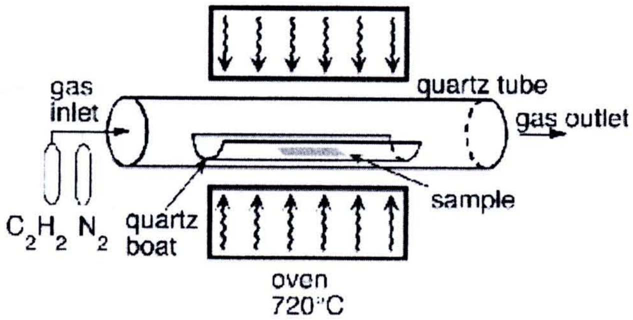


Figure 2.5 Carbon nanotubes synthesis using chemical vapor deposition technique[16].

2.3 Surface modification of carbon nanotubes

According to the van der Waals force between nanotubes surface, carbon nanotubes tend to aggregate to each other as a bundle. Therefore, this major problem lead carbon nanotubes hardly dispersed in any kind of solvent and induced the next problem which was how to disperse carbon nanotubes before applying in any application. The necessary properties of carbon nanotubes and even the other nanomaterials were provided the high specific surface area and their individual unique property. The surface modification of carbon nanotubes were the important solution to overcome this problem by reducing the van der Waals force of intertubes for improving their dispersion and provide the ionic functional groups on nanotube surface for improving their stability in aqueous solution. From the relevant literatures, there have been proposed two main approaches for modifying carbon nanotubes surface; *i)* noncovalent and *ii)* covalent surface modification. To provide a wide variety of functional groups on carbon nanotubes surface, covalent surface modification were the impact method for dispersion and stability improvement. However, the disadvantages of this technique are that the abundant of conjugated bond which were the important for the electronic property of carbon nanotubes, were loose during the favor chemical reaction on nanotubes surface.

While the noncovalent surface modification still provided the carbon nanotubes integrity using polymer, surfactant, biomolecules base on the interaction as electrostatic, hydrogen bonding, hydrophobic, and even van der Waals. However, the noncovalent surface modification still provide the weak interaction between the dispersing species and carbon nanotubes surface when compare with covalent surface modification, it's possible to loose their stability when the condition were not suitable.

2.3.1 Noncovalent surface modification

Several ways of dispersion have been explored and can be basically devided in two main approaches. One procedure consists on the noncovalent modification of CNTs with surfactant, nucleic acid, peptides, and polymers. The noncovalent interactions are based on van der Waals, hydrophobic and π-π stacking interactions. The advantage of this method is the preservation of the electronic structure of CNTs surface.

Chengguo Hu et al. [18] demonstrated a new noncovalent approach for the dissolution and exfoliation of SWNTs in water by a rigid, planar and conjugated diazo dye, Congo red (CR). The mixture of SWNTs and CR can be dissolved in water with a solubility as high as 3.5 mg/ml for SWNTs. High-resolution transmission electron microscope images showed that the SWNTs bundles were efficiently exfoliated into individual SWNTs or small ropes. The pi-stacking interaction between adsorbed CR and SWNTs was considered responsible for the high solubility.

Individual single-walled carbon nanotubes (SWNTs) have been suspended in aqueous media using various anionic, cationic, nonionic surfactants and polymers were reported by *Valerie C. Moore et al.* [19]. The surfactants are compared with respect to their ability to suspend individual SWNTs and the quality of the absorption and fluorescence spectra. For the ionic surfactants, sodium dodecylbenzene sulfonate (SDBS) gives the most well resolved spectral features. For the nonionic systems, surfactants with higher molecular weight suspend more SWNT material and have more pronounced spectral features.

Junping Zhang et al. presented their work that focuses on manipulating the dispersion of pristine CNTs with a series of versatile derivatives of chitosan (CTS) by using *pH* as a stimulus [20]. Derivatives of CTS could be used to disperse CNTs homogeneously while endowing them with biocompatibility and maintaining their intact electronic structure. The substitution degree of CTS derivatives could also be used to manipulate the dispersion of CNTs more specifically. *pH* sensitivity of the CTS/CNTs, CMCTS/CNTs and NSC/CNTs systems as well as completely homogeneous dispersion of CNTs by using HACC may open new possibilities for using CNTs for various biomedical applications.

Moreover, polyelectrolyte multilayers can be immobilized onto carbon nanotubes via electrostatic interaction by Layer-by-Layer technique to disperse carbon nanotubes. *Decher et al.* have developed a new tèchnique for the preparation of polymer thin film from polyelectrolyte solution by Layer-by-Layer technique or electrostatic self-assembly technique (ESA) [21]. The principle of this technique can be summarized as follow. A substrate is successively dipped in dilutes solution of oppositely charged polyelectrolyte leading to a Layer-by-Layer deposition mode. Each adsorption step leads to a reversal of the charges allowing the deposition of the next layer until it becomes polyelectrolyte multilayer thin films (PEMs) [22]. PEMs have been fabricated using mainly electrostatic attraction as the driving force for multilayers. There are many other interactions that have been used successfully for multilayers deposition such as donor-accepter interaction, hydrogen bonding, covalent bond, etc. *Agata Zykwinska et al.* demonstrated that a new general procedure for carbon nanotube modification based on polyelectrolyte layer-by-layer assembly [23]. They demonstrated noncovalently modified surface of carbon nanotubes by layer-by-layer deposition with synthetic polyelectrolytes. The thickness of the adsorbed polyelectrolyte layers increases linearly with the bilayers number up to reach 6 nm. The adsorbed polyelectrolyte layers were used as anchoring ones to subsequently graft a natural biopolymer. This opens the promising way to design new biodevices based on carbon nanotubes. *Alvaro Carrillo et al.* described a strategy for functionalizing graphite and carbon nanotube surfaces with multilayered polymeric films [24]. Poly(amphiphiles) adsorb noncovalently onto these surfaces from aqueous solutions, due to hydrophobic interactions. The covalent attachment of a second polymer layer to this initial adsorbed layer results in the formation of a cross-linked polymer bilayer; additional layers can be deposited by the covalent or electrostatic attachment of polyelectrolytes. They used these multilayered polymer films to mediate the attachment of gold nanoparticles to graphite, single-walled nanotube (SWNT), and multiwalled nanotube (MWNT) surfaces. This approach provides a convenient method for attaching other nanostructures, biological molecules, or ligands to carbon nanotubes.

2.3.2 Covalent surface modification

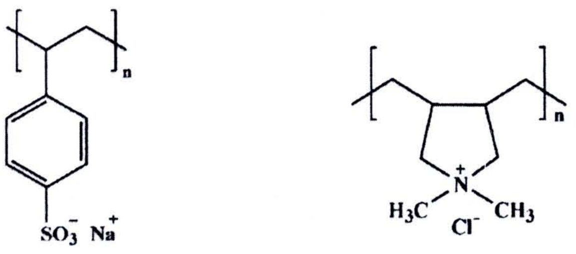
Another approach is based on CNTs covalent functionalization. First, CNTs are cut and oxidized to generate a certain number of carboxylic groups subsequently dramatized with different types of molecules. Alternatively, CNT side walls can be directly functionalized by addition reactions.

Maxim N. Tchoul et al. demonstrated that oxidation of single-walled carbon nanotubes (SWNTs) with nitric acid increases their dispersability in water, methanol, and N,N-dimethylformamide [25]. The dispersability of all types of nanotubes increased substantially after 1 hr of sonication and after 2-4 hr of reflux. Longer treatments resulted in little further improvement in dispersability and at reflux degraded the SWNTs. Concurrent with improved dispersability, oxidation resulted in smaller diameters and shorter lengths show mostly bundles rather than individual tubes. Functionalization of carbon nanotubes via 1,3-dipolar cycloadditions was demonstrated by *Nikos Tagmatarchis and Maurizio Prato* [26]. The organic functionalization of carbon nanotubes has opened new avenues with opportunities to fabricate novel nanostructures by improving both their solubility and processibility. The 1,3-dipolar cycloaddition of azomethine ylides onto carbon nanotube (CNT) networks may play a relevant role towards this direction. CNT-based materials have been synthesized possessing differently functionalized solubilizing chains and hold strong promise as useful building blocks for the construction of novel hybrids for nano- and bio-technological applications.

2.4 Theory of Layer-by-Layer self assembly

2.4.1 Definition and general description of polyelectrolyte [27]

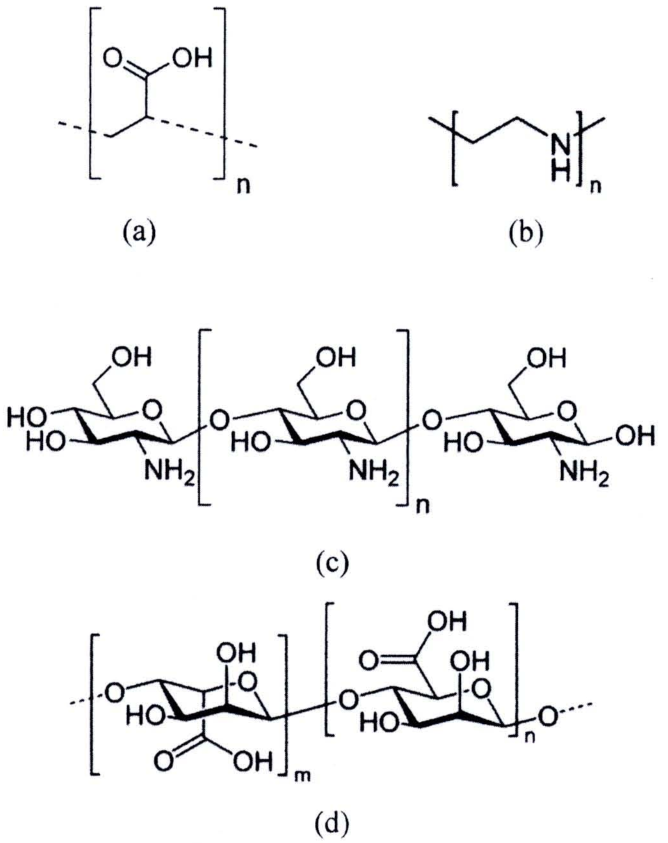
The term "polyelectrolyte" (PEL) is employed for polymer systems consisting of a macroion i.e., a macromolecule carrying covalently bound anionic or cationic groups, and low molecular "counterions" securing for electroneutrality. Example of an anionic and a cationic polyelectrolyte (PEL) are presented in Figure 2.6.



(a) (b)

Figure 2.6 Chemical structure of (a) sodium poly(styrene sulfonate) and (b) poly(diallyldimethylammonium chloride).

Both Na-polystyrene sulfonate and poly(diallyldimethylammonium chloride) are dissociated into macroion and counterion in aqueous solution in the total *pH* range between 0 and 14. Also polymers like poly(acrylic acid) and poly(ethylene imine) are usually classified as polyelectrolytes, in spite of the fact that they form a polyion-counterion system only in a limited *pH* range, and remain as an undissociated polyacid in the acid range or undissociated polybase in the alkaline range, respectively (Figure 2.7 (a), (b)), a behavior typical for weak polyelectrolytes (Figure 2.7 (c), (d))and quite analogous to weak low molecular electrolytes.



(a) (b) (c) (d)

Figure 2.7 Chemical structure of the weak synthetic polyelectrolytes (a) poly(acrylic acid) and (b) poly(ethyleneimine) and weak natural polyelectrolytes (c) chitosan and (d) alginate.

A special case of polyelectrolytes, the "polyampholytes," carrying both anionic and cationic groups covalently bound to the macromolecule, are presented in nature by an abundant number of proteins but can also be obtained by various synthetic routes.

In principle, any macromolecular chemical structure can be transform into a polyelectrolyte structure by covalently attaching a reasonable number of ionic groups to the polymer backbone, with linear or branched macromolecules at a compound soluble in an aqueous medium of appropriate *pH* after introducing a sufficient number of ionic groups.

Today's commercial polyelectrolytes are predominantly obtained by a polymerization, polycondensation, or polyaddition process. Also numerous important

PEL also originate from nature, such as gelatin, as a representative of the widespread class of proteins or pectins belonging to the group of anionic polysaccharides. Furthermore, some PEL of practical importance result from a chemical modification of nonionic natural polymers such as cellulose or starch.

In contrast to the huge variability of the polymer backbone structure, the number of different chemical structures of anionic or cationic sites responsible for the preculiar behavior of PEL in solution is rather small (Table 2.1)

Table 2.1 Structures of ionic sites of polyelectrolyte.

Cationic groups	Anionic groups
$-COO^-$	$-NH_3^+$
$-CSS^-$	$=NH_2^+$
$-OSO_3^-$	$\equiv NH^+$
$-SO_3^-$	$- NR_3^+$
$-OPO_3^{2-}$	

These ionic groups are usually classified as anionic and cationic; a further subdivision into weakly and strongly acid and basic groups is reasonable in analogy to "strong" and "weak" acids and bases of low molecular chemistry with the sulfonate, the sulfonate-half ester, and the tetraalkylammonium group being representative for the so-called "strong PEL."

Besides the acid or base strength of the ionic site, the average distance between the adjacent anionic or cationic charges along the polymer chain is a decisive parameter determining PEL behavior, especially in the dissolved state. This charge carrier density or charge density is defined as the average distance between ionic sites, taking into account chain bond geometry, or as the average number of ionic sites per monomer unit in the case of copolymers, with the latter definition yielding comparable data only within the same class of copolymer with an ionic component. Besides this average charge density, the regularity of distribution of ionic sites along the chain can also influence PEL properties significantly, for example, with regard to solubility. As a rule, typical PEL behavior can be expected if more than 1 ionic site per 10 monomeric units is present in a copolymer.

2.4.2 Formation of polyelectrolyte multilayer thin films

Polyelectrolyte multilayer films created via Layer-by-Layer (LbL) deposition are currently used to modify the surface properties of materials. These polyelectrolyte based films are capable of self-organization. The self-organization process of polyelectrolyte films, also referred to as electrostatic self-assembly (ESA), has been well documented over the past ten years.

Starting in the early 1990s, Decher's group began work on the realistic method for the ESA of nanolayers over charged substrate. The process developed by Decher has increased in popularity since its introduction. This is a result of the method's simplicity and the fact that polyelectrolytes as well as charged nano objects can be deposited in a controlled manner. Biological compounds, conducting and light emitting polymers, and dyes have also been deposited onto suitable substrates via ESA.

The LbL process is based on the alternating adsorption of charged cationic and anionic species. The process begins by properly charging a substrate. The charged substrate is then primed by adsorbing a layer of a polyelectrolyte with an opposite charge sign to that imparted to the substrate. Once the substrate is primed, it is then dipped into a solution of a counterion polyelectrolyte. A rinse step is included between the two adsorption processes to remove excess as well as to prevent cross-contamination of the polyelectrolyte solutions. These simple steps complete the LbL deposition of the nanolayers. Multiple layers can be created by simply dipping the substrate in alternating anionic and cationic baths [28].

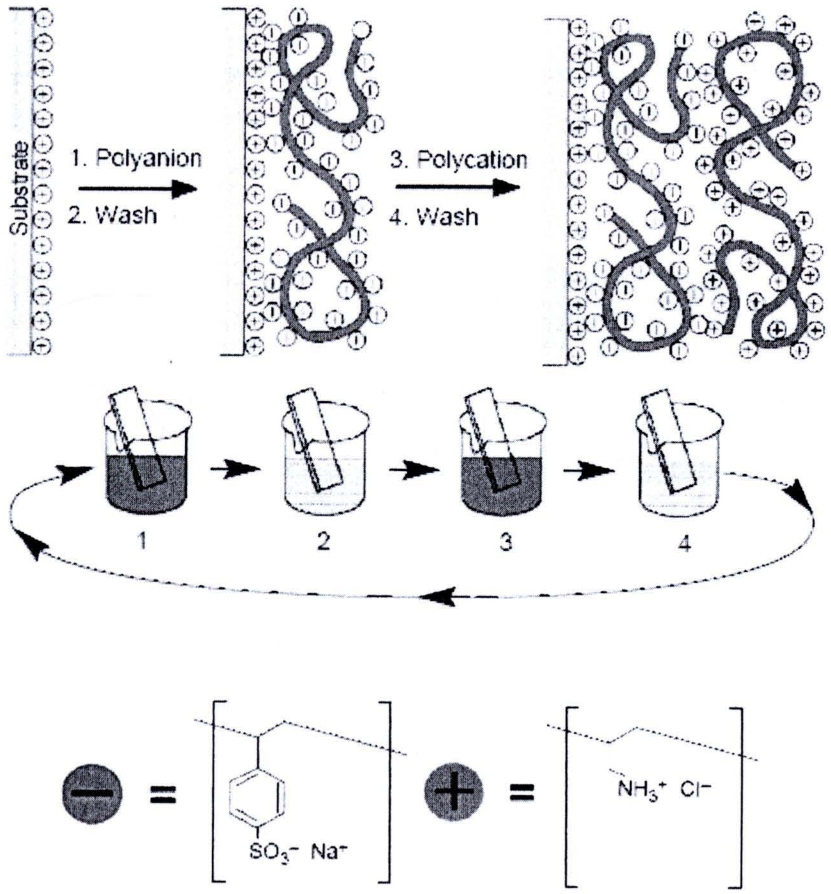


Figure 2.8 Schematic of the electrostatic self-assembly (ESA) [21].

From Figure 2.8 top: Simplified molecular concept of the first two adsorption steps depicting film deposition starting with a positively charged substrate. The polyion conformation and layer interpenetration are an idealization of the surface charge reversal with each adsorption step which is the basis of the electrostatically driven multilayer build up depicted here. Counterions are omitted for clarity. Figure 2.8 Bottom: Schematic of the film deposition process using glass slides and beakers. Steps 1 and 3 represent the adsorption of a polyanion and polycation respectively, and steps 2 and 4 are washing steps. The four steps are the basic buildup sequence for the simplest film architecture (A/B)n where n is the number of deposition cycles. The construction of more complex film architectures requires additional beakers and an extended deposition sequence.

Therefore, Layer-by-layer technique is the most versatile and facile approach based on electrostatic self-assembly between oppositely charged polyelectrolytes [29]. This technique can produce the multilayers thin film on any shape, any size and any substrate as shown in Figure 2.9.

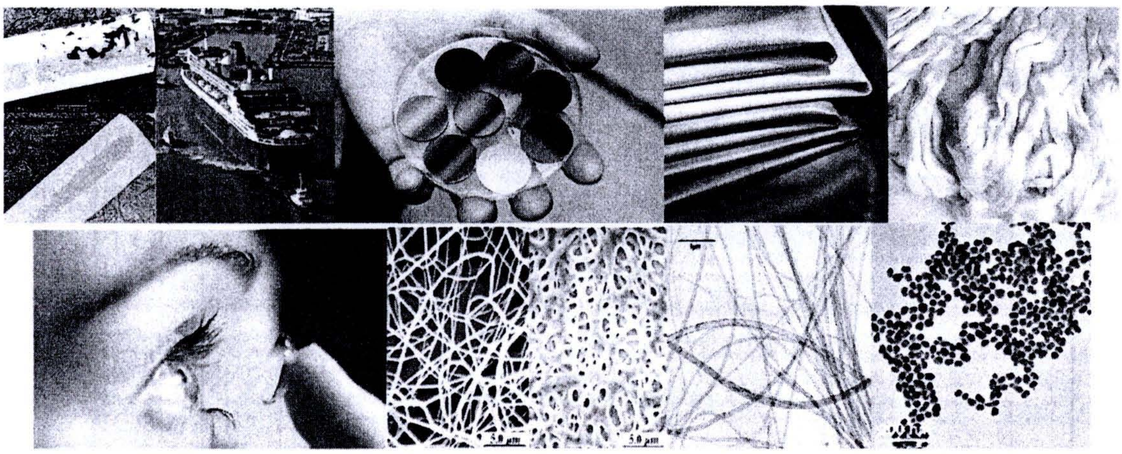


Figure 2.9 Variety of substrates for deposition polyelectrolyte multilayers via layer-by-layer technique.

2.4.3 Parameters controlling the growth of PEM [30]

The parameters controlling the growth of PEM were studied because there are important for the multilayer formation.

2.4.3.1 Type of polyelectrolyte

The type of polyelectrolyte affects the total thickness. For instance, the multilayer thickness increases in the order: poly (acrylamide sulfonate)/poly (diallyldimethylammonium chloride) (PAMS/PDADMAC) < poly (styrene sulfonate) /poly (allylamine hydrochloride) (PSS/PAH) < PSS/PDADMAC. All these polyelectrolytes are flexible. The intrinsic persistence length for PSS, PAMS and PAH is similar (approx. 1 nm) while the intrinsic persistence length of PDADMAC is slightly higher. Therefore the chain stiffness cannot be the only reason for the differences in multilayer thickness. It is assumed that the balance between hydrophobicity and hydrophilicity of the polyelectrolytes plays an important role for the thickness. While PSS has a hydrophobic backbone and is not water soluble below a degree of charge of 0.33 even the neutral PAMS is water soluble.

The type of multilayer growth depends also on the type of polyelectrolytes. The thickness of PSS/PAH multilayers increases linearly with the number of deposition cycles, while the thickness of PSS/PDADMAC multilayers increases linearly or exponentially depending on the charge density of PDADMAC. The exponential growth is related to a higher surface roughness and internal roughness than in the case of linear growth [31].

2.4.3.2 Effect of polymer charge density

A minimum charge density is required for the formation of multilayers. Below this charge threshold the charge reversal is not sufficient. In the case of strong polyelectrolytes the charge density is varied by changing the chemical structure. For instance, a PSS/PDADMAC multilayer can be built up at polycation charges ≥ 70%. Above this threshold the charge density does not affect the polymer density (electron density between 0.374 and 0.393 A° -3) [32].

Not only the average charge density, but also the distribution of the charges along the chains plays an important role for building up multilayers. The adsorption of block-copolymers showed that a short strongly charged block (10–20% of the total number of monomer units per chain) is sufficient for the formation of multilayers, even if the average charge density is below the charge threshold that is required for multilayer formation [33].

2.4.3.3 Influence of ionic strength

The total multilayer thickness can be controlled with angstrum precision by adding salt to the aqueous polyion solutions. Due to the screening of the charges along the polyelectrolyte chains the polymer molecules are more entangled with increasing salt concentration. The results are in a larger thickness and a stronger internal and external roughness of the adsorbed layers. The increase in thickness d is proportional to IB (I: ionic strength). Most of the studies in the literature report an exponent B of the salt dependence between 0.5 and 1 for different polyelectrolytes. *Lo¨sche et al.*, showed by neutron reflectivity that the thickness of a layer pair (PSS/PAH) varies linearly with the ionic strength of the dipping solutions in the concentration range 0.5–3 mol/l NaCl additive [34]. At low ionic strength, i.e.below 0.5 mol/l NaCl, a deviation from this linear behavior towards an I 0.5 dependence is stated. The latter behavior is also reported by other groups against air or water. Above a salt concentration of 1 mol/l the thickness increase is less pronounced, but nevertheless, d increases up to a concentration of 3 mol/l.

PSS/PDADMAC multilayers increases proportional to I or I 0.5 depending on the PDADMAC charge density.

Beside the segment–segment repulsion also the attraction between the polyelectrolyte and the oppositely charged interface is screened. Therefore, one would expect a decrease of adsorbed amount at high ionic strength. For some systems, as, e.g. PAMS/PDADMAC or PSS/PDADMAC, this decrease has been observed, but the thickness of PSS/PAH multilayers increases even above an ionic strength of 1 mol/l. There seems to be a paradox: On one hand a minimum polymer charge density is required to form multilayers, on the other hand multilayers can be built up at high ionic strength where the electrostatic interactions are screened. These results indicate that macroscopic mean field theories like the *Gouy Chapman* theory do not describe the multilayer formation at high ionic strength. Two other explanations for the adsorption of polyelectrolytes are possible: Firstly, beside enthalpy contributions also the gain in entropy plays an important role due to the release of counterions during multilayer formation. Furthermore, charge (or ion) fluctuations near the surface should be taken into account. They make the surface 'visible' for the oppositely charged polyelectrolyte despite of (mean field) screening.

2.5 Layer-by-layer surface modification of carbon nanotubes

An interesting issue for noncovalent surface modification of carbon nanotubes was layer- by-layer deposition technique. The coating CNTs with polyelectrolyte from this technique provided a wide variety of ionic functional groups on CNT surface lead to obtain high dispersion efficiency and their stability in aqueous solution. In 2004, *Bumsu Kim et al.* [35] were successfully functinalized carbon nanotubes with gold nanoparticle composites. Treated carbon nanotubes were deposited with cationic polyelectrolyte; poly(diallyldimethylammonium chloride) alternate with anionic polyelectrolyte; polystyrene sulfonate for bilayers. *Alexander B. Artyukhin et al.* [36] has been reported noncovalent surface modification of carbon nanotubes by deposit the primer layer as pyrene ionic derivative. PDADMAC and PSS were used to alternately deposit on the modified carbon nanotubes. *Hao Kongfor et al.* [37] were proposed preparation, characterization and layer-by-layer self-assembly of polyelectrolyte-functionalized multiwall carbon nanotubes. The results confirmed that multiwall carbon nanotubes have a high efficiency loading polyelectrolytes by the layer-by-layer approach as shown in Figure 2.10 and Figure 2.11.

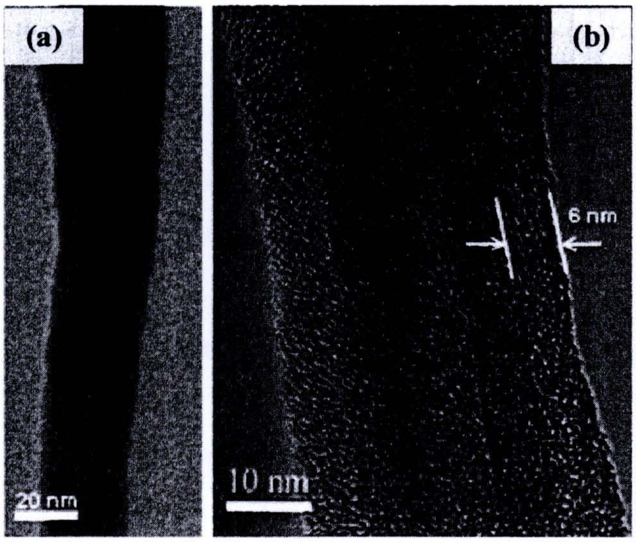


Figure 2.10 TEM image of coating multiwall carbon nanotubes with polyelectrolyte [37].

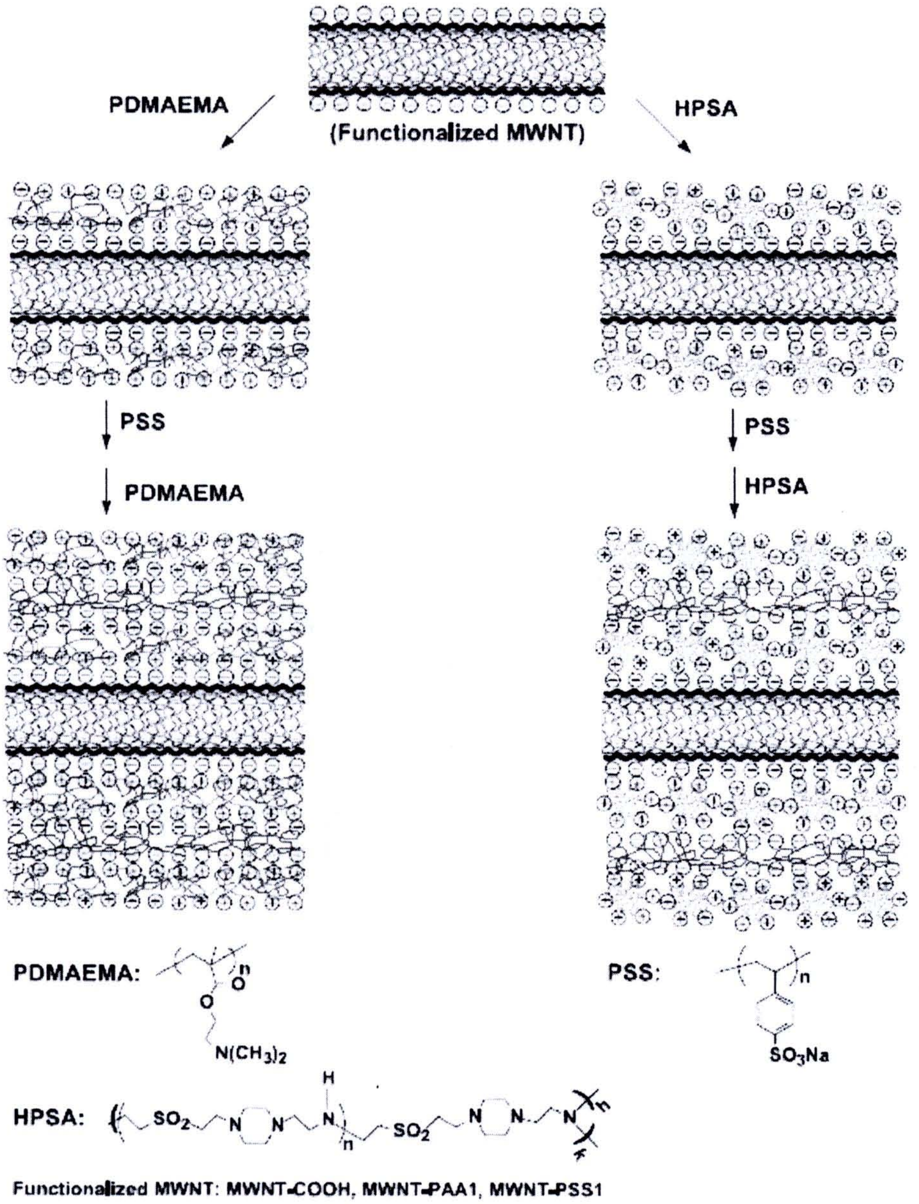


Figure 2.11 Representative the deposition of PDMAEMA, PSS, and HPSA [37].

To apply coating carbon nanotubes with polyelectrolyte multilayers on their surface, there are many application. *Lijun Liu et al.* [38] found that water-soluble multiwall carbon nanotubes coating poly(allylamine hydrochloride) were successfully coated as bionanomultilayers with a model enzyme; horseradish peroxidase (HRP) by layer-by-layer technique as shown in Figure 2.12 The bionanomultilayers were constructed as highly sensitive phenolic biosensor which having the detection limit of 0.6 μM. Therefore, the developed bionanomultilayer biosensor exhibited a fast, sensitive, and stable detection.

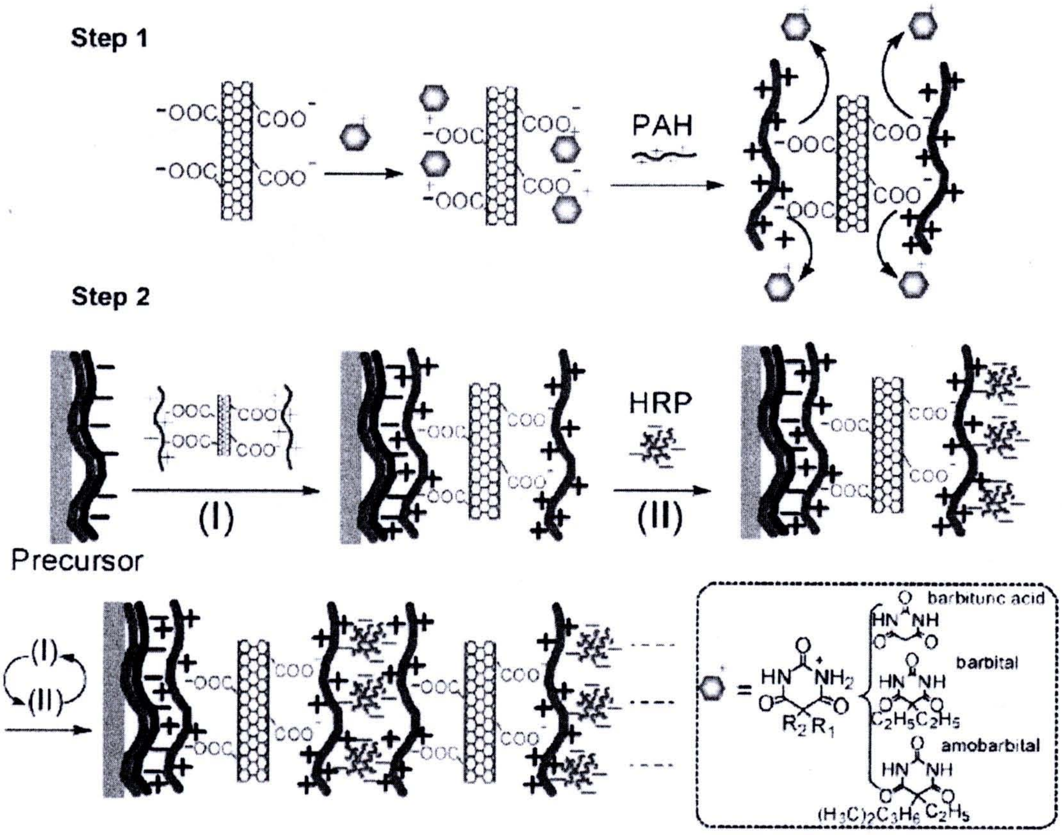


Figure 2.12 The process of solubilizing PAH-MWCNTs and assembly bionanomultilayers on PAH-MWCNTs [38].

Sai Bi et al. [39] found that treated multiwall carbon nanotubes were coated with many ingredients; poly(diallyldimethyl ammonium chloride) (PDDA), horseradish peroxidase, alpha phetoprotein, and alpha phetoprotein primary and secondary antibody via layer-by-layer technique as shown in Figure 2.13. The results showed the detection limit which was two orders of magnitude lower than standard ELISA method. Therefore, this hybrid material can be used as a biolabel for ultrasensitive chemiluminescence immunoassay of cancer biomarker.

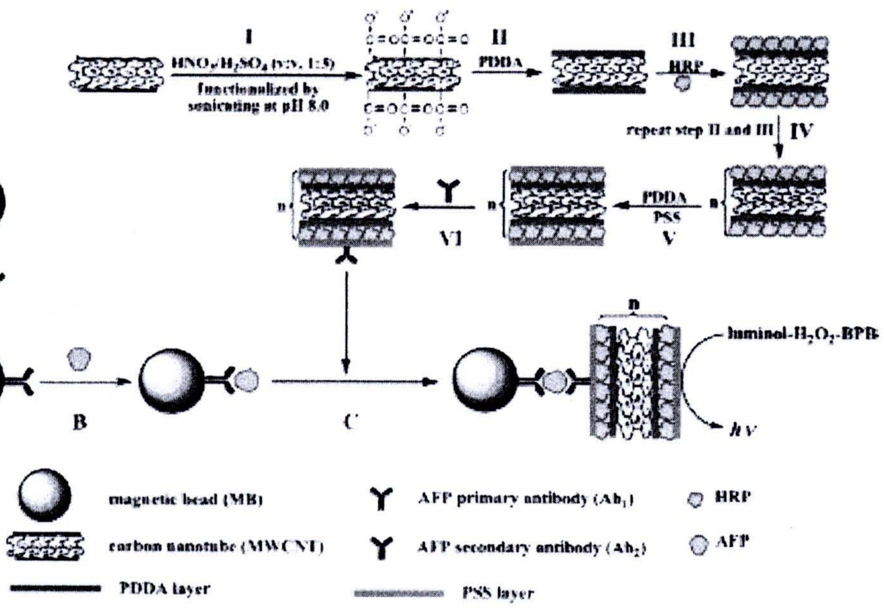


Figure 2.13 The schematic illustration of the detection for AFP based on sandwich-type CLIA. The upper part I–V is the schematics of layer-by-layer electrostatic self-assembly of HRP on carbon nanotube template: (I) treatment of MWCNTs generating negatively charged carboxylic functionalized groups; (II) assembling of positively charged PDDA; (III) assembling of negatively charged HRP; (IV) repetition of II and III until the desired layers are obtained; (V) additional assembling of positively charged PDDA layer and negatively charged PSS layer; (VI) adsorption of AFP secondary antibody (Ab2) [39].

Recently, *Xiaoke Zhang et al.* [40] have been reported that treated singlewall carbon nanotubes were deposited with polysaccharides which were polycation chitosan and polyanion alginate via layer-by-layer technique. The coating carbon nanotubes were successfully controlled release anticancer drug; doxorubicin to cancer cells as shown Figure 2.14.

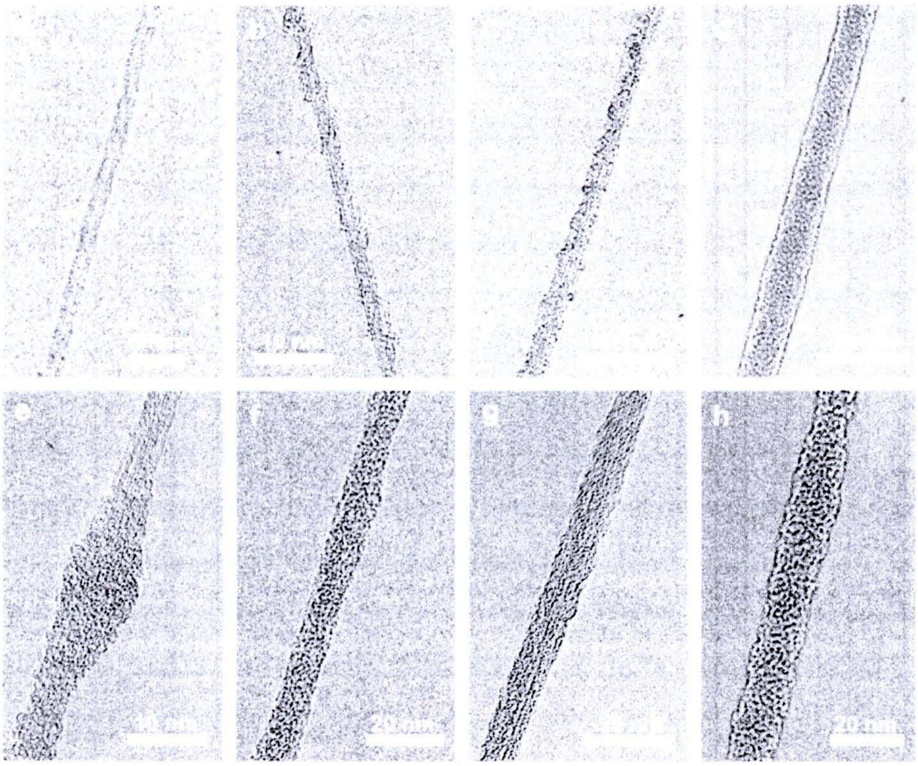


Figure 2.14 TEM images of modified SWCNTs. (a) Cut SWCNTs, (b) Alginate-SWCNTs, (c) Chitosan-SWCNTs, (d) Chitosan/Alginate- SWCNTs, (e) Doxorubicin-SWCNTs, (f) Doxorubicin-Alginate-SWCNTs, (g) Doxorubicin-Chitosan-SWCNTs and (h) Doxorubicin-Chitosan/Alginate-SWCNTs [40].

2.6 Wrapping carbon nanotubes with polymer by noncovalent surface modificatuion: Molecular Dynamics Simulation

Molecular dynamics (MD) simulation is a specific tool used to demonstrate and understand the dynamics and thermodynamics in many fields of science (e.g. biological and material systems). They can afford molecular information that is complicated or unfeasible to achieve from experimental techniques alone. The wrapping phenomenon of modified CNTs with polymer has been proposed as a general phenomenon in both of previous theoretical and experimental publications [41, 42]. Not only synthetic polymer but natural polymer has also been proposed wrapping phenomenon on CNT surface by the molecular dynamics simulation study.

Molecular dynamics (MD) simulations are performed on the complex amylose-nanotube system to study the mode of interaction between the initially separated amylose and SWNT fragments, which can be either wrapping or encapsulation. *Y.H. Xie et al.* [43] found that the van der Waals force is dominant and it always plays an important role in promoting non-covalent association. The influence of the size of nanotube on MD simulation is also studied. Our study illustrates that amylose molecules can be used to bind with nanotubes and, thus, favor non-covalent functionalization of carbon nanotubes.

Recently, *Yingzhe Liu et al.* [44] have been reported that carbon nanotubes coated with alginic acid through noncovalent functionalization have been shown to be soluble and dispersed in water. Alginic acid can wrap around SWCNT by virtue of van der Waals attractions and organize into a compact helical structure, a process induced in the gas phase by hydrogen-bonding interactions. In contrast, in an alginate aqueous solution, a loose helical wrapping mode is found to be favored by virtue of electrostatic repulsions in conjunction with the weakening of hydrogen-bonding interactions. This work shed meaningful light on the potential of noncovalent functionalization for solubilizing carbon nanotubes, and open exciting perspectives for the design of new wrapping agents that are envisioned to form the basis of innovative nanomaterials targeted at chemical and biomedical applications.

2.7 Carbon nanotubes in drug delivery application

The one of familiar application of modified carbon nanotubes which was put attempt to deep study was biomedical application especially drug delivery application.

The application of modified CNTs as new nanocarriers for drug delivery was apparent immediately after the first demonstration of the capacity of this material to penetrate into the cell. An important characteristic of modified CNTs is their high propensity to cross cell membranes. Two routes of internalization have been proposed. It has been found that modified CNTs penetrate following a passive diffusion across lipid bilayer similar to a “nanoneedle” able to perforate the cell membrane without causing cell death [45]. Alternatively, when CNTs were used to deliver proteins by adsorbing them onto their external surface, they seem to be uptaken by endocytosis [46, 47].

Alberto Bianco et al. were successful in preparing CNTs containing both fluorescein and amphotericin B (AmB) [48]. Their studies revealed that AmB covalently linked to CNTs is taken up by mammalian cells without presenting any specific toxic effect. Modified CNTs with AmB, one of the most effective antibiotic molecules for the treatment of chronic fungal infection, are rapidly internalized by mammalian cells with a reduced toxicity in comparison to the drug administered alone. In addition, *Hongjie Dai et al.* [49] showed that the property of CNTs to adsorb near infrared irradiation was used to kill cancer cells. Pristine SWNT were wrapped with poly(ethylene glycol)(PEG) modified with a phospholipid (PL) moiety and folic acid (FA). Because tumor cell are known to overexpress folate receptors, the PL-PEG-FA/SWNTs construct was only internalized inside cancer cells, which were then destroyed by using a laser wavelength of 808 nm.

Recently, supramolecular chemistry on water-soluble carbon nanotubes for drug loading and delivery was proposed by *Hongjie Dai et al.*[50]. Water-soluble SWNTs with poly(ethylene glycol) (PEG) functionalization via these routes allow for surprisingly high degrees of π-stacking of aromatic molecules, including a cancer drug (doxorubicin). Binding of molecules to nanotubes and their release can be controlled by varying the pH. The strength of π -stacking of aromatic molecules is dependent on nanotube diameter, leading to a method for controlling the release rate of molecules from SWNTs by using nanotube materials with suitable diameter. Soluble Single-Walled Carbon Nanotubes as Longboat Delivery Systems for Platinum(IV) Anticancer Drug Design were demonstrated by *Stephen J. Lippard et al.* [51]. SWNTs tethered to substrates by disulfide linkages use the reducing environment of endosomes into which they are taken to selectively release their cargo only following cellular internalization. By combining the ability of platinum(IV) complexes that resist ligand substitution with the proven capacity of SWNTs to act as a longboat, shuttling smaller molecules across cell membranes, they have constructed a SWNT tethered platinum(IV) conjugate that effectively delivers a lethal dose of cis-[$Pt(NH_3)_2Cl_2$] upon reduction inside the cell. *Balaji Panchapakesan et al.* [52] hypothesized that monoclonal antibodies that are specific to the IGF1 receptor and HER2 cell surface antigens could be bound to single wall carbon nanotubes (SWCNT) in order to concentrate SWCNT on breast cancer cells for specific near-infrared phototherapy. SWCNT modified with HER2 and IGF1R specific antibodies showed selective attachment to breast cancer cells compared to SWCNT functionalized with non-specific antibodies. After the complexes were attached to specific cancer cells, SWCNT were excited by ~808 nm infrared photons at ~800 mW cm^{-2} for 3 min. Cells incubated with SWCNT/non-specific antibody hybrids were still alive after photo-thermal treatment due to the lack of SWNT binding to the cell membrane. All cancerous cells treated with IGF1R and HER2 specific antibody/SWCNT hybrids and receiving infrared photons showed cell death after the laser excitation. Following multi-component targeting of IGF1R and HER2 surface receptors, integrated photo-thermal therapy in breast cancer cells led to the complete destruction of cancer cells.

2.8 Carbon nanotubes cytotoxicity: *In Vitro*

Toxicity of carbon nanotubes has been an important issue that attracted the researcher in laboratory and even in public to realize and consider advantages and disadvantages in the same time before integrating carbon nanotubes in any applications. Nowadays, carbon nanotubes's toxicity still be argued and discussed in academic research by world wide researcher because of their different results. Especially, the attempt to integrate carbon nanotubes in biomedical application such as drug carrier, toxicity and biocompatibility of carbon nanotubes was an important that should be considered as well. However, the beginning conclusion was that the toxicity of carbon nanotubes depends on factors which were size, shape, surface area, surface chemistry, solubility and impurity as a transition metal catalyst. *Kostas Kostarelos* [53] has been reported as news and views that experimental evidence to date clearly indicates that long and rigid carbon nanotubes should be avoided for in vivo applications and that chemical functionalization should be optimized to ensure adequate dispersibility, individualization, and excretion rates sufficient to prevent tissue accumulation as shown in Figure 4.15.

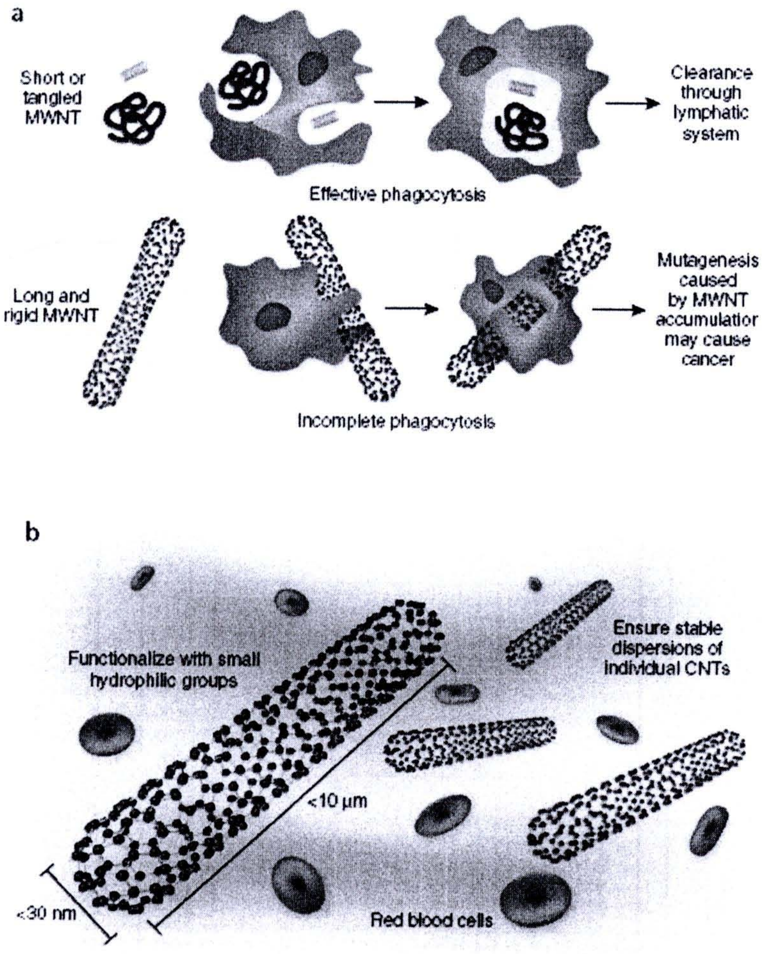


Figure 2.15 (a) The effect of CNT structure on phagocytosis by macrophages and clearing from tissues. Whereas macrophages can engulf MWNTs with a low aspect ratio (ratio of length to width) before their clearance by draining lymph vessels, MWNTs with a high aspect ratio cannot be cleared and accumulate in tissues, where they promote carcinogenesis. (b) In addition to their dimensions, other considerations relevant to the safety of CNTs include increasing their solubility and preventing their aggregation, to facilitate urinary excretion and thereby prevent tissue accumulation [53].

Guang Jia et al. [54] found that the cytotoxicity of carbon nanomaterials with different geometric structures exhibited quite different cytotoxicity and bioactivity in alveolar macrophage. The cytotoxicity in vitro follows a sequence order on a mass basis: SWCNT > MWCNT > Quartz > C_{60}.

Christie M. Sayes et al. [55] reported that cytotoxicity of singlewall carbon nanotubes; *In Vitro* depend on the functionalization density of carbon nanotubes surface. The modified CNT surface consist of SWNT-phenyl-SO_3X (ratio of CNT/ phenyl-SO_3X equal 18, 41, and 80), SWNT-phenyl-$(COOH)_2$ (ratio of CNT/ phenyl-$(COOH)_2$ equal 23) and underivatived SWNT stabilized in 1% Pluronic F108. The results showed that the degree of sidewall functionalization increases, SWCNT become less cytotoxic as shown in Figure 2.16

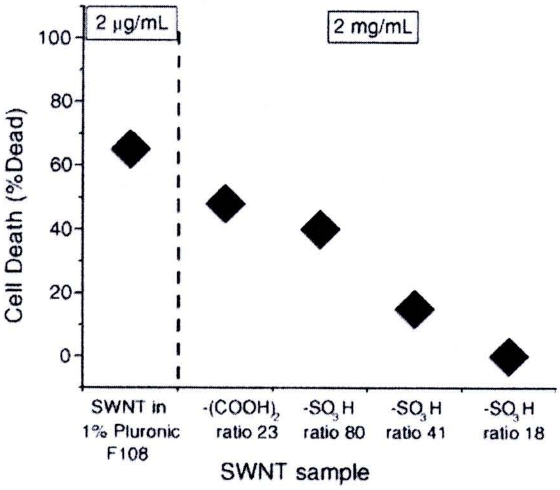


Figure 2.16 Effect of functional groups of SWCNT on cell viability [55].

While *Alexandra Porter et al.* [56] have found that acid treated CNT were less aggregated within the cell when compared with pristine CNT. After 4 days of exposure, bundles and individual acid-treated CNT was found inside the lysosomes and cytoplasm where the caused no significant changes in cell viability or structure. *Peter Wick et al.* [57] reported that the well-dispersed carbon nanotubes effect to their cytotoxicity. Suspended carbon nanotubes-bundles were less toxic than asbestos, ropes like agglomerated CNTs induced more cytotoxic effect than asbestos fiber at the same concentrations.

In addition, the cytotoxicity testing technique was a crucial problem as well because for cell viability test, indicator dyes such as MTT, WST-1, Neutral red, Alamar blue, and Commassie blue were needed to assess. *A. Casey et al.* [58] has been reported the indicator dyes are not appropriate for the quantitative toxicity assessment because carbon nanotubes can interact with colorimetric indicators resulted in a false positive toxic effect. *Larisa Belyanskaya et al.* [59] also reported the limit of the MTT reduction assay for carbon nanotubes-cell interaction. Improvement of carbon nanotubes suspension with polyoxyethylene sorbitan monooleate and sodium dodecyl sulfate still interfered with MTT assay as well. Therefore, the question how toxic is CNT remain unanswered and will remain uncertain until new screening techniques are developed which do not involve the use of colorimetric dye. To avoid using colorimetric dyes for cytotoxicity studies, *Eva Herzog et al.* [60] has been proposed the clonogenic assay which was the new approach for toxicity test. Employing the clonogenic assay, without any such interaction, this technique was more reliable method for in vitro cytotoxicity test which measure the colony surface area and colony number.