CHAPTER II
LITERATURE REVIEW

2.1 Carbon allotropes

Carbon allotropes are the different structural forms of carbon, initiated by different bonding formations. There are 3 main allotropes of carbon which have been applied widely in the nanotechnology, which are buckminsterfullerene, graphene, and carbon nanotube.

Buckminsterfullerene, or fullerene, is the hollow and spherical carbon molecules, discovered by Sumio Iijima (Iijima 1980) Each carbon atom is bonded to three other carbon atoms and, consequentially, is sp^2 hybridized. Hexagonal rings are the dominant structures, whereas pentagonal rings are required for the sphere to complete its closed spherical structure.

Graphene is a one-atom-thick planar sheet of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. Graphene can actually be wrapped to form graphite, carbon nanotube, or fullerene.

Carbon nanotube is the cylindrical tube of sp^2-bonded carbon atoms, with hollow interior, whose length to diameter can be upto 132,000,000:1 (Wang et al., 2009).

2.2 Applications of carbon allotropes

2.2.1 Applications of Fullerene

Fullerene, in the mesophase, has been used as a n-type semiconductor, used in the p-type polymer. Together they are formed into the active layer called bulk heterojunction (Reyes-Reyes et al., 2005) that is used in photovoltaic application. Fullerene can reduce the excessive weight of the layer and enhance the efficiency of the layer by 2.4% - 5.2%

It is a component of functional organic field-effect transistor, or OFET, which has lower production cost and promising wide range of applications, including information storage, ligth emission and detection, medical analysis, and etc. (Guo et al., 2010)

Wang and coworkers (Wang et al., 1999) have evaluated the potential of fullerene as anti-oxidant, which can be utilized in the biomedical field to neutralize the free radicals, the source of molecular mutation and cancer

2.2.2 Applications of Carbon nanotubes

Zhang and coworkers (Zhang et al., 2007) had synthesized the Carbon nanotube fibre, which had 5.3 times higher strength and 4.3 times higher stiffness than the strongest and the toughest engineering fibres at that time. The properties seemed to come from the individual high strength and stiffness of Carbon nanotubes themselves. Munoz and coworkers (Munoz et al., 2004) also produced the Carbon nanotube fibre with the coagulation-based Carbon nanotube spinning method. The produced fibre was claimed to has the strength of 1.8 gigapascals, which is extremely high.

Gong and coworkers (Gong et al., 2000) had produced the surfactant assisted Carbon nanotube/ Poly-oxyethylene-8-lauryl composite, which results in the composite with higher glass transition temperature and elastic modulus than the conventional composite.

Yang and coworker (Yang and Gupta 2005) synthesized the carbon nanotube – poly-styrene foam, which was useful in the electromagnetic interference shielding and conducting electricity, as the composite shows the enhancement in weight, corrosion resistance, flexibility and cost.

Yu and coworkers (Yu et al., 2006) have verified the usage of transducer consisting of a piezoelectric poly-vinylidene fluoride (PVDF) thin film coated with compliant carbon nanotube - based transparent conductors. The transducer can work as both acoustic actuator and sensor.

Carbon nanotube is capable of being functionalized with specific biological molecules and acts as a near-infrared agent that can infiltrate the tumor cells and destroy them. Kam and coworkers (Kam et al., 2005) have functionalized the carbon nanotube with the phospholipids groups to make it accessible for the cell, via endosytosis. The entered carbon nanotube will absorb the exterior radiation and specifically kills the tumor cell.

Carbon nanotube can also be used as the storage for fuel hydrogen. Dillon and coworkers (Dillon et al., 1997) suggested that the CNT can uptake the hydrogen, with the capillary effect, and the gas can condense itself inside the tube's cavity, further enhancing the storage capacity of the tubes.

Carbon nanotube, with the high stiffness, low density, very small cross-section and defectlessness, is appropriate to be modified to Nano-Electro-Mechanical Systems (NEMS) oscillator. Sazonova and coworkers (Sazonova et al., 2004) has reported the actuation and detection of the translational oscillation of the doubly clamped carbon nanotube oscillator. The resonance frequency was tunable and the oscillator can transduce the tremendously small forces.

Like Teflon, the aligned carbon nanotubes can exhibit the superb non-wettability, and thus can be used as the slick surface. Feng and coworkers (Feng et al., 2002) have found that the water-contact angle of the aligned carbon nanotube film can be upto 158.5°, which was comparatively high.

Infrared photo-response is the consequential property of carbon nanotube's electrical conductivity. Pradhan and coworkers (Pradhan et al., 2008) enhanced the electrical conductivity of the electrically and thermally insulating poly-carbonate by adding trace amount of single-walled carbon nanotube (SWNT), resulting in significant increase in both the electrical conductivity and infrared illumination.

2.2.3 Application of Graphene

Graphene is known to have very good electron mobility that reaches 10 000 $cm^2 V^{-1} s^{-1}$ at room temperature, and one-atom thickness that leads to large surface area and large interface. Liu and coworkers (Liu et al., 2008) used the organic solution-processable functionalized graphene as an electron acceptor, and used poly-3-octylthiophene (P3OT) and poly-3-hexylthiophene) (P3HT) as electron donor. The power conversion efficiency increases from 5% - 6%, by 1.4%

Graphene's conductive and hydrophobic properties are helpful in preventing corrosion by repelling water and inhibiting electro-chemical reactions. Chen and coworkers (Chen et al., 2011) demonstrated the ability of the graphene film to protect the metal from the oxidation with the oxidant. The extent of protection can go up to 200 °C and 4 hours in the presence of air, as characterized by SEM, Raman spectroscopy, and XPS

Xia and coworkers (Xia et al., 2009) detected the potential profile within a p-type graphene transistor via a photocurrent imaging technique. In the n-type conduction regime, the graphene close to the contacts stayed p-type, forming p-n-p channel, which was the experimental evidence of the conduction behavior in the p- and n-branches of graphene transistors.

2.3 Graphene

2.3.1 Graphene as potential alternative nanomaterial

With the advantage of lower production cost over other well-known carbon allotropes (Xu et al., 2008), which are fullerene and carbon nanotube, graphene has caught the interest in the industrial-scale market. Another advantage is its high surface area, derived from its high aspect ratio (Jia et al., 2005), that allows more surfactant to adhere on the surface, without concerning on the effect of diameter-related curvature that is normally concerned with other allotropes (Gotovac et al., 2007), since the curvature can disturb the formation of sp^3 hybridization between the foreign molecules and carbon atoms on the surface (Zhang et al., 2010). Apart from that, graphene has morphological advantage, since its planar structure maximizes the π- π binding with the surrounding (Bao et al., 2010).

2.3.2 Different forms of graphene used

General forms of graphene used in any industries are in the form of, either, pure graphene, obtained directly from graphite and its different forms, or, graphene oxide (GO), or, partially reduced GO (RGO). The reason behind the existence of GO is the requirement for industrial scale production and the non-productive method of pure-graphene production (Novoselov et al., 2004; Geim and Novoselov 2007). At present, the method to produce GO, in mass production, is the chemical reaction that alters graphite to GO (Schniepp et al., 2006; Stankovich et al., 2006; Verdejo et al., 2008; Wang et al., 2008). However the GO loses significant original electrical conductivity that belongs to non-oxidized form. It can be reduced to graphene via reduction (Novoselov et al., 2004; Berger et al., 2006; Li et al., 2008; Li et al., 2008; Ponomarenko et al., 2008; Xu et al., 2008) to partially restore intensive properties. This incompletely restored graphene is sometimes referred to as chemically converted graphene (CCG) or RGO. Apart from the oxidation, reaction with potassium can also create the alternative graphene-functionalization reactant (Chakraborty et al., 2008), since it acts like an in-situ reducing agent. There have been different methods and attempts to initiate the decent dispersion of graphene and its derivative in the applications where dissolving is required, since the solution-phase production of both graphene and its derivative has been obligatory.

2.4 Conventional methods of graphene dispersion stabilization

The methods, used to functionalize the graphene and its derivative, assemble the ones used with carbon nanotube. Alexander A. Green and Mark C. Hersam (Green and Hersam 2010) produced graphene with controlled thickness using density gradient ultracentrifugation technique (DGU), and functionalised it with sodium cholate, which was similarly used in DGU stabilisation for carbon nanotube (Green and Hersam 2007). Davide and coworkers (Pantarotto et al., 2004) used single-stranded plasmid DNA to functionalize the carbon nanotube, and made it water soluble due to the sticking-out hydrophilic phosphate group. This idea was re-applied with RGO, and its dispersion was stabilized for a very long period of time (Patil et al., 2009). The satisfying results showed that the techniques might be interchangeable between these two carbon allotropes. However, the interchangeability of the surfactants used between graphene and CNT may not work always. Stankovich and coworkers (Stankovich et al., 2006) claimed that addition of sodium dodecylsulfate (SDS) and TRITON X-100 failed to stabilize the dispersion of RGO in water, thus the idea of interchangeability may not be absolutely verified yet. The anomaly maybe derived from increment of C/O atomic ratio; less O available, leading to consequential increase of intermolecular Van der Waal's force of attraction (Similar to coking effect).

There are generally 2 cases of the solution-related problems of graphene's dispersion. One involves organic solvents, and another involves polar solvents. The condition varies according to the applications.

2.4.1 In organic solvent

The main principle of dispersing the graphene and its derivatives in the organic solvent is to attach the sterically-hindered and hydrophobic molecules to their surfaces.

Stankovic and coworkers (Stankovich et al., 2006) had a vision on GO's utility as nanofiller, and tried to make it soluble in the more organic substance for higher usage flexibility. The GO was treated with organic isocyanate, reducing the hydrophilicity of hydroxyl group initially in place, with derivatization of both the edge carbooxyl and surface hydroxyl functional groups via formation of amides (Blagbrough et al., 1986) or carbamate esters (Stankovich et al., 2006). The modified GO resulted in decent exfoliation in the polar aprotic solvents, which were dimethylformamide (DMF), n-methylpyrrolidone (NMP), dimethyl sulfoxide (DMSO), and hexamethylphosphoramide (HMPA), but it did not disperse in the less polar solvents, which were tetrahydrofuran (THF), acetone, methylene chloride, and toluene and the polar protic solvents, which were methanol and ethanol. Xu and coworkers (Xu et al., 2009) functionalised RGO, prepared by conventional Hummer method, with the amine-terminated 5-4 (aminophenyl)-10, 15, 20-triphenyl porphyrin (TPP). The final result was the production of organic-solvent-soluble graphene.

Niyogi and coworkers (Niyogi et al., 2006) utilized the same technique applied to disperse single-walled carbon nanotube, to disperse graphite. The graphite was oxidized by acid reaction, with a mixture of hydrochloric acid (HCl) and nitric acid (HNO_3), before being functionalized with octadecylamine (ODA) to form octadecyl-amido graphite, which was soluble in THF, tetrachloromethane (CCl_4) and 1, 2-dichloroethane (CH_2Cl_2).

Subrahmanyam and coworkers (Subrahmanyam et al., 2009) also did the dispersion test on the similar solvents, the general procedure, involving the acid treatment and reaction with $SOCl_2$ of graphene, was followed, then the acidified and reactive graphene was functionalized with the aliphatic amine to form amide-derivatised graphene, which was soluble in CCl_4, CH_2Cl_2, and THF. Compton and coworkers (Compton et al., 2010) also used hexalamine, a type of aliphatic amine, to increase hydrophocity of graphene.

Whilst the other researchers reported the functionalisation – derived dispersion, Hamilton and coworkers (Hamilton et al., 2009) had reported on the possibility of homogenous dispersions of unfunctionalized and nonoxidized graphene nanosheets in ortho-dichlorobenzene (ODCB), which was realized by sonication and centrifugation. However, there were attempts to dissolve the unmodified graphene in other organic solvents; benzene, toluene, xylenes, chlorobenzene,and pyridine, but they were unsuccessful. This posts the critical dependence of dispersion on the type of solvent. In the similar case, but with functionalization, Subrahmanyam and coworkers (Subrahmanyam et al., 2009) had modified the acid-treated graphene with hexadecyltrimethoxysilane (HDTMS) and dibutyldimethoxytin (DBDT), with the same molar ratio of 1:1, and then dissolved the products in CCl_4. The result shown on figure 1 indicates that HDTMS promoted better dispersion than DBDT. The difference in structure of these chemicals seems to be the factor that led to such incidence.

There has been a case where the theory of steric hindrance was proven applicable. Liang and coworkers (Liang et al., 2009) have done the experiment to evaluate the effect of sterically-hindered functional group towards the ionic interaction of water, as polar solvent, by observing the transfer activity of three different types of functionalized GO, which were treated with three quarternary ammonium salts; tetradecyltrimethylammonium bromide (TTAB), didodecyldimethylammonium bromide (DDAB), and tetradodecylammonium bromide (TAB) with 1, 2, and 4 alkyl chains. The results were the dispersion in water of TTAB and DDAB-fuctionalised GO, but not TAB-functionalised one, due to the steric hinderance effect of four akyl chains that TAB possessed. The resulting graphene was further utilized as the very electrically conductive flexible film. Larger-aromatic ring planar stabilizers were suggested as the further development of this research. The fruit of this result realized the production of the smooth monolayer graphene sheet that possessed high conductivity and was easy to produce economically and environmentally-friendly.

Polymers are also one of the interesting surfactants, and they are applied according to hydrophobia and hydrophilia. Polystyrene, the hydrophobic and sterically-hindered polymer, was used by Ding and coworkers (Ding et al., 2003) to adhere on the GO by in-situ radical-driven polymerization of styrene. The coagulation occurred steadily in the water-surrounded environment, showing diminished water-affinity of GO.

2.4.2 In polar solvent

The attempts to dissolve the graphene in the polar solvent were the idea prior to that of organic-solvent dispersion. The main principle of this dispersion is to attach the hydrophilic (or amphiphilic) molecules to the graphene's and its derivatives' surfaces, in order to create ionic interaction of the polar solvent, resulting in of attraction and dispersion, or to attach the sterically hindered molecules on the surface to keep the molecules apart from each other, by like-pushes-like repulsion force. GO naturally possesses hydroxyl, carboxyl, epoxide, and carbonyl groups (He et al., 1996; Lerf et al., 1998). Therefore, it is naturally hydrophilic. However, as mentioned before, this form deteriorates the significant properties, thus several pre-treatments are required to partially regain such properties, and to prepare the carbonaceous substance for surface emulsification as well.

Xu and coworkers (Xu et al., 2008) researched on the ionic functionalisation of graphene, by reducing the conventional GO, obtained via Hummers method (Hummers and Offeman 1958). The GO was mixed with sodium hydroxide (NaOH) and pyrenebutyric acid and then mixed with hydrazine monohydrate for reduction. After cleansing, the 1-pyrenebutyrate-functinonalised graphene was obtained and dispersed in water. The stable dispersion was observed. Similarly, Lomeda and coworkers (Lomeda et al., 2008) reduced the GO with hydrazine, before functionalizing it with aryl diazonium salts and dispersing it in DMF, NMP and N,N'-dimethylacetamide (DMAc). The satisfying dispersion was achieved, demonstrating the applicability of aryl diazonium salts as stabilizer. Similarly, Hao and coworkers (Hao et al., 2008) functionalized the RGO with

7,7,8,8-tetracyanoquinodimethane (TCNQ), followed by centrifugation in water. Si and Samulski (Si and Samulski 2008) implanted sulfonic-acid functional group, using p-phenyl-SO_3H precursor, upon RGO. The water-attracting acid group helped to distribute the RGO sheets, in both cases. Park and coworkers (Park et al., 2010) equipped the RGO with polyoxyethylene sorbitan laurate (TWEEN), which is normally used to prevent unspecific binding of biological substatnce, Due to its high selectivity, it created very stable water-dispersion for the RGO

The surfactant used may have larger structure in order to ensure the steric hindrance of the enhanced graphene. Bonaccorso and coworkers (Bonaccorso et al., 2010) had used sodium deoxycholate, a sodium salt of deoxycholic acid, as the dispersant. The outstanding of this application is the control over the thickness of the graphene exfoliated, when in collaboration with DGU technique. Ghosh and coworkers (Ghosh et al., 2010) performed non-covalent functionalization of grapehene using fluorescent coronene carboxylate, the aromatic molecule. The products were water-soluble, and the procedure has shown the comparison, between the different graphene samples, which were thermal exfoliation of graphite oxide (EG) and the arc evaporation of graphite in a hydrogen atmosphere (HG). The observation under UV/Visible illumination indicated that the stabilizer was not completely immobilized on the surface of EG, unlike HG that shows no sign of luminescence. The difference was evaluated to be due to difference in number of layers, where EG had more number of layers than HG. Higher number of layers depreciates the bonding between the carboxylate molecules and carbon molecules, due to higher stability.

The idea of using the metal hydroxide precursor was quite promising. Hao and coworkers (Hao et al., 2008) replaced NaOH and pyrenebutic acid with potassium hydroxide (KOH), and reduced the GO with the same reductant. The stable dispersion of the RGO was also observed eventually. Fan and cowrokers (Fan et al., 2008) had confirmed that, by chance, the mere addition of NaOH or KOH alone can initiate the dispersion for GO suspension. The cause of dispersion was characterized to be deoxygenation of GO. This method also has a potential to be an environmentally-acceptable alternative water-based graphene solution.

Subrahmanyam and coworkers (Subrahmanyam et al., 2009) utilized poly-oxythylene(40)nonylphenylether (IGP), an organosilane, SDS and cetyltrimethylammonium-bromide (CTAB), an organotin, to functionalise GO. The resulting product was water-soluble. From this experiment, the fact about the proportionality of the surfactant's concentration on dispersibility was observed, and IGP was the best since it required the least concentration to initiate the stable dispersion (at 1 mM). Apart from the role of concentration, temperature also played the role in dispersion. Chen and coworkers (Chen et al., 2001) had functionalized CNT with 1-pyrenebutanoic acid succinimidyl ester (PYBS) and the result was satisfactory, thus Subrahmanyam and coworkers (Subrahmanyam et al., 2009) employed the same method with graphene and dissolve it in DMF. However, the duration of dispersion stability varied upon the temperature at which the mixing took place. At 200 °C, the dispersion had lasted for many days, whilst at room temperature; the dispersion had lasted only for few hours. Zhang and coworkers (Zhang et al., 2009) used the same method to produce the ethanol-disperse graphene that was filled in polyvinylidene fluoride (PVDF) to form nanocomposite polymer.

Han and coworkers (Han et al., 2010) also used the organic molecules to disperse the graphene. They grafted diphenylalanine in 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) on the RGO solution, forming the dispersant . However, there was the investigation on the pH that ensured the dispersion. It was found that at pH below 3.7, aggregation occurs, since the negativity was neutralized by the overwhelming positive charges in acidic environment, so the point was to maintain the charge of the functional group, in order to stabilize the intermolecular repulsive force. This shows the significance of pH on dispersion stabilization. Another organic molecule used was HFBI protein. Laaksonen and coworkers (Laaksonen et al., 2010) fixed this molecule upon graphene, via a uniquely developed method of exfoliation that creates the graphene directly without oxidation, and functionalize it simultaneously. That helps to upgrade the safety and operation. Such liquid-phase exfoliation also promotes capability of up-scaling and independence of growth promoter (Bonaccorso et al., 2010).

The, so-called, ionic liquid (IL), which possesses the amphilicity and environmental safety, was used to produce the polar solvent-dispersible graphene, produced via electrolysis, with the mixture of IL and water as electrolyte. This preparation method was claimed to be environmental-friendly, since it involves less application of hazardous chemicals. Liu and coworkers (Liu et al., 2008) utilized 1-octyl-3-methyl-imidazolium hexafluorophosphate ($[C_8mim]^+[PF6]^-$), 1 octyl-3-methyl-imidazolium tetrafluoroborate ($[C_8mim]^+[BF4]^-$), 1-octyl-3-methyl-imidazolium chlorine ($[C_8mim]^+Cl^-$), and 1-butyl-3-methyl imidazolium hexafluorophosphate ($[C_4mim]^+[PF6]^+$) as the IL. The results showed that all of these liquids can initiate the dispersion in DMF.

A polymer like poly-ethylene glycol (PEG), was also used as the functional group of the graphene to make it water-soluble, since it is hydrophilic polymer (Liu et al., 2008), acidified graphene was treated with excessive PEG and concentrated hydrochloric acid under solvothermal conditions. The -OH group of PEG readily attracted H^+ ion in the water and started dispersion. With further modification on PEG, Chakraborty and coworkers (Chakraborty et al., 2007) functionalized the acidified potassium graphite (C_8K) with amine PEG. The result showed that the modification will not deteriorate the dispersion, as long as the additional molecule is also hydrophilic. Stankovich and coworkers (Stankovich et al., 2006) coated the RGO with poly-(sodium 4-styrenesulfonate), which possesses both sterically hindered structure and amphiphilicity. Such morphology allowed the RGO to remain unattached to water molecules and disperse in the water.

Mentioning about the role of mechanical treatment towards the dispersibility, similar to the previously stated experiment carried out by Hamilton and coworkers, J. I. Paredes and coworkers (Paredes et al., 2008) relied plainly on the mechanical treatment, which was sonication. Mechanical treatment can overcome the intermolecular force of attraction in the agglomerate to certain extent. The opposition towards the application of stabilizing agent arose from the deterioration of application when they are present (Li et al., 2008). With the technique, the GO was able to dissolve and disperse in N, N-dimethylformamide, N-methyl-2-pyrrolidone, THF, and ethylene glycol stably, while it was not dispersible in dichloromethane, n-hexane, methanol and o-xylene. In the middle of those extreme cases, acetone, ethanol, 1-propanol, DMSO, and pyridine spurred the middle term dispersion. Eventually, it was also proposed that the sonication time is directly proportional to the dispersion stability and ethylene glycol and THF had comparatively less solubility towards GO compared with water and the rest of the stable solvents, induced from higher amount of precipitation formed after a while. There is even an extreme case where neither mechanical treatment nor chemical functionalization is needed. Behbtu and coworkers (Behabtu et al., 2010) claimed that the liquid-phase graphite dispersion, of three differently-manufactured types of graphite; graphoil, microcrystalline graphite and highly ordered pyrolytic graphite, was accomplished by simple mixing with super acid. In this case, the acid was chlorosulphonic acid. The mixing, without sonication and other mechanical treatments, resulted in much more concentrated and stable solutions, than the one produced with mechanical treatment and chemical functionalization.

2.5 Surfactant

As previewed previously, surfactant plays an important role in chemical functionalisation and dispersion stabilization. The principal characteristic of surfactant is amphiphilicity, having one hydrophilic end and hydrophobic end in the same molecule. There are lots of surfactants that catch the interest of researchers, but some are toxic and some are not industrially productive. There are few, which are qualified, to be promising in large-scale application that is sodium dodecyl sulfate.

2.5.1 Sodium Dodecyl Sulfate (SDS)

It is any compounds that possess the formula $NaC_{12}H_{25}SO_4$. This salt is wildly used as a surfactant. Its major use is as laundry detergent (Smulders et al., 1997), with the production capacity up to billions of kilograms. It is produced from the neutralization of hydrogen lauryl sulfate with either sodium hydroxide or sodium carbonate. Hydrogen lauryl sulfate is produced by the reaction between lauryl alcohol with sulfur trioxide gas, chlorosulfuric acid, or oleum.

The feedstock of SDS production can be obtained from natural vegetable oils, such as palm oil, or coconut oil, making it biodegradable product. SDS is neither carcinogen nor mutagen, but it causes mild dermal irritaion after very long and constant exposure.

2.6 Molecular simulation

2.6.1 Study of SDS Aggregates

Even with the availability of many sophisticated techniques and numerous methods of dispersion stabilization, the actual atomic-level behaviors of the surfactants and nano-meterials are still vague. Therefore computer simulation was invented and has been used to visualize the microscopic phenomenon. It has been utilized to characterize the nature of dispersion and obtain the data concerning surfactant-nanomaterial interactions and surfactant morphology. Several applications have been made on the study of carbonaceous nanoparticles and surfactants.

Tummala and Striolo (Tummala and Striolo 2009) used molecular dynamics (MD) simulation to observe that the morphology of SDS surfactant aggregates on single-walled carbon nanotube (SWNT), and its dependence on the tube's diameter and the surface coverage (The amount of surface occupied by an individual surfactant molecule). Along with Xu and coworkers (Xu et al., 2010), they attempted to clarify how the SDS aggregate on SWNTs contributes to effective SWNT-SWNT interactions. These studies showed that the structure of the nano-materials affects the aggregation, as mentioned before that curvature of the surface affects the adhesion of surfactant on (Gotovac et al., 2007). Tummala and coworkers (Tummala et al., 2010) used GROMACS simulation package to display the self-assembly of flavin mononucleotide (FMN) adsorbed on SWNTs. They found that the aggregation morphology of aqueous FMN on SWNTs depended on nanotube diameter, in other words, the surface area of the tube. However, in the case of graphene sheet or graphite, where curvature is absent, different outcomes are possible.

Konatham and coworkers (Konatham et al., 2011) utilised MD simulation of the dispersion of graphene sheets in n-octane, using LAMMPS simulation package. The work was concluded with the advice to utilize chemical functionalization on the sheets to avoid agglomeration. Konatham and coworkers (Konatham et al., 2012) also used simulation package GROMACS to simulate the effect of architecture of surface functional group on dispersion stability.

Samamakolpi and coworkers (Sammalkorpi et al., 2008) examined the SDS and C_{12} aggregate's structure and dynamic on the infinitely large multi-layered graphite at various surface coverages. The simulation result suggested that the presence of the anionic hydrophilic heads in SDS affects its orientation on the graphite's surface.

With the scale of the substrate reduced to several nanometers. The effect of lateral confinement of the graphene nano-sheets on surface aggregate can be observed. Tummala and coworkers (Tummala et al., 2010) have carried out the MD simulation of SDS aggregation on graphene nanosheets (GS) and graphene nano-ribbons (GN) of different sizes, at the same surface coverage.The study showed the dependence of the aggregate morphology on the dimension of the carbonaceous nano-sheets.

However, due to large amount of details in the simulation configuration, it is impractical to run the MD simulation with large simulating dimension, for long time. Thus, the idea of simplifying the details of molecular simulation configuration was proposed by Groot and Warren (Groot and Warren 1997). Their idea includes grouping, or coarse-graining, the components in the simulation into isotropic soft beads, whose interactions are governed by the repulsion parameters.

2.6.2 Study of Graphene Agglomeration

The theoretical explanation for the agglomeration of graphetic materials in a solution has been mentioned earlier in this section. However, the proper visual inspection of the in-situ mechanism with experiments remains impractical, due to small scale and haste of the process. Therefore, some molecular simuations about the agglomeration of the graphene nanosheets were conducted.

Konatham and coworkers (Konatham et al., 2011) have simulated the system of graphene sheets submerged in n-octane (oil), resulting in agglomeration of the nanosheets, for which they proposed the solution by functionalising the sheets with alkane functional groups (Konatham and Striolo 2008).

Apart from oil, other solvents have been simulated to observe their capability of dispersing the graphene sheets. Shih and coworkers (Shih et al., 2010) simulated the solution of graphene sheets, or pristine, and N-methylpyrrolidone

(NMP), N,N′-dimethylformamide (DMF), dimethyl sulfoxide (DMSO),γ-butyrolactone (GBL), and water. The result suggested that NMP has the highest ability to disperse the pristines and water has the lowest ability. However, the nano-sheets insisted to agglomerate in any cases. With NMP as the solvent, the mechanism of agglomeration of two graphene sheets was studied. The visual inspection of the outcome suggested that the slightest touch between two sheets was the necessary to induce the agglomeration. The sheets then slid parallel to each other and agglomerated.

Park and Aluru (Park and Aluru 2011) observed the agglomeration mechanism of the graphene sheets in water. The result yielded the similar mechanism in agglomeration, for which the first slight and direct contact between sheets was the necessary step to initiate agglomeration. The parallel sliding of the sheets, similar to the observation in the work of Shih and coworkers, was observed.

Currently, the simulation that involves dynamic graphene nanosheets in SDS-water solution is very rare. Min and coworkers (Min et al., 2012) have carried out the coarse-grained simulation of SDS aggregation on a mobile graphene nanosheet. However, they never demonstrated the multiple-graphene nanosheets simulation to illustrate the surfactant-aided stabilization of the nanosheets. Thus, the simulation of the SDS-aided graphene nanosheets stabilization is conventionally an undiscovered topic.