Unit-IV
NANO CHEMISTRY

1. Introduction:- Nanomaterials are cornerstones of nanoscience and nanotechnology. Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It is already having a significant commercial impact, which will assuredly increase in the future as shown in Fig.1.

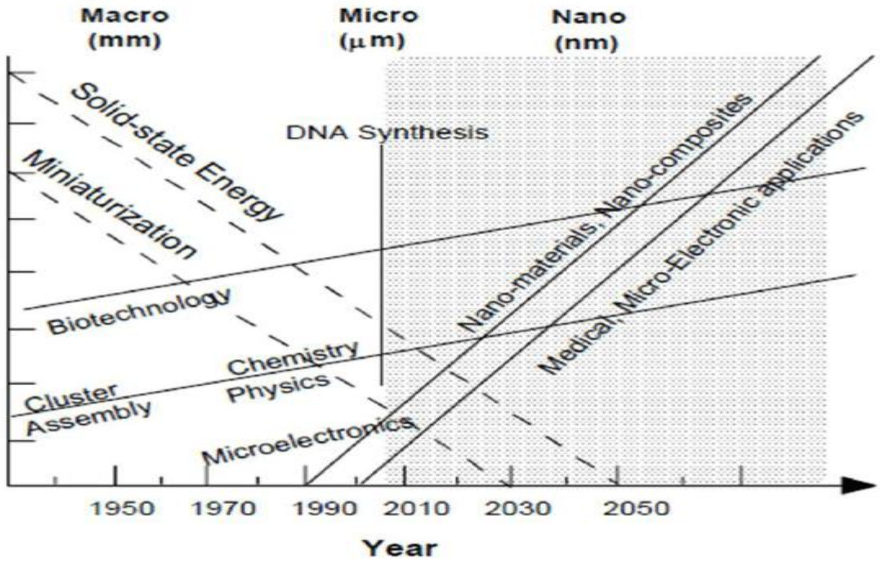


Fig.1 Evolution of science, technology and future

1.1. What are nanomaterials?

Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers (100 nm). A nanometer is one millionth of a millimeter i.e. (10^{-9} m) and approximately 100,000 times smaller than the diameter of a human hair. Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts and applications in electronics, medicine, and other fields.

1.2. Where are nanomaterials found?

Nanomaterials are already in commercial use, with some having been available for several years or decades. The range of commercial products available today is very broad, including stain-resistant and wrinkle-free textiles, cosmetics, sunscreens, electronics, paints and varnishes. Nanocoatings and nanocomposites are finding uses indiverse consumer products, such as windows, sports equipment, bicycles and automobiles. There are novel UV-blocking coatings on glass bottles which protect beverages from damage by sunlight, and longer-lasting tennis balls using butylrubber/nano-clay composites. Nanoscale titanium dioxide, for instance, is finding applications in cosmetics, sun-block creams and self-cleaning windows, and nanoscale silica is being used as filler in a range of products, including cosmetics and dental fillings.

1.3. Nano-Science/ Chemistry and Nanotechnology:- The word nano means dwarf. The nano-Science/ Chemistry deals with the study of relationship between various phenomena, physical, physical properties and material dimensions at nano scale, on the other hand nanotechnology deals with application of nanomaterils and study of principles which makes application of nanomaterials possible.

2. Advances in Nanomaterials:- The history of nanomaterials began immediately after the big bang when Nanostructures were formed in the early meteorites. Nature later evolved many other Nanostructures like seashells, skeletons etc. Nanoscaled smoke particles were formed during the use of fire by early humans.

The scientific story of nanomaterials however began much later. One of the first scientific report is the colloidal gold particles synthesised by Michael Faraday as early as 1857. Nanostructured catalysts have also been investigated for over 70 years. By the early 1940's, precipitated and fumed silica nanoparticles were being manufactured and sold in USA and Germany as substitutes for ultrafine carbon black for rubber reinforcements. Nanosized amorphous silica particles have found large-scale applications in many every-day consumer products, ranging from non-diary coffee creamer to automobile tires, optical fibers and catalyst supports. In the 1960s and 1970's metallic nanopowders for magnetic recording tapes were developed. In 1976, for the first time, nanocrystals produced by the now popular inert- gas evaporation technique was published by Granqvist and Buhrman. Recently it has been found that the Maya blue paint is a nanostructured hybrid material. The origin of its color and its resistance to acids and biocorrosion are still not understood but studies of authentic samples from Jaina Island show that the material is made of needle-shaped palygorskite (clay) crystals that form a superlattice with a period of 1.4 nm, with intercalates of amorphous silicate substrate containing inclusions of metal (Mg) nanoparticles. The beautiful tone of the blue color is obtained only when both these nanoparticles and the superlattice are present, as has been shown by the fabrication of synthetic samples. Today nanophase engineering expands in a rapidly growing number of structural and functional materials, both inorganic and organic, allowing to manipulate mechanical, catalytic, electric, magnetic, optical and electronic functions. The production of nanophase or cluster-assembled materials is usually based upon the creation of separated small clusters which then are fused into a bulk-like material or on their embedding into compact liquid or solid matrix materials. e.g. nanophase silicon, which differs from normal silicon in physical and electronic properties, could be applied to macroscopic semiconductor processes to create new devices. For instance, when ordinary glass is doped with quantized semiconductor "colloids," it becomes a high performance optical medium with potential applications in optical computing.

3. Classification of Nanomaterials:- According to Richard W. Siegel, Nanostructured materials are classified as Zero (0-D), one (1-D), two (2-D) and three (3-D) dimensional nanostructures. Nanomaterials are materials which are characterized by an ultra fine grain size (< 50 nm) or by a dimensionality limited to 50 nm. Nanomaterials can be created with various modulation dimensionalities as defined by Richard W. Siegel: zero (atomic clusters, filaments and cluster assemblies), one (multilayers, nanowire & nanotubes), two (ultrafine-grained overlayers or buried layers-Thin films and sheets), and three (nanophase materials consisting of equiaxed nanometer sized grains- polycrystals & foams etc.) as shown in the below in Fig. 2.

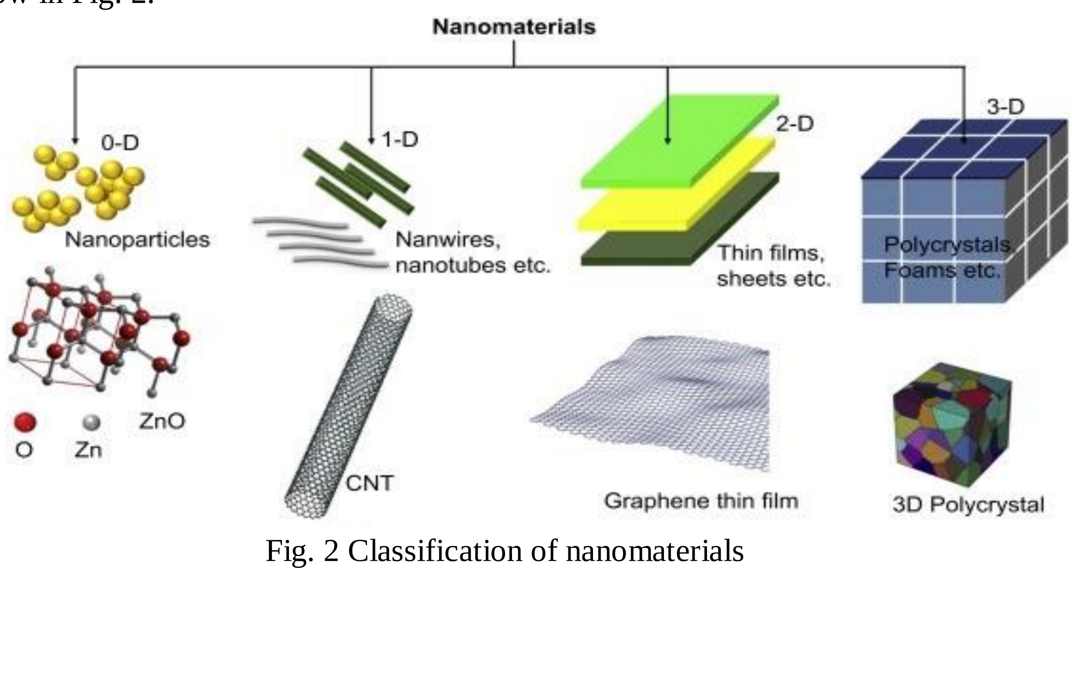


Fig. 2 Classification of nanomaterials

4. Important properties of nanomaterials:- These materials have created a high interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties. Some examples are given below:

i. High surface area to volume ratio of nanomaterials provides a tremendous driving force for diffusion, especially at elevated temperature.

ii. High surface energy due to reduced dimensions, spatial confinement, reduced imperfections and super paramagnetic behavior.

iii. Highly effective sintering (process of compacting and forming a solid mass) at lower temperature and in shorter duration as compared to larger particles.

iv. Optical properties:- Nanostructured semiconductors are known to show various non-linear optical properties. Semiconductor Q-particles also show quantum confinement effects which may lead to special properties, like the luminescence in silicon powders and silicon germanium quantum dots as infrared optoelectronic devices.

v. Catalytic properties:- Nanostructured metal clusters and colloids of mono- or plurimetallic composition have a special impact in catalytic applications with enhanced activity, selectivity and lifetime in chemical transformations and electrocatalysis (fuel cells). Enantioselective catalysis was also achieved using chiral modifiers on the surface of nanoscale metal particles.

vi. Sensing properties:- Nanostructured metal-oxide thin films are receiving a growing attention for the realization of gas sensors (NO_x, CO, CO_2, CH_4 and aromatic hydrocarbons) with enhanced sensitivity and selectivity.

vii. Nanophase ceramics are more ductile at elevated temperatures as compared to the coarse-grained ceramics.

viii. Nanostructured metal-oxide (MnO_2) finds application for rechargeable batteries for cars or consumer goods.

ix. Nanocrystalline silicon films for highly transparent contacts in thin film solar cell and nano-structured titanium oxide porous films for its high transmission and significant surface area enhancement leading to strong absorption in dye sensitized solar cells.

x. Polymer based composites with a high content of inorganic particles leading to a high dielectric constant are interesting materials for photonic band gap structure.

4. Synthesis of nanomaterials:-There are two approaches applied for synthesis of nanomaterials namely: bottom up approach and top down approach. The 'bottom up' approach involves assembling the atoms/particles together while the 'top down' approach involves dis-assembling (break, or dissociate) of bulk solids into finer pieces until they are constituted of only a few atoms. This domain is a pure example of interdisciplinary work encompassing physics, chemistry, and engineering up to medicine.

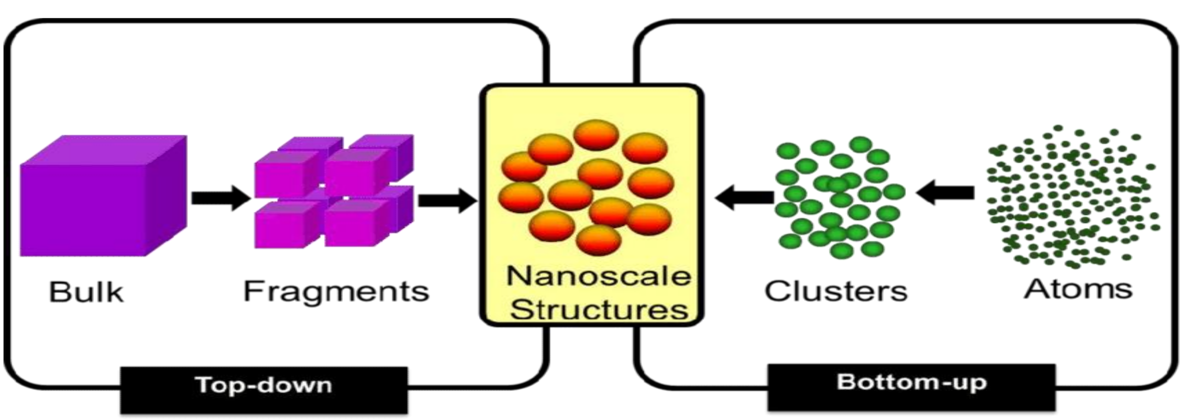


Fig. 3 Top-down and Bottom up approach for Nanoparticles synthesis

4.1. **Mechanical grinding:-** It is a top-down approach for preparation of nanoparticles by applying mechanical energy. This involves crushing of solid materials using hardened steel, silicon carbide (SiC) or tungsten carbide (WC) balls in stainless steel container. The crushing is carried out for 100 to 150 hours to get uniform powder. This method is easy, inexpensive and produces nanoparticles of 2-20 nm range but at the same time problems like control on shape and purity is lacking.

4.2. **Thermal Evaporation-Condensation:-** It is top-down method which for used for synthesis metal and alloy nanoparticles. This was very fist technique used for synthesis of nanoparticles which involves thermal evaporation of target material in electron beam evaporation devices or Joule heated refractory crucibles at 1-50 m bar pressure. Ultra-fine nanoparticles are formed due to gas phase collision and nucleation (condensation) at high residual pressure. The problem associated with these techniques is non-uniform heating resulting inhomogeneous nanoparticles.

4.3. **Microwave/ Gamma irradiation**:- It is a top-down approach for preparation of nanoparticles which involves heating and evaporation the target material by microwave radiations. The microwave/ gamma radiations provide uniform heating without heating the environment and produces homogeneous nanoparticles.

4.4. **Sputtering:-** This is a top-down process of nanoparticles synthesis in which a solid surface is bombarded with high energy particles (Argon ions) resulting in surface erosion of the solid surface with formation of atoms due to collision of energetic particles and the solid surface.

Mechanism of Sputtering:-

It can be well understood by two theoretical models:

(i) According to thermal vaporization theory it is the heat of bombardment of high energy particles that cause vaporization of the solid surface.

(ii) The momentum-transfer theory believes in transferring of the kinetic energy/ momentum of high energy particles to the atoms of solid surface.

Factors influencing sputtering:-

(i) Energy of the bombarded ions or particles.

(ii) Type of the target surface.

(iii) Angle of reflection of particles incident.

(iv) Crystal structure of solid surface.

Types of sputtering:- Its mainly of three types:

(i) DC diode sputtering.

(ii) RF radio sputtering.

(iii) Magnetron sputtering

4.5. **Pulsed Laser Ablation (PLA) Method:-** In this bottom-up method a pulsed laser beam is focused on the target material to ablate nanoparticles. The properties of nanoparticles dependant on laser parameters like wavelength, pulse duration, flounce, and repetition rate and material properties etc. The rate of ablation Increases with increase in laser energy. The advantages of PLA over the other methods are: simple and safe techniques, wide range of target materials, can be carried out at room temperature, no chemical solution required, nanoparticles with complicated stoichiometry, high purity and narrower particle can be produced. The only disadvantage of PLA is its high cost.

4.6. **Plasma Method:-** It is very effective bottom-up approach to prepare nanoparticles. This involves heating of metal in evacuated chamber above its evaporation temperature using high high-temperature plasma. The high-temperature plasma is produced by heating of Helium (He) gas using heating coils operated at radio frequency (RF). The vapor of the metal nucleates on to the helium atoms and gets collected on the cold collector rod and passivated by oxygen.

4.7. The Polyol Technique:- A bottom-up approach used for preparation of metal, metal oxide, semiconductor and bimetallic alloy nanoparticles by employing non aqueous solvent (polyol). The polyol acts as solvent, reducing and passivating agent. The polyol provides control over size, texture, and shape of nanoparticles with minimized surface oxidation and agglomeration. Ethylene glycol is used as solvent for preparations of metal oxide nanoparticles due to its useful properties i.e., high boiling point, high dielectric constant, crosslinking ability and strong reducing capability.

4.8. Micro-Emulsion Technique:- Micro-emulsion method is a bottom-up approach and widely applied for the preparations of inorganic nanoparticles. The emulsions are liquid in liquid dispersions formed by reduction of interfacial tensions with the help of energy and adding sufficient amount of surfactant. The surfactant stabilizes the particles and helps in size control. The polymers also produce emulsions in liquid state which are of three types depending on the size of droplet, i.e., micro-emulsions, mini-emulsions and macro-emulsions. The metallic nanoparticles are synthesized using water in oil micro-emulsion by mixing of micro-emulsions of a metal salt with other micro-emulsions containing a reducing agent. The collisions among the reactants in the mixture of two micro-emulsions due to Brownian motion results into mixing, coalescence and fusion. The formation of metal nuclei by the reaction among solubilizates. The nanodroplets size, shape and type of surfactant used greatly affects the morphology of nanoparticles.

4.9. Electrodeposition or Electrochemical Method:- Electrochemical synthesis is the bottom-up approach for preparation of metal nanoparticles in an electrochemical cell. This method involves use of aprotic solvent for dissolution of a metallic anode. The target metal ions then reduced electrochemically to produce nanoparticles. The size of nanoparticles can be controlled by varying counter electrodes and current density. The main advantage of electrochemical synthesis is the ability to tune with the preferred potential accurately and rejection of the potential wasteful alternative half-reaction.

4.10. Chemical Precipitation Technique:- The bottom-up approach in which nanoparticles size is controlled through arrested precipitation methodology. It involves in situ synthesis of nanomaterials which doesn’t allow physical changes and helps in size control by blocking aggregation. The Oswald ripening and thermal coagulation can be controlled by use non-aqueous solvents by inducing double layer repulsion of tiny crystallites at lower temperatures. The surfactant is applied to maintain space between the particles. Nanoparticles so formed are recovered by centrifugation, washed and dried in vacuum.

4.11. Sol-Gel Technique:- It is a bottom-up approach for synthesis of Silicon, Zirconium and Yttrium oxide nanoparticles. This technique involves interaction of colloidal suspension called sol and gelatin to obtain continuous liquid phase network called gel. The solvent used is mostly alcohol while metal alkoxides and aloxysilanes are used as starting materials. The sol gel technique starts with a homogeneous alkoxides solution. The pH of process controlled using a suitable catalyst. The Sol-gel method is comprises of following stages:

(i) Hydrolysis - replacement of [OR] group with [OH-]group

(ii) Condensation - formation of monomer, dimer, cyclic tetramer, and high order rings

(iii) Growth of particles and Agglomeration of particles – formation of nanoparticles.

4.12. Sonochemical Reduction Method:- The sonochemical reduction method is bottom-up and green methodology for synthesis of metal nanoparticles. It involves interaction of matter and energy by ultrasound irradiation of precursors (sonochemical synthesis) in presence or absence of some stabilizer. The stabilizer so used is starch, gelatin polyvinyl, pyrrolidone and polyethylene glycol (PEG). The process is consisting of three steps: formation, growth and in the end bubbles collapse implosively. There slight increase in pressure and temperature for few seconds due to bubbles collapse followed by cooling. The important properties of nanoparticles viz. particle shape, particle size, and purity can be controlled by solvent, sonication power, chemical species and temperature.

5. Application of nanomaterials:-Nanomaterials having wide range of applications in the field of electronics, fuel cells, batteries, agriculture, food industry, and medicines, etc... It is evident that nanomaterials split their conventional counterparts because of their superior chemical, physical, and mechanical properties and of their exceptional formability.

5.1. Fuel cells:- A fuel cell is an electrochemical energy conversion device that converts the chemical energy from fuel (on the anode side) and oxidant (on the cathode side) directly into electricity. The heart of fuel cell is the electrodes. The performance of a fuel cell electrode can be optimized in two ways; by improving the physical structure and by using more active electro catalyst. A good structure of electrode must provide ample surface area, provide maximum contact of catalyst, reactant gas and electrolyte, facilitate gas transport and provide good electronic conductance. In this fashion the structure should be able to minimize losses eg. Carbon nanotubes (CNT) - microbial fuel cell.

5.2. Catalysis:- Higher surface area available with the nanomaterial counterparts, nano-catalysts tend to have exceptional surface activity. For example, reaction rate at nano-aluminum can go so high, that it is utilized as a solid-fuel in rocket propulsion, whereas the bulk aluminum is widely used in utensils. Nano-aluminum becomes highly reactive and supplies the required thrust to send off pay loads in space.

5.3. Phosphors for High-Definition TV:- The resolution of a television, or a monitor, depends greatly on the size of the pixel. These pixels are essentially made of materials called "phosphors," which glow when struck by a stream of electrons inside the cathode ray tube (CRT). The resolution improves with a reduction in the size of the pixel, or the phosphors. Nanocrystalline zinc selenide, zinc sulfide, cadmium sulfide, and lead telluride synthesized by the sol-gel techniques are candidates for improving the resolution of monitors. The use ofnanophosphors is envisioned to reduce the cost of these displays so as to render highdefinition televisions (HDTVs) and personal computers affordable to be purchase.

5.4. Next-Generation Computer Chips:- The microelectronics industry has been emphasizing miniaturization, whereby the circuits, such as transistors, resistors, and capacitors, are reduced in size. Nanomaterials help the industry to break these barriers down by providing the manufacturers with nanocrystalline starting materials, ultra-high purity materials, materials with better thermal conductivity, and longer-lasting, durable interconnections (connections between various components in the microprocessors). Example: Nanowires for junctionless transistors.

5.5. Drug delivery device:- Today's most harmful side effects of treatment are due the drug delivery methods that don't pinpoint their intented target cell accurately. Now nanotechnology made it possible to deliver the drug to particular infected cell eg. cancer therapy by use of drug filled nanosized RNA strands.

5.6. Elimination of Pollutants:- Nanomaterials possess extremely large grain boundaries relative to their grain size. Hence, they are very active in terms of their chemical, physical, and mechanical properties. Due to their enhanced chemical activity, nanomaterials can be used as catalysts to react with such noxious and toxic gases as carbon monoxide and nitrogen oxide in automobile catalytic converters and power generation equipment to prevent environmental pollution arising from burning gasoline and coal.

5.7. Sun-screen lotion:- Prolonged UV exposure causes skin-burns and cancer. Sun-screen lotions containing nano-TiO_2 provide enhanced sun protection factor (SPF) while eliminating stickiness. The added advantage of nano skin blocks (ZnO and TiO_2) arises as they protect the skin by sitting onto it rather than penetrating into the skin. Thus they block UV radiation effectively for prolonged duration. Additionally, they are transparent, thus retain natural skin color while working better than conventional skin-lotions.

5.8. Sensors:- Sensors rely on the highly active surface to initiate a response with minute change in the concentration of the species to be detected. Engineered monolayers (few Angstroms thick) on the sensor surface are exposed to the environment and the peculiar functionality (such as change in potential as the CO/anthrax level is detected) is utilized in sensing.

6. Disadvantages of Nanomaterials

(i) Instability of the particles:-Retaining the active metal nanoparticles is highly challenging because thermodynamically metastable hence retained by encapsulated in some other matrix. They are prone to attack and undergo transformation this leads to deterioration in properties and retaining the structure becomes challenging.

(ii) Unsafe:-Fine metal particles act as strong explosives owing to their high surface area coming in direct contact with oxygen. Their exothermic combustion can easily cause explosion.

(iii) Impurity:-Because nanoparticles are highly reactive, they inherently interact with impurities as well. Formation of oxides, nitrides, etc can also get aggravated from the impure environment/ surrounding while synthesizing nanoparticles. Hence retaining high purity in nanoparticles can become a challenge hard to overcome.

(iv) Biologically harmful:-Nanomaterials are usually considered harmful as they become transparent to the cell-dermis. Toxicity of nanomaterials also appears predominant owing to their high surface area and enhanced surface activity. Nanomaterials have shown to cause irritation, and have indicated to be carcinogenic. If inhaled, their low mass entraps them inside lungs, and in no way they can be expelled out of body. Their interaction with liver/blood could also prove to be harmful (though this aspect is still being debated on).

(v) Difficulty in synthesis, isolation and application:-It is extremely hard to retain the size of nanoparticles once they are synthesized in a solution. Hence, the nanomaterials have to be encapsulated in a bigger and stable molecule/material. Hence free nanoparticles are hard to be utilized in isolation, and they have to be interacted for intended use via secondary means of exposure.

(vi) Recycling and disposal :-There are no hard-and-fast safe disposal policies evolved for nanomaterials. Issues of their toxicity are still under question, and results of exposure experiments are not available. Hence the uncertainty associated with affects of nanomaterials is yet to be assessed in order to develop their disposal policies.

Surface Characterization Techniques for Nanoparticles:- In the past few years, nanotechnology research has expanded out of the chemistry department and into the fields of medicine, energy, aerospace and even computing and information technology. With bulk materials, the surface area to volume is insignificant in relation to the number of atoms in the bulk, however when the particles are only 1 to 100 nm across, different properties begin to arise. The nanoparticles have superior UV blocking properties when compared to the bulk material, making them useful in applications such as sunscreen. Many useful properties of nanoparticles rise from their small size, making it very important to be able to determine their surface area. Various techniques have been developed for surface characterization of nanoparticles like SEM, TEM, XRD, BET etc.

1. Transmission Electron Microscopy (TEM)

Introduction:- Microscopy is a means by which an object is transformed in to magnified image. There are different ways for magnifying the images of very small objects by large amounts. In any type of microscopy (optical microscopy or electron microscopy), a wave of wavelength λ (light wave or electron wave) interacts with the matter and as a result of this interaction we get the microstructural information about the object. Electron Microscopy becomes a very important physical characterization tool at the nano-metric level. Electron Microscopy stands far ahead of the optical microscopy as it can provide the much improved resolution and depth of focus compared to optical microscopy. Transmission electron Microscopy (TEM) operates on the same basic principles as the light microscope but uses electrons as “light source” and their much lower wavelength makes it possible to get a resolution thousand times better than with a light Microscopy. Transmission electron microscopy (TEM) is the original form of electron microscopy and analogues to the optical microscope. It can achieve a resolution of ~ 0.1 nm, thousand times better resolution, cannot be reached by the light microscope. The beam of electrons passes through the specimen and analyzes the internal structure of the specimen in the form of images. The electron has the poor penetrating capability and gets absorbed in the thick specimen. Therefore, the thickness of the specimen should not be more than few hundred Angstroms (one angtron = 10-10 m) However sometimes, slightly thickens samples are used in High Voltage Electron Microscope.

Principle:- The TEM operates on the same basic principles as the light microscope but uses electrons instead of light. Because the wavelength of electrons is much smaller than that of light, the optimal resolution attainable for TEM images is many orders of magnitude better than that from a light microscope.

The transmission electron microscopy (TEM) principle, as the name suggests, is to use the transmitted electrons. Electrons are made to pass through the specimen and the image is formed on the fluorescent screen, either by using the transmitted beam or by using the diffracted beam.

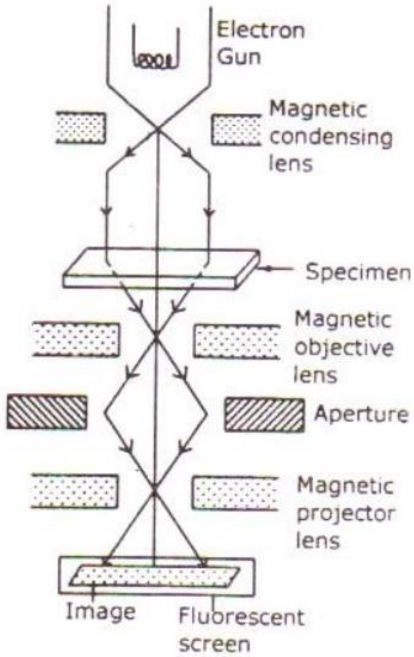
Instrumentation:- It consists of an electron gun to produce electrons. Magnetic condensing lens is used to condense the electrons and is also used to adjust the size of the electron that falls on to the specimen. The specimen is placed in between the condensing lens and the objective lens as in the figure.

The magnetic objective lens is used to block the high angle diffracted beam and the aperture issued to eliminate the diffracted beam (if any) and in turn increases the contrast of the image.

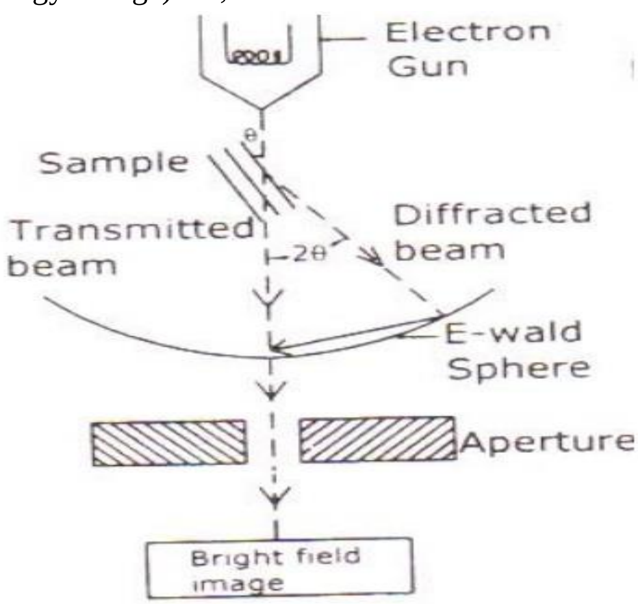
The magnetic projector lens is placed above the fluorescent screen in order to achieve higher magnification. The image can be recorded by using a fluorescent (Phosphor) screen or (CCD – Charged Coupled device) also.

Working:- TEM images are formed using transmitted electrons (instead of the visible light) which can produce magnification details up to 1,000,000 x with resolution better than 10 A°.

Stream of electrons are produced by the electron gun and is made to fall over the specimen using the magnetic condensing lens. Based on the angle of incidence the beam is partially transmitted and partially diffracted. Both these beams are recombined at the E-wald sphere to form the image. The combined image is called the phase contrast image. In order to increase the intensity and the contrast of the image, an amplitude contrast has to be obtained. This can be achieved only by using the transmitting beam and thus the diffracted beam can be eliminated.



Now in order to eliminate the diffracted beam, the resultant beam is passed through the magnetic objective lens and the aperture. The aperture is adjusted in such a way that the diffracted image is eliminated. Thus, the final image obtained due to transmitted beam alone is passed through the projector lens for further magnification. The magnified image is recorded in fluorescent screen or CCD. This high contrast image is called Bright Field Image. Also, it has to be noted that the bright field image obtained is purely due to the elastic scattering (no energy change) i.e., due to transmitted beam alone.

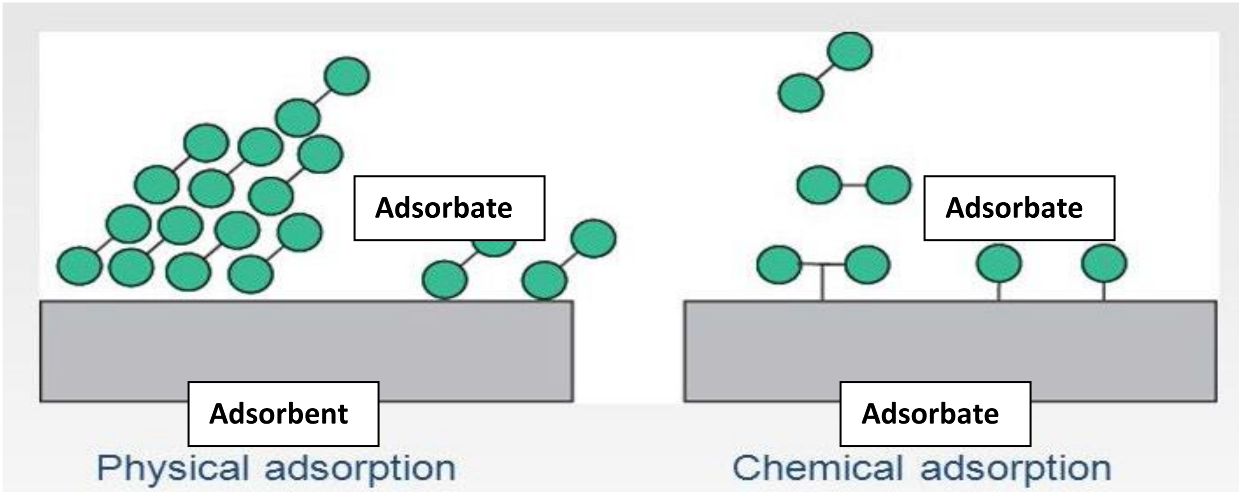


Application of TEM:

TEM is an established technique for examining the crystal structure and the microstructure of materials. It is used to study all varieties of solid materials: metals, ceramics, semiconductor, polymers, and composites. TEMs provide topographical, morphological, compositional and crystalline information.Future trends include the use of ultrahigh vacuum TEM instruments for surface studies image analysis and computerized data acquisition for quantitative image analysis.

2. Brunauer–Emmett–Teller (BET)- Surface Area Analysis of Nanoparticles

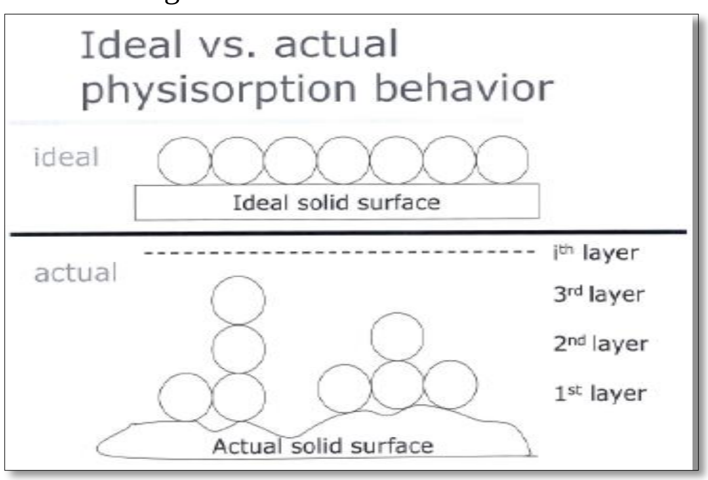
Introduction:- Brunauer-Emmett-Teller (BET) theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of materials. The observations are very often referred to as physical adsorption or physisorption.



BET Theory

The BET theory was developed by Stephen Brunauer, Paul Emmett, and Edward Teller in 1938. The BET theory was an extension of the Langmuir theory, developed by Irving Langmuir.

Langmuir surface area depends on adsorption capacity of the adsorbent. BET Theory extends the Langmuir theory from monolayer adsorption to multilayer adsorption. BET isotherm is determined from the monolayer formation of gas molecules adsorbed on the surface of adsorbent, multilayer formation not taken into account for calculating the surface area.



BET equation to determine the monolayer absorbed gas volume (vm):

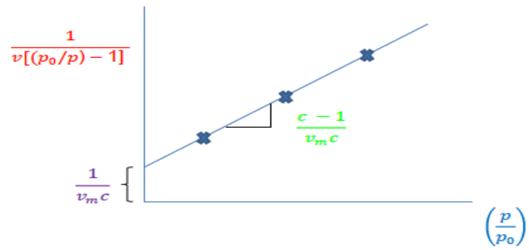
$$\frac{1}{v[(p_0/p)-1]} = \frac{c-1}{v_m c}\left(\frac{p}{p_0}\right) + \frac{1}{v_m c}$$

v = adsorbed gas quantity
p_0 = saturation pressure of adsorbate
p = equilibrium pressure of adsorbate
c = BET constant = $\exp\left(\frac{E_1-E_L}{RT}\right)$
E_1 = heat of adsorption for the first layer
E_L = heat of vaporization

BET equation can be plotted to determine monolayer adsorbed gas quantity and the BET constant

$$\frac{1}{v[(p_0/p)-1]} = \frac{c-1}{v_m c}\left(\frac{p}{p_0}\right) + \frac{1}{v_m c}$$

$$y = mx + b$$



Take numerical values for slope and intercept to solve for vmand c

$$slope = \frac{c-1}{v_m c}$$

$$\text{intercept} = \frac{1}{v_m c}$$

$$v_m = \frac{1}{slope + intercept}$$

$$c = 1 + \frac{slope}{intercept}$$

From the monolayer absorbed gas volume (*Vm*), we can determine total and specific surface area

$$S_t = \frac{v_m N s}{V}$$

S_t = total surface area of sample material
v_m = monolayer absorbed gas volume
N = Avogadro's number = 6.02×10^{23} molecules/mol
s = cross-sectional area of adsorbed gas molecule
V = molar volume of adsorbed gas

$$S_{BET} = \frac{S_t}{a} \; [=] \; \mathrm{m^2/g}$$

S_{BET} = specific surface area
a = mass of sample

BET Technique for Surface Analysis:

BET theory applies to systems of multilayer adsorption that usually utilizes a probing gas (called the adsorbate) that do not react chemically with the adsorptive (the material upon which the gas attaches to and the gas phase is called the adsorptive) to quantify specific surface area. Nitrogen is the most commonly employed gaseous adsorbate for probing surface(s). For this reason, standard BET analysis is most often conducted at the boiling temperature of N_2 (77 K). N2 is used as the adsorbate. The size of nitrogen molecule is very well known. When the instrument measures how many nitrogen molecules are adsorbed, then it is easy to compute the surface area of the adsorbent. Nitrogen is also inert and suitable to work with for BET measurements. Other probing adsorbates are also utilized, albeit less often, allowing the measurement of surface area at different temperatures and measurement scales. These include argon, carbon dioxide, and water. Specific surface area is a scale-dependent property, with no single true value of specific surface area definable, and thus quantities of specific surface area determined through BET theory may depend on the adsorbate molecule utilized and its adsorption cross section.

Experimental Setup

BET Surface Area & Pore Volume Analyzer is an instrument to determine the specific surface area of powders, solids and granules. Prior to any measurement the sample must be degassed to remove water and other contaminants before the surface area can be accurately measured. Samples are degassed in a vacuum

at high temperatures. A minimum of 0.5 g of sample is required for the BET to successfully determine the surface area. After the sample is degassed, the cell is moved to the analysis port. Dewars of liquid nitrogen are used to cool the sample to obtain detectable amounts of adsorption and then maintain it at a constant temperature. A low temperature must be maintained so that the interaction between the gas molecules and the surface of the sample will be strong enough for measurable amounts of adsorption to occur. The adsorbate, nitrogen gas in this case, is injected into the sample cell with a calibrated piston. Relative pressures less than atmospheric pressure is achieved by creating conditions of partial vacuum. After the saturation pressure, no more adsorption occurs regardless of any further increase in pressure. Highly precise and accurate pressure transducers monitor the pressure changes due to the adsorption process. After the adsorption layers are formed, the sample is removed from the nitrogen atmosphere and heated to cause the adsorbed nitrogen to be released from the material and quantified. The dead volume in the sample cell must be calibrated before and after each measurement. To do that, helium gas is used for a blank run, because helium does not adsorb onto the sample.
The data collected is displayed in the form of a BET isotherm, which plots the amount of gas adsorbed as a function of the relative pressure.

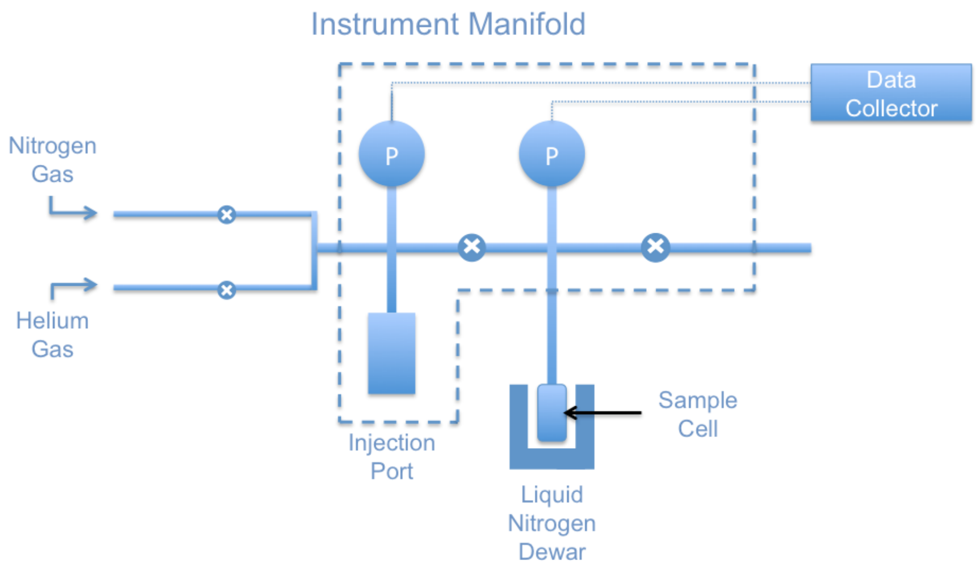


Figure: Schematic representation of the BET instrument. The degasser is not shown.

Applications

Currently, the BET method is used to determine the specific surface area of porous materials, including amorphous and crystalline materials. BET is used to determine surface area of nanoparticles.