



Nanomaterials

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1 Introduction

Nanomaterials describe, in principle, materials of which the smallest dimension of a single unit is sized between 1 and 100 nm (termed as the nanoscale). The prefix ‘nano’ is derived from Greek means ‘dwarf’. It is a rapidly growing field with tremendous potential in multiple fields such as medicine, electronics and computer science. At the nanoscale materials exhibit different properties when compared to the chemically identical material in cluster or bulk. These properties are due to two broad sets of nanoscale effects:

1. Effects that are due to higher surface to volume ratio that scale smoothly with decrease in volume.
2. Quantum effects by virtue of which there is a discretized behavior.

Nanosystems can be divided by dimensionality, that is, the number of dimensions that exceed the nanoscale. 0D nanomaterials, for example silver nanoparticles are within the nanoscale in all three dimensions. Similarly examples of 1D and 2D nanomaterials are carbon nanotubes and graphene respectively. 3D nanomaterials are bulk materials composed of nanostructures arranged in a regular pattern, where the distance between particles is within the nanoscale.

There are two ways to manufacture nanomaterials. One is the ‘top-down’ approach which involves deconstructing a bulk material into nanoparticles. The other is a ‘bottom-up’ approach, which refers to the formation of nanoparticles from smaller subunits, driven by the physical and chemical properties of the subunits themselves.

This report covers the preliminary thermodynamics, kinetics and transport required for studying phenomenon at the nano-scale as well as the spectroscopic techniques used for characterisation. Next it touches upon surface effects and intermolecular forces that are involved in self-assembly of nanomaterials. It also briefly covers some surface and quantum effects. It concludes by exposing the reader to the properties and applications of graphene, a novel nanomaterial, in order to give a glimpse of the vast scope of this field.

2 Thermodynamics at the Nanoscale

2.1 Thermodynamic Terminology and Variables

Thermodynamics is concerned with heat and work and explains, on a macroscopic level, relative stability and the feasibility of a change. Following are some thermodynamic terminology

- **System** denotes an identifiable macroscopic collection; a subset of the universe that is the region of interest. **Surrounding** denotes the rest of the universe which has a perceptible effect on the system. An **isolated** system is one from which no matter or energy can be exchanged with the surroundings. An **open** system can exchange both matter and energy with the surrounding whereas a **closed** system can exchange energy and not matter. Actual systems rarely fit into any of these categories, however for theoretical treatment systems can be approximated as such.
- A **process** is the transformation from one thermodynamic state to another. A process which occurs with no heat transfer between system and surrounding is termed as an **adiabatic** process. Similarly an **isothermal** process is one in which there is no temperature change in the system and surroundings, while an **isobaric** process is a process that occurs under constant pressure. Again, real life processes are rarely completely adiabatic, isothermal or isobaric.
- A **Reversible** or Quasi-static process is a process that can be reversed in its direction by an infinitesimal change in one or more state variables. An **Irreversible** process proceeds in only one direction.
- A thermodynamic property is a **State** function if its value depends solely on the system's current state and not the path which the system took to reach the current state. **Path** functions depend on the path as well.
- **Intensive** properties are independent of mass and **Extensive** properties are mass dependent.

Following are some important thermodynamic variables:

- **Work(W)** work performed by a system is energy transferred by the system to its surroundings, by a mechanism through which the system can spontaneously exert macroscopic forces on its surroundings. Sign convention: Work done on the system is positive.

$$W = - \int_{r_1}^{r_2} F_{\text{ext}}(r) dr$$

- **Heat(q)** is energy in transfer to or from a thermodynamic system, by mechanisms other than thermodynamic work or transfer of matter. Sign convention: heat transferred to the system is positive.
- **Internal Energy(U)** of a system is identified with the random, disordered motion of molecules and excludes the macroscopic potential energy and kinetic energy. It is a state function. From the first Law of Thermodynamics,

$$\Delta U = W + q$$

- **Enthalpy(H)** is defined as $H = U + PV$. It is a state function. The change of enthalpy from one state to another is defined as the heat exchange involved in an isobaric process with same initial and final states.
- **Entropy(S)**: Entropy is a state function. Qualitatively, entropy is a measure how much the energy of atoms and molecules disperse out in a process and can be defined in terms of statistical probabilities of a system or in terms of the other thermodynamic quantities.

$$\Delta S = \int \frac{dq_{\text{rev}}}{T}$$

- **Gibbs' Free Energy(G)** predicts the direction of a process under the condition of constant temperature and pressure. $G = H + TS$; $\Delta G < 0$ for a spontaneous, irreversible process.

2.2 Thermodynamics and Size Effects

2.2.1 Relative Temperature Fluctuations

In macroscopic systems, temperature of the entire system is defined based on the average kinetic energy of the particles of the system. The equations of thermodynamics are valid only for such systems consisting of a large number of particles. For dealing with thermodynamics of nanoscale systems, relative temperature fluctuations for a cubic particle of length L and N atoms per unit volume is defined by

$$\frac{\Delta T}{T} = \sqrt{\frac{1}{NL^3}}$$

For relative temperature fluctuations below 1% (0.01), classical thermodynamics is considered a valid approximation.

2.2.2 Breakdown of Thermodynamics at the Nanoscale

Phase transitions, being bulk phenomena, are not sharp when dealing with nanoparticles. They behave more like molecules than as bulk matter. Rather than of phases it may be more useful to think of different structural isomers which coexist over a range of temperatures. Different parts of a cluster might behave as different 'phases' which fluctuate with position and size. When phases are no longer well defined the Gibbs phase rule loses its meaning. New phases may appear which are characterised by discrete chemical potentials and separated by so-called layering transitions.

Nanoparticles are also able to exhibit negative heat capacities. This means that the temperature drops over a certain range when heated. It is understood in the following way: temperature relates to kinetic energy, heat capacity to total energy; thus, temperature drops when a fraction of kinetic energy is converted to potential energy. For example, when more and more energy is deposited on an isolated S_8 ring this corresponds to heating and is seen by higher amplitudes of vibrational and rotational motion. At some point, sufficient energy may be localised in a single bond so that this bond breaks, converting a hot S_8 ring into a colder linear S_8 chain. This also means that temperature fluctuates at constant energy and is no longer well defined for small isolated species. It may impose a principal limit to certain applications of nanotechnology.

2.3 Surface Effects

Bonding in a small cluster of atoms differs from that in the bulk. Moreover, an atom at the smooth surface of a sizable single crystal is different from an atom at the surface of a small cluster of the same element. These properties are exhibited due to fact that nanomaterials have a larger fraction of atoms at the surface as compared to their bulk counterparts.

2.3.1 Dispersion

The surface of a sphere scales with the square of its radius, but its volume scales with r^3 . The total number of atoms N in this sphere scales linearly with volume. The fraction of atoms at the surface is called dispersion F , and it scales with surface area divided by volume, i.e. with the inverse radius or diameter, and thus also with $N^{-1/3}$. For cubes of n atoms along an edge and a total of $N = n^3$ atoms, where the number of atoms at the surface is $6n$ corrected for double counts at the 12 edges and for reinstalling the 8 corners. For large N the edge and corner corrections become negligible, leading to the $N^{-1/3}$ scaling:

$$F = \frac{6n^2 - 12n + 8}{n^3} \approx \frac{6}{N^{1/3}}$$

All properties which depend on the dispersion of a particle lead to a straight line when plotted against r^{-1} , d^{-1} , or $N - 1/3$. Examples of such properties are density, cohesive energy, melting point, etc.

2.3.2 Cohesive Energy

Cohesive energy is the bond energy per atom. Fig. 3 represents an average value. In reality, however, the atoms in the interior of the cluster are more highly coordinated, form more bonds and are therefore more stable than those at the cluster surface and have a higher cohesive energy. Therefore, for cubic crystals, the corner atoms have the highest reactivity and are often found to be missing.

To understand the behavior, consider the total cohesive energy holding n number of atoms in solid material together. If N is the number of surface atoms, then the number of bulk interior atoms is $n - N$. E_o is the cohesive energy per atom of the bulk material. Hence the contribution of the bulk atoms to the total cohesive energy is $E_o(n - N)$

The number of atom-atom interactions on the surface is one half of the number atom-atom interactions in the bulk. Half of the total bonds of each surface atom are dangling bonds. As a result, their contribution is $\frac{1}{2}NE_o$. Let \bar{E}_b be the cohesive energy per mole

of the bulk material and \bar{E}_n be the cohesive energy per mole of the nanomaterial as a whole. Then

$$\bar{E}_n = \bar{E}_b(1 - \frac{N}{2n})$$

Both the cohesive energies \bar{E}_n and \bar{E}_b measure the strength of interaction between the atoms increase linearly with the melting temperature.

2.4 Melting Point of Nanomaterials

The melting temperature of nanoparticles increases with size and eventually levels off to a value corresponding to the bulk phase melting temperature. This is also a smooth scalable surface effect and has a similar relation as cohesive energy. In order to derive this relation, a few concepts need to be introduced first.

2.4.1 Chemical Potential

The chemical potential(μ) of a system measures the change of Gibbs' Energy with number of moles n while keeping other variables constant.

$$\mu = (\frac{\partial G}{\partial n})_{P,T}$$

This concept becomes important while dealing with a multi-component system. For a multi-component system, the total Gibbs' free energy is given by $\sum_i \mu_i n_i$. Chemical potential is a useful concept in thermodynamics in that it helps understand how multi-component systems evolve toward equilibrium. Chemical potential is analogous to electrical potential, where charge flows from a region of high electrical potential to a region of low electrical potential. In the case of chemical potential, transfer of matter always occurs from a region of high chemical potential to a region of low chemical potential.

2.4.2 Gibbs' Energy and Surface Tension

The Gibbs energy of the surface is directly proportional to the surface area. The proportionality constant is known as the surface tension of the material in question.

$$\bar{G}_{\text{surf}} = \gamma \bar{A}$$

where \bar{A} is the molar area and γ is the surface tension. The Gibbs' energy represents the work done to increase the surface area.

$$\bar{G}_{\text{surf}} = \gamma \frac{\partial A}{\partial n} = \gamma \frac{\partial V}{\partial n} \frac{\partial A}{\partial V}$$

For a spherical particle of radius r

$$\frac{\partial A}{\partial V} = \frac{8\pi r}{4\pi r^2} = \frac{2}{r}$$

The corresponding surface molar Gibbs energy in terms of molar volume of a nanoparticle is therefore

$$\bar{G}_{\text{surf}} = \frac{2\gamma\bar{V}}{r}$$

2.4.3 Phase Equilibria in Bulk Materials

When two phases (1) and (2) are in equilibrium

$$d\bar{G}(1) = d\bar{G}(2)$$

Since $d\bar{G} = \bar{V}dP - \bar{S}dT$,

$$\bar{V}(1)dP - \bar{S}(1)dT = \bar{V}(2)dP - \bar{S}(2)dT$$

Rearranging,

$$\frac{dP}{dT} = \frac{\Delta\bar{S}_{\text{trans}}}{\Delta\bar{V}_{\text{trans}}}$$

Since $\Delta\bar{S}_{\text{trans}} = \frac{\Delta\bar{H}_{\text{trans}}}{T_{\text{trans}}}$,

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_{\text{trans}}}{T\Delta\bar{V}_{\text{trans}}}$$

Taking vapor pressures of components (1) and (2) as P_1 and P_2 ,

$$\ln \frac{P_2}{P_1} = \frac{\Delta\bar{H}_{\text{trans}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

2.4.4 Phase Equilibria in Nanomaterials

In the treatment of phase changes within nanoparticles, assume that the particle is made up of a single element. The total chemical potential of a nanoparticle must be a sum of the bulk chemical potential and the surface chemical potential.

$$\mu_{\text{particle}} = \mu_{\text{bulk}} + \mu_{\text{surf}}$$

For a particle with radius r , expressions for chemical potentials in solid and liquid phases are

$$\mu_{\text{particle}}^{\text{L}} = \mu_{\text{bulk}}^{\text{L}} + \frac{2\gamma^{\text{L}}\bar{V}^{\text{L}}}{r}$$

$$\mu_{\text{particle}}^{\text{S}} = \mu_{\text{bulk}}^{\text{S}} + \frac{2\gamma^{\text{S}}\bar{V}^{\text{S}}}{r}$$

At the melting temperature of the nanomaterial, the two phases will be in equilibrium, that is,

$$\mu_{\text{particle}}^{\text{L}} = \mu_{\text{particle}}^{\text{S}}$$

$$\mu_{\text{particle}}^{\text{L}} - \mu_{\text{particle}}^{\text{S}} = \frac{2}{r}(\gamma^{\text{L}}\bar{V}^{\text{L}} - \gamma^{\text{S}}\bar{V}^{\text{S}})$$

Since $\Delta\bar{G}_{\text{trans}}^{\text{bulk}} = \mu_{\text{bulk}}^{\text{L}} - \mu_{\text{bulk}}^{\text{S}}$ and $\Delta\bar{G}_{\text{trans}}^{\text{bulk}} = \Delta H_{\text{trans}} - \frac{T\Delta H_{\text{trans}}}{T_{\text{trans}}}$

$$\Delta\bar{H}_{\text{trans}}\left(1 - \frac{T}{T_{\text{trans}}}\right) = \frac{2}{r}(\gamma^{\text{L}}\bar{V}^{\text{L}} - \gamma^{\text{S}}\bar{V}^{\text{S}})$$

$$\frac{T}{T_{\text{trans}}} = 1 - \frac{1}{r} \frac{2}{\Delta H_{\text{trans}}}(\gamma_{\text{L}}\bar{V}_{\text{L}} - \gamma_{\text{S}}\bar{V}_{\text{S}})$$

Where T is the melting point of the nanoparticle and T_{trans} is the melting point of the bulk material To obtain surface tension and molar volume for solid phase, the following relations exist

$$\gamma_{\text{S}} = 1.25\gamma_{\text{L}_{\text{mpt}}} + \frac{\partial\gamma_{\text{L}}}{\partial T}(T - T_{\text{mpt}})$$

$$\bar{V}_{\text{S}} = \left(\frac{\bar{V}_{\text{L}}}{1 + \beta}\right)$$

where β depends on the element. In an experiment to detect melting point of indium confined in controlled-pore glass and in Vycor of various pore diameters, it is clearly seen that there is a second peak which shifts to lower temperatures as the pore diameter decreases. It belongs to indium inside the pores. Furthermore it broadens, which is another characteristic of small particles. Since the pore size is well defined this broadening cannot be ascribed to a pore-size distribution. Rather, it reflects that melting is a cooperative phenomenon which is not well defined for a small number of members of the ensemble. A sharp melting point is only obtained in the thermodynamic limit of an infinite number of particles.

3 Kinetics and Transport at the Nanoscale

Chemical kinetics, the study of the rates of reactions and the implication of these rates, relies on the experimental observation of reactions and the effects of changing conditions on their rates. While thermodynamics dealt with the feasibility of reactions, kinetics deals with how reactions occur and the rates at which they occur.

3.1 Basics of Chemical Kinetics

3.1.1 Rates of Chemical Reactions

Rate of a reaction can be quantified as measuring changes in concentration of reacting species over time. Consider the general reaction



The rate of the reaction can be defined as

$$v(t) = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

where $[A]$, $[B]$, $[C]$, $[D]$ represent concentrations of respective species.

The experimentally determined rate law of a reaction shows the dependence of the rate of the reaction on the different reacting species (and catalysts). For the general reaction introduced above,

$$v(t) = k[A]^n[B]^m$$

where k is the rate constant, n and m are the orders of the reaction with respect to A and B respectively.

The Arrhenius equation gives us the temperature dependence of the rate constant

$$k = Ae^{-\frac{E_a}{RT}}$$

where A is the pre-exponential factor and E_a is the activation energy. These two concepts will be elaborated on in the following subsections.

3.1.2 Collision Theory

Using the Kinetic Theory of Gases, which deals with molecular speeds, collision density and collision cross-section of a sample of gas in a particular container, a deeper understanding of reaction kinetics can be obtained. In a typical gas phase reaction, the collision density is in the order of 10^{30} collisions per liter second, which would correspond to a reaction rate of about $10^6 \text{ mol dm}^{-3} \text{ s}^{-1}$ if every collision resulted in the formation of the product.

However, many reactions are known to proceed much slower, implying that only a fraction of these collisions actually lead to product formation. For a collision to form a product, the reactant species must have sufficient kinetic energy as well as a suitable relative orientation. The minimum energy required for a reaction to take place is E_a .

At greater temperatures, a larger fraction of molecules have an energy exceeding the activation energy, resulting in a higher yield of the product. The pre-exponential A factor in the Arrhenius equation deals with the fraction of molecules that will have a suitable relative orientation for the reaction to occur. Orientation is not important for spherically symmetric atoms or nanoparticles, but becomes a critical factor for particles with more complex shapes.

Transition state theory provides a more robust interpretation of the activation energy. This theory is based on the premise that reactant particles come together to form a very short-lived high-energy complex (the transition state) that very quickly leads to product formation.

3.1.3 Catalysis

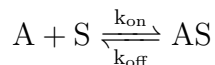
A catalyst is a species that when added to a reaction mixture speeds up the rate of the reaction. Catalysis has great relevance to reactions such as nanoparticle synthesis, quantum dot functionalization, and to reactions on surfaces. A catalyst increases the rate of a reaction by lowering its activation energy.

There are two types of catalysts: homogeneous (always in same phase as reactants) and heterogeneous (in different phase as reactants). Catalysts for a particular reaction lower the activation energy of the reaction by providing an alternative pathway to the slowest step (rate determining step) in the mechanism of that reaction.

3.2 Bimolecular Binding Kinetics

3.2.1 Kinetics of Reversible Binding

Consider the binding of a molecule A onto a solid surface composed of S . Let k_{on} and k_{off} be the rate constants for the forward and backward direction of binding respectively.



The reaction can be set up such that an aqueous solution of the protein is continuously flowing over the solid substrate, thereby maintaining a constant value of $[A]$. The rate of formation of the surface bound protein is:

$$\frac{d[AS]}{dt} = k_{\text{on}}[A][S] - k_{\text{off}}[AS] = k'_{\text{on}}[S] - k_{\text{off}}[AS]$$

where $k'_{\text{on}} = k_{\text{on}}[A]$.

3.2.2 Cooperativity of Binding

Consider a complex ML_n in which n small molecules(or ligands) bind to distinct sites of a large nanoassembly(or macromolecule) The equilibrium constant of the process is

$$K = \frac{[ML_n]}{[M][L]^n}$$

Since at any time, the total amount of species M in solution is $[M] + [ML_n]$, we can describe the fraction of the bound molecules as

$$f = \frac{[ML_n]}{[M] + [ML_n]} = \frac{K[L]^n}{1 + K[L]^n}$$

This can be rearranged to

$$\frac{f}{1-f} = K[L]^n$$

From this the Hill equation is obtained:

$$\log \frac{f}{1-f} = n \log[L] + \log K$$

The value n is known as the Hill coefficient and its value represents how the bound molecules are interacting with each other. A value $n > 1$ is interpreted as cooperative binding. This means that once L is bound to M , it promotes the binding of other L molecules to M . If $n < 1$ the binding is anticooperative—the bound ligand prevents the binding of other ligands. If $n = 1$, the binding is noncooperative—the bound ligand does not affect the binding of other ligands.

The theoretical maximum value of n is the total number of binding sites on M . In a Hill plot describing the binding of a small molecule to a polymer nanofilm, It can be seen that the binding goes from noncooperative to cooperative at some critical concentration shown by the X . A loosely packed layer of L on M at low concentrations, where the molecules are too far from each other to interact. At sufficiently high concentration we have a transition to a more densely packed layer, where the bound molecules are interacting strongly with their neighbors.

If all of the sites on the macromolecule are identical, independent, and noninteracting, then $n = 1$, the Scatchard equation is obtained:

$$\frac{f}{1-f} = K[L]$$

3.3 Diffusion Control

3.3.1 Diffusion

Diffusion is an entropically driven spontaneous process which results in the net movement of particles of a substance from a region of higher concentration to a region of lower concentration. Fick's first law for diffusion in one dimension states

$$J = -D \frac{dc}{dt}$$

Where J is the concentration flux (moles of species flowing per unit time per unit area) , D represents the diffusion coefficient and c is the concentration of the diffusing species. Fick's second law of diffusion states:

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2}$$

For particles diffusing through a test surface with surface area A let $\Phi = JA$. Thus, for a particles diffusing through a sphere of radius R ,

$$\Phi = 4\pi R^2 D \frac{dc}{dr}$$

The diffusion coefficient is temperature dependant and is related to frictional coefficient f by Einstein's Law of Diffusion as

$$D = \frac{k_B T}{f}$$

For a spherical particle flowing through a fluid with viscosity η

$$D = \frac{k_B T}{6\pi\eta r}$$

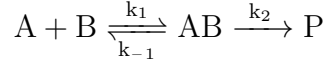
Another important relation is Einstein's equation which states that average displacement $\langle x \rangle = \sqrt{2Dt}$. For a spherical particle flowing through a solution

$$\langle x \rangle = \sqrt{\frac{RTt}{3\pi\eta r N_A}}$$

3.3.2 Kinetics of Diffusion Control

In a reaction in which species approach each other slowly, the rate of the reaction would depend on the speed at which molecules approach each other. This is common

in solution phase reactions, where diffusion is much slower due to collisions. The reactions in which the rate-determining step depends on the diffusion of reactants through the solution are said to be diffusion controlled reactions. Since, in such reactions the formation of products from activated complexes is much faster than the diffusion of reactants, the rate is governed by the collision rate between reactant species. Heterogeneous reactions are also often diffusion-controlled, as reactant molecules must reach the interface to participate in the reaction and are therefore common for reactions in which solid nanomaterials react with other species in solution. Consider the reaction



Reactants A and B diffuse to form a complex AB in the rate determining step ($k_2 \gg k_1, k_{-1}$) after which the complex forms the product P . Therefore the observed rate constant $k_{\text{obs}} \approx k_1$. To find the rate of B diffusing towards A , we define the critical radius r_c which can be approximated as $r_c = r_A + r_B$. At $r = r_c$, $[B] = 0$ and at $r \rightarrow \infty$, $[B] = [B]_b$, that is the bulk concentration. At a particular r

$$\Phi = 4\pi r^2 D_B \frac{d[B]_r}{dr}$$

Under steady state conditions, Φ is independent of r which gives

$$d[B]_r = \frac{\Phi}{4\pi r^2 D_B} dr$$

which on integrating with r_c and ∞ as limits obtains

$$\Phi = 4\pi r_c D_B [B]_b$$

Taking into account diffusion of A

$$\Phi = 4\pi r_c (D_A + D_B) [A]_b [B]_b$$

Comparing with the rate law of the reaction

$$\frac{d[P]}{dt} = k_{\text{obs}} [A] [B]$$

we obtain the value of k_{obs} as

$$k_{\text{obs}} = 4\pi r_c (D_A + D_B)$$

4 Fundamentals of Surface Nanoscience

4.1 Surface Tension

Surface tension measurements provide a simple but powerful method for determining a variety of characteristics of adsorbed monolayers, including the density of the monolayer. Surface tension measures the stability of a surface. A more rigorous way to define surface tension is to say that it is the free energy required to transport a molecule from the bulk phase to the surface and hence expand the area of the surface (dA). This surface free energy (dG_{surf}) is given by

$$dG_{\text{surf}} = \gamma dA$$

where the proportionality constant γ is the surface tension. Surface tension can be interpreted as a two-dimensional analog to a spring—it is the measure of the resistance of a surface to increase its area. The larger the surface tension, the greater the resistance to increase the surface area, which in turn fundamentally depends on the interplay between various inter-molecular interactions occurring on the surface.

4.1.1 Contact Angles and Wetting Phenomena

When a drop of liquid is placed on a planar solid surface, it may at one extreme completely spread to cover the entire surface, or at the other extreme form a spherical droplet on the surface. These situations represent either complete wetting or complete dewetting. Usually the degree of wetting is intermediate between these extremes and depends largely on the interfacial energy (or surface tension) between the liquid and the solid surface. The contact angle is the angle at which the liquid–vapor interface meets the solid surface. If the planar surface is horizontal and the droplet is not moving, this angle is called the static contact angle. If the liquid is in motion because the surface is tilted, then we can identify two dynamic contact angles, the advancing contact angle and the receding contact angle. This picture is similar to a raindrop running down the surface of a window. Usually the advancing contact angle is much larger than the receding angle, and the difference between the two values is called contact angle hysteresis. The Young equation provides a relationship between these various surface tensions and the static contact angle:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

γ_{LV} and θ can be easily measured. The plot of $\cos \theta$ versus γ_{LV} is linear with a negative slope. The line can be extrapolated to the value $\cos \theta = 1$ and the corresponding surface tension measured is called critical surface tension and corresponds to complete wetting. Since in this condition $\gamma_{SL} = 0$, the Young equation

gives $\gamma_c = \gamma_{sv}$. It is worth noting that surfaces can be hydrophobic (water hating) or hydrophilic (water loving). The surface of glass, for example, is considered hydrophilic due to being terminated by polar hydroxyl groups and Teflon hydrophobic due to being terminated with non-polar fluorocarbons.

4.1.2 Nanomaterials and Superhydrophobicity

A superhydrophobic surface enables the contact angle of a drop to approach 180° and move along the surface with no friction. Superhydrophobic surfaces each have two distinct states of wetting, each governed by separate equations and having separate characteristics. The first type was outlined by Wenzel in 1936 and describes a wetting state in which water rests on a surface whose morphology has been altered so that in a given area, water is in contact with more hydrophobic surface than if the surface were completely flat. Wenzel states are described by the equation

$$\cos \theta^W = r \cos \theta$$

where θ is the contact angle on an unmodified surface, θ^W is the Wenzel contact angle (on the rough surface), and r is the ratio of the actual surface area of the substrate to the projection of that surface onto a horizontal surface. However, if the surface is hydrophilic ($\theta < 90^\circ$), then Wenzel wetting actually increases the hydrophilic properties of the surface. Also, because water is present between perturbations, water in a Wenzel state is less likely to roll off the substrate than on a flat surface of the same material. Thus, Wenzel wetting relies on two factors—an already hydrophobic substrate and an increase in the surface area of that substrate.

The other major type of wetting was discovered by Cassie and Baxter in 1944 and describes a wetting state in which water rests on nano- or micro-sized “pins” with air spaces in between. Unlike Wenzel wetting, Cassie–Baxter states have a smaller area of substrate in contact with the water than a planar surface and rely on the air gaps in between regions on the surface of the substrate to form a superhydrophobic surface. In fact, Cassie–Baxter surfaces can be fabricated with hydrophilic substrates and still display superhydrophobicity. Unlike Wenzel surfaces, water in Cassie–Baxter states rolls off surfaces much more easily than on a flat surface of the same material. These properties are reflected in the equation governing Cassie–Baxter wetting:

$$\cos \theta^C = \varphi_s (\cos \theta) + (1 - \varphi_s) \cos \theta_X$$

where φ_s represents the fraction of surface present at the top of the protrusions (where the water is in contact with the substrate), and θ_X is the contact angle over the air gaps, which is approximated at 180° , and θ_C is the Cassie–Baxter contact angle (on the rough surface). Thus, there are two ways to increase superhydrophobicity of a

Cassie–Baxter surface—either increase the value of θ by increasing the inherent superhydrophobicity of the substrate, or decrease φ_s by making bigger air gaps. Interconversion between these two states is possible, but there is an energy barrier to overcome much like any transition state between two energy minima. This phenomenon comes into play when Cassie–Baxter surfaces display Wenzel wetting, which is possible if water falling from a great distance is forced into the crevices between roughness features. The final important feature of superhydrophobic surfaces that must be mentioned before a more thorough description of the specifics is the advantage of multiple-scale roughness, in which perturbations range from the nanoscale to the microscale. Recent study has shown this kind of surface to increase the ease with which drops roll off the surface (in other words, decreasing the contact-angle hysteresis), the prevention of conversion from Cassie–Baxter to Wenzel states, and the tendency to convert from Wenzel to Cassie–Baxter states.

Another interesting feature that is unique to a specific fabrication method is the ability of certain hydrophobic semiconductors to be crystallized into a superhydrophobic surface that exhibits superhydrophobicity in the dark but superhydrophilicity in the light. One likely explanation for this phenomenon is that superhydrophilicity is generated by the excitation of electrons on the surface, which suggests that there are surface properties that can be changed by applying a voltage. Instead of excitation due to ultraviolet (UV) radiation, a voltage could be used, thus allowing for materials that can be dried instantly at the flick of a switch or wetted completely with another flick.

Superhydrophobic structures can be synthesized via generation of fractal solids through crystal growth and diffusion-limited growth. The second method, by randomness, creates small disturbances on the surface of the flat substrate, which then cause more particles to attach to these perturbations. The process continues until large bumps form, which then have small disturbances on their surfaces that create subbumps, and so on. The greatest benefit of these kinds of assemblies is that being fractal, these surfaces have multiple-scale roughness. The main bumps can act as Wenzel-type surfaces, while the smaller bumps can act as Cassie–Baxter surfaces. Another important benefit of fractal solids is their ease of fabrication—because these surfaces are usually created by chaotic movement of material, they require less specialized machinery and can be made with a variety of materials. In fact, fractal superhydrophobic surfaces have been reported using semiconducting polymers, giving these particular surfaces the ability to switch properties under the influence of UV light or an applied voltage. However, fractal solids tend to be opaque, limiting their range of applications. This problem is not present in another type of superhydrophobic surface fabrication—uniform nanostructures. These structures can be generated in many ways, from carbon nanotube growth to lithographic etching. The drawback of these kinds of materials is that they are much less effective at

repelling water than fractal structures. They lack multiscale roughness, and even methods that generate more random arrays are less hydrophobic than fractal surfaces.

4.2 Adsorption Phenomena

A molecule approaching a surface may experience a net attractive force and consequently become trapped or confined at the surface. Such a species is called the adsorbate, and adsorption is the physical process by which adsorbate molecules accumulate onto a solid surface. Solid substrates can be chemically modified so that adsorption can be selective. This modification is known as surface functionalization and may be as simple as oxidizing a metal surface to render it hydrophilic and change the surface energy so that polar molecules are spontaneously adsorbed to the surface. Many solids have the property of adsorbing large quantities of gases and solutes from liquid solutions. This process is generally very specific both with respect to the adsorbent and the material adsorbed and driven largely by thermodynamic considerations. Adsorption is usually an exothermic process and can be divided into two kinds: chemisorption (chemical adsorption) and physisorption (physical adsorption). In the chemisorption process, bonds are broken in the adsorbate molecules and new covalent bonds are formed between the adsorbent and the adsorbate until a complete monolayer has been irreversibly established. The resulting substrateadsorbate bond strengths range from 200 to 500 kJmol⁻¹. If adsorption is nonspecific and if only small amounts of heat are liberated, comparable to the heat of vaporization of the adsorbed material, the process is physisorption. The interaction between the adsorbent and adsorbate is reversible and much weaker (≈ 20 kJmol⁻¹) in a physisorbed film compared to a chemisorbed film. It should be noted that although physisorption is typically nonspecific, thermodynamic considerations remain very important for physisorption processes. Chemisorption has a shorter bond length and deeper potential well compared to physisorption. Moreover, the chemisorption interaction is repulsive at larger distances than bond length. This results in the physisorbed state being a precursor to the chemisorbed state. The adsorption capacity of solid surfaces is determined from measurements of the mass (or moles) of material adsorbed and the area available. for adsorption per unit mass of adsorbent. Usually the amount of solute adsorbed from solution per unit mass of adsorbent depends on the solute bulk concentration up to its saturation point.

4.2.1 Absorption Isotherms

An adsorption isotherm is a mathematical relationship between surface coverage (i.e., the fraction of the adsorbent surface covered by the adsorbate) versus the bulk concentration of the adsorbate. The “isotherm” term means that these measurements

are carried out at constant temperature. If the bulk phase is a gas, then the adsorption isotherm can be represented by a plot of surface coverage as a function of gas pressure at a constant temperature. Adsorption isotherms allow us to determine some important characteristics of the adsorption process such as equilibrium constants, the number of adsorption sites available for adsorption on the substrate, and the enthalpy of adsorption. The Langmuir adsorption isotherm, presented by Langmuir in 1918, is the simplest adsorption isotherm. The Langmuir adsorption isotherm assumes that there are a finite number of identical adsorption sites on the solid substrate and that each site is taken up by a single adsorbate molecule. During the adsorption processes, these sites are taken up until a point of saturation is reached in which all sites have been taken up by adsorbate molecules. This point represents complete monolayer coverage, at which further adsorption ceases. Furthermore, the Langmuir adsorption isotherm assumes that there are no interactions between the adsorbate molecules during the adsorption process and that the enthalpy of adsorption is independent of surface coverage. This is in contrast to cooperative adsorption, in which the formation of the adsorbed layer promotes the adsorption process further and can result in a multilayer. The Langmuir adsorption can be quantified as

$$\frac{1}{V} = \frac{1}{V_m} \left(\frac{kT}{KP} + 1 \right)$$

where V is the volume of gas adsorbed to the surface, V_m is the volume corresponding to monolayer coverage, K is the equilibrium constant of the reaction and P is the pressure of the gas. The Langmuir isotherm makes a number of assumptions that may not apply to all adsorbates and adsorbents. For instance, strong intermolecular interactions may cause deviations from Langmuir adsorption behavior. Many systems display multilayer adsorption. The Brunauer Emmett Teller, or BET, isotherm is useful for modeling such behavior. The key assumptions made in the BET isotherms are that physisorption on a solid is infinite, that there are no interlayer interactions in the multilayer film, and that each layer can be described by the Langmuir model. The BET isotherm takes the form shown as

$$\frac{V_m}{V} = \frac{cz}{(1-z)[1-(1-c)z]}$$

The term $z = P/P^*$, where P^* is the vapor pressure above the adsorbate before any adsorption occurs. The constant c is related to the enthalpy of adsorption of the first layer (ΔH_1) and the enthalpy of vaporization of the subsequent layers (ΔH_{vap})

$$c = \exp\left(\frac{\Delta H_1 - \Delta H_{\text{vap}}}{RT}\right)$$

4.3 Surfactant Chemistry

Surfactants describe a class of molecules that have a tendency to adsorb to surfaces and interfaces and lower the interfacial tension. Surfactants are amphiphilic, which means that one part of the molecule is soluble in a specified fluid (the lyophilic part) and the other part of the molecule is insoluble (the lyophobic part). If the fluid is water, then the soluble part is called the hydrophilic part, and the insoluble part is the hydrophobic part. Thus, the structure of a surfactant has a region that is largely nonpolar, typically hydrocarbon or fluorocarbon in nature, and another region that is polar, charged, and interacts strongly with water. These two regions are commonly referred to as the hydrophobic tail (or chain) and the hydrophilic head group, respectively. The hydrophobic region is insoluble and the surfactant molecules are forced to accumulate on the surface and expose these nonpolar chains away from the water and toward the air. The number density of the molecules at the surface increases with bulk concentration. As with other adsorbates on surfaces, each surfactant has a concentration for which no more surfactant molecules can pack at the interface and a saturated monolayer is formed. The packing density of surfactant molecules within the monolayer will depend on the intermolecular interactions between neighboring head groups and the hydrophobic interactions between the tail groups. The formation of the monolayer represents a thermodynamically favorable situation: polar head groups are buried in the aqueous phase and the hydrophobic tails are avoiding contact with water. This scenario explains why surfactants lower the surface tension of the air–water interface. It is easy to see that surface tension decreases as the surfactant concentration increases, but then levels off to a constant value when a saturated monolayer is formed.

4.3.1 Micelle and microemulsion formation

After increasing the surfactant concentration beyond the saturation point, the surfactant molecules start aggregation in bulk to form nanostructures known as micelles. The concentration at which a full monolayer is present at the interface and micelles begin to form in the bulk solution is known as the critical micelle concentration, or CMC. The process of micellization is in some ways similar to precipitation, but the precipitate itself has a very narrow size distribution and is stable and soluble in water. This property is because the micelle structure is such that the hydrophobic chains are aggregated in the core while the polar head groups form the exterior part of the structure. The delicate balance between inter-head group interactions and the geometry of the surfactant molecule result in a micelle with a particular shape, size, and aggregation number. The CMC of a particular surfactant solution is very sensitive to impurities and other physical conditions. The

addition of salt decreases the CMC of ionic surfactant solutions because the added ions screen the charged head groups of the surfactant, thus making it easier to form micelles. As the chain length of the surfactant increases, the CMC decreases due to the reduction in solubility of the surfactant. In a nonpolar solvent, surfactant molecules can self-assemble to form “reverse micelles.” In this situation, the molecules are aggregated in such a way that the hydrophobic moieties form the exterior of the micelle and the polar regions of molecules form the core of the micelle. Micelles in aqueous solution are capable of solubilizing small amounts of oil added to the aqueous surfactant solution above its CMC. As a result, the micelles swell with oil and increase in size. This swollen micellar phase is thermodynamically stable and is known as a microemulsion. In essence, tiny oil droplets are solubilized in water. Microemulsion phases are generally made by putting an aqueous surfactant phase in contact with an oil phase. A complex equilibrium is established between the oil phase, a monolayer at the oilwater interface, and the aqueous micellar solution. It is also possible for reverse microemulsion aggregates to be present in the oil phase.

4.3.2 Determination of Surface Excess

Surface tension measurements allow the determination of a quantity known as surface excess. The difference between the concentration of the surfactant at the interface and in a two dimensional plane in the bulk is known as the surface excess. The value tells us how much extra surfactant we have on the surface compared to a two-dimensional plane in the bulk phase. Surface excess is, to a good approximation, a measure of the concentration of molecules on the surface. For nonionic amphiphiles, the Gibbs’ adsorption equation relates surface tension γ to surface excess Γ at a given temperature T , and is given by

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d \ln C}$$

For ionic amphiphiles, a slightly different equation is used because the presence of the counterion has to be taken into account and the surface-surfactant-counterion system as a whole must be electrically neutral.

$$\Gamma = -\frac{1}{2RT} \frac{d\gamma}{d \ln C}$$

5 Inter-molecular Interactions and Self-Assembly

5.1 Inter-molecular Forces

Inter-molecular interactions play a central role in surface chemistry and the process of self-assembly, both of which affect the structure and properties of nanomaterials. Such interactions also determine the properties of surfactants, influence adsorption phenomena, and even affect interactions between molecules and electromagnetic radiation. Various inter-molecular interactions with examples for some are listed below:

- **Ion-Ion Interactions:** Formation of a charged polymer nanofilm on the surface of Si due to deprotonation of oxide nanolayer generating a negative charged surface that interacts with a polycation such as Polyethylenimine.
- **Ion-Dipole Interactions**
- **Dipole-Dipole Interactions:** Use of polar molecules as the stationary phase in column chromatography, in which the rate of flow of the mobile phase depends on the polarities of the components.
- **Interactions Involving Induced Dipoles**

In dense systems relevant to nanoscience, such as liquids, solids, and colloids, these interactions are affected by the presence of their neighbors. These complex interactions can be treated by averaging these interactions into a simple parameter. When molecules are exposed to an electric field, E , whether that field is external (e.g., a beam of light or a voltage applied to a pair of electrodes) or internal (e.g., other molecules/ions in the system), the molecules reorient and polarize to minimize their energy of interaction with the field. The dielectric constant ϵ is a dimensionless quantity that reflects the system's ability to polarize.

5.1.1 Dispersion Forces

Aside from the forces that are essentially electrostatic in nature, a force also exists between all molecules, regardless of charge or polarity, which results from the quantum mechanical correlation between electrons in neighboring molecules. This force is called the dispersion or London force. Even though a neutral, non-polar molecule has no permanent dipole moment, at any given moment the distribution of its electrons may be asymmetrical, resulting in an instantaneous or momentary dipole moment. This instantaneous dipole moment creates an electric field that perturbs the electrons of neighboring molecules, producing induced dipole moments and resulting

in attractive forces between the molecules. The approximate potential energy of interaction due to dispersion between two molecules can be calculated in terms of their electronic polarizabilities, α , and their ionization potentials I

$$U(r) = \frac{-3}{2(4\pi\epsilon_0)^2} \frac{\alpha_1\alpha_2}{r_{12}^6} \frac{I_1I_2}{I_1 + I_2}$$

The dispersion forces do not vary much between different types of molecules, and therefore aren't very influential in processes such as phase separation and self assembly in the condensed phase.

5.1.2 Total Inter-Molecular Potentials

Ultimately, the total interaction potential energy between two molecules is the sum of all the different interactions. In a very basic treatment of the interactions between two atoms or molecules, the total inter-molecular potential is often modeled by the Lennard-Jones potential, which is the sum of a soft sphere overlap repulsion term and an attractive term analogous to the London Dispersion interaction. It is given by:

$$U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]$$

where $-\epsilon$ is the minimum energy and σ is a constant parameter. A more complete total intermolecular potential would be the sum of all interaction potential energies.

5.2 Self-Assembly

Self-assembly is the process during which discrete structures such as molecules spontaneously and often reversibly organize themselves into nanomaterials. The organization of these molecular building blocks is driven by a combination of thermodynamic factors and kinetic factors. The interactions may be covalent in nature, leading to strong bonds between the molecules and resulting in an irreversibly self-assembled nanostructure. However, many self-assembly processes involve weaker non-covalent interactions, which can have significant influence on the thermodynamics and kinetics of selfassembly due to being ubiquitous and varied in type and range of interaction distances. It is important to appreciate that self-assembly can be spontaneous and directed.

5.2.1 Inter-molecular Forces and Aggregation

Supramolecular chemistry is dominated by the host of noncovalent interactions present in molecular subunits. The organization of the building blocks into more

complex structures will largely be driven by thermodynamics, whether energetics or entropy. Self-assembly in a solution will lead to a three-dimensional aggregate, but if the assembly is occurring on a surface, then a two-dimensional aggregate will form. A planar support will also impose some restrictions on the exact structure. A thermodynamically stable structure will be formed based on the conditions of the assembly process (temperature, the presence of a surface, pH, concentration, etc.). If the structure is formed in a solvent such as water, it is important to appreciate that the molecules comprising the aggregate may be in dynamic equilibrium with “free monomers” in solution. One consequence of this is that the aggregate size and shape may change with monomer concentration and other conditions such as pH, temperature, and salt concentration.

5.2.2 Hydrophobic Effect

Amphiphilic molecules, such as lipids and surfactants, have a tendency to accumulate on the surface of water. The closely packed monolayer is in dynamic equilibrium with individual molecules in the bulk aqueous phase, and so the packing density of the film increases as the concentration of molecules in the bulk phase increases. However, structural and thermodynamic constraints often limit the packing density, and a saturated monolayer is usually formed when the bulk concentration is sufficiently high. The thickness of such a film is approximately the length of the amphiphilic molecule (nanoscale). Due to this short dimension, the monomolecular film is often described as a two-dimensional nanoassembly.

When the length of the hydrophobic hydrocarbon chain of amphiphilic molecules increases, it defines the solubility and dominates the intermolecular reactions involved. If the hydrocarbon chain is long enough the molecules may drop out of solution (precipitate) and interact with themselves instead of the water molecules. The hydrophobic effect refers to the tendency of like non-polar molecules to form aggregates in water. Often when organic molecules containing large nonpolar hydrocarbon moieties are placed in water they spontaneously self-organize themselves into larger aggregates because this arrangement minimizes overall contact between the hydrocarbon part of the molecule and the water molecules of the solvent. The origin of this phase separation is primarily to maximize the water–water intermolecular interactions because the dipole–dipole interactions are stronger than the interactions between nonpolar molecules. In other words, the enthalpic force is in the water, not the nonpolar phase, meaning that this type of phase separation is enthalpically driven.

A collection of water molecules confined and “ordered” within a small region of space will have smaller entropy. compared to the same molecules “disordered” and occupying a larger volume. Since entropy changes are positive for spontaneous

processes, it is favorable for a water molecule to be “released” from a small space and enter a larger volume, especially if such a process leads to a loss of order. Water molecules, in avoiding contact with the hydrocarbon chain, form a cage around the chain. This cage contains ordered water molecules essentially immobilized around the organic molecule. When two such “hydrated” molecules approach each other and make contact, this cage is disrupted and the confined water molecules are liberated into the bulk solution. This process is accompanied by an increase in entropy of the water molecules. In a sense the van der Waals attractions between the two hydrocarbon chains is driven in part by the large increase in entropy due to the disruption of the cage. If this process occurs among many organic molecules it will lead to aggregation, typically resulting in nanoscale entities dispersed within the aqueous solution. The hydrophobic effect is paramount in many self-assembly processes, including some biological processes such as the formation of the cell membrane.

5.2.3 The Electric Double Layer

The electrostatic double layer is the term given to the diffuse layer of counter-ions in a solution that are associated with a charged surface. When a surface comes into contact with a liquid, it may become charged by adsorbing ions from solution or releasing ions into solution. Many surfaces, for instance, are pH labile, and at either high or low pH might become positively or negatively charged. The surface charges are balanced by appropriate counterions from the solution. The first region is a compact layer of counterions that is closely bound to the charged surface called the Stern or Helmholtz layer. The second region is a more diffuse and extensive layer of counterions that is in rapid equilibrium with the surrounding solution. This region is referred to as the electrical double layer or the diffuse electrical double layer. The compromise between energy minimization (due to charge neutralization) and entropy maximization (due to free movement) of the system produces the diffuse double layer with an equilibrium concentration of counterions that gradually decreases with distance away from the charged surface until it reaches a value equivalent to that of the bulk solution. The actual distribution of the counterions at equilibrium can be calculated by the Poisson–Boltzmann equation

$$\frac{d^2\Psi}{dx^2} = \left(\frac{e}{\varepsilon\varepsilon_0}\right)\sum_i z_i \rho_{i0} \exp(-z_i e\Psi(x)/kT)$$

where z_i is the valency of the i th electrolyte and $\Psi(x)$ is the electrostatic potential at a distance x away from the surface. ρ_{i0} is the number density of the i th electrolyte at

that same distance x . For $ze\Psi(x)/kT \ll 1$ then the equation reduces to

$$\frac{d^2\Psi}{dx^2} = \kappa^2\Psi(x)$$

where

$$\kappa = \left(\frac{\sum_i \rho_{i0} z_i^2 e^2}{\varepsilon \varepsilon_0 kT} \right)^{1/2}$$

of which the solution is

$$\Psi(x) = \Psi_0 e^{-\kappa x}$$

where Ψ_0 is surface potential. The characteristic length $1/\kappa$, also known as the Debye length can be used as a rough approximation for the thickness of the double layer. When a charge is within the Debye length it experiences the effect of the charged surface. Beyond the Debye length screening effect of the counterions is much more significant. The Debye length is independent of the properties of the surface itself—that is to say for a given liquid at a certain temperature it depends only on the concentrations and valencies of ions in the bulk solution, not on the surface charge or surface potential. When packing of aggregates is dense enough, the electronic characteristics of the material may change due to electron coupling across monomers. For example, molecular building blocks may result in a nanostructure in which the electrons are delocalized over the entire aggregate. This will change the material's optical and electronic properties, which will be determined by the shape and size of the aggregate.

6 Quantum Effects at the Nanoscale

At the nanoscale classical physics models aren't able to accurately represent individual particles, so there is a need to take into account quantum mechanical effects as well. Quantum confinement at the nanoscale leads to size dependant discretisation of accessible energy levels which affects the electronic and optical properties of nanomaterials. Such properties can be explained using quantum mechanical models such as particle in a box, rigid rotor, harmonic oscillator, etc. For example, quantum dots, which can be explained by the particle in a box model, (in which energy levels are inversely proportional to L^2) vary their colours with change in size as the energy, and by extension, wavelength of electronic transitions is size dependant.

6.1 Density of States

The density of states (DOS) is essentially the number of different states at a particular energy level that electrons are allowed to occupy, i.e. the number of electron states per unit volume per unit energy. Atoms have their well known atomic orbitals. Depending on the extent of overlap in a solid they remain mostly unperturbed, as in noble gases, or they combine to extended band structures, as in metals or semiconductors. Each of N atoms contributes with its atomic states to a band so that, although the width of a band increases slightly when more atoms are added, the density of states (*DOS*) within a band is basically proportional to the number of atoms of an ensemble with an extended band-like state. The band width amounts typically to a few eV. Thus the *DOS* is higher for larger clusters and smaller for nanoparticles. As the size of the particle is reduced, it loses the band like characteristics and exhibits discrete energy states. This leads to interesting optoelectronic properties.

6.2 Pseudo Atoms

Because of the quantised states of electrons and holes nanocrystallites are often called quantum dots, pseudo-atoms or superatoms. Experimental and theoretical support for the pseudo-atom character of small metal clusters comes from properties such as ionisation potentials and electron affinities which reveal shell structures akin to those of conventional elements. Pseudo-atoms can even be regarded as new elements which can be combined with others, leading to a completely new chemistry.

7 Spectroscopic Characterisation Techniques

Spectroscopy is the study of the ways in which electromagnetic radiation interacts with matter. Spectroscopy is an invaluable field of chemical analysis, and different spectroscopic methods are able to determine identity, concentration, and structural information of chemical compounds, among other useful information.

7.1 Absorption and Emission

Molecules exist in only a finite number of discrete states which are the sum of several quantized aspects of the molecule such as the energies of its electrons around their respective nuclei, the interatomic vibrations that exist in the molecule, and the rotations of the molecule around its center of mass. Molecules can absorb/emit photons corresponding to transitions between these states whose energy difference must be $\Delta E = h\nu$.

When electromagnetic radiation is incident on a substance its velocity varies due to interaction of electric field with permanent and induced dipoles within the substance. However when the frequency of the EM wave matches the energy required for a transition, then it might be absorbed by the molecule. Both these behaviors are encompassed by the complex refractive index $\tilde{n} = n + ik$ where k is called extinction index and represents absorption. The nature of the frequencies at which a molecule or substance absorbs the incoming radiation and the amount of radiation absorbed at those frequencies provides valuable information about that molecule, such as the type and strength of different bonds that exist in the molecule. While all optical transitions follow similar rules, different types of transitions can be used to provide complementary information (e.g., geometry and concentration).

For example, absorption of light in the ultraviolet and visible region of the electromagnetic spectrum typically causes transitions between electronic energy states of a molecule. Alternatively, absorbed infrared radiation causes a transition between vibrational states of the molecule.

Apart from the energy of the EM wave exactly matching the transition energy of the atom, the transition must conserve spin and angular momentum and must involve a shift in the charge distribution. The last criterion will be elaborated in the following section.

7.1.1 Transition Dipole Moment

The interaction energy of a dipole having moment $\mu = \sum_j q_j r_j$ with an electric field ϵ is

$$E = -\mu \cdot \epsilon$$

According to the the postulates of Quantum Mechanics, the expectation value of the interaction energy

$$\langle E \rangle = \langle \psi | -\hat{\mu} \cdot \hat{\epsilon} | \psi \rangle$$

where $\hat{\mu}$ and $\hat{\epsilon}$ are the quantum mechanical operators that correspond to their classical counterparts μ and ϵ and ψ is the wavefunction of the molecule. For a transition from an initial state ψ_i to a final state ψ_f , the expectation value of the interaction energy involved in the transition is given by

$$\langle E \rangle = \langle \psi_f | -\hat{\mu} \cdot \hat{\epsilon} | \psi_i \rangle$$

For molecules significantly smaller than wavelength, ϵ can be takes as constant over the molecule, which gives

$$\langle E \rangle = -\epsilon \cdot \langle \psi_f | -\hat{\mu} | \psi_i \rangle = -\epsilon \cdot \mu_T$$

where μ_T is called the transition moment integral. If $\mu_T = 0$ the transition is said to be electron-dipole forbidden, as it has a zero or weak intensity. Note that while the transition dipole moment represents an induced polarization in the molecule as it interacts with the electric field of the light and absorbs a photon, it does not imply that either the ground or excited state must have a permanent dipole moment. For a single electron in a 1D system

$$\mu_T = -e \int \psi_f^* x \psi_i dx$$

7.1.2 Oscillator Strength

Oscillator strength f gives the strength (relative probability) of a transition

$$f = \left(\frac{8\pi^2 m_e \Delta E}{3h^2 e^2} \right) \langle \mu_T | \mu_T \rangle$$

The concept of oscillator strength connects the molecular or nanoscale property of the transition dipole to the bulk optical properties of a system. Oscillator strength is related to the complex refractive index as

$$\tilde{n}(\nu)^2 = 1 + \frac{N_{\text{elec}} e^2}{4\pi^2 m_e \epsilon_0} \sum_i \left(\frac{f_i}{\nu_i^2 - \nu^2 - i\gamma\nu_i} \right)$$

Where:

- N_{elec} is the density of electrons participating in the transition
- ν_i is the frequency of the transition
- γ is a line width parameter that can represent various sources of broadening, including quantum mechanical, differences in the environment of each molecule or nanosystem, interaction with other states, etc

7.1.3 Relaxation Processes

absorption is not the only important process involving light in molecules and nanomaterials. After the molecule has absorbed the incoming radiation, it ordinarily returns to the ground state after some short amount of time due to one of several relaxation processes. Fluorescence: is the process of re-emission of light, usually of a higher wavelength. Fluorescence is typically observed in the ultraviolet–visible region of the electromagnetic spectrum. Nonradiative relaxation is the most common relaxation process, in which the excited molecule relaxes without reemitting any electromagnetic radiation. This process typically occurs in small steps by the conversion of the excited energy into kinetic energy through collisions with nearby molecules, producing heat. Phosphorescence is another relaxation process that typically occurs in the UV–vis region. It is observed when an excited electron undergoes nonradiative intersystem crossing to a lower-energy excited state in which the electron in the excited state and the remaining electron in HOMO have the same spin (a triplet state). Relaxation is much slower since the electron needs to flip its spin again to return to the ground state while obeying the Pauli exclusion principle. When the excited electron then relaxes back to a state of lower energy, a photon is produced at a longer wavelength than the absorbed light. Phosphorescence is a much rarer phenomenon than fluorescence.

7.2 UV-Visible Spectroscopy

7.2.1 Absorbance and Extinction Coefficient

Photons with wavelength in the ultraviolet and visible range (190nm to 800nm) generally correspond to electronic transitions. The region of a molecule that absorbs the light and contains the electrons that undergo the electronic transition is called the chromophore. When EM waves are incident on a solid, the intensity of the transmitted wave is less than the incident wave, the difference corresponding to the absorbed waves. Absorbance is defined as

$$A = \log\left(\frac{I_0}{I}\right) = -\log T$$

where I_0 , I and T are the original intensity, transmitted intensity and transmittance respectively. For samples with relatively low concentrations of chromophores, the absorbance of the sample can be directly related to its concentration. This relationship is known as the Beer–Lambert law and is given by

$$A = c\varepsilon l$$

where c is the concentration of the sample and l is the path length of the beam in the sample. ε is the molecular absorptivity or extinction coefficient and is proportional to the probability of the chromophore (in a particular environment) absorbing a photon for a particular molecule at a specific wavelength of light

$$\varepsilon(\lambda) = \frac{4\pi k}{\lambda c}$$

where k is the complex component of the refractive index. It is also related to oscillator strength as

$$f = 4.3 \times 10^{-9} \int \varepsilon(\nu) d\nu$$

where integral is over the width of the absorption peak. In addition to solutions, this type of spectroscopy can be used to characterise solid materials (like thin films) as well, in which case density becomes analogous to concentration.

7.2.2 Setup of UV-Vis Spectrophotometer

At a basic level, a UV–vis spectrophotometer consists of a light source, a dispersive device for selecting wavelengths of light, a sample holder, and a detector, along with several optical components. Many spectrophotometers use a double-beam configuration, in which a beam splitter allows the light beam to pass through a sample cell and a reference cell alternately throughout the measurement process. The beam is diverted into the reference cell by the splitter several times per second, and the absorbance of the reference cell is measured and automatically compared with the absorbance of the sample cell to correct for fluctuations or variations in the lamp intensity over time and improve the accuracy of the measurement. In practice, UV–vis spectrophotometer contain two different light sources, one to produce light in the UV range and one to produce visible light. Except in spectrophotometers capable of measuring multiple wavelengths simultaneously, the light sources are never run simultaneously. Instead, as the spectrophotometer measures the absorbance of a sample across a predetermined range of wavelengths, the light source switches from the visible source to the ultraviolet source. The light change is generally set to occur around 360 nm to allow for the highest light intensity at each wavelength.

7.3 Molecular Fluorescence Spectroscopy

7.3.1 Principles of Fluorescence & Fluorescence Quantum Yield

Molecules that exhibit the property of fluorescence are termed as fluorophores. For each excitation wavelength, the fluorophore has a characteristic fluorescence emission profile, which is the range and intensity of wavelengths that are produced when that excitation wavelength is used to excite the fluorophore. Alternatively, for each emission wavelength there also exists an excitation profile, which is the range of wavelengths that produce fluorescence of that emission wavelength and the intensities of emission associated with each of those excitation wavelengths. Both excitation and emission profiles give valuable information about a molecule and its surroundings. Fluorescence Quantum Yield Φ_f is the ratio of photons absorbed to photons emitted. It is usually determined by comparison with a standard material.

$$\Phi_f = \Phi_{\text{std}} \frac{g_a n_a^2}{g_{\text{std}} n_{\text{std}}^2}$$

where,

$$g = \frac{\partial I}{\partial A}$$

that is, derivative of the total fluorescence intensity of a fluorophore with respect to its absorbance of the excitation light (a measure of how the total fluorescence intensity changes with respect to absorbance). For low concentrations of the fluorophore, the relationship is usually linear (i.e., g_x is constant), so g_x can be calculated by integrating the total fluorescence spectrum for a certain excitation wavelength and then plotting integrated fluorescence intensity versus absorbance of the excitation wavelength for a number of different concentrations.

7.3.2 Setup of a Fluorometer

The fluorescence emission spectrum is gathered by shining a beam of a certain excitation wavelength on the sample and then scanning the output (emission) wavelength range with the detector while recording the intensity of fluorescence at each emission wavelength. Alternatively, the excitation spectrum can be obtained by setting the detector to monitor a specific emission wavelength and recording the intensity of fluorescence while scanning the input (excitation) wavelength range. A photomultiplier is used when emitted radiation is of a low intensity. A photomultiplier tube contains a photocathode surface that emits electrons when exposed to radiation. It also has multiple other electrodes, called dynodes. Each photoelectron that strikes a dynode causes many more electrons to be emitted. This creates an avalanche effect that results in millions of electrons for each initial

photoelectron to be collected at an anode. The resulting current is measured in terms of voltage and is related to the wavelength being scanned.

For bulk phase measurements, the solution phase sample is generally placed into a fluorescence cuvette and fluorescence measurements are made at 90° to the incident beam. For thin films, a substrate on which the thin film has been built is placed so that the incident light shines on the surface of the substrate at a large angle of incidence (i.e., more parallel to the surface) and fluorescence is detected at a different angle than the angle of reflection.

7.4 Vibrational Spectroscopy

The absorption of IR radiation corresponds to a change in energy of approximately 20 kJ/mol. This is the amount of energy required to cause covalent bonds to stretch, bend, and twist, particular combinations of which are called the vibrational modes of a molecule. Only those frequencies of IR radiation that match the natural vibrational frequencies of the covalent bonds of the molecule lead to IR absorption by the molecule. These frequencies are called vibrational modes. For vibrational transitions, the transition dipole moment is the change in the dipole moment as the atoms in the molecule vibrate. Therefore, symmetric diatomic molecules that have no dipole moment do not absorb IR radiation, since their vibration cannot produce a nonzero transition dipole. frequency of the vibrational bond is given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

where μ is the reduced mass of the system. Molecules that have more than two atoms have multiple vibrational modes. Only those frequencies are absorbed which correspond to vibrational modes that generate a dipole moment The number of vibrational modes is given by $3N - 6$ for a free, non-linear molecule in the bulk. The subtracted degrees of freedom represent rotation or translation of the molecule. Linear molecules have $3N - 5$ vibrational modes since they have one fewer rotational degree of freedom due to their symmetry. By plotting absorption or transmission versus incident IR frequency, one can map out the exact absorption frequencies for a sample containing the molecule of interest. This infrared spectrum provides a fingerprint of the molecular structure of the molecule.

7.5 Light Scattering Methods

7.5.1 Scattering Mechanism

Apart from absorption, scattering is another phenomena that occurs when EM waves interact with matter. When light passes through a solution or suspension, much of the light is transmitted directly through the solution, but some of the light is scattered in different directions. To better understand this scattering process, the process is modelled as a photon promoting the species to a short-lived, virtual excited state. The photon is then emitted in a random direction. The promotion to the virtual excited state is a result of a momentary interaction with the photon and the entire process is not quantized, unlike absorption.

7.5.2 Rayleigh and Raman Scattering

Most commonly, light is scattered elastically (or without losing or gaining any energy), in a process described as Rayleigh scattering. Rayleigh scattering is a wavelength-dependent process, meaning that some wavelengths are scattered to a greater extent than others. Rayleigh scattering is strongest for the shorter wavelengths of light that are closer in size to the dispersed phase molecules. This is the reason the sky has its blue appearance.

Raman scattering occurs when light is scattered inelastically by a molecule, that is, when the scattered light is of a higher or lower energy after it has been scattered than before. This increase or decrease in energy is generally due to a change in the vibrational energy of the molecule. According to the model of light scattering, this type of Raman scattering might occur when the molecule relaxes from the virtual excited state to a vibrational state that is higher or lower in energy than the state at which the molecule was previously. The shift in energy between vibration states directly matches that of the IR-absorption. However, instead of requiring a change in the dipole moment, Raman scattering requires a change in polarizability of the molecule. This allows vibrational frequencies that cannot be excited using infrared spectroscopy, such as the stretching of homonuclear diatomics. Paired with IR-spectroscopy Raman spectroscopy can provide detailed information about the structure of the molecule and its environment. According to naming convention, frequency shifts to a lower energy (which are more probable) are known as Stokes' shifts, whereas shifts to higher energy are called anti-stokes shifts.

A Raman spectrum that maps intensity versus frequency of the scattered light has a centralized and strong peak that represents the Rayleigh scattering of the incident light. The Rayleigh peak is symmetrically surrounded by a distribution of much smaller peaks that represent the Stokes lines at the lower frequencies and the anti-Stokes lines at the higher frequencies. This peak is often blocked from the

detector by a filter.

7.5.3 Scattering by Nanoparticles

Apart from Rayleigh and Raman scattering particles can also undergo two other types of inelastic scattering, known as Mie scattering and geometric scattering. The type of scattering depends on the size of the particle interacting with electromagnetic radiation. Consider the unitless parameter, x , defined as,

$$x = \frac{2\pi r}{\lambda}$$

where r is the radius of the particle and λ is the wavelength of the incident light. Rayleigh scattering occurs when $x \ll 1$ or when the particles are small compared to the wavelength of light. Mie scattering occurs when the particles are the same size as the wavelength of light (i.e., $x \approx 1$) and geometric scattering occurs when the particles are relatively large (i.e., $x \gg 1$).

7.5.4 Determining Particle Size using Scattering of Light

The intensity, angular distribution, and polarization of the scattered light depend on factors such as the shape and size of the particles, as well as on the interactions between them and thus provide valuable information on these properties. The measurements are generally instantaneous, noninvasive, and allow representative sampling of polydisperse samples. However, the presence of small particle impurities, particularly those that have a tendency to scatter the light, can impose serious errors in the measurement. In practice, a collimated beam of light of a given wavelength (λ) and intensity (I_0) passes through a solution containing the dispersed nanoparticles. The intensity of the scattered light is then measured as a function of the angle (ϕ) between the incident beam and the scattered beam. The variation of the refractive index of the dispersed phase (n_{dp}) and dispersed medium (n_{dm}) gives rise to the scattering. The intensity of the scattered light depends on the intensity and wavelength of the incoming light, the solution refractive index increment and the average number density of particles in the solution (N). These parameters can be determined experimentally and are used to obtain the optical constant K_0

$$K_0 = 2\pi^2 \frac{n^2}{\lambda^4 N} \left(\frac{dn}{dc} \right)^2$$

In order to understand how the intensity of light varies with the scattering angle ϕ , we need to describe the incoming unpolarized light as being composed of two mutually perpendicular polarized components. For small scattering angles $\phi \rightarrow 0$, these

components will contribute equally to the scattered intensity. At very large scattering angles, one of the two polarized components contributes to a greater degree to the scattering. In fact, when $\phi = 90^\circ$ the component polarized along the direction of the scattered beam has no contribution to the scattered intensity. The Rayleigh ratio can be obtained from these measurements and is defined as

$$R_\phi = \frac{d^2}{1 + \cos^2 \phi} \frac{I}{I_0}$$

where d is the distance between sample and detector. The difference of the Rayleigh ratio of the colloid and that of the pure solvent is given as

$$\Delta R_\phi = \frac{2\pi^2 n^2}{\lambda^4} \left(\frac{dn}{dc} \right)^2 RTc \sqrt{\frac{d\Psi}{dc}}$$

where the term $RTc \sqrt{\frac{d\Psi}{dc}}$ is known as the concentration fluctuation factor and describes the free-energy cost in creating an inhomogeneity in concentration. ΔR_ϕ is related to both the critical micelle concentration (*CMC*) of the surfactant and the concentration of the surfactant monomers (c_m).

$$\Delta R_\phi = \frac{K_0(c_m - CMC)}{10^3/M + 2B(c_m - CMC)}$$

M represents the molecular weight of the micelle and B is a constant known as the second virial coefficient. The sign of B provides information on the intermolecular interactions between micelles. A negative value indicates a net attraction between the micelles and a positive value indicates a net repulsive interaction. A value of zero indicates an “ideal” micellar solution in which there are intermicellar interactions.

7.5.5 Dynamic Light Scattering

Dynamic light scattering (DLS), also known as photon correlation spectroscopy, is a method used to determine the size distribution of particles in a solution. This is a powerful technique that can accurately report the sizes of particles present across several orders of magnitude. Furthermore, measurements are typically easy to make. DLS works by shining a laser at a sample solution and observing the scattered light. If the particles in the solution are small compared to the wavelength of the light ($x < 10$) then this phenomenon will proceed primarily through Rayleigh scattering. Scattered light is observed in a distribution centered on the expected wavelength. The reason for this is that the particles in solution are undergoing Brownian motion which causes red/blue shift because of the Doppler Effect. The total observed intensity also fluctuates in time. This is because Brownian motion causes the distance

between any two adjacent atoms to vary in time. The light emitted from these atoms experiences interference; the distance between the atoms determines whether this interference is constructive or destructive.

Successive measurements are taken and correlation of intensity is measured, which gives information on the rate of diffusion of a particle. The quicker the correlation decreases, faster the movement of the particle. The hydrodynamic radius of a particle can be obtained from its diffusion coefficient, and thus, from dynamic light scattering data via rearrangement of the Stokes–Einstein equation:

$$r_H = \frac{k_B T}{6\pi\eta D}$$

. It must be noted that apart from size of the particle, some other factors also affect diffusion such as extent of hydration, ionic strength of the solution, surface morphology and geometry of the particle. One important limitation to DLS is that the signal intensity received from a given particle is proportional to the sixth power of the particle's diameter. Thus, if one has a solution containing a 1:1 mixture by molar concentration of 10-nm particles and 100-nm particles, the peak area corresponding to the larger particles will be a million-fold larger than that for the smaller particles despite the solution containing an equal number of each.

7.6 X-Ray Spectroscopy

7.6.1 Absorption and Fluorescence of X-Rays

In the x-ray region of light, enough energy is available to ionize the molecules that the photons interact with. When x-ray energy corresponding to the binding energy of a core (nonvalence) electron is absorbed, the core electron is ejected from the atom. This results in an excited ion. There is a higher probability of this happening when an x-ray beam with energy equal to the binding energy of the core electron is used. The excited ion, which is a result of the x-rays' ejecting of a core electron, will fluoresce through transitions of electrons in higher energy levels to the vacancy left by the ejected core electron. These transitions allow the excited ion to return to its more stable ground state. This fluorescence is measurable and is often used in concert with nanoscience techniques such as fluorescence recovery after photobleaching (FRAP), fluorescence resonant energy transfer (FRET), and fluorescence interference contrast microscopy (FLIC).

7.6.2 X-Ray Diffraction

When x-rays pass through matter, the radiation interacts with electrons in the matter in such a way that the path of the x-rays can be altered. This scattering effect

of matter on x-rays is known as diffraction. In a crystal or any ordered sample, the x-rays scatter in ways that distinct interference patterns, which gives information about the crystal structure as well as the spacing between lattice points of the crystal. Bragg's Law gives the condition for constructive interference

$$2d \sin \theta = n\lambda$$

where n is an integer, d is the lattice spacing and θ is the angle of incidence between the X-Ray beam and the plane of the atom layer.

8 Nanomaterial Study: Graphene and its Applications

In this section, the scope of the study is narrowed down to graphene and its applications, especially in energy storage devices. Graphene is considered as part of the advanced type of carbon nanomaterials. It is two-dimension solitary sheet of carbon atoms. These atoms are packed in an hexagon network. It has outstanding properties in terms of high electrical conductivity, mechanical stability, thermal conductivity, and solar radiation absorptivity. Graphene demonstrates outstanding performance in several applications such as catalysis, catalyst support, CO₂ capture, and other energy conversion and energy storage devices. The atomic structure for this material can serve as the platform for other materials made up of carbon. The layer can also be bent into fullness, nanotubes and further stacked into graphite. The electronic characteristics of graphene is also largely influenced by 2pz orbitals present π symmetry orientation. Under ambient conditions, solitary layer graphene's thermal conductivity occurs as a result of acoustic phonons. This thermal conductivity occurs because there is no crystal defect. In terms of mechanical characteristics, they are considered as a material with high strength. Their yield strength is 42 N/m with a mechanical strain of approximately 25%.

8.1 Synthesis of Graphene

The earliest type of graphene around a decade ago came in the flakes via mechanical exfoliation of graphite. Graphene produced via this techniques is of higher quality but there are challenges relating to the mass production because a fabrication method is needed for the breaking down of wafer scale graphene. Mechanical exfoliation, chemical exfoliation, chemical synthesis, as well as thermal chemical vapour deposition (CVD) remain some of these techniques used. There are other methods like unzipping nanotubes as well as microwave synthesis. Synthesis of graphene chemically also include breakdown of graphite oxide, diffusion in a solution and as well as the application of hydrazine.

8.1.1 Mechanical Exfoliation

This is unconventional way for extraction of graphene flakes in single layers on substrates. This is one of the earliest means of graphene synthetization. This method is a top down techniques in nanotechnology where there is the creation of transverse stress. Graphene is also manufactured via the process of separating graphite derivatives. An external force of approximately 300 nN/ μm^2 is needed for splitting of one single – atomic layer from a graphitic structure. Different thickness of graphene

are also manufactured by mechanical exfoliation as well as removing layers from graphite like the highly ordered pyrolytic graphite (HOPG). The exfoliation is carried out with the aid of different agents like tape as well as printing techniques etc. Optical microscopy is also a common means of mono layer graphene identification. The colour of graphene tend to change with respect to the thickness of the graphene. The fastest method as well as accurate approach in finding graphene thickness is using Raman spectroscopy. This same technique is used for determination of quality of the crystal.

8.1.2 Chemical Exfoliation

This technique is considered as the best approach for the graphene synthesis. Polymer composites, energy storage materials as well as paper like material have all utilized chemical method for producing graphene. Chemical exfoliation involves two main stages. The interlayer van der Waals forces is reduced for enhancing interlayer spacing. Graphene intercalated compounds (GICs) are produced via this technique. The graphene is then exfoliated via a very fast heating process. Synthetisation of graphene can also be done using polycyclic aromatic hydrocarbons. Again the application of dendriect precursor changed by cyclodehydrogenation as well as planarization can be used to produce graphene. Larger flakes are generated when polydispersed hyper branched polyphenylene are used as the precursor. Oxidative cyclodehydrogenation using FeCl_3 is another one of the processes used in graphene production. Thermal exfoliation and laser exfoliation are also techniques to produce quality graphene.

8.1.3 Graphene Oxide

A well-known method for production of graphene in larger quantities is through chemical reduction of graphite oxide. With the aid of concentrated sulfuric acid, nitric acid as well as potassium permanganate using Brodie method, Staudenmaier method or Hummers' method, graphite oxide synthesized. Graphene is also produced via sonication as well as reducing graphene oxide. This approach involves reducing agents like phenyl hydrazine and pyrrole being used. Another approached used to synthesize graphene on large scale is electrochemical reduction. The hydrophilicity of graphene oxide layers makes them very useful in comparison to graphite. The graphene oxide is first suspended in water via sonification and then deposited on to the surface via spin coating.

8.1.4 Graphene Pyrolysis

Manufacturing of graphene can also be done via chemical synthesis in the bottom up process. The process involves thermal reaction using an equimolar ratio of ethanol and sodium in an autoclave. Pyrolyzation of sodium ethoxide via sonication can be used to detach graphene smoothly. The process leads to the production of graphene which is 10 μm . The advantages of this approach is enormous. Some of these merits include low cost as well as easily fabricated for high purity. In spite of these advantages other limitations using this approach include large number of defects being produced.

8.1.5 Chemical Vapour Deposition

Chemical vapour deposition (CVD) is a coating process that uses thermally induced chemical reactions at the surface of a heated substrate, with reagents supplied in gaseous form. Substrate is first diffused onto a thermally disintegrated precursor at elevated temperatures. The deposition is done on a thin film, crystalline, solid, liquid or gaseous precursors. This process is usually carried out on metals such as Cu, Ni, Pd, Ru, and Ir with primary reagents like methane.

8.2 Applications of Graphene in Energy Storage

8.2.1 Fuel Cells

Fuel cells are devices that used for the direct conversion of the chemical energy of the fuel into electricity with high efficiency and exhibited promising results in different applications. Graphene is extensively used in fuel cells mainly for support material of the anode catalyst, support, as well as even replace the cathode catalyst, composite and standalone electrolyte membrane. The support for catalyst on the membrane for fuel cells especially Proton Exchange Membrane fuel cells are usually made from graphene because of their conductivity, area of the surface being high and adhesion to particles of the catalyst. It is ideal for decreasing the loading of the catalyst or even replacing the Pt with non-platinum catalysts. Apart from this, graphene is considered as a promising material for the reinforcing and improving the electrical conductivity, mechanical, and thermal stabilities of the bipolar plates.

8.2.2 Dye Sensitized Solar Cells

Dye sensitized solar cells are formed from three compositions namely, dye adsorbed TiO_2 photo anode, counter electrode as well as iodide electrolyte. The iodide can undergoes oxidation into triiodide under light beam on TiO_2 photo anode. This

results in the release of an electron into TiO_2 . There is movement of the electron via the external circuit to the counter electrode where it meets the triiodide hence reducing the triiodide to iodide. To speed up the process, platinum catalyst is required. It is considered that graphene can replace such expensive platinum catalyst with accepted performance and stability. Graphene was found to improve the efficiency and stability of the DSSCs through application at photoanode, electrolyte and the counter electrode. Graphene has high thermal stability, low impedance level, high transparency, and high-temperature carrier mobility and hence is used as transparent conductors, electron promotor in the semiconductor layer, and as an additive in dye sensitizers.

8.2.3 Batteries

Anodic material ideal for lithium ion batteries are made up of graphitic carbon. Graphite carbon having high crystallinity as well as arrangement of the graphene layers leads to LiC_6 being formed and this is the highest intercalation state of the battery. There is a transfer of electrons between the Li and Carbon, which are stored between two sheets. However, Graphitic material possesses long-range crystal order which creates large diffusion distances. Reduced graphene oxide is therefore the best alternative, having high charge capacity. However, graphene has a lower efficiency, which remains a major setback for the material.

Li air batteries are capable of storing more energy compared to existing lithium ion batteries. They come in prototypes made up of Li anode, membrane as well as cathodic region made up of a porous electrode. Main issue with lithium air battery is noticeable at the cathodic region. During operation, the Li reduces O_2 forming lithium oxide. This serves as a blockage on the electrolyte as well as flow path of the oxygen hence reducing the lifespan. Aggregation of the carbon as well as the binder particles being tight also leads to low O_2 diffusion rates hence affecting the rate performance. Graphene made up of high surface area coupled with open pore structure. is therefore viable to mitigate these challenges. Their strong conduction can ensure that the porous electrode is properly utilized.

8.2.4 Supercapacitors

The future of electrochemical device which is double layered is guaranteed due to the advancement in graphene. Several research work has been conducted using graphene and the capacitance recorded between 100 and 200 F/g. Investigations conducted also show that an assembly of graphene into supercapacitor is able to improve electrode surface area of graphene and also enhance network conductivity. These phenomenon leads to large macropore channels being created and this supports ionic

transport via the electrolyte. This therefore shows that freestanding network of graphene is capable of reducing inactive electrode mass originated from polymer binders as well as additives and the current collectors. Different graphene-based electrodes with different graphene structures such as zero-dimension (free-standing particles or dots), one dimension (fiber and yarn types), two dimensions (graphenes and graphene-based films), and three dimensions (graphene foams, aerogels, and sponges) used for super capacitors.

8.3 Other Applications of Graphene

8.3.1 Composite Materials

Graphene are used as functional materials in composites and this tend to improve the characteristics as well as the performance of the composite. Graphene having good elasticity, strength and porosity have positive effect on the composites when combined together. The strength of some graphene increases under compression. These types of graphene shows strong compression under crosslinked conditions. The spongy structure in these graphene makes them ideal for reinforcement of polymer matrices. It implies that the matrices for graphene provides high strength, increase hydrophobicity as well as high conductivity.

8.3.2 Superhydrophobicity

Sheets of graphene are hydrophobic in nature. Production of superhydrophobic surface via the application of graphene is one of the latest technological mile stone chalked in recent times. This is executed via combining of tunable laplace(excess pressure inside drop) pressure because of its pore size being controlled. The hydrophobicity of graphene can be increased via an increase in roughness of the surface. Graphene has high porosity as well as surface roughness hence it is possible for them to exhibit super hydrophobic characteristics. This rough surface causes an increase in laplace pressure and when the surface energy is low

8.3.3 Electrochemical Sensors

The advantages of electrochemical sensors are enormous compared to biosensor transducer due to the fact that they are able to sense materials without destroying the surrounding systems. Effective detection requires that the distance between the redox centres as well as the electrode surface reduced to the barest minimum. This process is usually carried out through the addition of nanoparticles, carbon nanotubes or nanowires/fibers. Graphene is very good in terms of electron transfer characteristics as well as excellent catalytic activities for the detection of many molecular analytes.

Detection of trace targets is achievable using graphene exhibiting good conductivity as well as the surface area being high. There is increase in analyte transport because of the large pores hence supporting detection of binding targets. When graphene is used in direct sensing systems, they are able to detect useful biological moieties at lower concentrations. It is also biocompatible with no toxicity hence good for biomedical purposes. The recent development in this field has immensely contributed to direct electron transfer sensors. The novel sensors have long term stability as well as high sensitivity detection [126]. An electrode surface being two dimensional such as that of metals as well as glassy carbon electrodes have always been a challenge for electrochemical electrodes. Graphene can be used to mitigate these challenges.

8.3.4 Absorbers

3 dimensional graphene shows high surface area. Its characteristics make them ideal for absorption events. Graphene has good in take for organic liquids in comparison to other materials and also advantageous in terms of reusability. Again graphene sheets have proven to be able to absorb some gases at lower concentrations. The functional group of graphene is also capable of reducing gas exposure for trapping as well as converting unwanted gases even in that industry.

Graphene oxide due to their functionality can serve as platform for reduction events. These characteristics results in physical as well as resistive detection of the gases.

This is very predominant especially when graphene oxide is used to catalyze the oxidation of SO_2 to SO_3 absorbed at room temperature. The brown graphene oxide becomes black during this process. The SO_3 that was trapped is normally transformed back into sulfuric acid when exposed to water. This allows easy filtration of the reduced graphene oxide impurities. The process aided visual detection coupled storing any unwanted industrial gas.

Expanded graphite is the best alternative for lower cost oil removal due to it having higher loading of more than 83 times it's original weight. Research conducted shows that 70% of the oil collected is capable of being removed via vacuum filtration. In spite of these merits, the particulates does not show the organic solvents being absorbed in larger quantities. Again these materials can only be recycled just a few times. The future of oil spill clean-up is largely dependent on effectively as well as reversibly removing both organic solvents as well as oil spill contaminates. Graphene will therefore contribute significantly in this regard. Investigations have been conducted in the application of graphene as absorbers for many oils, alkanes, alcohols as well as organic solvents

8.3.5 Thermal Applications of Graphene

Graphene is also good in terms of thermal management of different energy storage/conversion devices. During such heat management applications, a high thermal conductive fluid plays important role. It is reported that the mixing of the fluid such as water with few fraction of nanoparticles such as graphene would enhance the thermal capabilities of the base fluid.

9 Conclusion

The field of nanomaterials opens a whole new world of possibilities in various areas. The ability to tune properties of nanostructures by varying different parameters adds a new dimension to our current technology. It is a field in research that is rapidly growing and will very likely see major developments in the coming years. This report offered an introductory study of the field by analysing the thermodynamics, kinetics and transport of the nano-scale and how they differ from the bulk scale. The mechanisms of the self-assembly of nanomaterials were touched upon to give an insight into synthesis of nanomaterials. Quantum effects were also briefly discussed. Spectroscopic techniques for bulk characterisation were also introduced. Lastly, synthesis and applications of graphene, especially in energy storage devices were elaborated on, in order to give the reader an idea of real-world applications of nanomaterials and current research.

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