



CHAPTER II

LITERATURE REVIEW

2.1 Single-Walled Carbon Nanotubes

2.1.1 Structure and Properties of Single-Walled Carbon Nanotubes

Offering exceptional mechanical strength (Lahiri *et al.*, 2009) and optical properties (Tabakman *et al.*, 2010), as well as high electrical and thermal conductivities (Amama *et al.*, 2008), single-walled carbon nanotubes (SWNTs) have been attracting great interest for a wide scope of possible applications, such as probes, bio-sensors, catalyst supports, hydrogen storage, gas separation, composites and multifunctional materials, and so on (Bhushan, 2006).

SWNTs can be imagined as a rolled graphene sheet (one planar layer of graphite) with its ends seamlessly attached (Figure 2.1). They are represented by a pair of indices (n,m) which represents the orientation of the circumference. As a convention, if $n = m$, the tube is called armchair nanotube. If $m = 0$, the tube is called zigzag nanotube. For any other (n,m) , the tube is called chiral nanotube. The typical nomenclature of SWNT is shown in Figure 2.2.

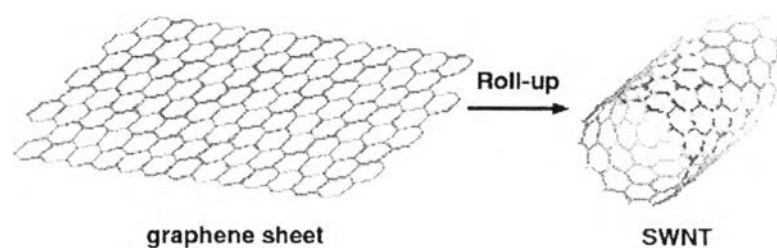


Figure 2.1 A single wall carbon nanotube by rolling-up a graphene sheet (Vaisman *et al.*, 2006).

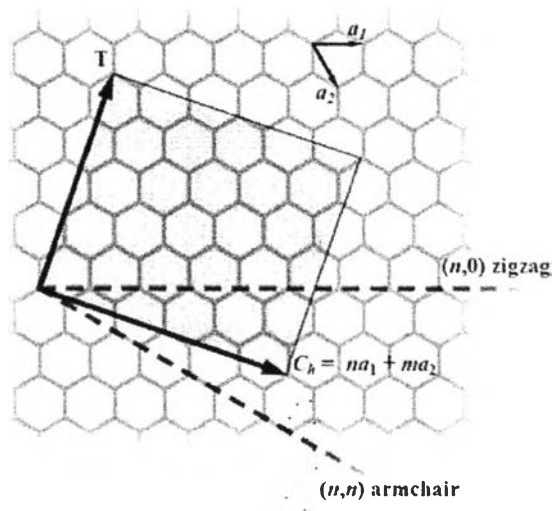


Figure 2.2 Nomenclature of SWNT (Prakash, 2005).

2.1.2 Aggregation and Poor Solubility of Single-Walled Carbon Nanotubes

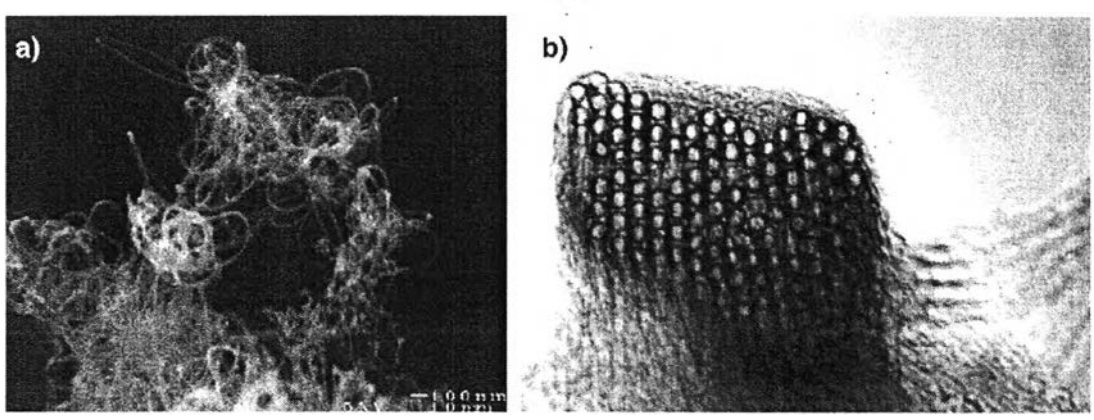


Figure 2.3 (a) SEM image of SWNT bundles and (b) TEM image of the cross section of a SWNT bundle (Thess *et al.*, 1996).

Because of high aspect ratios, combined with high flexibilities and strong van der Waals interactions of ~ 500 eV/ μm of tube-tube contact (Girifalco *et al.*, 2000), SWNTs tend to agglomerate into bundles or ropes (Figure 2.3) when dispersed in either water or organic solvents. Bundles typically contain thousands of

SWNTs, making them impossible to utilize the properties of individual nanotubes. For example, in areas such as nanotube-polymer composite, the presence of bundles reduces the effectiveness of SWNTs as mechanical reinforcement agents (Cadek *et al.*, 2004). Consequently, the separating and dispersing methods are required for SWNTs to achieve their full potential.

2.2 Dispersions of Single-Walled Carbon Nanotubes

There are two distinct approaches for dispersing SWNTs, including the mechanical method and methods that are designed to alter the surface energy of the solids, either physically (noncovalent functionalization) or chemically (covalent functionalization). Mechanical dispersion methods, such as ultrasonication and high shear mixing, separate nanotubes from each other, but can also fragment the nanotubes, decreasing their aspect ratios (Lu *et al.*, 1996).

Covalent functionalization, where the dispersing agent is covalently bound to the SWNT sidewalls, has been carried out by several research groups using various methods for attaching any number of functional groups to achieve suspensions in most any solvent. However, this technique can cause the SWNTs to lose their exceptional electronic properties because of the severe disruption of the π system (Zhao *et al.*, 2004). Noncovalent functionalization of SWNTs is particularly attractive, as it preserves the intrinsic properties of SWNTs (Grossiord *et al.*, 2007). In this approach, dispersing agents such as surfactants, polymers (O'Connell *et al.*, 2001; Vijayakumar *et al.*, 2010), or biomolecules (Minami *et al.*, 2006; Yan *et al.*, 2008; Zheng *et al.*, 2003) have been widely used in the preparation of either aqueous or organic solutions to obtain high weight fraction of individually dispersed nanotubes.

2.3 Aqueous Single-Walled Carbon Nanotube Dispersions Using Surfactants

2.3.1 Surfactants

“Surface active agents” are called surfactants. These are also called amphiphilic molecules possessing both hydrophilic and hydrophobic properties.

Amplilic molecules are used in a variety of applications such as fabrication of porous materials, structured materials, detergency, oil recovery, and many other technological applications, for their ability to aid in the formation of emulsions.

A surfactant is characterized by its tendency to adsorb at surfaces and interfaces, thus reducing the surface or interfacial tension. The interface can be between solid and liquid, between air and liquid, between air and solid, or between a liquid and a different immiscible liquid. The driving force for a surfactant to adsorb at an interface is to lower the free energy of that phase boundary. The interfacial free energy per unit area represents the amount of work required to expand the interface. The term interfacial tension is often used instead of interfacial free energy per unit area. When that boundary is covered by surfactant molecules, the surface tension is reduced.

All surfactant molecules consist of at least two parts, one which is soluble in a specific fluid (the lyophilic part) and one which is insoluble (the lyophobic part). When the fluid is water one usually talks about the hydrophilic and hydrophobic parts, respectively. The hydrophilic part is referred to as the head group and the hydrophobic part as the tail amount of work required expanding the interface. The structure of surfactant is shown in Figure 2.4.

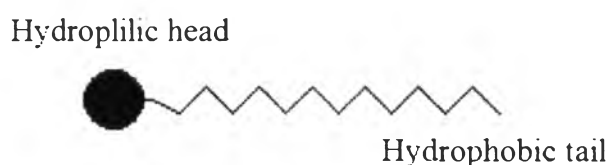


Figure 2.4 Schematic illustration of a surfactant.

According to the nature of the polar group, surfactants can be classified into four basic types as follows:

- Anionic: the hydrophile is a negatively charged group such as carboxyl ($\text{RCOO}^- \text{M}^+$), sulfonate ($\text{RSO}_3^- \text{M}^+$), sulfate ($\text{RSO}_4^- \text{M}^+$) or phosphate ($\text{ROPO}_3^- \text{M}^+$).

- Cationic: the hydrophile bears a positive charge, as for example, the quaternary ammonium halides ($R_4N^+X^-$), and the four R-groups may or may not be all the same, but will usually be of the same general family.

- Nonionic: the hydrophile has no charge, but derives its water solubility from highly polar groups such as polyoxyethylene (POE or $R-OCH_2CH_2O-$), alcohols, polyethers, esters, or their combinations.

- Zwitterionic: the molecule contains, or can potentially contain, both a negative charge and a positive charge, such as the sulfobetaines $RN^+(CH_3)_2CH_2CH_2SO_3^-$.

2.3.2 Surfactant Adsorption at the Solid-Liquid Interface

The adsorption of surfactants at the solid-liquid interface is strongly influenced by a number of factors (Rosen, 2004):

- The nature of structural groups on the solid surface: whether the surface contains highly charged sites or essentially nonpolar groupings, and the nature of the atoms which these sites or groupings are constituted.

- The molecular structure of the surfactant being adsorbed (the adsorbate): whether it is ionic or nonionic, and whether the hydrophobic group is long or short, straight-chain or branched, aliphatic or aromatic.

- The environment of the aqueous phase: its pH, its electrolyte content, the presence of any additives such as short-chain polar solutes (e.g., alcohol, urea), and its temperature.

Together these factors determine the mechanism by which adsorption occurs, and the efficiency and effectiveness of adsorption.

2.3.3 Surfactant Adsorption Isotherms

Adsorption is the process by which molecules attach to a surface. The molecule that adsorbs is the adsorbate and the surface is the adsorbent. There are two types of adsorption namely physisorption and chemisorption. Physisorption occurs when molecules physically interact with a surface through van der Waals forces, which are long-range, weak attractive forces. Chemisorption occurs when a molecule chemically bonds to a surface and usually through a covalent bond.

Generally, the non-covalent physisorption of surfactants is widely used to overcome the van der Waals interaction and to improve the dispersibility of the carbon nanotubes. In this case, the chemical structure of the carbon nanotubes remains unchanged and the dispersed carbon nanotubes are stabilized by the electrostatic repulsion or steric hindrance of the micelles formed around them.

A mechanism of nanotube isolation dispersing a nanotube bundle into individual tubes (Figure 2.5), with the combined assistance of ultrasonication and surfactant adsorption, was proposed. The role of ultrasonic treatment is likely to provide high local shear, particularly to the nanotube bundle end. Once spaces or gaps at the bundle ends are formed, they are propagated by surfactant adsorption, ultimately separating the individual nanotubes from the bundle (Vaisman *et al.*, 2007).

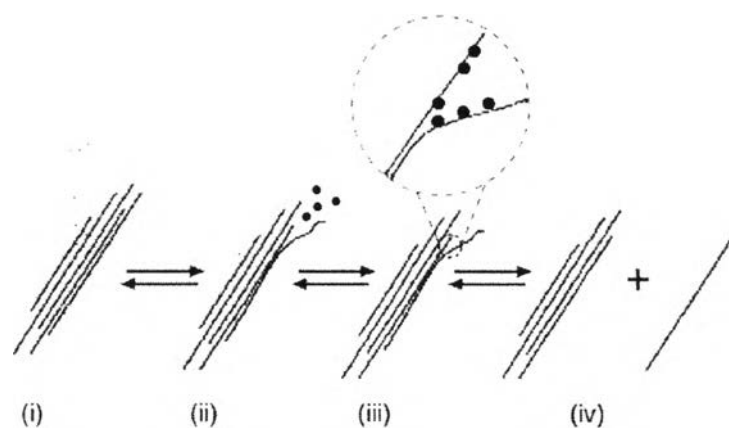


Figure 2.5 Mechanism of nanotube isolation from bundle (Vaisman *et al.*, 2007).

The adsorption of pure surfactants and surfactant mixtures onto inorganic and organic surfaces has been widely studied. The phenomenon usually depends on the chemical characteristics of the solid, the nature of surfactant molecules, and the nature of solvent. It has been extensively demonstrated that the main driving forces for adsorption of ionic surfactant molecules on charged surfaces are the Coulombic attractions between the surfactant heads and the charged surface groups from the solid, and the hydrophobic bonding between the surfactant tails.

Surfactant adsorption isotherms of SDBS onto SWNT surface were investigated by Matarredona *et al.* (2003). Measurements of the adsorption isotherm of SDBS on SWNTs were conducted at two different pH values, 4 and natural. At pH 4, it is enhanced the adsorption of SDBS due to the positive charge of the tube surface which can be achieved by lowering the pH below the point of zero charge (PZC). The actual isotherms are presented in Figure 2.6.

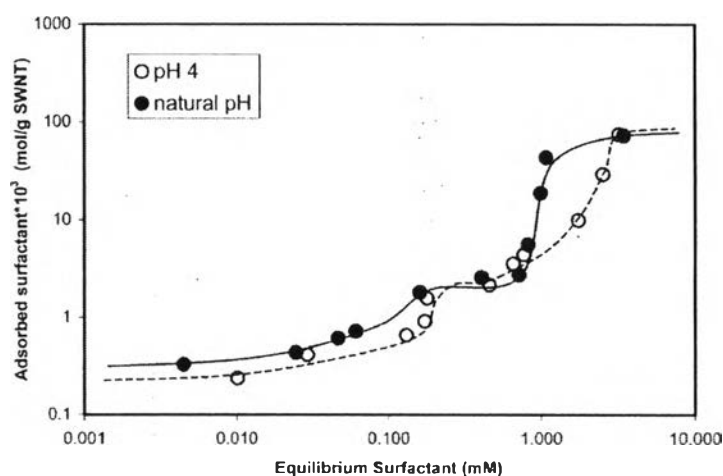


Figure 2.6 Adsorption isotherms of SDBS on HF-treated SWNT (PZC=5.5) at pH 4 and natural pH at 25 °C (Matarredona *et al.*, 2003).

The shapes of both isotherms seem to indicate a two step mechanism of adsorption and reach the saturation plateau at the same maximum adsorbed concentration. Both isotherms conducted below and above the PZC of the nanotubes show no significant differences, particularly at low concentrations, Coulombic forces between the negatively charged headgroups of surfactant and the charged surface of nanotubes do not govern the adsorption process. For concentration above 0.1 mM, until the surface becomes saturated with surfactant molecules, the hydrophobic forces between the surfactant tail and the nanotube walls play an important role.

In addition, Utsumi *et al.* (2007) have contributed a great deal of understanding in the mechanisms that control the dispersion of SWNTs in aqueous solution using surfactant. The adsorption isotherms of SDBS on SWNTs were measured using ultraviolet-visible spectroscopy (UV-Vis). The isotherms (Figure

2.7) reveal a two-step adsorption process where the first step was attributed to adsorption on bundles and the second step was attributed to the exfoliation of bundles via sonication and subsequent surfactant adsorption on individual tubes.

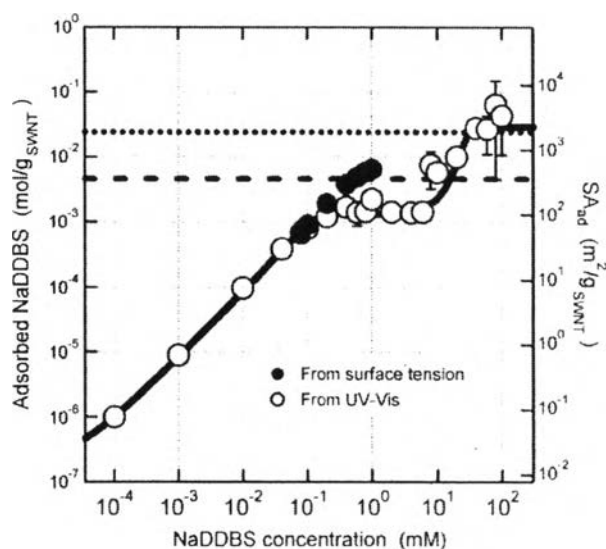


Figure 2.7 (Left axis) SDBS amount adsorbed on 1 g of SWNT determined by (●) surface tension and (○) UV-Vis measurements (Utsumi *et al.*, 2007).

2.3.4 Surfactant Self-Assembly Structures on Single-Walled Carbon Nanotubes

Molecular self-assembly, by definition, is the spontaneous organization of molecules under thermodynamic equilibrium conditions into structurally well-defined and rather stable arrangements through a number of noncovalent interactions. These molecules undergo self-association forming hierarchical structures. For the self-assembly of surfactant molecules onto nanotube surface, it is mainly through hydrophobic/hydrophilic interactions, in which the hydrophobic tail of the surfactant molecule adsorbs on the surface of SWNT bundles while the hydrophilic head associates with water for dissolution.

There are three common models for surfactant adsorption onto nanotube surface, as illustrated in Figure 2.8; carbon nanotube encapsulation within a

cylindrical micelle, hemimicellar adsorption of surfactant on to carbon nanotubes, and random adsorption of molecules onto the tube surface.

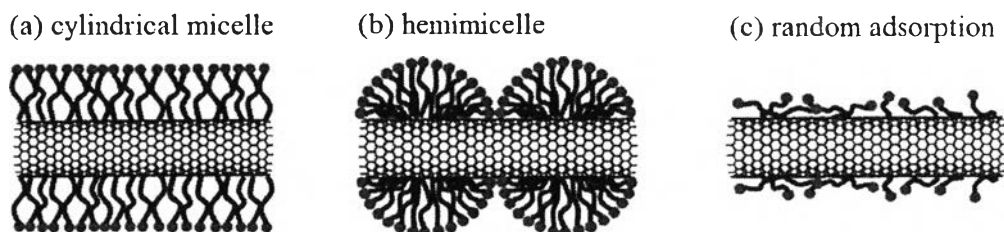


Figure 2.8 Illustrations of (a) the cylindrical micelle, (b) hemimicelle, and (c) random adsorption models (Wallace and Sansom, 2009).

Several researchers have tried to find model for surfactant-nanotube interaction. For instance, Yurekli *et al.* (2004), they demonstrated that surfactant molecules randomly adsorbed on nanotube surface without preferential head-tail orientation for the stabilization of the dispersion. Islam *et al.* (2003) investigated the suspensions of surfactant-stabilized SWNTs in water and they suggested that the tubes are stabilizes by hemimicelles illustrated in Figure 2.9. Matarredona *et al.* (2003) performed a detailed study on aqueous SDBS-SWNT dispersions and reported that each nanotube is covered by a monolayer of surfactant molecules in which the head form a compact outer surface while the tails remain in contact with the nanotube walls described as a cylindrical micelle.

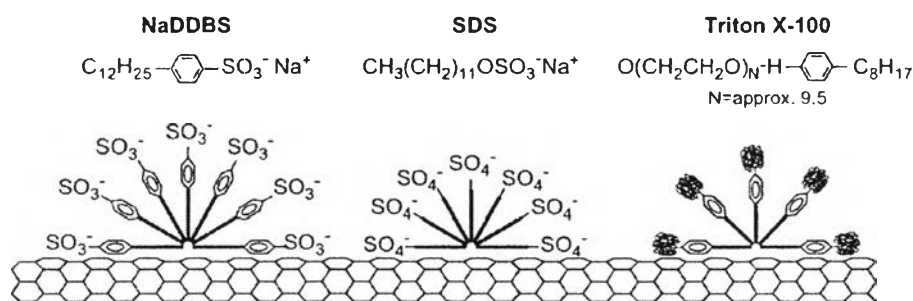


Figure 2.9 Schematic representation of how surfactants may adsorb onto the nanotube surface (Islam *et al.*, 2003).

2.3.5 Experimental Studies of Aqueous Single-Walled Carbon Nanotube Dispersions Using Surfactants

A large number of amphiphilic molecules, including sodium dodecyl sulfate (SDS) (Blanch *et al.*, 2010; Clark *et al.*, 2011; Haggenueller *et al.*, 2008; McDonald *et al.*, 2006; Tan and Resasco, 2005; Yurekli *et al.*, 2004), sodium dodecylbenzene sulfonate (SDBS) (Blanch *et al.*, 2010; Clark *et al.*, 2011; Haggenueller *et al.*, 2008; Islam *et al.*, 2003; Matarredona *et al.*, 2003; Okazaki *et al.*, 2005; Tan and Resasco, 2005; Utsumi *et al.*, 2007), hexadecyl-trimethyl ammonium bromide (CTAB), octyl phenol ethoxylate (Triton X-100) (Clark *et al.*, 2011; Tan and Resasco, 2005), sodium cholate (SC), and sodium deoxycholate (DOC) (Blanch *et al.*, 2010; Haggenueller *et al.*, 2008), have been shown to stabilize SWNT dispersions, with varying effectiveness.

The dispersion of SWNTs in aqueous SDS solution with the aid of ultracentrifugation was first reported by O'Connell *et al.* (2002). It has been shown that SDS can remove tube bundles and stabilize tube in water media. Salzman *et al.* (2007) used different dispersing agents namely SDBS, SDS, single stranded salmon DNA and ZrO₂ nanoparticles for quantifying SWNTs dispersions by Raman spectroscopy. The dispersions are evaluated quantitatively by comparison of the areas of carbon nanotubes G-band and they found that the concentration dependence of the normalized G-band areas. Haggenueller *et al.* (2008) employed optical absorption and fluorescence spectroscopy to evaluate the amount of individual SWNTs suspended by various surfactants and reported that bile salt DOC provides better suspension quality compared to other surfactants.

Markovic *et al.* (2009) studied on surfactant-stabilized SWNTs dispersion such as SDBS and melamine sulfonate superplasticiser (MSS) by using Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM). The result from Raman analysis was shown that the upshift of G-band of nanotubes/SDBS dispersion is greater than nanotubes/MSS dispersion. FTIR was shown the existing of sulfonate group in SWNTs dispersed by SDBS and MSS. AFM study indicated the debundling into small bundles carbon nanotubes after modified nanotube dispersion.

Among various surfactants, SDBS is commonly used to stabilize aqueous SWNT dispersions without showing strong diameter dependence (Okazaki *et al.*, 2005). It was reported that SDBS can disperse up to 20 mg/mL of individual SWNTs (Islam *et al.*, 2003). The benzene ring in the SDBS molecule is believed to provide superior dispersive ability due to π - π interactions with the SWNTs, despite being located near the hydrophilic end of the molecule (Clark *et al.*, 2011; Islam *et al.*, 2003; Tan and Resasco, 2005). Matarredona *et al.* (2003) analyzing their experimental data suggested that hydrophobic interactions dictate for the most part the agglomeration of SDBS on SWNTs.

Moreover, Utsumi *et al.* (2007) demonstrated the ability to suspend individual SWNTs by using SDBS. They studied means of surface tension measurement, ultraviolet-visible spectroscopy (UV-Vis), scanning electron microscopy (SEM), and transmission electron spectroscopy (TEM). It has been observed that the external surface of SWNT bundle is fully covered with adsorbed. This dispersion state was confirmed by SEM and TEM observations (Figure 2.10).

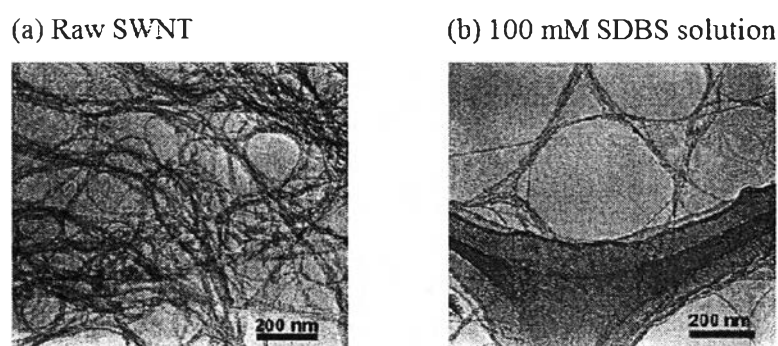


Figure 2.10 TEM images of raw SWNT and 100 mM SDBS solution in high magnification (Utsumi *et al.*, 2007).

2.4 Molecular Dynamics Studies of Aqueous Single-Walled Carbon Nanotube Dispersions Using Surfactants

2.4.1 Introduction to Computer Simulations

Due to experimental limitations at the nanoscale to elicit connections between chemical structure and properties, experimental studies cannot provide the detailed structural information and interactions between SWNTs and surfactant molecules in aqueous solutions. Generally, experimental studies can only hypothesize and suggest about these phenomena. Understanding of surfactant-aided SWNT dispersion with detailed atomic-level information regarding interactions and packing is crucial to secure progress, for example the design of any SWNT reinforced polymer nanocomposite materials, electronic devices, and biological applications.

Computer simulations have been a powerful technique to study the properties of assemblies of molecules in terms of their structure and microscopic interactions between them which provide a valuable complement to experiment. One of simulation techniques commonly used to study the formation of surfactant aggregates on the SWNT surface is molecular dynamics in which atoms are treated as particles moving under the influence of classical mechanics. Molecular dynamics has the great advantage that dynamical behavior and transport properties are readily calculated. In addition, the molecular motions occur naturally under the influence of the intermolecular forces and any external fields, making it possible to directly observe diffusive, convective, and other modes of motion at the molecular level.

2.4.2 Single-Walled Carbon Nanotubes Self-Assembly with Surfactants: Molecular Dynamics Simulations

One example of simulations is the study of SDS surfactant aggregates on SWNTs carried out by Tummala and Striolo (2009). They used extensive all-atom molecular dynamics method to investigate the self-assembly of SDS on (6,6), (12,12), and (20,20) SWNTs at room conditions. The simulation results suggest that the morphology of the surfactant aggregates strongly depends on the nanotube diameter, as well as on the surface coverage.

At the small nanotube diameter, SDS molecules are difficult to wrap the nanotubes due to higher bending of SDS molecules, encountering an energetic barrier. As the nanotube diameter increases, it is easy for the adsorbed SDS to wrap around the tubes because of smaller bending and more surfactant tail-carbon atom contacts. In addition, a variation of structures has been observed when the number of molecules in the simulation box was increased. At low coverage, SDS molecules form “ring” with the SDS molecules lying flat on the tube surfaces and parallel to the tube axis. High coverage favors the formation of adsorbed micelles with disordered internal structure, as shown in Figure 2.11.

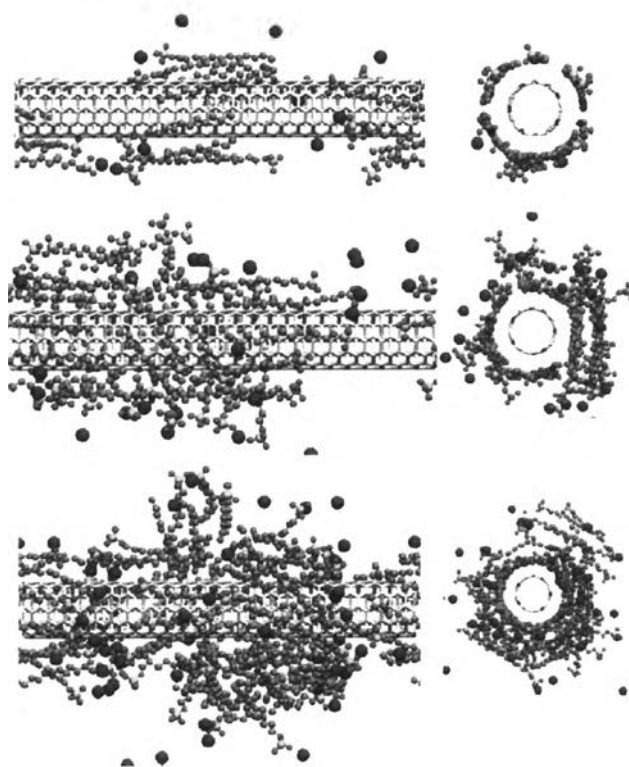


Figure 2.11 Side (left panels) and front views (right panels) of representative simulation snapshots obtained for SDS surfactants adsorbed on (6,6) SWNTs at increasing surface density. From top to bottom, the surface per surfactant headgroup is 0.98, 0.44, and 0.25 nm² respectively (Tummala and Striolo, 2009).

Besides the simulation snapshots, they also investigated the density distribution of surfactant head groups, surfactant tail segments, and counterions

around the SWNTs (Figure 2.12). The surfactant tails segments accumulate near the hydrophobic SWNT surfaces. At low surface density, there is the formation of one layer of surfactant tails segments. For the head groups, they are contact with the hydrophobic SWNT surfaces at low surface density. As the surfactant density increases, there is the formation of a second shell of surfactant tails segments around the tubes and the surfactant heads extend toward the aqueous medium. Some head groups are still nearby the tube surfaces. Moreover, they obtained that SWNTs are not charged in which the counterions are attracted by the surfactant heads.

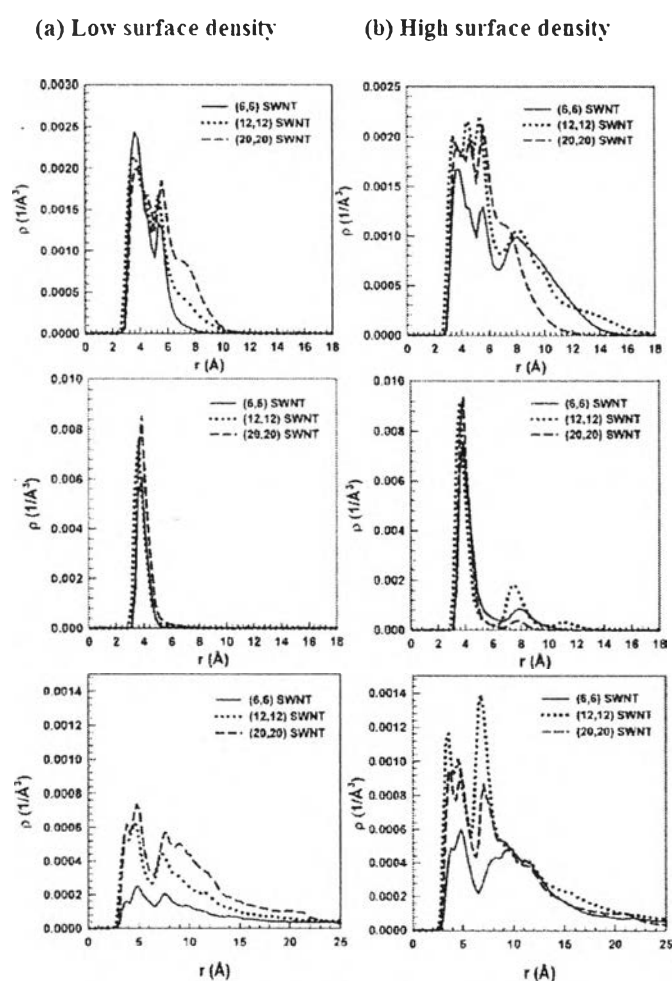


Figure 2.12 Density profiles of surfactant (a) low surface density and (b) high surface density: head groups (top panels), surfactant tail segments (center panels), and counterions (bottom panels) around the SWNTs (Tummala *et al.*, 2009).

Along with Xu *et al.* (2010), they attempted to clarify how the aggregate SDS structures on SWNTs determine effective SWNT-SWNT interactions using the LAMMPS code under constant temperature, pressure, various surface coverages, and nanotubes curvatures. The (6,6), (18,18), and (24, 24) SWNTs were considered with diameter. At high surface coverage, the equilibrium snapshots suggest that SDS can form a cylindrical-like monolayer on small-diameter SWNTs and the stable hemimicellar structure on larger-diameter SWNTs. As surfactant coverage decreases, it is shown that the tail and head groups of surfactant molecules almost located at the same position.

Tummala *et al.* (2010) used MD simulations to describe the self-assembly of flavin mononucleotide (FMN) adsorbed on SWNTs. They found that the aggregation morphology of aqueous FMN on SWNTs depends on nanotube diameter. Aqueous dispersions of SWNTs stabilized using the bile salt surfactant SC were investigated via MD simulations by Lin and Blankschtein (2010). The results showed that the cholate ions wrap around the tubes with a small tendency to orient perpendicularly to the tube axis (Figure 2.13).

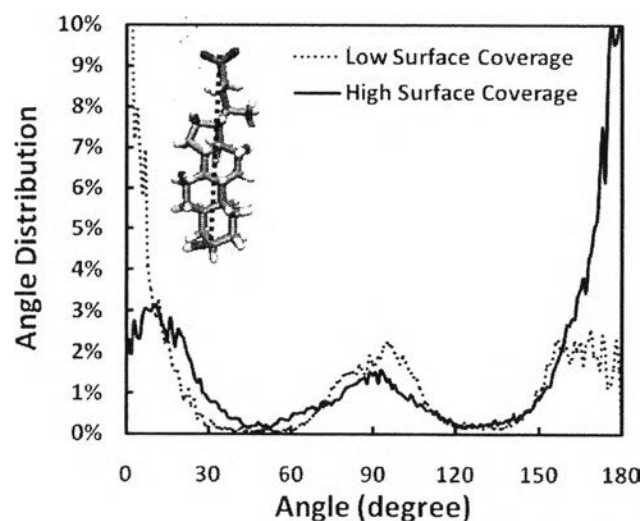


Figure 2.13 Simulated distribution profiles of the angle, θ , between the principal axis of the cholate ions and the cylindrical axis of the SWNT (Lin and Blankschtein, 2010).

Despite their technological importance, alkylbenzene sulfonates have rarely been studied by MD simulations. Jang *et al.* (2004) simulated sodium hexadecane benzenesulfonate at the water-decane interface. They found that surfactant 4-C16 has a more compact packing, in terms of the interfacial area and molecular alignment at the interface, than other simulated surfactants. Furthermore, surfactant 4-C16 leads to the most stable interface by having the lowest interface formation energy. As well as He *et al.* (2010), they simulated monolayers of a series of linear and branched alkylbenzene sulfonates at the water-air interface and observed that the length of alkyl chain and the position of attachment of the benzene ring on the alkyl chain affect the aggregate morphology and the surface tension of alkylbenzene sulfonates at water/air interface. These results are important because they point at the effect of surfactant morphology on practical quantities, specifically the surface tension.