South Valley University

Faculty of Science

Chemistry department

Chemistry and nanotechnology

for

2nd year students

Biochemistry Group

2022/2023

Chemistry and nanotechnology

Nanotechnology has become one of the most interesting fields of research and as a high-technology, it has attracted intensive interest among researchers and also induced massive investments from the industry and research foundations around the world and as a result of that, the applications of nanoscience covering many fields like chemistry, physics engineering, biology and the related areas.

Nanotechnology is basically a general purpose technology and this makes it so attractive. This means that it may has a direct significant impact on different industries and products for many applications became possible using nanotechnology. These products certainly can be more efficient, smarter, better built and longer lasting compared to conventional products.

By using nanotechnology and utilizing the bottom-up self-assembly approach processes, the atoms and molecules can be integrated to construct devices and circuits which are significantly different from their counterparts related to the traditional top-down approach of fabrication strategy. Moreover, during devices fabrication, much less waste is produced and extremely high energy efficiency can be achieved by the bottom-up self-assembly approach processes.

As it is known, when the dimensions of some material particles are reduced to the nanoscale, and below a critical value, the properties of these materials change dramatically. The unique properties furnished by the materials due to the careful manipulation and production of materials at this level of dimensions enables the synthesis of many products. These products have higher performance compared to the conventional ones.

As was mentioned previously, this area of research and technology covers many research fields and a very wide range of applications. Therefore, cooperation of researchers from different fields is important. This is because of that the level of fundamental knowledge and understanding of the many phenomena associated with the reduction of materials size to the nanolevel need to be vast and profound and covering a number of basic science branches.

In other words, because most of the applications related to nanotechnology are complementary in nature, it is required that one has a suitable basic scientific background in different areas of science beside a large practical experience. This requirement is basically important to understand how the characteristics of matter change when one of the dimensions of its particles is changed from the bulk size to the nanoscale (1 – 100 nm) and also the impact of that on the applications of these nanoparticles. It is important to notice that these changes in properties accompanying particle size reduction are most significant when the length of the material particle becomes comparable to the critical length associated with a certain phenomenon.

In this context, the basis of quantum mechanics, electron microscopy, interaction of the different types of electromagnetic radiation with matter including ultraviolet and x-rays spectroscopy, surface chemistry and other branches of chemistry like the basics of analytical and physical chemistry is important for one to synthesize, characterize and manipulate matter on the nanoscale. Moreover, the fundamental knowledge of biology is not only required because nanosize species exists in biological systems and one can learn much from biology about nanscience, but also due to safety considerations. One should be aware of the possible adverse effects of nanomaterials on health.

The term nanotechnology is modern; however, nanosize materials existed with the existence of life. A phenomenon like the change of the color of elements when the dimensions of their particles change was observed in the past and scientists tried to understand and explain them. The development of science on the theoretical and practical levels and the inventions of advanced tools and instruments enabled the understanding of the nature and characteristics of materials on the bulk and nanosize levels and now such phenomena is relatively easy to understand and explain.

The appearance of nanoscience followed the famous lecture by Richard Feynman (there is a plenty of room at the bottom). However, the field of colloids (a colloidal system is a biphasic one consists of a dispersion medium and a dispersed phase; the particles sizes of which are in the range of 10-1000 Angstrom) was developed far before the development of the modern term of nanotechnolgy.

Colloids

Soluble substances were classified as colloids and crystalloids by Thomas Graham. This classification was based on the ability of the solutions to diffuse across vegetable or animal membranes. Crystalloid solutions were able to pass across such membranes but colloid solutions weren’t. However, later, it was recognized that by using suitable methods and conditions, any substance can be prepared in the colloidal conditions. Particle sizes in colloidal solutions are between those of true solutions (less than about 10 Angstrom) and those of coarse suspensions (more than about 1000 Angstrom, 1 nm = 10 Angstrom). Particles in a colloidal solution therefore cannot be seen by the ordinary microscope (compare particle size in a colloidal solution with the wavelength of visible light). However, colloidal particles scatter light. The halos formed around them when illuminated by a converging beam of light (in the ultra-microscope) can be seen. Colloidal particles therefore can be seen under the ultra-microscope which uses an intense converging beam of light as hallows in a dark background. However, the photographs of the colloidal particles can be obtained by using the electron microscope which uses a beam of electrons of very short wavelength ($\lambda=h/mv$).

Colloidal solutions are heterogeneous systems. Therefore, different systems can be encountered due to different combination of phases. However, because two gases cannot form a heterogeneous system, due to the high diffusion rates, a system in which a gas is dispersed in a gas cannot exist.

A sol is a heterogeneous colloidal system in which a solid, having particles in the range 1-100 nm, is dispersed in a liquid. Sols formed by dispersing a solid in water, as the dispersion medium, are called hydrosols. Hydrophilic sols are formed when substances directly give sols with water. Generally, these are reversible sols meaning when precipitated, (coagulated) they are directly reconverted to the colloidal state. Hydrophobic sols, on the other hand, are formed when the substances to be transformed to the colloidal sate do not directly give sols with water. They need some more complicated procedures to reform. These are irreversible sols and therefore, when precipitated they cannot directly be reconverted to the colloidal state.

Preparation of colloidal solutions

A colloidal solution can be prepared either by breaking up a substance (existing originally in its bulk form) to get it dispersed in the dispersion medium with its particles in the range of colloidal by allowing ions or molecules of a substance to form larger particles having their dimensions in the colloidal range. These two approaches may be referred to as the dispersion methods and the condensation methods, respectively, for the preparation of colloidal solutions (compare these with the top-down and bottom-up approaches of nanotechnology).

A number of methods like the mechanical dispersion, ultrasonic dispersion, electro-dispersion and peptization can be used to reduce the dimensions of the particles of a substance to the dimensions of the particles in the colloidal state (1-100 nm). On the other hand, excessive cooling, lowering the solubility (by exchanging of the solvent), passing of a vapor of an element into a liquid and the chemical action belong to the second approach.

Dispersion methods

Mechanical dispersion

In mechanical dispersion, the substance is grounded, shaken with the dispersion medium and then passed to the colloid mill to transform the substance to a colloid dispersion. The disc mill and the ball mill can be used for this purpose. The disc mill consists of two metal discs (nearly touching each other) rotating at a high speed in opposite directions. Particles of the coarse suspension (due to the shearing force between the two discs) yield particles having sizes in the colloidal range. The ball mill is used for preparation of colloidal solution due to the special design of its internal surface and the high speed rotation of the ball mill. A coarse suspension under these conditions is transformed into a colloidal dispersion.

Dispersion by ultrasonic vibrations

Ultrasonic vibrations can cause the transformation of a coarse suspension to the colloidal dimensions. The mercury sol in water, in the presence of a stabilizing agent like citrate, can be prepared by this method.

Electro dispersion

The Bredig's arc method is an example. It consists in striking an arc between two electrodes (immersed in the dispersion medium) of a metal. Due to the intensive heating of the arc (a metal), which is to be transformed into the colloidal state, itis vaporized at first and then immediately condensed in the cooled dispersion medium. Traces of an electrolyte (like KOH) are used to stabilize the obtained sol.

Peptization

Peptization is the converse of coagulation. Coagulation occurs when a colloidal solution is broken down due to aging or removing the charge from the surface of dispersed particles. In this case, a colloidal solution is obtained as a result of the dispersion of a coagulated sol. A freshly prepared $Fe(OH)_3$-for example-when treated with $FeCl_3$ (used as a peptizing agent) forms a sol.

Condensation methods

Excessive cooling: A colloidal solution of ice in an organic solvent can be prepared by freezing a solution of water in the organic solvent.

Chemical actions: Precipitation, oxidation, reduction, hydrolysis…etc. are examples of this approach.

Precipitation

When the solubility of the substance is small (like As_2S_3) it can be prepared by precipitation. This occurs when the activity product of the ions exceeds the solubility product of the precipitate to be formed:

$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$

Oxidation

$H_2S + O \rightarrow H_2O + S$

Reduction

$2AuCl_3 + 3SnCl_2 \rightarrow 3SnCl_4 + 2Au$

$2H_2S + SO_2 \rightarrow 2H_2O + 3S$

Hydrolysis

$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$

Properties of colloidal solutions

1- Heterogeneity: A colloidal solution is a heterogeneous system consists of the dispersion medium like water and the dispersed phase (small particles of a substance). The ultra-microscope can be used to detect particles of the colloidal solution while photograph of the particles in a colloidal solution can be obtained by using the electron microscope.

2- The large increase in surface area: The size of particles in colloidal systems is very small. As a result of the small particle size, the surface area is very high. Due to the high surface area of colloidal systems, they exhibit a large increase in the surface chemical energy, adsorption capacity and catalytic efficiency.

3- Osmotic pressure: When a true solution is transformed to a colloidal solution, the osmotic pressure of the resulting colloidal solution becomes less than that of the original true solution. This is because of that osmotic pressure depends on the number of species in the solution. The number of species is greater in the original true solution.

4- Tyndall effect: Particles of the colloidal solution scatter light. As a consequence, the path of a beam of light passing through the colloidal solution becomes illuminated and visible when observed from the side.

5- The Brownian movement: The suspended particles are in a constant zig-zag motion. This can be explained by the collision between particles of the dispersed phase with those of the dispersion medium. The Brownian movement becomes more intense when the particle size of the dispersed phase decreases.

6- Filterability: Colloidal solutions are heterogeneous systems.Thecolloidal particles can be separated mechanically as by using ultrafilters.

7- Electrical properties: Particles of colloidal solutions have a charge on them due to:

(1) The selective adsorption: When preparing a colloidal solution of (XY), the charge on (XY) depends on the adsorbed ion, whether it is X^+ or Y^-. This largely depends on which of these two ions exist in excess during preparation

(2) Self-dissociation: Soap molecules, $C_nH_{2n+1}COONa^+$, dissociate in solution to give ions. The hydrocarbon parts of these molecules have high affinity for one another and as a result they form molecular aggregates having sizes of the colloidal state.

(3) Presence of acidic or basic groups: e.g. the protein molecule, $H_2N\text{-}X\text{-}COOH$.The ionization and charge on it depend on the pH value. The molecules become positive $^+H_3N\text{-}X\text{-}COOH$ or negative $H_2N\text{-}X\text{-}COO^-$ depending on the pH value of the medium.

Isoelectric point

Because of the charge they carry, the particles of the colloidal solution move under the effect of an electric field. The protein molecules for example are positive or negative depending on the pH. By changing the pH value, the type of charge on the molecule can be changed for example from positive (+) to negative (-) and as a result, the direction of motion in the field is reversed. The isoelectric point is the pH when the protein molecule is neither negative nor positive. At this point they do not move under the effect of the electric field.

8- Cataphoresis (electrophoresis): Because colloidal particles carry a charge on them, they migrate to the electrode of the opposite charge in an electric field. Cataphoresis is thus used to determine the type of charge on the colloidal particles.

9- Electro osmosis: When the charged particles of a colloid is maintained stationary in the electric field, by using a diaphragm in a U-tube used for the experiment, the dispersion medium would move. This happens because the medium is oppositely charge due to neutrality of the system.

10- Color: The color of the colloidal solution depends on the wavelength of the scattered light. This in return is dependent on the particles sizes.

11- Coagulation: Coagulation occurs when the particles of the dispersed phase precipitate due to breaking up of a colloidal solution. This can be a result of the addition of an electrolyte to the colloidal solution. Addition of the electrolyte leads to the neutralization or the removal of the charge from the colloidal particles surface. Aging also may result in the breaking up of a colloidal solution and its coagulation.

Rydberge equation

The Rydberge equation describes the energy of the hydrogen atom. It is given in the form:$1/\lambda= R\ (1/n_1^2 - 1/n_2^2)$ where R is the Rydberge constant = $1.097\ 10^7\ m^{-1}$, λ is the wavelength of the electromagnetic radiation energy emitted when the excited electron jump back to the ground state following the excitation process and n is an integer (n_1 is always less than n_2).

Bohr equation

Bohr equation also describes the energy of the hydrogen atom. It is given in the form: $1/\lambda= R\ (1/n_1^2 - 1/n_2^2)$ with the different variables has the same meaning as mentioned in case of the Rydberge equation. However, the derivation of Bohr equation is based on the basic idea that the atom consists of a positive nucleus and an electron orbiting it. From a basic postulate that the orbital angular momentum of the electron $mvr = nh/2\pi$, Bohr could derive his equation for the hydrogen atom.

Mosely equation

Moseley equation describes the energy of the characteristic x-ray lines. Moseley equation is given as: $1/\lambda = a(Z-b)^2$ where (a) and (b) are constants and (Z) is the atomic number of the element (the characteristic x-ray line belongs to this element in the Coolidge tube used for the production of x-rays).

Comparing the Moseley and Bohr equations, and taking into consideration the fact that in Bohr equation the term $(1/n_1^2 - 1/n_2^2)$ is a constant for a certain transition leading to the appearance of a characteristic x-ray line (e.g. for transition from the second to the first level it = 1-(1/4) = 3/4, for transition from the third to the first level it = 1 – (1/9) = 8/9 … and so on), a general formula can be used to calculate the wavelength of radiation energy or characteristic x-ray line as follows: $1/\lambda = R(Z-b)^2 (1/n_1^2 - 1/n_2^2)$. The term $(Z-b)^2$inthe previous equation accounts for the shielding effect of the electrons on a part of the nucleus charge.

A particle in a box

The energy of such a system is given by the following equation: $E_n = (h^2/8mL^2)n^2$, where h is Blanks constant, m is the mass of the particle, L is the length of the distance between two walls of the box. This equation implies that the transitional motion is quantized in small dimensional space. If the dimensions of the box are in the same order of the electron orbital in the hydrogen atom, the energy calculated using the previous equation would be in the UV range. It is also known that rotations and vibrations of molecules (which include small displacements or transitional motion, in the range of a fraction of the bonds in the molecule in case of vibration) are quantized and the reason is related to the small dimensions involved in such movements.

The Schrodinger equation in the simplest form is given as: $H\psi = E\psi$ where H is known as the Hamiltonian, ψ is the wave function and E is the energy of the system (e.g. the hydrogen atom). It is used as a basis in some programs in theoretical computational chemistry. The Schrodinger equation can be solved for the hydrogen atom. This means that it can be used to describe the energy of the hydrogen atom the energy obtained agrees with that calculated from the Bohr equation, however, it takes into account the dual property of the electron. It is worth mentioning that quantum numbers are naturally obtained in the case of solving the Schrodinger equation for the hydrogen atom.

The electronic configuration of the atoms follows certain rules. These rules are all familiar to chemistry students.

The arrangement of elements in the periodic table follows taking Moseley equation as a basic property of elements.

Bonding

The different kinds of bonding; ionic, covalent, coordinate, hydrogen bonding are simple and can be discussed in the light of the electron configuration of the atoms and their position in the periodic table. Bonding in organic molecules includes sigma and pi bonding and the relative energy of the molecular orbitals are simple. The concept of HOMO and LUMO are familiar to organic chemistry students.

In solids, bonding is usually described by similar approaches like the metallic bond. It is more appropriate however to consider the concept of valence band and conduction band in solids. The energy of the gap between bands in this context determines the electrical properties of the solid. Conductors are characterized with low band gap values (in the order of less about 1 eV). Insulators have band gasps more than about 5 eV while semiconductors are in between. The properties of the band gap and type of semiconductor can be determined from the relevant E- K plots and the band gap energy can be calculated from the UV-Vis. spectra.

Quantum effects

It is important to consider the evolution of quantum confinement size effects with the development of size of particles towards the nanosize range. It is also important to realize the effects of quantum confinement on the electronic structure of semiconducting nanostructures. These quantum confinement size effects develop with synthesis of nanosize materials via two approaches: the top-down and a bottom-up approach where the confinement refers to the spatial confinement of electrons in a nanomaterial.

The significant length scale in this context is the exciton (electron hole pair) and Bohr's radius, a_o. The effect of quantum confinement accompanies the spatial extension of the excitons within semiconducting nanostructures. The cause of confinement and its impact on the electronic structure of a semiconductor nanostructure is an important aspect of nanoscience. The understanding of the electronic structure of bulk materials is also important in this respect. The bands separation significantly increases due to transformation of particle size from bulk size to nanosize. This is reflected on the UV spectra which undergo blue shift. It is worth mentioning that the confinement begins with different nanocrystal sizes for different semiconductors as a_o varies broadly within semiconductor nanomaterials and also that a_o and E_g, are interrelated. As a particle gets smaller, its surface area gets larger compared to its volume. Therefore, nanomaterials have relatively larger surface areas and surface atoms in comparison to bulk materials. The large surface area compared to volume and the quantum effects are main reasons for the unique and exceptional properties of materials at the nanolevel.

It is noteworthy that other characteristics like the strength and electrical properties of materials are also significantly modified at the nanoscale. Also, the materials become more chemically efficient at this scale as compared to those in bulk size. This can be explained by the following example. For a cube of unit dimension (I cm) the surface to volume ratio is 6. This means that a total of 6 cm^2 surfaces per unit volume are exposed for interaction with molecules around. For the higher ratios characterizing nanoparticles, higher values of surface per unit volume are exposed for interaction with the surrounding molecules. This is important in some phenomena like adsorption and the related applications like catalysis. It is also important to notice that friction and electrostatic forces also become more pronounced at the nanoscale level as will be discussed later.

Nanoparticles

An example of nanostructures is the nanoparticles (NPs). They are particles with a diameter size less than 100 nm. NPs and nanostructured materials have been a source of inspiration for a long time. The reason for this is their applications in many areas like imaging, photonics, photography, and surface analysis etc. Moreover, the optical properties of NPs also significantly different from that of bulk materials despite that they have the same chemical structure. Two groups NPs are important. These are organic NPs and inorganic NPs. A n example of the former is fullerenes while metal NPs like those of silver, gold, magnetic NPs, and semi-conductors NPs such as zinc and titanium oxide are example of the latter group. Quantum dots are nanoparticles having size less than about 10 nm.

Computational chemistry and nanoparticles

Two broad areas of computational chemistry can be considered. These areas are related to (a) molecular mechanics and (b) the electronic structure theory. The two areas of computational chemistry are concerned with the structure of molecules and their reactivity. Programs related to both of these two areas basically perform the same types of calculations like geometry optimization of particular molecular structure and the energy and related properties of these moleculesthus **(i)** they compute the energy of molecules. As a result of that the properties which are related to the energy of the molecular structure can be predicted. **(ii)** they perform geometry optimization. Geometry optimization determines the molecular structure of the lowest energy. **(iii)** they compute the vibrational frequency of molecules. Frequency calculations may permit prediction of other properties.

It is worth mentioning that frequency calculations are not possible or predictable for all computational chemistry methods.

Molecular mechanics

Computations or simulations belonging to molecular mechanics utilize the laws of physics to determine the structures and properties of molecules. There are different molecular mechanics methods. Each one is characterized by its particular force field.

A force field has: (i) a set of equations, (ii) a series of atom types and (iii) one (or more) parameter set

The set of equations define how the potential energy of a molecule varies with the locations of atoms. Atom types define the characteristics of an element in a certain chemical context. As a result of that atom types prescribe different characteristics and behavior for an element depending on its surrounding atoms. They therefore depend on hyperdization, charge and the types of the other atoms to which it is boded. The parameter sets fit the equation and the atom types sued to experimental data and define force constants. Force constants are values used in the equations to relate atomic properties to energy components and structural data (bond lengths and angles).

It is important to notice that molecular mechanical calculations make computations based on the mutual interactions among the nuclei. This means that it does not treat the electrons in the molecular systems in an explicit manner. However, through parameterization in the force fields, the electronic effects may be involved. One result of this treatment is that molecular mechanics simulations are computationally inexpensive. This and allows large systems to be handled. Molecular mechanics computations, on the other hand, have several limitations: Among these are the following:

- Molecular properties which depend on electronic details are not reproducible or practical in the methods of molecular mechanics. Therefore, molecular mechanics methods are not used to study chemical systems in which electronic effects are important i.e. systems which involve bond formation and bond breaking. This is a direct consequence of the neglect of electrons in their calculations.
- There is no force field which can be used for simulations of all molecular systems. This is because of that each force field gives satisfactory results only for a limited class of molecules. This class is related to those for which the force field was originally parameterized.

Electronic structure methods

Electronic structural methods utilize the laws of quantum mechanics as the basis of their computations. The energy (and other properties of a molecule) may be obtained by solving the Schrodinger equation: $H\psi = E\psi$ for the system.

However, it is well known that Schrodinger equation can be solved only for the hydrogen atom which is the simplest system. Therefore, the exact solutions of this equation are not possible for the more complicated systems. Electronic structural methods therefore are characterized by their many mathematical approximations to the solution of Schrodinger equation and there are two major classes of electron structure methods. These are semi-empirical methods and ab initio methods.

Semi-empirical methods

To simplify the computation, semi-empirical methods use parameters derived from experimental data. Thus, they solve an approximate form of the Schrodinger equation.

These forms depend on using appropriate parameters for the type of chemical system to be investigated. Different semi-empirical methods therefore are characterized by their different parameters sets and these semi-empirical methods are used in many programs like MOPAC and Gaussian.

It is important to notice that semi-empirical calculations are relatively inexpensive and when there are good parameters sets used, these calculations give acceptable qualitative results for molecular systems. Relatively accurate quantitative values of energies and structures for systems are also obtainable.

Ab initio methods

Ab initio methods do not use experimental parameters in their computations. The ab computations are based on the laws of quantum mechanics beside a number of physical constants. They compute solutions to the Schrodinger equation using a series of careful mathematical approximations. It is important also to notice that they are not limited to a specific class of systems but their computations give high quality quantitative results for a broad range of systems. In a few minutes, the energies and related properties for systems containing many heavy atoms can be calculated. Also, they are basically capable of performing simulations and handling any type of atoms including metalsand can investigate molecules in their excited state and in solution.

Density functional methods (DFM).

DFM is related to the electronic structure methods. They therefore are similar to the ab initio methods. It is well known that the electrons in a molecular system react to one another's motion. This means that they try to keep out of one another's way. This behavior is considered in DFM models. Therefore, DFM include the effects of electron-correlation. Methods including electron correlation can account for the instantaneous interactions of pairs of electrons with opposite spin. It is important to notice that Hartree-Fock calculation (belongs to the ab initio methods) consider this effect in an average sense where, an electron reacts to an averaged electron density. This approximation makes Hartree-Fock results to be relatively less accurate for some types of systems.

Applications

Electronic structural methods are used to investigate many chemical phenomena. Some computational chemistry programs are able to perform calculations to predict some molecules properties. Calculations can be carried out in the gas phase, in solutions, in the ground state or in the transition state. For these reasons they are considered as powerful means for exploring fields like reaction mechanism and excitations energy.

Properties that can be studied include energies and structures of molecules and transition states, molecular orbitals, bonds and energy of reactions, reactions pathway, atomic charges and electrostatic potentials, multipole moments, vibrational energies, Raman and IR spectroscopy, NMR properties, polarization and thermochemical properties.

Application related to nanoparticles

Determination of the type of atoms which constitute the building blocks of nanostructures (the chemical composition) and the way in which these atoms arrange themselves or attach one anther (in bonds and crystal structures) is important to understand the properties of nanostructures.

The chemical composition can be investigated by relevant methods like atomic absorption, atomic emission and x-rays. On the other hand, because most nanostructures are crystalline, a basic knowledge of crystallography is required. Crystal lattices can be described by assigning the positions of the atoms in a unit cell. Unit cells of different systems are characterized by some parameters, a, b, c and an angle theta. Crystal structures of samples can be determined from the XRD data. Some simple and important unit cells for nanostructures include the simple cubic lattices, the face centered cubic lattices, and body centered cubic lattices. The hexagonal close-packed structure results from stacking planner hexagonal layers in a certain manner. Stacking of these planner hexagonal structures leads to the formation of the face centered cube structure. Some nanostructures properties (and applications) depend on the type of crystal structure. The catalytic activity and the adsorption enthalpy for example depend on the surface exposed.

It is also important to notice that nanoparticles can be studied theoretically. It is known that some elements like phosphorus and sulfur in the vapor phase form clusters. Cluster of metal atoms also can be synthesized, identified and studied. Sodium clusters for example form stable structures containing 2 and 8 atoms. These are more stable than other clusters containing other number of atoms. The stability of such small atom number clusters is described by magic electron numbers. Such clusters can be considered as super atoms. The energy of such structures is described by the jellium model. The energy pattern from such model (obtained through solving the Schrodinger equation) is a one in which the following order of energy levels can be obtained: 1s 1p 1d 2s 1f 2p (compared to the energy levels for the hydrogen atom resulting from quantum calculations, 1s 2s 2p 3s 3p 4s 3d …etc). It is worth mentioning that the stability of larger clusters is determined by structural magic numbers. Nanoparticle forming a crystal having 13 atoms is an example. The next particle of the same shape (as the previous one containing 13 atoms) formed by adding another layer of atoms to that of the 13 atoms, contains 55 atoms. As was mentioned previously, the Schrodinger equation can be used for calculating the energy levels of the hydrogen atom. The energy levels of the positive charge (spherically distributed) of the nanostructure is similar to that of the hydrogen atom. However, the order of the energy levels is different. In the jellium model, the magic numbers correspond to these structures having a size in which all the energy levels are filled. Another approach that is used to investigate the structure and properties of a metal cluster is based on considering them as molecules. Molecular orbital theory, such as in the density functional theory methods mentioned previously, can be used to calculate the properties of these structures.

Nanaoelectronics

It is known that an electronic circuit incorporates many components. These components are usually present on a printed circuit board assembly (PCBA). The very large-scale integration (VLSI) technology enables adding all these components into a single chip. The purpose of this is to improve miniaturization and increase the overall performance and functionality. VLSI therefore is a process of integrating thousands of objects like transistors onto a single silicon semiconductor microchip. In other words, VLSI refers to an integrated circuit technology with numerous devices on a single chip and the remarkable growth of the electronics industry is basically due to the advances in this technology.

VLSI technology has some advantages like production of smaller size circuits, the lower cost of devices, the higher reliability of these devices, the improved performance and the fulfillment of the requirement for miniaturization. This makes VLSI a vital subject of electronics engineering and their circuits are used everywhere. One can find such in microprocessors, in chips in cell phones, personal computers, digital cameras, medical electronic devices etc.

The technology of metal oxide semiconductor (MOS) is promising for VLSI implementation with higher packing capacity and significantly lower energy consumption. The integration of carbon nanotube (CNT) fabrication with standard CMOS VLSI on a single substrate suitable for the emerging hybrid nanotechnology applications was reported. This co-integration combines the advantages of CMOS and CNTs.

Nanotechnology therefore may enable many novel devices and circuit architectures which are different from microelectronics circuits. Quantum computing is an example. Thus, it presents another technology revolution to the traditional CMOS VLSI technology. This is logically true because nanotechnology introduces many new fabrication strategies, such as the bottom-up molecular self-assembly strategy. In this context, the VLSI and nanoscience fields overlap to some extent and VLSI can be an important application in nanotechnology where nanoparticles of Si and other semiconductors are used for fabrication of IC's.

It is important to notice that VLSI industry constantly deceases the size of transistors. Therefore, larger number of them can be built into the same chip. Nanotechnology is the next step in order to maintain this trend for years to come. As a consequence of that nanotechnology has the potential to enable fabrication of many novel devices and circuit architectures which are totally different from microelectronics circuits.

Micromachining and Micro Electro-Mechanical System (MEMS)

Technologies of micromachining and micro-electromechanical system (MEMS) can be used to produce complex structures, devices and systems on the scale of micrometers. Basically, micromachining techniques are related to the integrated circuit (IC) industry and the development in fields like lithography and metal deposition methods significantly contribute to this technology.

Microsensors have smaller size, improved performance, better reliability, and lower production costs compared to other forms of sensor. They belong to the micro-electromechanical systems (MEMS) devices. As was mentioned above, MEMS is a chip-based technology. Silicon is a main material used in MEMS technology. MEMS technologies allow electronic circuits and mechanical devices to be manufactured on a silicon chip. This is similar to the process used for integrated circuits and allows the construction of items such as sensor chips with built-in electronics that are significantly small in size. MEMS therefore can be regarded as ultra-compact systems composed of micromechanical components such as sensors, actuators and electronic circuits on a silicon wafer. It uses semiconductor fabrication technologies to produce miniaturized mechanical and electromechanical elements. The size of these may be in the order of one micrometer. (MEMS) have been widely used to develop high-performance transducers. MEMS pressure sensors, MEMS angular rate sensors and MEMS magnetic field sensors are examples. The attractive features of MEMS include small size, light weight, cost effective batch fabrication, and precision control of the physical dimensions.

In this context it is important to realize that the ratio of surface area to volume of a certain component in the micro world is significantly higher than that of the component in devices of the conventional size. As was previously mentioned, some features like friction becomes very significant in this case. Also, the molecular attraction forces between the small or microscale objects exceed the mechanical restoring forces. These properties are taken into consideration during fabrication of microscale devices for various applications.

It is worth mentioning that, MEMS are not a part of nanotechnology. However, understanding their behavior can be used in nanotechnology. Therefore, while MEMS stands for micro-electromechanical system, NEMS stands for nano-electromechanical system. NEMS would be used in nanotechnology. NEMS is preferred for the high efficient applications like high frequency resonator and ultrasensitive sensors due to the most attractive features of NEMS; i.e. smaller mass, higher electrical efficiency, and higher surface area to volume ratio.

Molecular sensors

Molecular sensors are molecular or supramolecular-based systems. These are able to transform probe-analyte interactions into signals. These signals (optical or electrochemical changes) allow analyte sensing. The important components of a certain type of biosensor are (1) a bioreceptor (e.g., enzymes, antibody, microorganism, a cell); (2) a transducer of the physicochemical signal, and (3) a signal processor to interpret the data. It is worth mentioning that (i) selectivity and sensitivity are important features to take into consideration during the design and optimization of electrochemical biosensors (ii) the efficiency of a sensor surface is governed by the type of sensing surface, non-specific binding and the detection limit.

Nucleation and crystal growth

Devices performance is governed by the specific properties of its components materials. The full knowledge of structure and properties of these materials, allow tailoring new composite materials of certain desired features for the specific application. In this context single crystals of substances can be grown and they have a fundamental role in modern technology. Nucleation (the formation of a new structure) is the first stage in this process. Particle growth follows nucleation. Particle growth therefore is the process of increasing the size of a pre-existing nucleus. This means that crystals are formed through a number of stages including nucleation as the first stage. Nucleation is the initial process occurring in the formation of a crystal in a solution, a liquid, or a vapor. In this process a small number of species (ions, atoms, or molecules) arrange themselves in a certain pattern. Creation of liquid droplets in saturated vapors, formation of gas bubbles or ice in water, formation of amorphous or crystalline clusters in solids are examples.

It is important to notice that:

(i) the crystallization process occurs through certain mechanisms and as a crystal grows, preferential sites upon which other particles to be added are formed.

(ii) seed crystals can provide nucleation sites for crystal growing.

(iii) the nucleation process influences the crystal size distribution.

(iv) among the factors that influence the nucleation process (in a certain case) are the viscosity and surface tension beside the thermodynamic state variables like pressure and temperature. Nucleation rate decrease significantly as the temperature increases and low nucleation rates results in larger and more perfect crystals.

(v) at low supersaturation conditions, the rate of crystal grow is high while the rate of nucleation is lower. Under these conditions, crystals of large size result.

(vi) at high supersaturation conditions, the process of nucleation dominates the process of crystal growth and as a result smaller crystals are formed.

Mechanism and thermodynamics of crystallization

Mechanism

Crystallization mechanisms consist of nucleation, growth, and maturation of the crystals. These stages take place when there are suitable conditions for that to happen like when a solution becomes supersaturated. In such a case and at these conditions, the extra substance in the medium is converted into crystals.

As was mentioned before, the first step in the process of crystal formation includes nucleation from an unstable supersaturated solution. To obtain this state of supersaturation one can cool down the solution and in other cases some of the solvent is left to evaporate. The process of crystal growth, on the other hand, is governed by the transport and the kinetics of the crystal components (atoms, ions,..) from the surrounding environment into the crystal nuclei.

It is important to notice that perfect crystals grow slowly and they do not include defects. The rapid growth of imperfect crystals is due to that these crystals contain defects (e.g. dislocations). These defects catalyze the addition of the components particles to the growing crystalline structure.

Some points need to be considered in the process of phase transition:

- the reason for the phase transformation (from solution to solid and in case of nucleation or growth) is related to the free energy. Phase transition starts when the free energy of the initial solution phase is higher than the sum of the free energies of the final crystalline phase beside that of the final solution phase.
- The reason for phase transition also can be explained by considering the activities (or concentrations) of the species to be transformed from one phase to the other. It is known that precipitation (crystallization) starts when the activity product of the reactants exceeds the equilibrium activity product (equilibrium constant) of those reactants.
- Another point of view in some cases considers the chemical potential of the system. The driving force for crystallization sometimes is related to the change in chemical potential of the crystallizing species. The greater the chemical potential difference is, the greater is the driving force for crystallization.

Thermodynamics

Changes in thermodynamic function like enthalpy and entropy are important to be considered in these processes. For example, it is important to consider the structural water molecules during the process. These water molecules are released when the ions or molecules join a growing crystal. In other cases, water molecules are trapped during crystal formation. The release or trapping of water molecules exhibit a significant enthalpic and entropic consequences and this effect varies significantly from one system to the other.

The contribution of surface molecules to the free energy of the new phase is greater than those of the bulk molecules and this destabilizes the nucleus formed especially in the first stage where at very small size (when many of the molecules are at the surface) the nucleus is unstable. At this stage of the process, adding more molecules increases the free energy of the nucleus and under these conditions the nucleus tends to dissolve. However, at the moment the nucleus reaches a certain large volume, there is a large decrease in free energy. The surface free energy at this size is not significant and in such a case addition of a molecule to the new phase lowers the free energy.

The critical size (at which the free energy of the system is decreased or dropped) is reduced if there is a state of high supersaturation. In this case, the initial phase becomes unstable and a very small change in density for example, leads to the appearance of the new phase and the rate of generation and growth of the new phase then is limited only by the rate of transport of mass or energy.

It is important to notice that:

(i) nucleation take place as a result of a change that bring together a suitable and sufficient number of molecules to exceed the critical size.

(ii) nucleation can be controlled by adjustment of the critical size because the probability of nucleation is affected by the value of the critical size.

(iii) by varying the degree of supersaturation, the probability of nucleation can be controlled. As was mentioned before, the critical size is reduced if there is a state of high supersaturation.

(iv) the smaller the interfacial energy, the smaller is the critical size and the more likely is the process of nucleation. Therefore, foreign surfaces can be used to control nucleation. This is because of the fact that the interfacial energy between a nucleus and a solid substrate is lower than that of it in contact with a solution. In the former case, the molecules of the crystal form bonds with the substrate. These bonds are stronger than those between molecules and solvent. Stronger bonds lead to a smaller interfacial free energy.

It is important to notice that in case of using a substrate, the strength of bonding at the interface is dependent on the structure and also the chemistry of the substrate surface. As a result, when a property (like the lattice strain) is decreased due a similarity of the atomic structure of the substrate surface and a certain crystalline plane of the phase nucleating, nucleation occurs preferentially on that crystal plane. This is especially favoured when the substrate surface presents chemical functionalities which promote strong bonding to the nucleus surface formed.

Self-assembly

Biological systems give ideal examples of the phenomenon of self-assembly. In a protein, for example, the sequence of amino acids in the poly peptide chain is an example of this phenomenon. Each poly peptide chain is formed by the successive addition of many amino acids. In this process each amino acid arrives to the attachment site with a certain mechanism. When arrives, it spontaneously attaches to the growing chain to form the protein.

This process of self-assembly occurs spontaneously in other systems when there are the suitable conditions. Small molecules can organize themselves spontaneously to form well defined structures. These structures of some ordered molecules aggregations can be well defined and also significantly stable. The equilibrium state for this process is attained through reversible weak interactions and a relevant process of spontaneous replacement of improperly attached species. An example of this process of self-assembly is the spontaneous adsorption of molecules on some surfaces in a systematically and ordered fashion.

It is important to notice that self-assembled monolayers are stable and relatively easy to synthesize. These self-assembled monolayers are formed on suitable substrates surfaces like those of metals and metal oxides. For example, RS-M or RCOO-MO are obtained due to interactions between metal (M) and metal oxide (MO) surfaces with RSH and RCOOH. The first step in the process is to prepare the substrate. For example, a metal vapor on a surface of glass forms a suitable crystalline layer that is used as the substrate. Some metals form a suitable regions of a planner hexagonal close-packing atomic arrangements. The sites of adsorption of molecules to be used to form the monolayer are those between the triplets of the surface atoms. It is important to notice that the adsorption process is spontaneous and involves organization of molecules in systematic manner, resulting in a well ordered mono layer and to form and attain equilibrium, this process involves weak reversible interactions.

Supramolecular structures

Supramolecular structures are large molecules formed through bonding together a number of smaller molecules. Supramolecular chemistry has been developed significantly on the level of science and technology and it constitutes a major field in chemistry. The design of functional supramolecular devices in photoactive, electroactive, or ionoactive components is a relevant subject where the design and function of these devices can be treated at the molecular and supramolecular levels.

Supramolecular chemistry is interested in systems undergoing self-organization under the control of molecular recognition processes. The design of such systems, which are functional self-assembling and molecular information-controlled, provides an important link to nanoscience and nanotechnology. Thus, the synthesis of well-defined, functional molecular and supramolecular structures having a nonosize through the processes of self-organization may offer a very powerful compliment to nanofabrication and nanomanipulation.

It is important to notice that supramolecular chemistry is recognized as a dynamic chemistry. This is due to that the interactions connecting the molecular components of a supramolecular species are labile and these species have the ability to exchange their constituents. Thus, the continuous change in constitution (by reorganization and exchange of building blocks) is possible through the noncovalent interaction which is an important issue of supramolecular chemistry. The mechanism of such interactions is important for different applications like supramolecular catalysis.

It is important to consider the following:

(i) molecular motors are related to supramolecular chemistry. In this context the application is based on the fact that a chemical or electrochemical signal triggers a mechanical action.

(ii) supramolecular structures containing transition metals like palladium and platinum in the form of squares with high degree of symmetry are important examples. These and other structures are formed by the process of self-assembly.

(iii) dendritic molecules also can form supramolecular structures. These are formed in the branched form by the process of divergent growth. They are formed in the form of a central core plus a number of wedges. An example is the amino amine dendrimer having two wedges and the poly amino amine dendrimer (has 3 wedges). The size of these dendrimers is in the nanosize range and their structures are determined using the crystallographic data.

(iv) the individual dendritic molecules can also be linked together to form larger structures called supramolecular dendrimers formed by what is called supramolecular self-assembly.

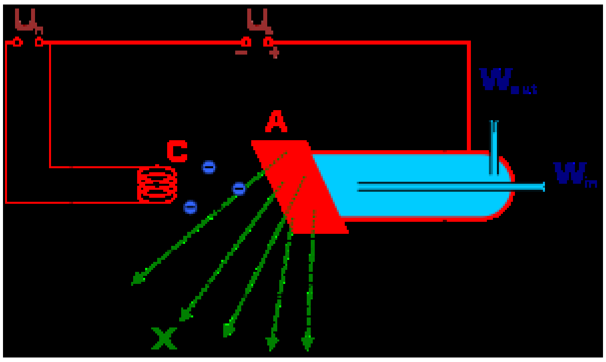
(v) an important structure that one meets in colloidal systems is the micelles. These are arrays of molecules of the colloidal dimension (or nanosize dimensions). Dendrimers have been made as unimolecular micelles. These contain hydrophobic tails that form a cluster on the inside and hydrophilic heads that point award (towards the surrounding matrix). An example is micellanoic acid dendrimer which forms a micelle containing terminal hydrophilic acid groups.

X-Rays and nanomaterials

Inner electrons (those of K and L levels) excitations and the following electron transitions are accompanied with characteristic x-ray lines emissions (K_α, K_β, ….etc.). These characteristic x-ray lines are used for elements identification. For inner electrons excitations, high- energy electrons, radioactive energy or x-rays of suitable energy can be used.

Production of x-rays

x-ray can be produced using the Coolidge tube. The tube is evacuated and contains a tungsten filament that can be heated using an electric current. The heated cathode generates electrons. These electrons are accelerated to high velocities in an electric field. The accelerated electrons strike the anode and lose their energies. About 1- 2% of their kinetic energy ($1/2mv^2$) is converted to x-rays as a result of the rapid deceleration. The remaining of the electrons energy (about 98%) is transformed to heat so, the target requires cooling (by water).



X-Ray spectra-

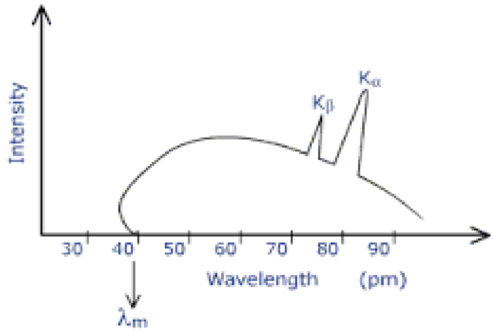
Spectra of X-rays generated using the Coolidge tube are continuous and are similar. This means that they cannot be used as a means of identification for the elements. When the accelerating voltage of the electrons is increased above a certain value (characteristic for the element) intense emission lines appear (superimposed on the continuous spectrum). These sharp emissions appear when the bombarding electrons have the sufficient kinetic energies to knock out an electron from the K or L shell of the target atoms. These x-ray lines are characteristic for the element of the anode in Coolidge tube.

Characteristic x-ray lines

- The characteristic K_α line appears when an L electron falls to fill the vacancy in the K shell while K_β is emitted when an electron from the M shell falls into the K shell. The energy of a given K or L line increases with atomic number, Z: $1/\lambda = a(Z-b)^2$ (the Moseley equation).

Spectra cut off

The sharp cut off at the short wavelength limit (corresponding to λ_{min}) of the spectrum is independent on the nature of the target but it depends on the accelerating voltage of the tube (when all the energy of acceleration (eV) is converted to an x-ray photon): $eV = 1/2mv^2 = hc/\lambda_{min}$ and therefore λ_{min} (Å) = 12396/V. Therefore it cannot be used fro elemental identification.



Analytical graph of X-rays emitted

Moseley equation

In Mosely equation ($1/\lambda = a(Z-b)^2$), a and b are constants, Z is the element atomic number. It is important to realize that as the characteristic spectral lines (K_α, K_β, ….etc) are related to the energy levels of the innermost atomic orbitals, they are independent of the physical or chemical combination in which the element is. The following relation is used to calculate the emitted characteristic radiation of elements: $1/\lambda = R(Z-b)^2 (1/n_1^2 - 1/n_2^2)$

The term $(1/n_1^2 - 1/n_2^2)$: For K_α = 1- ¼ = 3/4, for K_β=1-1/9 = 8/9. As was mentioned previously, comparison with the Bohr equation:$1/\lambda = R (1/n_1^2 - 1/n_2^2)$, the term $(Z-b)^2$

accounts for the shielding effect of the electrons on the nuclear charge. b, in the term (Z-b) is the number of electrons between the electron falling to fill the vacancy and the nucleolus. Examples, for K_α, b = 1 and for K_β, b = 9.

1- Calculate the wave length of K_α of an element (Z = Z) ($R= 1.097\times10^7$)

Answer: $1/\lambda= R(Z-b)^2 (1/n_1^2 - 1/n_2^2)$

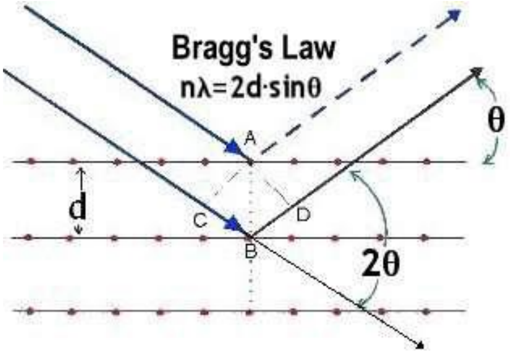
$1/\lambda= 1.097\times10^7 (Z-1)^2 (3/4) =$ ……….nm

2- Calculate the potential required for the production of K_α ($\lambda = \lambda$ nm) $eV=hc/\lambda$

$V= hc/e\lambda= 6.63\times10^{-34}$ (J.s) $\times 3\times10^8$ (ms^{-1})$/1.6\times10^{-19}$ (C) $\times\lambda\times10^{-9}$ (m)= …….. Volts

Diffraction of x-rays

An important fact is that the x-ray wavelengths are of the same order as the distance between planes of atoms in crystalline materials and so, crystals act as diffraction grating for x-rays. A portion of a beam of x-rays striking a crystal surface is scattered by the first layer atoms. Another fraction of it is scattered by the second layer and so on. The requirement for constructive interference is given by Bragg's equation ($n\lambda = 2d \sin\theta$).



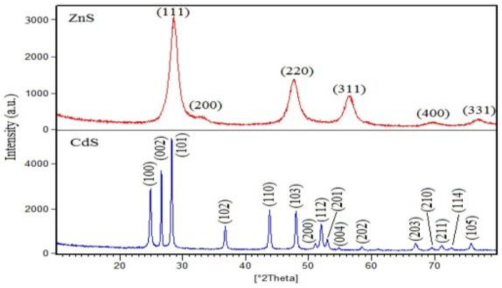
X-ray diffraction (XRD) is used for the identification of different phases of crystalline compounds and useful information can be obtained from the diffraction pattern (like the crystallite size, d spacing, miller indices, micro strain etc.).

Notice that, the wavelength of x-rays can be calculated if the angel of diffraction θ and d-spacing are known ($\theta = \theta$ and $d = d \times10^{-10}$ m).

Example: for n = 1; $\lambda= 2 \times d \times 10^{-10} \sin\theta =$ ………Å

Applications

XRF is usually used as a powerful means of elemental analysis: all elements above calcium can easily be analyzed. XRD is used for the identification of phase composition of crystalline compounds and useful information can be obtained from the XRD results like the crystallite size, d spacing, Miller indices microstrain, lattice type, the unit cell dimensions etc. X-ray is also used in medicine to view images of bones. Data of x-ray diffraction also are used to calculate the crystallite size of nanomaterials using the Scherrer equation.



It is worth mentioning that the XRD patterns can clarify the nanosize nature of a substance. Sharp lines or peaks indicate large or perfect crystals while small crystallite size materials are characterized by broad peak. The absence of peaks from the XRD pattern characterize amorphous samples.

Scherrer´s equation ($\tau = K\ \lambda/\beta\cos\theta$) is used to calculate the crystallite size from the XRD pattern data: τ is the size of the crystal, β is the line broadening at half the maximum intensity (full width at half maximum (FWHM) in radians, λ is the wavelength of x-rays (Cu K_α = 0.154 nm), K is the shape factor (a number) and θ is the Bragg angle.

The unit cell dimensions (for the cube system)

For the cube system, the following equations are suitable:

$(d^2_{hkl})= 1/(h/a)^2 +(k/a)^2 + (l/a)^2$

$d_{hkl}= a/(h^2+k^2+l^2)^{1/2}$

$a= d_{hkl}\ (h^2+k^2+l^2)^{1/2}$

Example:

- The first two lines in the XRD pattern of NaCl are at $\theta = 20^o\ 36´$, $\sin\theta = 0.3518$, d= 3.256 and $\theta = 23^o\ 58´$, $\sin\theta = 0.4062$, d = 2.820.

The value of a:

$a= d_{hkl}\ (h^2+k^2+l^2)^{1/2}$

For (100) plane as the first reflection line:

a= 3.256 (1+0+0) = 3.256

using this value for a for the second reflection

$3.256/2.820 = (h^2+k^2+l^2)^{1/2}$

$1.156 = (h^2+k^2+l^2)^{1/2}$

$(h^2+k^2+l^2) = 1.336$

No group of integer numbers for miller indices can fulfill this requirement and as a result, the assumption that the first reflection line is (100) is not correct.

For (111) plane as the first reflection line:

$a = 3.256\ (1^2+1^2+1^2)^{1/2} = 5.64$

for the second line:

$(h^2+k^2+l^2)^{1/2} = 5.64/2.820 = 2$

(002) , (020) and (200) planes fulfill this requirement

The assumption that the first line is the (111) is correct.

The value of a = 5.64 can be used to determine miller indices for the rest of reflections in the pattern

It is worth mentioning that, for the face centered cube (and also for the body centered cube) system, not all crystal planes give reflections in their XRD pattern. The FCC lattices have diffraction lines corresponding to Miller indices (hkl) which are all even or all odd. For BCC lattices, diffraction lines correspond to Miller indices such that the summation of which is odd.

Spectral methods

Ultraviolet and visible molecular spectrometry

Principle

Absorption in this region of the spectrum corresponds to transition between electronic energy levels. The energy involved covers the range100-800 nm. However, in practice, UV-Vis spectrometers operate between 200-800 nm.

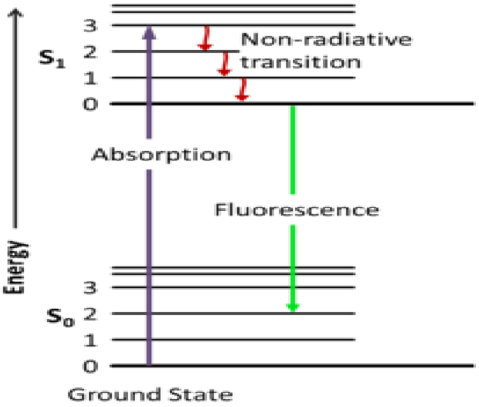
Transition metals have partially occupied d orbitals and they often show absorption bands at the visible region. Organic molecules, on the other hand, contain c-c bonds and c-other atoms and also, they may contain multiple bonds (double and triple bonds). In this case, different transitions ($\rho \rightarrow \rho^*$, $\pi \rightarrow \pi^*$, n→ higher energy levels) are possible. $\pi \rightarrow \pi^*$ occurs in molecules containing multiple bonds. The greater the extent of conjugation in the molecule, the closer the energy levels are and the higher the wavelength is.

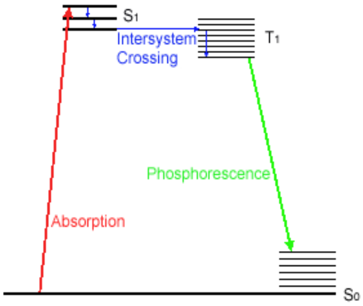
UV and visible spectra of solutions, due to solvents effects on vibrational and rotational levels of molecules, give broad bands. The peak wavelength λ_{max} is determined for analytical purposes and the absorption obeys Beer law.

After excitations by a photon of sufficient energy, faster transitions to lower excited states (involving vibrational levels of the excited state) takes shorter times and hence they are favorable. Further transition to the ground state results in the emission of lower energy (fluorescence (involves a singlet state) and phosphorescence (involves triplet states)).

Fluorescence and phosphorescence

Fluorescence which involves a singlet state is a short-lived phenomenon and the luminescence basically ends immediately. Phosphorescence, on the other hand, involves change in electron spin (triplet state) and therefore lasts for longer time (several seconds). In most cases, photoluminescence tends to be at longer wavelengths than excitation energy.





Molecular Multiplicity, M

$M = 2S + 1$

S = spin quantum number of the molecule = summation of the net spin of the electrons in the molecule. Most organic molecules have S = 0 because molecules have an even number of electrons. As a result, the ground state must have all electrons paired so, $M = 2 \times (0) + 1 = 1$. Molecules in the ground state have a singlet state.

While the molecules are in the excited state, one electron may reverse its spin. Therefore, $S = (+1/2) + (+1/2) = 1$ and $M = 2(1) + 1 = 3$ (triplet state).

Notice that a molecule with an even number of electron cannot have a ground triplet state because all electrons are paired. While molecules with one unpaired electron are in the doublet state (For example, organic free radicals)

It is worse mentioning that the allowed absorption process will result in a singlet state. A change in electron spin is a forbidden process meaning unlikely to happen.

Instrumentation

Light source, optical parts (like, cuvettes, monochromators or wavelength selector (mirrors and a grating) and detector. The source of radiation is the deuterium lamp: the electrical excitation of deuterium at low pressure produces a UV spectrum. Deuterium and hydrogen gives radiation in the UV range. Quarts windows and cuvettes must be used in this range. For visible radiation, the tungsten halogen lamp is used. Silicate glass can be used for these longer wave lengths.

Detectors

A photomultiplier tube or a photodiode array is used. A photomultiplier tube; multiply the current produced by the incident radiation in the order of about 10^8 times. A photdiode is a semiconductor device that converts light into electric energy.

Applications in nanoscience

The absorption of photons in this range causes electron transition from the valance band to the conduction band in semiconductors. The band gap energy of a semiconductor can be estimated from their UV-vis. absorption spectra. Shifts in the band can be related to the particles sizes and this phenomenon can be used to confirm the nanosize nature of a particles. For example, samples can be analyzed at different times during the synthesis of a nanosize substance. The change of the particles sizes during synthesis is accompanied with a shift in their absorption edge. When the particles sizes increase during synthesis there will be a red shift while when their sizes decrease a blue shift is observed in their UV-Vsi spectra.

Photocatalysis

Semiconductors like TiO_2, ZrO_2 and ZnO, can be used as efficient catalysts in the presence of light of suitable wavelengths. The efficiency of the catalyst depends on many factors like surface area, catalysts phase composition, crystallite size, particles shape and availability of active sites. As solid catalysts, the properties of them are significantly modified when synthesized in the nanosize and generally they are used in this form. Characterization of the catalysts provide valuable information about different properties affecting their efficiency. The phase composition and crystallite sizes can be calculated from the XRD date using the Scherrer equation. The UV-vis spectra enable the calculation of the band gap energy: $E_g=1240/\lambda$ and may be used to confirm the nanosize of the photocatalysts particles from the shift in the absorption edges during preparation or through comparison with bulk materials. The surface area and pore type can be obtained from the adsorption isotherms at liquid nitrogen temperature by the BET method. The pore type and size of the catalysts can be obtained from the adsorption data. The electron microscope can be used to confirm the nanosize nature of the photocatalysts and obtain some surface characteristics of them.

In the presence of the suitable energy electrons in the photocatalysts particles are excited from the valence ban to the conduction band. Formation of excitons (electron-hole pairs) initiate the photocatalytic process and therefore these excitones are required to have suitable life time. The holes in the valence bands can participate in the process of catalysis as oxidizing agents. Hydroxyl radicals and other reactive oxygen species also can be formed due to interactions involving oxygen and water. Organic molecules on the surface of such photocatalysts may be degraded under these conditions. In some cases, the complete mineralization (transformation of the organic molecules to CO_2 and H_2O) of the organic content can be achieved.

It is important to notice that preparation conditions of the photocatalysts affect their characteristics. Therefore, the photocatalytic efficiency of the catalysts depends largely on their preparation conditions. Addition of small amount (usually less than about 5%) of some elements to the photocatalysts (doping) significantly modify the photocatalysts characteristics. Catalysts doping is an important process to modify catalysts properties and increase their efficiency.

An important field in which nanoparticles are used is heterogeneous catalysis. The mechanism of catalysis is conveniently explained by the modern theory of contact catalysis. As was mentioned previously an important property that nanoparticles possess is the high surface area to volume ratio. A direct consequence of the high surface area to volume ratio is the modification of the surface properties and the unique properties of the nanosize particles. Adsorption phenomenon and catalysis, which are important topics for chemists, are significantly enhanced due to using nanoparticles (or colloidal particles).

Adsorption is a surface phenomenon in which some material molecules are concentrated at the surface of a solid (or a liquid). It is important in this context to distinguish adsorption which is a surface phenomenon from absorption. As was previously mentioned, adsorption is a surface phenomenon in which a layer (or more than one layer) of the molecules of a substance is formed on the surface of another substance. It is usually important to identify the nature of bonding between the surface and the molecules attached to it (the adsorbate). The expression absorption, on the other hand, refers to the homogeneous penetration of substance molecules into the body of a second substance as in the case of absorption of water in a sponge.

It is noteworthy that generally, porous materials are preferred in adsorption studies due to their high surface areas and also, when it is difficult or not important to distinguish adsorption from absorption, the expression sorption is used to mean adsorption and absorption.

There are many substances which are known as excellent adsorbents like charcoal which is well known to has high potential for the adsorption of large volumes of gases and also the removal of dyes from solutions. Alumina, silica gel, chromium oxide and zinc oxide are also known adsorbents. The amount of adsorbate and the strength of bonds they form with the surface depend on the nature of both the adsorbate and the adsorbent. The adsorbents are selective, for instance, nickel has high adsorption capacity for hydrogen but adsorbs other gases like nitrogen very little. Surface area and the nature of the surface play an important role in adsorption processes. The degree of adsorption of a gas increases with increasing pressure and decreasing temperature. Le Chatelier principle can be used to explain why adsorption decreases with increasing temperature. This is because of the fact that adsorption is an exothermic process and this means that heat is given out during adsorption. Gases has a definite value for the heat of adsorption on a certain solid, however, the value of heat of adsorption is dependent on the degree of surface coverage or the amount of substance adsorbed as will be discussed later.

Adsorption isotherm

The adsorption depends on many factors like temperature, the nature of the adsorbate and the adsorbent, the concentration or pressure of the adsorbate, the amount of adsorbent …etc. In the study of the phenomenon of adsorption it is frequently desired to obtain the adsorption isotherm. The results (data) of an adsorption experiment are presented in a graph known as the adsorption isotherm. In the adsorption experiment, the amount of gas adsorbed, at constant temperature, by a certain quantity of an adsorbent (e.g. one gram) as a function of the pressure is determined and the data are presented in a graph. The graph shows the pressure (cm Hg) on the abscissa and the amount of gas (volume, cc at STP) on the ordinate,

Freundlich adsorption isotherm

Freundlich adsorption isotherm can be used to study adsorption of gases on solid adsorbents and it also can be used to study adsorption from solutions. In the case of adsorption of gases on a solid, the effect of changes in gas pressure on the amount of it adsorbed by a certain amount of the adsorbent (e.g. 1 g) at constant temperature is studied. The empirical relation used is given as follows:

$a = KP^n$

a, is the amount of gas adsorbed by a mass unit of the adsorbent (1 g) at a pressure p of the gas. The constants K and n are specific for the adsorbent and adsorbate at the specified conditions. Freundlich equation can also be written in the logarithmic form:

$\text{Log } a = \log K + n \log P$

When the experimental results can be explained by Freundlich adsorption isotherm, n and K are determined (from slope and intercept of the straight line of log a vs. log P, respectively). It is known that Freundlich equation gives satisfactory results for experimental data in a narrow range of pressure. It also can be used for the study of the adsorption from solutions. Freundlich isotherm can be used to study the adsorption from solutions and the following form can be used: $a = KC^n$, where C is the concentration of the adsorbate.

It is noteworthy that adsorption from solution is more complex than adsorption of gases and only one layer is formed. It is important to notice that in chemical adsorption (chemisorption) it is supposed that only one layer of the adsorbate molecules is formed (monolayer). It is not practical to assume that more than one layer is formed in chemisorption because chemisorption requires a direct contact between the adsorbent surface and the molecules of adsorbate (contrary to physical adsorption). In physical adsorption many layers are presumably formed especially at low temperature and high pressure.

Langmuir adsorption isotherm

In this case, it is assumed that adsorption leads to the formation of a monolayer of the adsorbate on the adsorbent surface. Based on this assumption, Langmuir could obtain an important relation between the gas pressure and the amount of gas adsorbed at constant temperature:

$p/y = a/y_m + P/y_m$

where p is the gas pressure, y is the amount of gas adsorbed at any given pressure (P), y_m is the amount of gas required to form a monolayer and a is a constant. $1/y_m$ and a/y_m can be determined, respectively, from the slope and intercept of the straight line (p/y vs. p).

The Langmuir adsorption isotherm data can be used to estimate the surface area of solid adsorbent:

Slope = $1/y_m$ and intercept = a/y_m

If y_m is the amount of gas at STP required to form the monolayer, the number of adsorbate molecules adsorbed is:

$(y_m/22.4)\ (6 \times 10^{23})$

If the area covered by one molecule is (Z)

The total surface area of the adsorbent (1 g) is:

$(y_m/22.4)\ (6 \times 10^{23})(Z)$

It is important to notice that practically adsorption data are collected. Various isotherms are used to find out the best one the data fit. The isotherm which fit the experimental data is taken to explain the adsorption process under investigation

Light microscopes

Visible light and transparent lenses (like glass) are utilized in light microscopes which are used to see small objects. The sizes of these objects usually are in the range of micrometres. These light microscopes have a limited magnification capability (about 1000 times). Resolving objects separated by about 200 nm using these light microscopes is possible.

Electron Microscopes

Electron Microscopes have much higher magnifications power and also have a greater resolving power than light microscopes. This makes them able to image much smaller objects (at the molecular and atomic level) than those which can be seen by the light microscopes.

The scanning electron microscope

The scanning electron microscope and the optical microscope have the same functions. However, to take images of the specimen the electron microscopes use a beam of electrons instead of light. The wavelength of the moving electrons is given by the De Broglie equation. This equation define the wavelength of a moving particle as follows: $\lambda = h/mv$, λ= wavelength of particles, h= Planck's constant, m= mass of the particle, v= velocity of the particles. The shorter the wavelength of the illuminating source is the better is the resolution of the microscope. Shorter wavelengths of the electrons can be obtained using higher voltages values as can be expected from the De Broglie equation.

Principles of SEM

An electron source forms a beam of electrons. Using a positive electrical potential, these electrons are accelerated toward the specimen. Using metal apertures and magnetic lenses, the electron beam is confined and focused into a thin monochromatic beam. Electrons in the beam interact with the atoms of the specimen. This interaction results in the generation of some signals. These signals contain information about the specimen surface properties like topography and composition. To do this, the signals resulting from the interactions of the accelerated electrons and specimen surface are detected by suitable detectors and transformed into an image.

Components of SEM

Electron gun:

The gun is fitted with a tungsten filament cathode. When heated, the filament emits electrons.

Electron Column

It is where the electron beam is generated, focused to a small diameter, and scanned across the surface of a specimen. This is done using electromagnetic deflection coils. The specimen chamber exists at the lower part of the electron column.

Specimen Chamber:

Specimen stage and controls are located at the lower portion of the column. Specimens are mounted onto the specimen stage which is controlled by a goniometer.

Condenser Lenses:

After the electron beam passes the anode it is influenced by two condenser lenses. These lenses cause the beam to converge and pass through a focal point. The condenser lenses, therefore, are responsible for the determination of the intensity of the electron beam when it strikes the specimen.

Apertures:

The apertures are used to reduce or exclude extraneous electrons in the lenses. The final lens aperture is located below the scanning coils. It determines the spot size of the beam at the specimen. Decreasing the spot size results in an increase in resolution.

Scanning System:

Specimen images are formed by rastering the electron beam across the specimen using deflection coils inside the objective lens.

Electron Detectors:

The detectors used in this case collect the signal generated due to the interaction of the beam of electrons with a specimen. The secondary electrons from the specimen for example are attracted to the detector by a positive charge. Electronic detectors convert the signal into digital images.

It is important to notice that for better imaging, the gun column of electron microscope require vacuum. The presence of gases in the column environment results in scattering of the electrons due to collision with its molecules. This would lead to reduction of the beam intensity and stability.

As was previously mentioned, the electron gun produces an electron beam. This beam travels in the vacuum column through electromagnetic fields and lenses. These focus the beam down toward the sample. The electron beam scans the surface of the sample in a raster pattern through a special mechanism of deflection coils. Due to the interaction between the surface of the sample and the electron beam, signals are produced. These signals are collected by suitable detectors, converted to digital images and then displayed on a screen. It is important to notice that, beside the structural and morphological information, the production of characteristics x-ray lines provides information about samples elemental composition. X-rays generation due to the interaction of the electrons with the specimen was discussed in the XRD section. X-rays signal are detected by energy dispersive spectrometer (EDS) detector.

The generation of secondary electrons from the surface of a sample is the gaol of SEM. SEM therefore uses low accelerating voltages to prevent the electron beam to penetrate into the sample. When the primary electron beam interacts with the sample, the electrons lose energy by many scattering and absorptions within a teardrop-shaped volume of the specimen. This is known as the interaction volume. The size of the interaction volume depends on a number of factors. These include the atomic number of the specimen, the electrons energy, and the density specimens. It is therefore common to use low energy in the range 1-5kV.

Backscattered electrons are deflected back in the direction of the electron beam. These are highly energetic electrons and can be detected by backscattered electrons detectors. These detectors of the microscope trap the back scattered electron signals which are used to discriminate areas of different atomic numbered elements. This is because of that atoms with higher atomic number give off more backscattered electrons and appear brighter than those atoms with lower atomic number.

The secondary electrons have low energy. They are collected with the electron detectors used in SEM. These electrons are used basically to reveal topographical feature of a specimen. (A resolving power of less than 10 nm is possible).

As was discussed in the x-ray section, two important types of x-ray may be generated when the beam of electron interacts with the atoms of a specimen. These are (i) the continuous x-rays (or bremsstrahlung x-ray) and (ii) the characteristic x-rays. The intensity of x-ray energy depends on how close the accelerated electron comes to the nucleus. X-rays of various intensities are generated therefore. These intensities depend on the extent of electron penetration into the electron cloud towards the nucleus. These x-rays are used in some applications like measuring a specimen mass thickness.

Characteristics x-rays are generated when a high energy beam of electrons interact with the inner shell electrons of the specimen. This interaction may result in the ejection of an inner shell electron if the electron energy is high enough. The removal of such electrons ionizes the atom. As a consequence of that an outer shell electron drops into the vacancy to stabilize the atom. This result in the release of characteristic x-rays. The energy of these characteristics energies equals the difference in energy between the two shells involved in the process. The energy dispersive x-ray (EDX) detector and the wavelength dispersive x-ray (WDX) detector are used to detect these x-rays.

Also, Auger Electrons (low energy electrons**)** may be encountered and detected in the process. Auger electrons are generated from the upper layer of a specimen and these electrons carry information about its atomic composition. This constitutes a powerful technique for studying the distribution of the light elements on the surface of the specimen. A scanning auger electron spectrometer is used for this purpose.

Applications of Scanning Electron Microscopy

Investigation of topography, morphology, composition and the related properties of specimens are possible by SEM and there are many important advantages of SEM. Among these is the versatility of information collected using different detectors, the short time of analysis and the minimal sample preparation procedures. However**,** the microscope is large, pensive and requires experience to operate. It is also limited to solid samples and the procedures used for samples preparation may result in artifacts.

Tunneling through a barrier

We have seen that the energy of a particle in a box having a length L is given by the relation: $E_n= (h^2/8mL^2)n^2$. This equation can be derived also for the same system using the Schrodinger equation: $\partial^2\psi/\partial X^2 = (- 2mk/\hbar)\ \psi$.

When an electron having an energy E impinging on a barrier of height U and a width L, where E is less than U, and according to the classical mechanics it is not possible for the particle to penetrate the barrier because it has higher energy. According to the quantum mechanics however, penetration of the molecule through the barrier is possible regardless of the energy it possesses. This is because of the fact that the particle accompanying wave amplitude is not zero inside or behind the barrier, keeping in mind that the probability of finding the particle in some space is proportional to ψ^2. This means that the probability of finding the particle the other side of the barrier is not zero. The probability of finding the particle the other side of the box corresponds to the phenomenon of tunneling through a barrier.

The probability of tunneling can be described by the coefficient T.

Therefore, T+R =1

Where R is the reflectance coefficient.

T can be expressed as $T= e^{-2KL}$

where $K= (2m(U-E))^{1/2}/\ \hbar$

From $T= e^{-2KL}$, it is clear that with decreasing L value, T increases.

Scanning tunneling microscopy

The scanning tunneling microscopy (STM) is a powerful tool used for the investigation of electronic structures of the solid state. This is based on the tunneling phenomenon which allow the electron to tunnel through barriers of higher energy than the energy of the electron.

The scanning tunneling microscopy (STM) enables imaging the surfaces of conducting samples and studying their local electronic properties. Scanning tunneling microscopy also can be used to study many surface phenomena. For example, STM can be used to map out the electronic density of states of semiconductors.

The main components of the STM:

- a sharp probing tip.
- a piezoelectric scanning unit.
- a coarse positioning unit.
- a vibration isolation stage.
- a set of electronics.

The function of this set of electronics is to detect the tunneling current. It also controls the piezo-tube scanner with feedback and drives the coarse positioning.

The commands and the electronic signals in the microscope follow a certain sequence. The controller uses the computer to change the experimental settings. These includes the bias voltage, the tunneling current set point, the scanning speed, the scanning range and the proportional/integral gain for the feedback algorithm. it also transfers the feedback signal and tunneling current signal back to the computer to generate topographic images and tunneling spectra.

The STM tip is brought to about several angstroms from the sample surface to start the tunneling process. This is done by the coarse approach walker. Applying a bias voltage between the sample and the tip gives rise to a quantum mechanical tunneling current. The tunneling probability amplitude is an exponential function of the tip-sample separation. Therefore, the value of the tunneling current is largely sensitive to the corrugation of the specimen surface.

Imaging can be performed using a constant distance approach or a constant current approach. In the constant-current approach, the tunneling current is kept constant. The output voltages from a feedback loop to the piezo tube are used to deduce the vertical position of the tip as a function of its lateral position, z (x, y). By using the constant-current imaging approach, it is possible to identify the feature of interest. Investigation of the local electronic structure (local density of states) is possible. Changes in local density of states around an impurity, across a step-edge, or among grains with different crystalline orientations can be revealed through measurement of the tunneling spectra point by point on scanned target areas. Thus it is possible to investigate the spatially resolved local density of states.

The STM should perform measurements with atomic scale resolution reliability. Therefore, the setup of the microscope should fulfil the following requirement:

- The coarse approach mechanism must bring the probing tip into the tunneling range without crashing onto the sample.
- Throughout any measurement, the tip-sample separation must remain constant.

The design of the microscope therefore should be rigid enough to prevent vibrational couplings from changing the tip-sample distance and the possible mechanical disturbance from the environment which should be minimized as possible. To avoid artifacts in tunneling spectra due to noise contamination, the electronics must be well shielded from ambient electromagnetic interference. Also, it is required that the STM system have good thermal stability and therefore it requires good thermal isolation.

Atomic force microscopy (AFM)

The AFM is an advanced technique of studying surface properties of materials at the atomic scale. Thus, the technique plays an important role in many fields of science like material science, molecular biology and solid-state physics. STM arose from the scanning tunneling microscopy in order to study non-conductive materials. The inventors in this case focused on studying the force between the tip and the sample instead of measuring the tunneling currents. For this purpose, they incorporated a cantilever to hold the tip. This cantilever adjusts the tip to the sample surface.

It is important to notice nanoscale substances provides higher surface area of a material than in case of a micro or macro scales. Thus, a large portion of the scanned material is in contact with the probe. Therefore, valuable information concerning the properties of a sample can be collected.

Principles of AFM

Atomic force microscopy (AFM) is basically used to map the topography of materials. The study of the materials properties on the nanoscale is an important advantage of this technique. AFM uses a probing tip at one end of a cantilever to interact with the sample surface. The interaction between the sample surface and the tip gives rise to either attractive or repulsive forces. These forces give information about the topography of the sample.

If the tip and the sample are close to each other, the attractive force deflects the cantilever towards the sample. However, when the tip is brought into contact with the sample, the repulsive force deflects the cantilever away from the sample. The cantilever system therefore acts as a force sensor. These phenomena can be explained by the Pauli exclusion principle. According to this principle, one cannot have two electrons with the same quantum numbers in the same quantum state. In this case electrons will repel one another thus creating a repulsive force.

For cases of vibrations of the cantilever, the cantilever is vibrated at the resonant frequency. Since the resonance frequency is dependent on the force constant and the mass of the cantilever this means that the mass of the cantilever has to be minimized.

A laser beam detects the cantilever deflections. This happens when the incident laser beam is reflected off the surface of the cantilever. Any deflection will cause changes of the direction of the reflected beam. A high resolution deflection detector (position sensitive detector) is used to detect these changes. The changes can either be large or small. The detector is sensitive enough that it amplifies even the very small deflections.

A feedback loop maintains a predefined set point that is determined by the instrument. In this case, the feedback controls the deflection of the cantilever.

A piezoelectric xyz-scanner is responsible for the movements between the tip and sample in the x, y, z-directions. The piezoelectric scanner gives the access to do imaging in three dimension.

Modes of operation

There are three modes of operation in this case. The choice of the operation mode depends on the type of interaction between the cantilever tip and the surface.

a- Contact mode

In the contact mode, the tip touches the surface of the sample and this mode is suitable when the surface of the sample is not rigid. A surface imaging is attained by the deflections of the cantilever due to repulsive constant force. A feedback circuit regularly adjusts the height of the tip so that the force remains constant. The force of deflection is examined by the detector.

b- Noncontact mode

In this mode, the cantilever does not touch the surface of the sample. It maintains a distance of about 1-100Å. It vibrates close to the surface of the sample with a frequency higher than a resonant one and due to the attractive force, the amplitude and resonant frequency are reduced.

Tapping mode

This mode offers better quality for soft films and materials. It is similar to the contact mode. However, the tip of the cantilever alternates contacting the sample surface at resonant frequency. The tip of the cantilever vibrates with a lower frequency than a resonant one at a range of 200-1000 Å of amplitude. The cantilever tip touches the surface when it comes to its lowest point during the scanning swing. This contact lasts for a very short time.

Advantages and disadvantages

An important advantage of this technique is that no special treatment for the samples investigated is required. Also, this technique provides a 3D images for the specimen and also it offers a higher resolution compared to other techniques. However, this scanning technique is slow and expensive and soft samples may be damaged.

Applications

This imaging technique is used for nonconducting samples. Thus, it is useful for biological samples. The determination of some properties like the roughness and thickness of a crystal layer is possible.