CHAPTER III

THEORY

3.1Carbon nanoparticles (CNPs)

Since the first discovery of C_{60}, Buckminsterfullerene, by H. Kroto and R. Smalley in 1985 [21], it has initiated substantial attentions in many research areas particularly those of synthesizing carbon nanoparticles (CNPs) such as nanotubes (CNTs), nanohorns (CNHs), nanocapsules (CNCs) and so on. Among these structures, carbon nanotubes (CNTs) are currently the subject of intense research because of their extraordinary mechanical and electrical properties.

3.1.1 Buckminsterfullerene (C_{60})

60 carbon atoms in C_{60} are located at the vertices of a regular truncated icosahedron, 0.710 nm in diameter. Every carbon site on the C_{60} molecule is equivalent to every other site (see Fig. 3.1). The average nearest neighbor carbon-carbon (C-C) distance in C_{60} is very small (0.144 nm) and is almost identical to that in graphite (0.142 nm). Each carbon atom in C_{60} (and also in graphite) is trigonally bonded to three other carbon atoms, and 20 of the 32 faces on the regular truncated icosahedron are hexagons, the remaining 12 being pentagons. Thus we may consider the C_{60} molecule as a "rolled-up" graphene sheet (a single layer of crystalline graphite) which forms a closed shell molecular nanostructure, in keeping with Euler's theorem, which states that a closed surface consisting of hexagons and pentagons has exactly 12 pentagons and an arbitrary number of hexagons. The introduction of pentagons gives rise to curvature in forming a closed surface. To minimize local curvature, the pentagon become separated from each other in the self-assembly process, giving rise to the isolated pentagon rule, an important rule for stabilizing fullerene clusters.

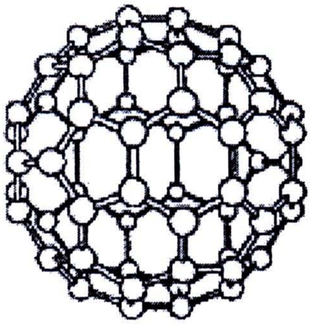

Figure 3.1 Structure of C_{60}, Buckminsterfullerene [22]

3.1.2 Carbon nanotubes (CNTs)

Carbon nanotubes (CNTs) are a very new allotrope of carbon. Carbon nanotubes can be described as graphene sheet rolled into a cylindrical shape. The chemical bonding of carbon nanotubes are composed entirely of sp^2 bonds, similar to those of graphite.

There are two main types of carbon nanotubes; single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) are following these; SWCNTs can be conceptualized by wrapping a one-atom-thick layer of graphite called graphene into a seamless cylinder which is shown in Figure 3.2(a). Meanwhile, MWCNTs consist of multiple layers of graphite rolled in on themselves to form a tube shape which is shown in Figure 3.2(b).

Interestingly, these nested tubes exhibit interlayer spacings of 3.4 A°, a value that is slightly greater than that of graphite (3.35 A°). Iijima attributed this difference to a combination of the tubule curvature and van der Waals interactions between the successive cylinders. Theoretically, it is possible to construct a carbon tube by rolling up a hexagonal graphene sheet in various ways. Two of these are 'non-chiral', so that the honeycomb lattices located at the top and bottom of the tube are always parallel. These configurations are known as 'armchair' and 'zigzag'. In the armchair structure, two C–C bonds on opposite sides of each hexagon are perpendicular to the tube axis, whereas, in the zigzag arrangement, these bonds are parallel to the tube axis (Fig. 3.3, b). All other conformations, where the C–C bonds lie at an angle to the tube axis, are known as 'chiral' or helical structures (Fig. 3.3 c).

Fig. 3.2 Structure of carbon nanotubes (a) SWCNTs and (b) MWCNTs

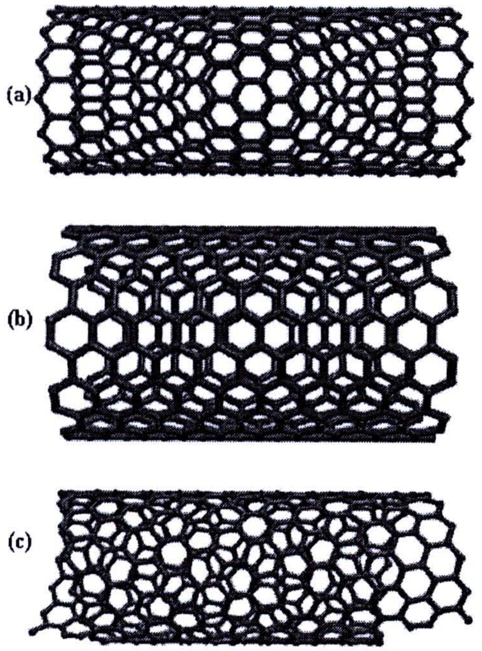

Figure 3.3 Molecular models of SWCNT exhibiting different chiralities a) zigzag arrangement; b) armchair configuration; c) chiral conformation

At present, carbon nanotubes can be obtained using various techniques: arc discharge, pyrolysis of hydrocarbons over catalysts, laser and solar vaporization, and electrolysis. These nanoscale materials can exhibit different morphologies such as straight, curled, hemitoroidal, branched, spiral, helix-shaped, etc. In 1992, two groups predicted theoretically that single-walled carbon nanotubes (SWNTs) might be metallic or semiconducting carbon nanowires, depending upon their helicity and diameter.

Recent examples of applications include the use of carbon nanotubes as:

- gas storage components of argon, nitrogen, and hydrogen
- AFM probes and field emission sources
- high power electrochemical capacitors
- chemical sensors
- magnetic data storage (e.g. iron filled nanotubes)
- nanocomposites, etc.

They exhibit extraordinary strength and unique electrical properties. Information of attraction properties of CNTs could be briefly summarized as follows,

- Strength property

Carbon nanotubes are one of the strongest and stiffest materials known, in terms of tensile strength and elastic modulus, respectively. This strength results from the covalent sp^2 bonds formed between the individual carbon atoms. A multi-walled carbon nanotube was tested to have a tensile strength of 63 GPa . In comparison, high-carbon steel has a tensile strength of approximately 1.2 GPa. Further, CNTs have very high elastic modulus, on the order of 1 TPa.

- Electrical property

Because of the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. In theory, metallic nanotubes can have an electrical current density more than 1,000 times greater than metals such as silver and copper.

- Thermal property

All nanotubes are expected to be very good thermal conductors along the tube, exhibiting a property known as "ballistic conduction," but good insulators laterally to the tube axis. It is predicted that carbon nanotubes will be able to transmit up to 6000 watts per meter per Kelvin at room temperature; comparing to copper, a metal well-known for its good thermal conductivity, which only transmits 385 watts per meter per Kelvin [14].

From these properties, carbon nanotubes have potentially useful in many applications in nanotechnology, electronics, optics and other fields of materials science. Many techniques have been developed to produce nanotubes in sizeable quantities, including arc discharge, laser ablation and pyrolysis of carbon-containing molecules. Comparison of these techniques, pyrolysis could be a possibility to produce nanotubes on a large scale at a very low cost [15].

3.1.3 Carbon nanocapsules (CNCs)

It has been suggested that carbon-coated magnetic nanoparticles might have important applications in areas such as magnetic data storage, xerography and magnetic resonance imaging. A typical example of carbon nanocapsule is shown in Fig. 3.4. It is a particle containing Fe encapsulated by graphene layers. The role of the carbon layer would be to isolate the particles magnetically from each other, thus avoiding the problems caused by interactions between closely spaced magnetic bits, and to provide oxidation resistance. In addition, the lubricating properties of the graphitic coatings might be helpful in magnetic recording and applications. The potential of important applications has motivated a significant amount of research on the encapsulation of magnetic materials in carbon nanoparticles.

Carbon nanocapsules which there are no metal as core particle can be called as multi-shelled nanoparticles. These particles consist several of graphene sheets in various shapes such as spherical, polyhedral, or short-tube.

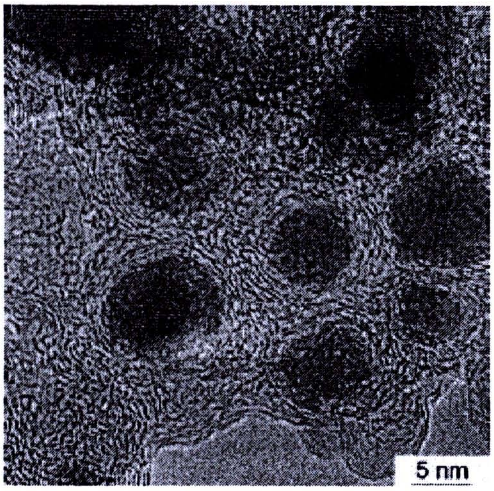

Figure 3.4 Carbon nanocapsules with iron particles in core [10]

3.1.4 Carbon nanohorns (CNHs)

Another type of carbon nanoparticles is named nanohorns due to their irregular horn-like shape, and were discovered by Sumio Iijima's research group. Nanohorns have the same graphitic carbon atom structure as normal carbon nanotubes. The main characteristic of the carbon nanohorns is that when many of the nanohorns group together an aggregate (a secondary particle) of about 100 nanometers is created. The advantage being, that when used as an electrode for a fuel cell, not only is the surface area extremely large, but also, it is easy for the gas and liquid to permeate to the inside. In addition, compared with normal nanotubes, because the nanohorns are easily prepared with high purity it is expected to become a low-cost raw material.

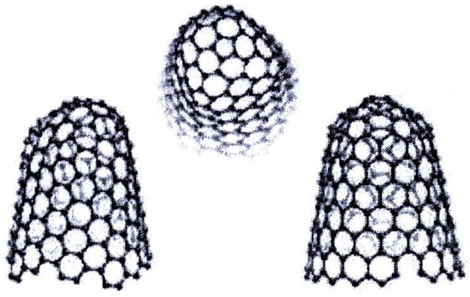

Figure 3.5 Carbon nanohorns (CNHs) model

3.2 Dye

A dye is a colored substance that can be applied in solution or dispersion to a substrate, thus giving a colored appearance. Dye molecules are colored because they are selectively able to absorb and reflect incident light. Organic molecules become colored, and thus useful dye molecules, if they contain at least one of each of the radicals called chromophores and auxochromes.

Chromophores are organic radicals containing unsaturated double bonds. A molecule possessing no chromophores would be colorless. Auxochromes are organic radicals that fulfill the following important functions: intensifies and deeps the hue of the dye molecule's color, makes the dye molecule more readily soluble in water because auxochromes tend to be polar, improves the color fastness properties of the dyed or printed fiber.

3.2.1 Classification of dyes according to application

3.2.1.1 Vat dyes

A vat dye is a water-insoluble colorant containing two or more keto groups. It can thus be brought into aqueous solution by a reduction process (vatting), which converts the vat dye into its alkali-soluble enolic (leuco) form. The major application is the dyeing and printing of cotton. The wash and light fastness of vat dye are excellent. They provide textile materials with the best color fastness of all dyes in common use. Vat dyes have grater exhaustion and fixation than most reactive dyes, and have less color in the effluent. The color removal of vat dyes is much easier owing to its insolubility in water.

3.2.1.2 Sulphur dyes

These dyes are so called because they contain sulphur atoms in their mulecules. These resemble the vat dyes in certain ways. The sulphur dyes contain the characteristic disulphide group in the insoluble form, which can be brought into the aqueous solution by reduction to the alkali-soluble (leuco) form. Sulphur dyes are mainly used for cellulosic fibers and the dyeing is employed for low cost fabrics. The effluent of sulphur dyeing is probably more toxic than any other, due to the presence of sulphide. The wet-fastness of sulphur dyes is usually good and the light-fastness satisfactory, but resistance to bleaching is poor.

3.2.1.3 Reactive dyes

These dyes are characterized by the presence of mobile reactive atoms or groups due to which they may enter into chemical reaction with certain functional group of fibrous materials. They are capable of reacting chemically with a substrate under suitable application conditions to form a covalent dye-substrate bond. The characteristic structural feature is thus the possession of one or more reactive groupings of various kinds. Dyeing with neutral reactive dyes eliminates the need for alkali in fixation and allows complete processing to be performed at a pH of around 7.0. Its application is the dyeing and printing of cellulosic fibers. Textile materials, which are colored with reactive dyes, have very good wash-fastness and light-fastness, however, they have to be thoroughly rinsed and washed-off to remove the unfixed and the hydrolysed dye molecules. If these molecules of dyes are not removed, poor wet-fastness and rub-fastness may result.

3.2.1.4 Direct dyes

These are defined as anionic dyes with substantivity for cellulosic fibers, normally applied from an aqueous dyebath containing an electrolyte such as sodium chloride. Sodium ions neutralize the negative surface charge of the fiber, enabling the dye anion of direct dye to enter the fiber more readily. The fibers most readily colored with direct dyes are cotton and viscose fibers. At least 70% of direct dyes are unmetallised azo structure. The poor wet-fastness of textile materials dyed with direct dyes are undesirable for many purposes. However, there are many methods to render it less soluble in water and therefore more fast to wet treatment.

3.2.1.5 Disperse dyes

These dyes have affinity for hydrophobic fiber (cellulose acetate) and they are normally applied from fine aqueous dispersion. Hydrophobic fibers can absorb disperse dyes from the vapour phase. This mechanism is the basis of many continuous dyeing and printing methods of application of these dyes. Textile materials which have been dyed with disperse dyes have a fair to good light-fastness and a moderate to good wash-fastness.

3.2.1.6 Basic dyes

Basic dyes are also called cationic dyes because, in solution, the dyes ionize and the colored component always constitutes the cation or positively charge radical. The Society of Dyers and Colorists defines a basic dye as characterized by its substantivity for the acidic types of acrylic fibers and for tannin-mordanted cotton. Acrylic materials dyed and printed with basic dyes have very good light-fastness and wash-fastness. This is attributed partly to the hydrophobic nature of acrylic fibers, which minimizes their absorption of water and their excellent resistance to sunlight.

3.2.1.7 Acid dyes

The acid dyes are so called because the original members of the class were applied under acidic conditions, and they are nearly all sodium salts of organic acids and the anion is the active colored component. These are defined as anionic dyes, characterized by substantivity for protein fibers. Wood, silk and nylon contain basic groups and the uptake of leveling acid dyes by nylon at acidic pH can usually be relate to the amine end-group content of fiber. As well as the dyeing and printing of nylon and protein fibers, acid dyes are important for the coloration of leather, paper, jute, wool and anodised aluminium. Metal toners are concentrated pigments prepared by precipitating anionic dyes, often of the unmetallised azo acid type, as their water-insoluble metal salts. Dyes and printed acid colors have good light-fastness.

3.2.1.8 Mordant dyes

The somewhat ambiguous term 'mordant dye' is defined as a dye that is fixed with a 'mordant'. A mordant is itself defined as 'a substance, usually a metallic compound, applied to a substrate to form a complex with a dye, which is retained by the substrate more firmly than the dye itself'. A more logical generic name for those chelatable anionic dyes capable of being fixed to wool after treatment with a dichromate would be the more popular term 'chrome dye' or 'chrome mordant dyes'.

3.2.1.9 Solvent dyes

Solvent dyes are characterized by their solubility in one or more organic solvents. Numerous media of interest in practice are alcohols, ethers, esters, ketones, chlorinated solvents, hydrocarbons, oils, fats and waxes.

3.2.2 Textile wastewater treatment methods

Textile processing includes sizing, desizing, scouring, bleaching, mercerization, weaving, dyeing, printing and finishing. The dyeing operation involves the use of chemicals, such as salt, alkalis, acids, reducing agents, oxidizing gents, soaps and detergents, and dye-fixing agents. Textile wastewater is generally colored, highly alkaline, highly in BOD or COD values, and high in suspended solids. One of the major problems concerning textile wastewaters is colored effluent. Though not particularly toxic, dyes have a visible effect. The presence of color will reduce aquatic diversity by blocking the passage of light through the water. There are many methods which have been applied for removed the color from wastewater such as coagulation, chemical flocculation, biological treatment, chemical oxidation, chemical reduction and adsorption.

One possible treatment for the removal of soluble dyes by an aerobic procedure may be biodegradation, but reactive dyes constitute an exception. The effluents containing azo reactive dyes are very difficult to treat in environmental systems, due to its high water soluble and polar.

Adsorption is one of the most effective physical processes for the removal of color and treatment of textile effluents. In the adsorption procedures the conventional materials used is activated carbon, but due to its complicacy in operation and separation. Then the alternative carbon material adsorbents, which are easier than in its operation and separation, have been studies.

3.3 Adsorption

When two phases are in contact, there is a region at their interface the composition of which is different from that of the bulk of either phase. The increase in the concentration of a substance at the interface as compared with the bulk concentration, is known as adsorption. On the surface of solid, substance can be adsorbed from a gaseous or liquid phase. The solid is known as the adsorbent and the gas or liquid is called the adsorbate.

Adsorption is brought about by the interactions between the solid and the molecules in the fluid phase.

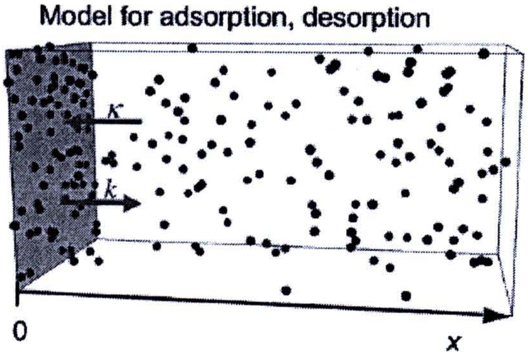

Figure 3.6 Model system for adsorption and desorption.

Figure 3.6 presents model for adsorption and desorption where molecules shown with dots, adsorb to the gray surface with the adsorption coefficient (K) and desorb with the rate constant (k’). Equilibrium would take place once the system is kept under a condition of constant temperature and pressure with the presence of sufficient amount of adsorbate molecules. Adsorption equilibrium would be affected by the adsorption capacity of the adsorbing surface and intensive properties of adsorbed molecules.

3.3.1 Types of adsorption

3.3.1.1 Physical adsorption, or Physisorption

It is relative nonspecific and is due to the operation of weak forces of attraction or van der Waals's forces between molecules. Here, the adsorbed molecule is not affixed to a particular site on the solid surface, but it free to move about over the surface because the surface does not share electrons with the adsorbate. When the molecular forces of attraction between the adsorbate and the adsorbent are greater than the forces of attraction between the adsorbate and the solvent, the adsorbate will be adsorbed onto the adsorbent surface. The adsorbent has numerous capillaries within the particles, and the surface available for adsorption includes the surface of the pores in addition to the external surface of the particle. Actually, most of the adsorption occurs on the pore surfaces. In addition, the adsorbed material may condense and form several superimposed layers on the surface of the adsorbent. Physical adsorption is generally quite reversible. Physisorption has a comparatively low enthalpy of adsorption, typically are only 2-20 kcal/mole.

3.3.1.2 Chemical adsorption, or Chemisorption

It is associated with exchange of electrons and the formation of a chemical bond between the adsorbed molecule (adsorbate) and the surface (adsorbent), which results in much stronger forces. Normally the adsorbed material forms a layer over the surface which is only one molecule thick, and the molecules are not considered free to move from one surface site to another. When the surface is cover by the monomolecular layer, the capacity of the adsorbent is essentially exhausted. Also, chemical adsorption is seldom reversible. Eckenfelder (2000) explained that the chemical adsorption results in the formation of a monomolecular layer of the adsorbate on the surface through forces of residual valence of the surface molecule [25]. A wide range of enthalpy changes may occur on chemisorption, though the typical chemisorption energies are 15-100 kcal/mole for simple molecules.

Therefore, a molecule is chemisorbed if the molecule's electronic structure is significantly perturbed upon adsorption, while a molecule is physisorbed if it adsorbs without undergoing a significant change in electronic structure. Molecules are often distorted when they adsorb on solid surfaces. Sometimes the molecules stay intact during the adsorption process, while at other times the bond break. A molecule can usually be physisorbed and chemisorbed on the same surface. The process may often be explained by an electrical attraction to the solid phase of components with a (minor) electrical change. The adsorption results in the formation of a molecular layer of the adsorbate on the surface and is sometimes followed by a slow diffusion into the particles of the adsorbent.

3.3.2 Adsorption isotherm

When an adsorbent is placed in a solution containing an organic solute and the slurry is agitated or mixed to give adequate contact, adsorption of the solute occurs. The solute concentration will decrease from an initial concentration, C_O, to an equilibrium value, C_e, if the contact time is sufficient during the slurry test. Adsorption isotherm is the relation between amount of solute adsorbed per unit mass of adsorbent (Q_e) and the equilibrium concentration (C_e) at a constant temperature. The isotherm can be graphically reduced to a straight line, for example, for the Langmuir equation and for the Freundlich equation. Thus correlation of equilibrium data by either theoretical or empirical equations is essential to practical operation. Two famous adsorption isotherm models have been proposed as follows.

3.3.2.1 Langmuir isotherm

In 1918, Irving Langmuir proposed another adsorption isotherm which explained the variation of Adsorption. It is an empirical isotherm derived from a proposed kinetic mechanism [32]. It is based on four hypotheses:

- The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.
- Adsorbed molecules do not interact.
- All adsorption occurs through the same mechanism.
- At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

The theoretical Langmuir isotherm is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface. The Langmuir equation is the most widely used parameter equation, as Eq. 3.1.

Langmuir equation:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \tag{3.1}$$

and

$$R_L = \frac{1}{1 + K_L C_0} \tag{3.2}$$

where C_e (mg/L) is the concentration of dye at equilibrium, Q_e (mg/g) is the amount of dye adsorbed at equilibrium, Q_m (mg/g) is the maximum adsorption capacity and K_L (L/mg) is the Langmuir constant. The values of Q_m and K_L can be calculated from plotting C_e/Q_e versus C_e.

The maximum adsorption capacity is corresponding to monolayer coverage. From Eq. 3.2, the separation factor or equilibrium parameter (R_L) also evaluated.

(i) $R_L = 0$: The adsorption process is irreversible
(ii) $R_L = 1$: Linear adsorption
(iii) $R_L > 1$: Unfavorable adsorption
(iv) $0 < R_L < 1$: Favorable adsorption

3.3.2.2 Freundlich isotherm

The Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage. It is the most important multisite adsorption isotherm for rough surface.

The Freundlich isotherm model is the earliest known equation describing the adsorption process. It is an empirical equation and can be used for non-ideal sorption that involves heterogeneous adsorption. The empirical Freundlich equation is given below by Eq. 3.3 or 3.4.

Freundlich equation: $Q_e = K_F C_e^{1/n}$ (3.3)

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \qquad (3.4)$$

where Qe (mg/g) is the amount of dye adsorbed at equilibrium, Ce (mg/L) is the concentration of dye in solution at equilibrium, K_F (mg/g $(mg/L)^{1/n}$) and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

The magnitude of $1/n$ quantifies the favorability of adsorption and the degree of heterogeneity of the CNTs surface. If $1/n$ is less than unity, indicating favorable adsorption and the adsorption is physical, then the adsorption capacity increases and new adsorption sites occur. Otherwise, the adsorption is chemical.