Concepts and Applications of Nano Science: Introduction - Nanomaterials – Classification based on dimensions, Synthesis – Top down and Bottom up-chemical precipitation, mechano-chemical method, micro emulsion method, reduction technique, chemical vapour deposition and solgel method, Hydrothermal synthesis(brief study)- Important methods for the characterization of nanomaterials – Scanning electron microscopy (SEM), transmission electron microscopy (TEM). Synthesis and applications of Quantum dots, Carbon nanotubes and Graphene (brief study).

'Nanotechnologies are the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale.'

Introduction

Nano is the Greek word for 'dwarf'. One nanometer (nm) is one billionth, or 10^{-9} of a meter. Just ten hydrogen atoms in a line make up one nanometer. Nanoparticles are sized between 1 and 100 nanometers. The smallest things visible to naked human eye are of the order 10,000 nm diameters. (Human hair measures 50,000-80,000 nm diameter gives us an idea of small the nanoscale is.) The term nanomaterials applied only to synthetic or artificially produced particles. (However several biological particles fall in this nanoscale range, eg. DNA: 2.5 nm, haemoglobin: 6.5 nm, viruses 10-100nm) Nanoparticles exhibit different physical, chemical and biological properties because of their characteristic size.

The first seeds of nanotechnology was sown by the Physicist Richard Feynman in his talk entitled "There is plenty of Room at the Bottom" in 1959. Feyman hypothesized that atoms and molecules could be manipulated like building blocks.

Classification of nanomaterials

2 types of classification are given below.

A) Classification based on nanoscale dimensionality. This Classification is based on the number of dimensions, which are not confined to the nanoscale range (<100 nm).

(1) zero-dimensional (0-D),

(2) one-dimensional (1-D),

(3) two-dimensional (2-D), and

(4) three-dimensional (3-D).

0-D:	All dimensions at the nanoscale
1-D:	Two dimensions at the nanoscale. one dimension at the macroscale
2-D:	One dimension at the nanoscale, two dimensions at the macroscale
3-D:	No dimensions at the nanoscale, all dimensions at the macroscale

i) Nanosystems confined in three dimensions

These include metal and metal oxide nanopowders, quantum dots and other nanostructured materials like fullerenes and dendrimers. 0D Nanomaterials, such as quantum dots has been extensively studied in light emitting diodes (LEDs), solar cells, single-electron transistors, and lasers

0-D

All dimensions (x,y,z) at nanoscale
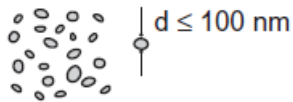
$d \leq 100$ nm

Nanoparticles

Materials wherein all the dimensions are measured within the nanoscale (no dimensions, or 0-D, are larger than 100 nm). The most common representation of zero-dimensional nanomaterials are nanoparticles.

ii) Nanowires and Nanotubes – Nanosystems confined in two dimensions

Nanowires include ultrafine wires or linear arrays of dots. Examples are semiconductor nanowires made of silicon, gallium nitride, indium phosphide etc. Nanotubes include carbon nanotubes, obtained by rolling graphite sheets. There are two types of carbon nanotubes (CNT): Single-walled and multi-walled CNT's.

1-D

Two dimensions (x,y) at nanoscale, other dimension (L) is not

$d \leq 100$ nm
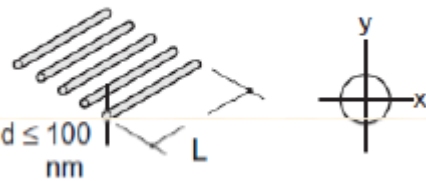
Nanowires, nanorods, and nanotubes

One dimension is outside the nanoscale.
_ This leads to needle like-shaped nanomaterials.
_ 1-D materials include nanotubes, nanorods, and nanowires, nanobelts, nanoribbons, and hierarchical nanostructures

iii) Nanolayers – Nanosystems confined in one dimensions

2D nanostructures have two dimensions outside of the nanometric size range. These include thin films, nanoprisms, nanoplates, nanosheets, nanowalls, nanodisks and surface coatings with thickness in nanoscale. These type layers are find in computer chips.

2-D

One dimension (t) at nanoscale, other two dimensions- (L_x, L_y) are not

L_x L_y

$t \leq 100$ nm
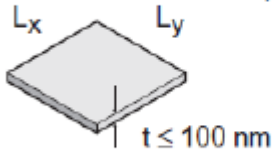
Nanocoatings and nanofilms

Two of the dimensions are not confined to the nanoscale.
_ 2-D nanomaterials exhibit plate-like shapes.
_ Two-dimensional nanomaterials include nanofilms, nanolayers, and nanocoatings.

iv) 3-Dimensional nanoparticles

Bulk nanomaterials are materials that are not confined to the nanoscale in any dimension. These materials are thus characterized by having three arbitrarily dimensions above 100 nm.

- Materials possess a nanocrystalline structure or involve the presence of features at the nanoscale.

- In terms of nanocrystalline structure, bulk nanomaterials can be composed of a multiple arrangement of nanosize crystals, most typically in different orientations.
- With respect to the presence of features at the nanoscale, 3-D nanomaterials can contain dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multinanolayers

B) *Commercial Classification*

i) Carbon-based nanomaterials

Nanomaterials composed of carbon in the form of hollow sphere and ellipsoids (eg. Fullerenes) or tubes (eg. CNT's).
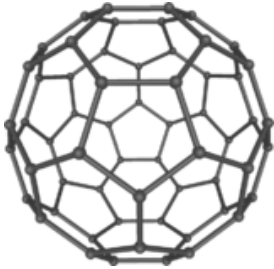
Fullerenes : Buckminsterfullerene C_{60}, also known as the buckyball, is the smallest member of the fullerene family.

C_{60} is a molecule that consists of 60 carbon atoms, arranged as **12 pentagons** and **20 hexagons**.

ii) Metal based nanomaterials

These include nanometals (eg. Nanogold, nanosilver), metal oxide nanopowders (eg. Silica SiO_2, titania TiO_3, alumina Al_2O_3 and iron oxides Fe_2O_3, Fe_3O_4, etc) and semiconductor nanocrystals or quantum dots (eg. Cadmium telluride CdTe, gallium arsenide GaAs)

iii) Dendrimers

These nanomaterials are nano size polymers. They are polymer based tree like structures that have sizes in nanoscale.

iv) Composites

These are formed by combining one or more separate components exhibiting best variety properties. They can be combinations of nanomaterials with other nanomaterials or with bulk materials. Such as nano sized clays, carbon fibres, bundles of multi-walled carbon tubes to enhance mechanical, optical, electrical, thermal and flame retardant properties.

Preparation (Nanofabrication)

Preparation of nanomaterials is commonly referred as *Nanofabrication*. Two approaches used for fabricating to nano scale particles are **Top-down nanofabrication** and **Bottom-up nanofabrication**.

Top-down method involves carving nanomaterials out of bulk materials. Large materials chop down to desired size. Techniques used to perform this method are *Precision Engineering* and *Lithography*. Top-down methods involves high energy usage such as *Mechanical grinding*.

The bottom-up method involves building up of materials atom by atom or molecule by molecule. *Positional assembly* is a technique, which involves using of scanning probe instruments like atomic force microscope to move atoms one by one into required arrangements. But this method is extremely laborious and time consuming. Another bottom-up approach is *Self-assembly*, a method in which atoms and molecules arrange themselves into lowest energy state product.

Chemical Precipitation :

Several nanomaterials can be prepared by chemical reactions. E.g., preparation of gold nanoparticles by reducing Au(III) using sodium citrate for 30 minutes.To 20 ml of chloroauric acid ($HAuCl_4$), 1% solution of trisodium citratedihydrate ($Na_3C_6H_5O_7.2H_2O$) is added with stirring. A gold sol is formed as citrate reduces Au(III) to gold. Heating is stoped when red colour is obtained (Au nanoparticles of 10-20 nm diameter). Upon adding 5-10 drops of 1M NaCl, the colour changes to purple. Similarly yellow silver nanoparticles can be synthesized by the reduction of silver nitrate using sodium citrate or borohydride.

Mechano-chemical method :

In this method nano particles synthesized by reacting chemical components by means of mechanical energy like grinding or milling.

$$A \ + \ B \ \xrightarrow[\text{milling}]{\text{grinding}} \ \text{AB Nano}$$
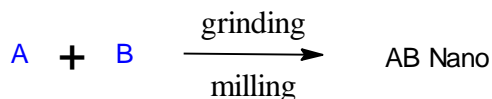
Micro emulsion method :

Microemulsions are isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a cosurfactant. The aqueous phase may contain salts and other ingredients, and the oil may actually be a complex mixture of different hydrocarbons and olefins. In microemulsions, where two immiscible phases (water and oil) are present with a surfactant, the surfactant molecules may form a monolayer at the interface between the oil and water, with the hydrophobic tails of the surfactant molecules dissolved in the oil phase and the hydrophilic head groups in the aqueous phase.

Micro-emulsion method is one of the recent and ideal techniques for the preparation of inorganic nano-particles. Oil and water are immiscible and they separate into two phases when mixed, each saturated with traces of the other component. If enough surfactant molecules are present, they align and create an interface between the water and the oil by decreasing the interfacial tension. An emulsion is formed when a small amount of an appropriate surfactant is mechanically agitated with the oil and water resulting in a two-phase dispersion where one phase exists as droplets coated by surfactant that is

dispersed throughout the continuous, other phase. As a general rule, the type of surfactant used in the system determines which phase is continuous. If the surfactant is hydrophilic, oil will be emulsified in droplets throughout a continuous water phase. The opposite is true for more lipophilic surfactants. Water will be emulsified in droplets that are dispersed throughout a continuous oil phase in this case.

Compared to other methods, the emulsion method has several advantages in producing nanoparticles with a spherical shape and narrow size distribution. In addition, the emulsion technique can reduce the cost of producing spherical powders of high purity. An emulsion is generally defined as a thermodynamically stable system composed of two immiscible liquids and a surfactant. There are other factors that affect the stability of an emulsion and further affect the morphology and size distribution of produced particles. These factors include type and amount of surfactant and co-surfactant, the concentration of precursor solution, the kind of oil phase, and the water-to-oil ratio. Surfactant is added to a mixture of oil and water in the reverse emulsion to reduce the interfacial tension between the water and oil phases. In water-in-oil emulsions, the aqueous phase is dispersed as nano-size water droplets covered with a monolayer film of surfactant and co-surfactant molecules in a continuous nonpolar organic solvent such as hydrocarbon. Not only water but also aqueous solutions of metal salts or ammonium hydroxide can be soluble in the reversed micelles. These aqueous droplets encapsulated with surfactant molecules can continuously exchange their components such as precursor and mineralizer with one another when they collide. Therefore, if two water-in-oil emulsions (one dissolves reactants A and another dissolves reactants B) are mixed, a reaction between them takes place during collisions of the water droplets in the emulsions. For the emulsion method, the particles with uniform small size and narrow size distribution can be obtained because the reaction field is limited to the fine reverse micelles.
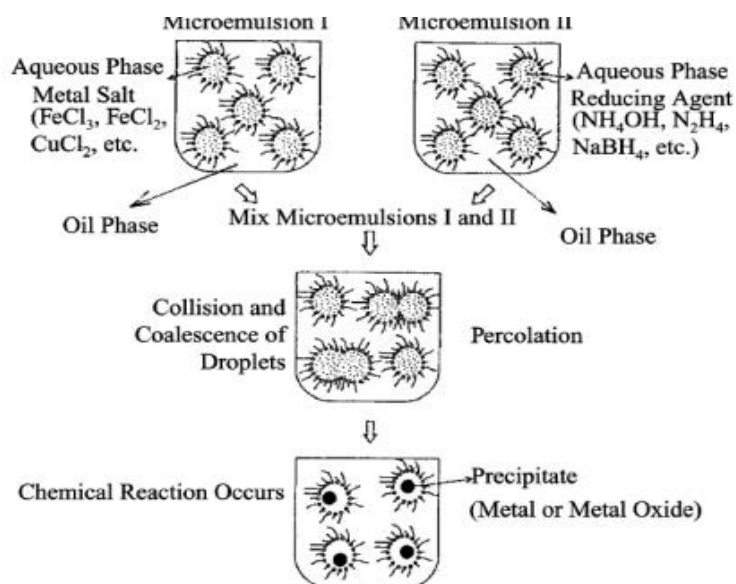
Hydrothermal method :

Hydrothermal method is usually carried out in a pressurized vessel, known as an "Autoclave". It can control the temperature as well as pressure. During the synthesis of nanoparticles, the temperature can be increased at the boiling point of water, which let the vapor to get saturated. Hydrothermal synthesis is broadly used for the synthesizing of graphene-ZnS nanocomposites which can be simply prepared by hydrothermal treatment of Go and ZnS precursor with water.

Hydrothermal synthesis involves the following steps:

1. Precursor Solution: A solution containing the desired metal salts or other precursors is prepared.
2. Autoclave: The precursor solution is sealed inside an autoclave, a high-pressure reaction vessel.
3. High Temperature and Pressure: The autoclave is heated to a specific temperature and pressurized. The elevated temperature and pressure conditions inside the autoclave are crucial for promoting the growth of nanoparticles.

Hydrothermal synthesis is a valuable technique for producing nanoparticles with well-defined properties. Its ability to control nanoparticle size, shape, and composition, coupled with the environmentally friendly nature of using water as a solvent, makes it a preferred method for many applications in the field of nanotechnology.
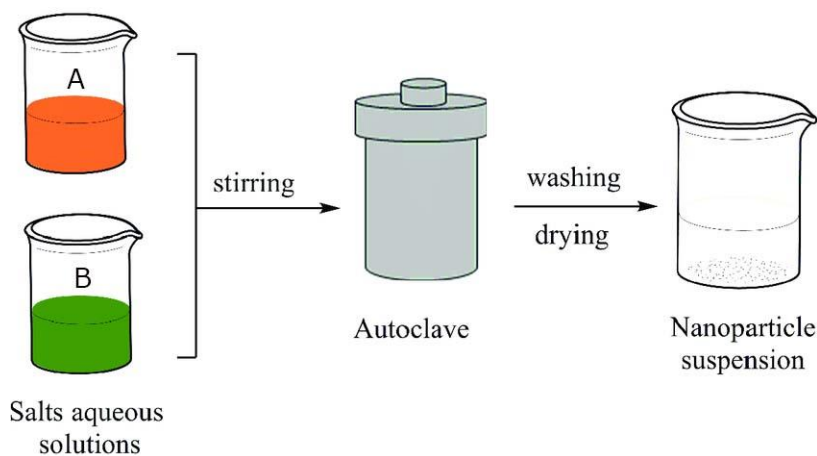

Chemical vapour deposition :

This is the method of depositing a solid material from a gaseous phase to a heated substrate. By this method, usually solid metal nano particles are obtained from the gaseous metal halides.

Metal halide $_{(g)}$ $\longrightarrow$ Metal $_{(solid\ nanoparticle)}$ + By product$_{(g)}$

The reaction vessel is heated to the desired temperature, which is typically well above the boiling point of water, often in the range of 100°C to 300°C or even higher. As the temperature increases, the water within the sealed vessel becomes supercritical. Supercritical water refers to water in a state where it exhibits both liquid and gas-like properties. This high pressure and supercritical state of water facilitate the dissolution and transport of the precursors, promoting chemical reactions.

Reduction technique :

In this reactants are chemically reduced to obtain nano particles. For example Ag nano particles can be obtained by reducing silver nitrate using hydrazine hydrate or glucose as reducing agents.

$$AgNO_3 \quad + \quad \underset{\text{reducing agent}}{N_2H_4} \quad \longrightarrow \quad Ag_{\text{ Nanoparticle}}$$
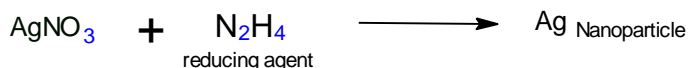
Sol-gel method :

The sol-gel process is a wet-chemical technique that use either a chemical solution (sol short for solution) or colloidal particle to produce an integrated network (gel).

A sol is a colloidal or suspension of solid particles of ions in a solvent. A gel is a semi-rigid mass, forms when the solvent from the sol begins to evaporate and the particles or ions left behind begin to join together as a network. Metal alkoxides and metal chlorides are typical precursors. They undergo hydrolysis and polycondensation reactions to form a colloid, a system of nanoparticles dispersed in a solvent. This sol evolves then towards the formation of an inorganic continous network containing a liquid phase (gel). Forms metal-oxo (M-O-M) or metal-hydroxo (M-OH-M) polymer in solution. After drying, the liquid phase is removed from gel.

A sol is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. A gel consists of a three dimensional continuous network, which encloses a liquid phase. Formation of stable sol solution occurs first then gelation starts through a polycondensation or polyesterification reaction. Gel kept for aging into a solid mass which causes contraction of the gel network. Then drying of the gel to remove liquid phases which can lead to fundamental changes in the structure of the gel. Then it is dehydrated at very high temperatures to remove M-OH groups for stabilizing the gel, i.e., to protect it from rehydration and also for removing organic contaminants.
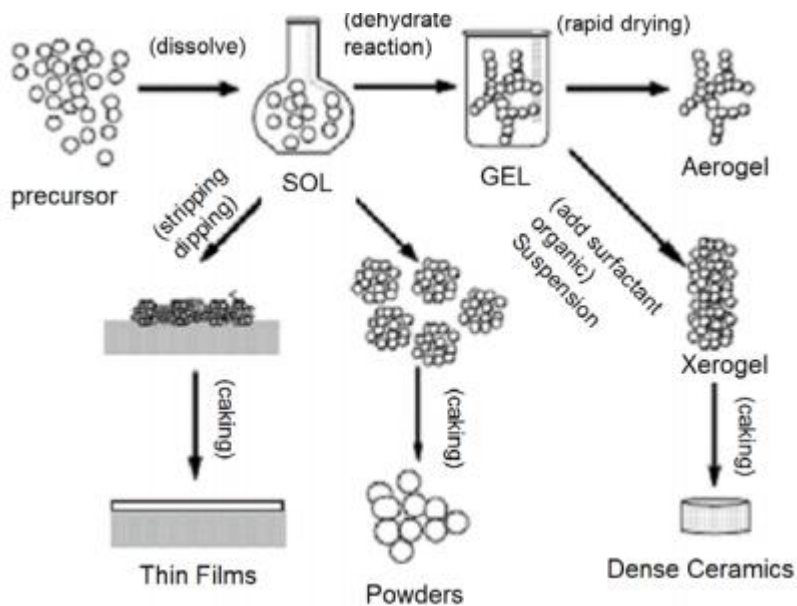
Properties

Materials reduced to the nanoscale can suddenly show very different properties compared to what they exhibit on a macroscale, enabling unique applications. For instance, opaque substances become transparent (copper); inert materials attain catalytic properties (platinum); stable materials turn combustible (aluminum); solids turn into liquids at room temperature (gold); insulators become conductors (silicon). Materials such as gold, which is chemically inert at normal scales, can serve as a potent chemical catalyst at nanoscales. Much of the fascination with nanotechnology stems from these unique quantum and surface phenomena that matter exhibits at the nanoscale.

Hence nanomaterials exhibit novel properties which are not exhibited by their corresponding isolated atoms or bulk materials. Modification of properties are not only due to diminishing size, but also by the phenomena like quantum size confinement, wave like transport etc. Novel mechanical properties of nanomaterials is a subject of nanomechanics research. Catalytic activities also reveal new behaviour in the interaction with biomaterials.

b) Thermal Properties:

Thermal properties depends on factors like small size, shape, large interfaces etc. and hence quite different from those exhibited by their bulk forms. Heat conduction is explained by lattice vibrational waves. Quantum of energy associated with lattice vibration is called a Phonon, similar to photon which is the basic energy quantum of electromagnetic wave. Similar to photons, phonons can be treated as both wave and particle. Any factor that increase the population of phonons cause an increase in thermal conductivity.

c) Chemical Properties:

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Nanomaterials have unique chemical reactivity along with catalytic activity. The chemical properties is due to the presence of increased surface and increased reaction sites. As particle size decreases, the percentage of atoms present at surface increases for chemical reaction.

d) *Mechanical Properties:*

Nanomaterials generally exhibit much improved mechanical properties as compared to corresponding macroscopic forms. Reduction in size generally leads to enhanced hardness, strength, elastic modulus, toughness and scratch resistance. For eg. The tensile strength and elasticity of carbon nanotubes is much higher than that of steel of the same diameter. Main reason for the enhancement in mechanical properties is the decrease in lattice defects (imperfections).

e) *Optical Properties:*

Optical properties of nanoparticles significantly differ from their bulk crystals. For eg., colour of gold nanoparticles shift from deep red through the intermediate colours to blue upon decreasing their size. The change of colour of metallic nanoparticles with their size is considered to be due to **Surface Plasmon Resonance**. A surface plasmon is a natural oscillation of the electron inside a given nanosphere. Absorption of energy occurs when the sphere is small compared to the wavelength of incident light and the frequency of light close to oscillation frequency of surface plasmon, lead to size-dependent colour.

f) *Electronic Properties:*

The electronic properties of a material are determined by electronic energy levels and the density of states. For nanomaterials, the energy levels and the density of states vary as function of size, resulting in dramatic changes.

Light emission from nanoparticles exhibit two important properties like *photoluminescence* and *electroluminescence*. In photoluminescence, light emission id photoinduced, ie, photoexcitation of the material give emission by de-excitation. In electroluminescence, light emission is electrically induced as a result of electron-hole combination. This light emission is the basis for their applications in visible and infrared lasers, optical sensors and LEDs.

Semiconductor nanocrystals or quantum dots made use in single electron transistors, computer chips and memory devices. The fluorescence and other properties of quantum dots are made use in bioimaging, solar cells and LEDs.

g) *Biological Properties:*

Because of their ultra small size , they can easily penetrate skin or cells and rapidly distribute in human body. E.g., Nanoparticles smaller than 20 nm can transist through blood vessel walls. Further because of their large surface area to mass ratio, they find high biochemical reactivity. Further, many nanomaterials have been designed for diagnostic or therapeutic medical use such as drug delivery, bio-

imaging devices etc. Certain nanostructures cause in vitro cell death, mitochondrial perturbations, membrane disruption, DNA mutation and chromosomal loss.

Applications

a) Catalysis:

Smaller the catalyst particle, greater would be the surface area and more would be the active centres. Hence greater the efficiency of nanoparticle as catalysts.

Eg. Compared to macroscopic Pt, nanoparticles of Pt supported on alumina surfaces show greater catalytic activity in the oxidation of CO to CO2, which is great importance in automobile industry.

Nanogold shows remarkable selectivity in partial oxidation reactions, like propylene to propylene oxide, which is not shown by its bulk counterpart.

b) Coatings:

Nanocoatings have widespread applications. Durable layer of titanium dioxide nanoparticles on glass, ceramic, metal or painted surfaces make them hydrophobic, antibacterial and makes surface so smooth that water runs off, dirt particles do not stick and germs do not survive.

A layer of silver nanoparticles, eg. Inside of a refrigerator can be effective against bacteria and fungi. Coating based on nanoscale calcium phosphate and proteins, which imitates natural tooth material, used to seal the microscopic cracks in tooth enamel. Nanocoatings have shown to improve toughness, thermal stability, hardness and make metallic surface gainst corrosion and scratch proof.

c) Plastics

It has been observed that nanocomposites made by the dispersion of inorganic nanoparticles can decrease the inflammability of plastics. Similarly introduction of conducting nanomaterials (0.05 to 0.1% carbon nanotubes) into plastics makes them electrically conductive.

d) Lubricants:

Fullerenes are well known lubricant nanomaterials. Mainly C_{60}, made from graphite are used as solid lubricants.

e) Imaging

Fluorescent nanoparticles like semiconductor quantum dots, fluorescent silica nanoparticles, silica coated fluorescent polymer particles, dye loaded latex nanobeds, fluorescent polystyrene particle, etc. have been used for imaging applications.

For eg. Quantum dots, the tiny light emitting semiconductor nanocrystals used for *biomolecular* and *cellular imaging*. It can be made nontoxic (by coating) to the body and large surface area to attach diagnostic and therapeutic antibodies.

In *bioimaging*, cadmium selenide-zinc sulphide quantum dots are used in targeting and imaging cancer cells. These quantum dots (5 nm diameter) are first coated with polymers (to protect the body and dot) and then attached with antibodies. When injected into body, the dots accumulate at the targeted tumour which could be detected by fluorescence imaging. Now a days nanoparticls have been employed for photography imaging also.

g) *Electronics:*

Quantum dots are used in electronic appliances such as LEDs, single electron tunneling devices like single electron transistors, computer chips, bioimaging devices and solar cells.

Properties of Fullerene Molecules

Fullerens:

Fullerenes are well known lubricant nanomaterials. Mainly C_{60}, made from graphite are used as solid lubricants.

- One example is the Buckminsterfullerene (Buckyball)
- It has a formula C_{60}
- It is a black solid
- Dissolves in petrol to make a red solution
- Free moving electrons so conducts electricity

The three-dimensional spherical fullerene molecule has unique chemical, physical, and physico-chemical properties, which include the following:

- The molecule can act as a semiconductor, conductor and superconductor under specific conditions
- Fullerenes can display the photochromic effect, which is a change in light transmission based on intensity
- Ability to form compounds with many different sorts of material including the ability to retain other substances inside the molecule and the ability to absorb free radicals
- Fullerenes are relatively safe and inert, and yet have properties that allow the substance to create active derivatives

1.Aromaticity

Aromaticity is the reactivity of the certain material or molecule with other in the different temperature. Fullerene also has aromaticity in different situations. A spherical fullerene has pi-bonding electrons

which are free to localize or delocalize in different chemical situations. According to the Huckel's rule the aromaticity of fullerene is three dimensional.

2.Chemical Properties

The carbon atoms within a Fullerene molecule are sp2 and sp3 hybridized, of which the sp2 carbons are responsible for the considerably angle strain presented within the molecule. C60 and C70 exhibit the capacity to be reversibly reduced with up to six electrons.

3.Physical Properties

Fullerenes are extremely strong molecules, able to resist great pressures—they will bounce back to their original shape after being subject to over 3,000 atmospheres. This property makes fullerenes become harder than steel and diamond. Fullerenes can withstand high degree of collisions, merely bouncing back and keeping their shapes; which explains the high stability of the molecule.

4.Optical Properties

Delocalized electrons in Fullerenes are known to provide exceptionally large nonlinear optical responses.

5.Chemistry

According to the researchers fullerenes are considered to be the stable molecules but not fully unreactive. In certain circumstances fullerene become reactive. The reactive characteristics of fullerene is electrophilic at double bonding, which reduces angle stress by changing hybridized carbons into sp3 hybridized ones. Due to the change in hybridized orbits, the bond angles tends to decrease from about 120° in orbitals of sp2 carbon atoms. This decrease in bond angles permits the bonds to bend lesser on closing the tube making fullerene molecule more stable.

6.Solubility

Fullerenes are soluble in many kind of solvents. The most Common solvents for the fullerenes include, carbon disulfide. Solutions of pure fullerene have a deep purple or voilet color. Color solutions of C70 are a reddish brown.

This set of special characteristics differs depending on the type of materials with <u>fullerenes</u> or fulleroid fragments and offers a very broad scope for their application.

APPLICATIONS

1 Solar Cells

The high electron affinity and superior ability to transport charge make Fullerenes the best acceptor component. A number of conjugated polymer–fullerene blends are known to exhibit ultrafast

photoinduced charge transfer. An important merit of organic solar cells is their flexibility. They can be rolled up, cut, and spread over any surface. Combining buckyballs, nanotubes, and polymers to produce inexpensive solar cells that can be formed by simply painting a surface. Similarly Fullerene can be used as organic photovoltaics

2 Fullerene Strengthening/Hardening of Metals

Fullerenes offer unique opportunities to harden metals and alloys. This is due to the unique characteristics of fullerenes, namely their small size and high reactivity.

3 Fullerenes Based Sensors

Fullerene-based interdigitated capacitors (IDCs) recently have been developed to explore sensor applications.

4 Fullerene in Medicine

Fullerene derivatives can be used in the photodynamic cancer therapy as antibacterial agents and medications of neuroprotective action. Because of their ability to enclose atoms, Fullerenes promise to be of great use as drug carriers. Fullerenes are powerful antioxidants, reacting readily and at a high rate with free radicals, which are often the cause of cell damage or death.

5 Polymer Additives

Fullerenes and fullerenic black are chemically reactive and can be added to polymer structures to create new copolymers with specific physical and mechanical properties. They can also be added to make composites.

6 Endohedral Fullerenes

Endohedral Fullerenes are created when an atom is inserted inside a Fullerene molecule. These Metallofullerenes are very stable molecules and can be use in many applications. For example in nano ball-bearing applications, Metallofullerenes ($K @C_{60}$) are more effective than fullerene.

6 Research

Buckyballs may be used to store hydrogen, possibly as a fuel tank for fuel cell powered cars. Researchers are attempting to modify buckyballs to fit the section of the HIV molecule that binds to proteins, possibly inhibiting the spread of the virus. Making bullet proof vests with inorganic (tungsten disulfide) buckyballs.

CARBON NANOTUBES

Synthesis: CNTs can be prepared in many ways, but the most important and common method is CVD. It is a technique in which the vaporized reactant (methane, ethylene, acetylene etc can be used as a

precursor or as a source of carbon) react chemically and forms a nanomaterial product that is deposited on the substrate. Substrate are materials on which CNTs are grown. Most commonly used substrates in CVD method are zeolite, silica, silicon plate coated with iron particles etc. To produce single-walled CNTs, metal catalyst nanoparticles such as Fe, Co, Ni, Mo, Fe-Mo alloys etc are used.

CNTs are also synthesised by electric arc discharge method which is also known as the Plasma Arcing method. CNTs found applications in the fields of sensors, and medicine such as gene editing, tissue engineering, artificial implantation, cancer cell tracing, and drug delivery.

Electrical And Optical Properties Of Carbon Nanotubes

Carbon nanotubes are particularly attractive, due to their tubular shape, low density, tuneable electrical properties, ballistic electron transport, lack of skin effect, current carrying capacity exceeding superconductors, mechanical strength/stiffness better than any metal, thermal conductivity exceeding diamond and many other properties. CNTs are composed of sp^2 bonds.

Optical properties of carbon nanotubes

Carbon nanotubes are hollow tubes made entirely from carbon with diameters in the nanometer range such as the one shown in the picture below. Nanotubes are promising candidates for nanoscale light-emitters and many other optical applications, especially in the infrared wavelength region of interest for e.g. optical communication. Because nanotubes can be both semiconductors and metallic depending on the diameter and "twist" they display highly interesting features. the optical properties of carbon nanotubes refer specifically to the absorption, photoluminescence (fluorescence), and Raman spectroscopy of carbon nanotubes. Spectroscopic methods offer the possibility of quick characterization of relatively large amounts of carbon nanotubes.
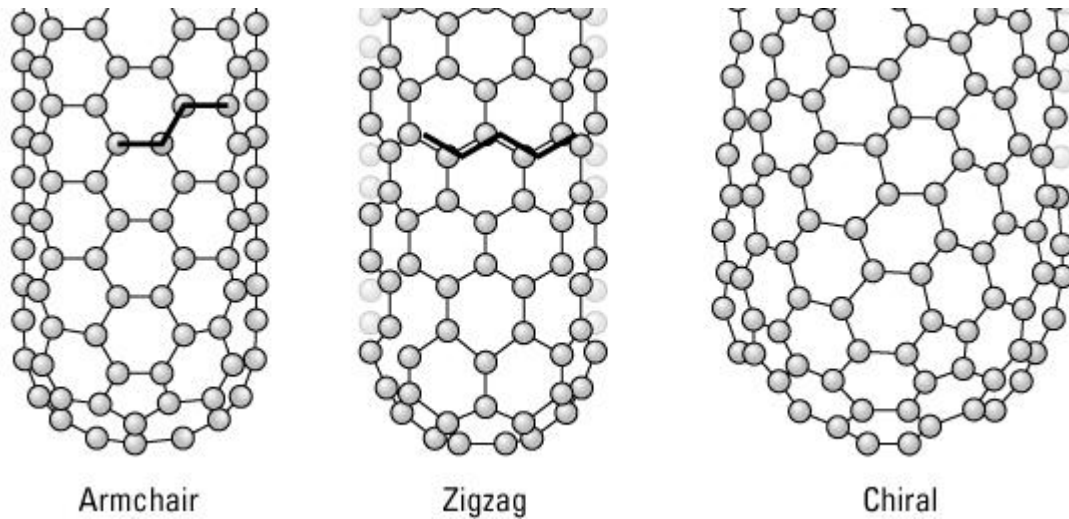
Electrical Properties of Carbon Nanotubes

The carbon nanotubes are long molecular wires that are able to conduct electrical current. They are constructed by rolling up a specified rectangular piece of a graphene sheet, with diameters from about 1 to 20 nanometres. Because of their small diameter and a typical length of a micro metre they are classified as 1D carbon systems, which electrical properties.

One very interesting potential application of carbon nanotubes is in electrical wiring. Conventional electrical wires made of copper and aluminium suffer from several problems including: weight (an issue in aerospace applications), skin effect (hindering their use in modern telecommunications),

mechanical performance (critical in overhead power lines), and electromigration (severely damaging microscopic wires in electronics applications).

The electrical properties of carbon nanotubes depend on how the hexagons are orientated along the axis of the tube. The following figure shows the three orientations that are possible: armchair, zigzag, and chiral.

Armchair   Zigzag   Chiral

Carbon nanotubes with the hexagons orientated in the configuration labeled armchair (hexagons are lined up parallel to the axis of the nanotube) have electrical properties similar to metals. When you apply a voltage between two ends of an armchair nanotube, a current will flow. An armchair carbon nanotube is, in fact, a better conductor than the copper normally used in electrical wire, or any other metal. The next two possible orientations of hexagons in carbon nanotubes share electrical properties similar to semiconductors. Those with the hexagons oriented in a circle around the nanotube have a configurations labeled zigzag. Those with a twist to the nanotube so the hexagons do not form any line are called chiral. These two configurations of nanotubes will only conduct an electric current when extra energy in the form of light or an electric field is applied to free electrons from the carbon atoms. Semiconducting nanotubes could be useful in building the ever smaller transistors used by the hundreds of millions in integrated circuits for all kinds of electronic devices.

For a given (n,m) nanotube, if $n = m$, the nanotube is metallic; if $n - m$ is a multiple of 3, then the nanotube is semiconducting with a very small band gap, otherwise the nanotube is a moderate semiconductor. Thus all armchair ($n = m$) nanotubes are metallic, and nanotubes (6,4), (9,1), etc. are semiconducting, i. e

- If the nanotube structure is armchair then the electrical properties are metallic

- If the nanotube structure is chiral then the electrical properties can be either semiconducting with a very small band gap, otherwise the nanotube is a moderate semiconductor

Metallic nanotubes can carry an electrical current density of 4×10^9 A/cm^2 which is more than 1,000 times greater than metals such as copper

Another interesting property of carbon nanotubes is that their electrical resistance changes significantly when other molecules attach themselves to their carbon atoms. Companies are using this property to develop sensors that can detect chemical vapors such as carbon monoxide or biological molecules.

Carbon Nano Tubes:

➢ Nano tubes are tiny tubes of carbon about 10,000 times thinner than human hair.
➢ these consist of rolled up sheets of multi layer carbon atoms in hexagon shape.
➢ They conduct electricity better than copper and are more stronger than steel wire .

Characterization of Nanoparticles
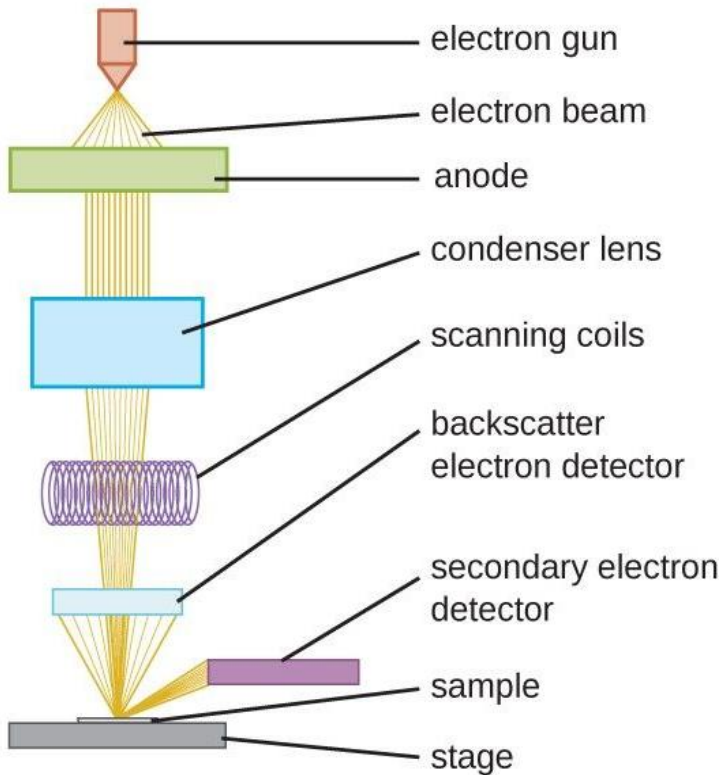
Various tools and instrumentation methods are used for the characterization for nanoparticles. Such as SEM and TEM.

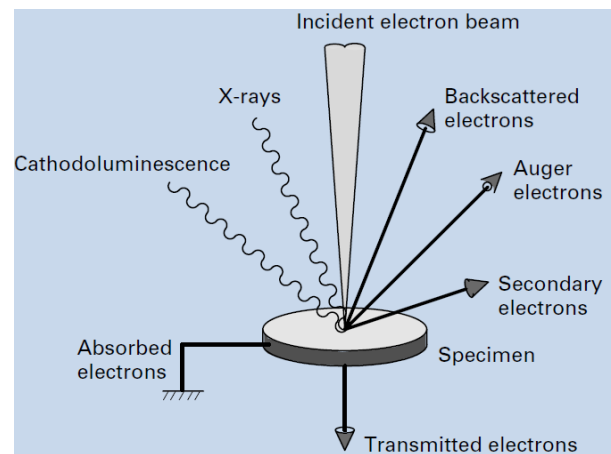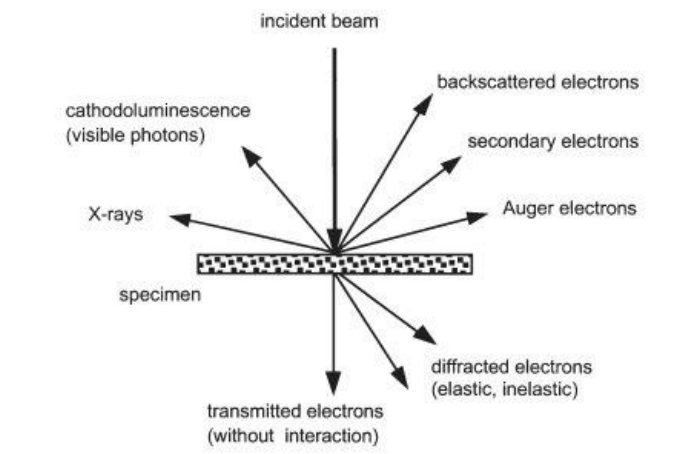## Scanning Electron Microscopy (SEM)

This electron microscopy based technique determines the size, shape and surface morphology with direct visualization of the nanoparticles. Therefore scanning electron microscopy offer several advantages in morphological and sizing analysis. However they provide limited information about the size distribution and true population average. During the process of SEM characterization, solution of nanoparticles should be initially converted into a dry powder. This dry powder is then further mounted on a sample holder followed by coating with a conductive metal (e.g. gold) using a sputter coater. Whole sample is then analyzed by scanning with a focused fine beam of electrons. Secondary electrons emitted from the sample surface determine the surface characteristics of the sample.

SEM

- electron gun
- electron beam
- anode
- condenser lens
- scanning coils
- backscatter electron detector
- secondary electron detector
- sample
- stage

The types of signals produced by an SEM include secondary electrons (SE), reflected or back-scattered electrons (BSE), photons of characteristic X-rays and light (cathodoluminescence) (CL), absorbed current (specimen current) and transmitted electrons.

Backscattered electron: Those electrons, which are deflected, back in the direction of the beam. The special detector in scanning and transmission electron microscope traps these signals. These are used

to discriminate areas of different atomic numbered elements. Higher atomic numbered elements gives off more backscattered electrons and appear brighter than lower numbered elements.

Secondary Electrons: These electrons are also collected with a special type of detector used in SEM and TEM. They are used primarily to reveal topographical feature of a specimen.

Auger Electrons: These are special types of low energy electrons that carry the information about the chemical nature (atomic composition) of the specimen. These are generated from the upper layer of specimen. It is a powerful tool in

the material sciences for studying the distribution of the lighter numbered atomic elements on the surface of the specimen.

Cathodoluminescent: This effect results when the energy of the impinging electrons in converted into visible light.

Characteristic X-rays: When high energy beam electrons interact with the shell electrons of the specimen atoms so that an inner shell electron is ejected. The removal of this electron temporarily ionizes the atom until an outer shell

electron drops into the vacancy to stabilize the atom. Since this electron comes from a higher energy level, a certain amount of energy must be given off before it will be accommodated in the inner shell. The energy is released as an x-ray,

the energy which equals the difference in energy between the two shells. Since this x-ray is of a discrete energy level, rather than a continuous. This means that since each element will generate a unique series of peaks, the spectrum may be used to identify the elements; such discrete x-rays are termed characteristic x-rays.

Applications of Scanning Electron Microscopy

Topography: The surface features of an object or "how it looks", its texture; direct relation between these features and materials properties (hardness, reflectivity... etc.)

Morphology: The shape and size of the particles making up the object; direct relation between these structures and materials properties (ductility, strength, reactivity...etc.)

Composition: The elements and compounds that the object is composed of and the relative amounts of them; direct relationship between composition and materials properties (melting point, reactivity, hardness...etc.)

Crystallographic Information: How the atoms are arranged in the object; direct relation between these arrangements and materials properties (conductivity, electrical properties, strength etc.)

Advantages of SEM

- ➢ It gives detailed 3D and topographical imaging and the versatile information garnered from different detectors.

- This instrument works very fast.
- Modern SEMs allow for the generation of data in digital form.
- Most SEM samples require minimal preparation actions.

Disadvantages of SEM

- SEMs are expensive and large.
- Special training is required to operate an SEM.
- The preparation of samples can result in artifacts.
- SEMs are limited to solid samples.
- SEMs carry a small risk of radiation exposure associated with the electrons that scatter from beneath the sample surface.

Transmission Electron Microscope

Transmission electron microscopy techniques can provide imaging, diffraction and spectroscopic information, either simultaneously or in a serial manner, of the specimen with an atomic or a sub-nanometer spatial resolution. TEM operates on different principle than SEM, yet it often brings same type of data. The sample preparation for TEM is complex and time consuming because of its requirement to be ultra thin for the electron transmittance. During the TEM characterization nanoparticles dispersion is deposited onto support grids or films. After dispersion they are fixed using either a negative staining material (phosphotungstic acid or derivatives, uranyl acetate, etc., or by plastic embedding). This is done to make nanoparticles withstand against the instrument vacuum and facilitate handling. When a beam of electrons is transmitted through an ultra thin sample it interacts with the sample as it passes through the surface characteristics of the sample are obtained.

TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine fine detail—even as small as a single column of atoms, which is thousands of times smaller than the smallest resolvable object in a light microscope. TEM forms a major analysis method in a range of scientific fields, in physical, chemical and biological sciences. TEMs find application in cancer research, virology, materials science as well as pollution, nanotechnology and semiconductor research. The transmission electron microscope is a very powerful tool for material science. A high energy beam of electrons is shone through a very thin sample, and the interactions between the electrons and the atoms can be used to observe features such as the crystal structure and features in the structure like dislocations and grain boundaries. Chemical analysis can also be performed.
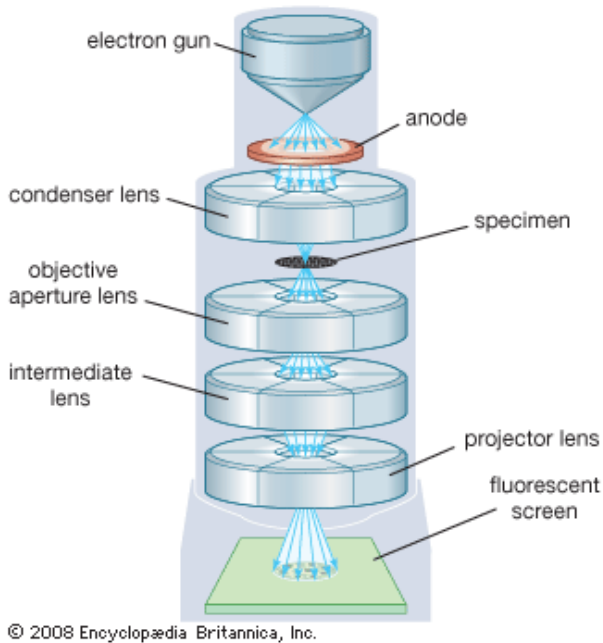
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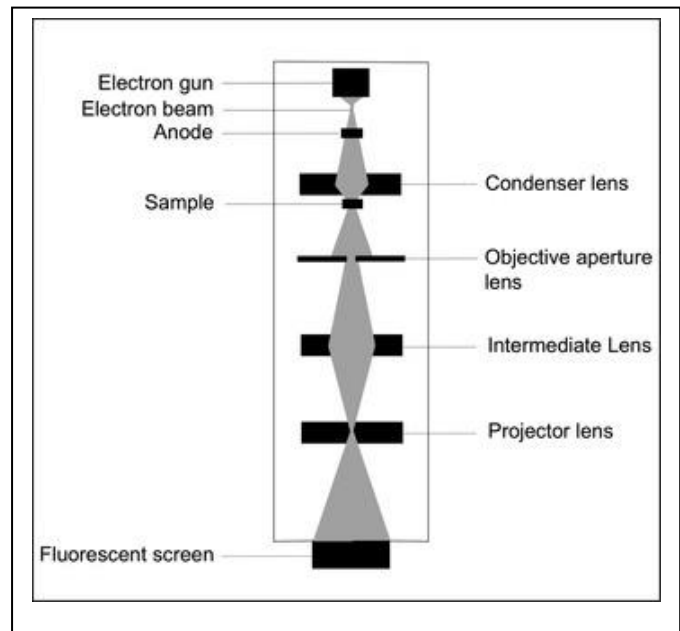
TEM can be used to study the growth of layers, their composition and defects in semiconductors. High resolution can be used to analyze the quality, shape, size and density of quantum wells, wires and dots. The TEM operates on the same basic principles as the light microscope but uses electrons instead 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. Thus, TEMs can reveal the finest details of internal structure - in some cases as small as individual atoms. At smaller magnifications TEM image contrast is due to absorption of electrons in the material, due to the thickness and composition of the material.

Working principles of TEM

Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through it. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a charge-coupled device.

Imaging:

The beam of electrons from the electron gun is focused into a small, thin, coherent beam by the use of the condenser lens. This beam is restricted by the condenser aperture, which excludes high angle electrons. The beam then strikes the specimen and parts of it are transmitted depending upon the

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thickness and electron transparency of the specimen. This transmitted portion is focused by the objective lens into an image on phosphor screen or charge coupled device (CCD) camera. Optional objective apertures can be used to enhance the contrast by blocking out high-angle diffracted electrons. The image then passed down the column through the intermediate and projector lenses, is enlarged all the way. The image strikes the phosphor screen and light is generated, allowing the user to see the image. The darker areas of the image represent those areas of the sample that fewer electrons are transmitted through while the lighter areas of the image represent those areas of the sample that more electrons were transmitted through.

As the electrons pass through the sample, they are scattered by the electrostatic potential set up by the constituent elements in the specimen. After passing through the specimen they pass through the electromagnetic objective lens which focuses all the electrons scattered from one point of the specimen into one point in the image plane.

Synthesis and applications of Quantum dots, and Graphene

Graphene synthesis methods are generally classified into two categories: top–down and bottom–up approaches. The top–down method is a destructive technique by which large starting materials are broken down by delaminating graphitic layers into graphene.

The bottom–up method is the assembly of graphene from smaller carbonaceous elements onto a substrate. Graphene can be synthesized using several bottom–up methods, namely, chemical vapour deposition (CVD). The chemical vapor deposition on transition metals (e.g., Fe, Co, Ni, Cu, Pd) is most common method used to prepare graphene, which requires a temperature as high as 1000 °C with a hydrocarbon (methane) gas flow as the precursor.

CVD is the deposition of gaseous reactants onto a substrate to form graphene. First, a gas-phase carbon precursor is adsorbed onto the surface of a transition metal catalyst, which undergoes catalytic decomposition to carbon atoms. Then the decomposed carbon species diffuse and dissolute into the metal at elevated temperatures. The dissolved carbon atoms are then precipitated out and segregated onto the metal surface. On cooling, surface nucleation initiates, followed by the graphene growth.

Graphene is technically a non-metal but is often referred to as a quasi-metal due to its properties being like that of a semi-conducting metal. As such, it has many unique properties that you don't find with other non-metallic materials. Each carbon atom is covalently bonded (sp^2 hybridized) to three other carbon atoms in a hexagonal array, leaving one free electron per each carbon atom. This free electron

exists in a p-orbital that sits above the plane of the material. Each hexagon in the graphene sheet exhibits two pi-electrons, which are delocalized, allowing for an efficient conduction of electricity. The holes in the structure also allow phonons to pass through unimpeded, which gives rise to a high thermal conductivity.

Graphene has many unique properties, making it an ideal material for use in electronic applications when compared to conventional materials. Electrical conductivity the most prevalent and important property of graphene.

Graphene found applications in the field of sensors (Due to the planar and consitent arrangement of atoms in a graphene sheet, every atom within the sheet is exposed to the surrounding environment.), batteries (graphene has been incorporated into lithium-ion batteries, lithium-sulphur batteries, supercapacitors and fuel cells). Graphene is incorporated into various composites for applications where strength and weight are limiting factors, for example in the aerospace industry (Graphene is being incorporated into many materials to make the existing material stronger and more lightweight). Graphene can be incorporated into polymeric materials to form graphene-polymer composite materials. Incorporation of graphene can help to increase the tensile strength of the polymers, increasing the shelf life of the polymeric material in commercial applications and also giving polymers electrical conductivity properties.

Quantum dots QD can be obtained by using top-down processing methods and bottom-up approach. Top-down processing methods include electron-beam lithography, and X-ray lithography. A number of different self-assembly techniques (bottom-up) have been used to synthesize the QDs, and they may be broadly subdivided into wet-chemical and vapor-phase methods.

QDs find biological application, including tracking different macromolecules in the cell, tracking various cells in the tissue, labeling organelles and cells, clinical applications, bioimaging, and other applications