Engineering Physics
Unit –V

Physics of Nanomaterials

Nanomaterials:

- Nano meaning that 10^{-9}
- A nanometer is billionth of a meter. i.e. a manometer equal to 10^{-9}m.
- "Nanomaterials could be defined as those **materials grain size is of the order of 1-100 nm** at least in one dimension"

Example:

1. carbon atom is approximately 0.15nm in diameter.
2. Diameter of Red Blood Cell (RBC) is approximately 7000nm.
3. Diameter of water molecule is around 0.3 nm. Thickness of human hair is around 80,000nm.

Nanoscience:-

Nano science can be defined as the study of phenomena and manipulation of materials at atomic, molecular and macros molecular scales, where properties differ significantly from those at a larger scale.

Nanotechnology:-

Nanotechnology can be defined as the design, characterization, production and application structures, devices and systems by controlling shape and size at the nano scale.

Types of Nanomaterials

Nanomaterials are those materials, whose grain size is the order of **1-100nm at least in one dimension**.

There are three types of Nanomaterials

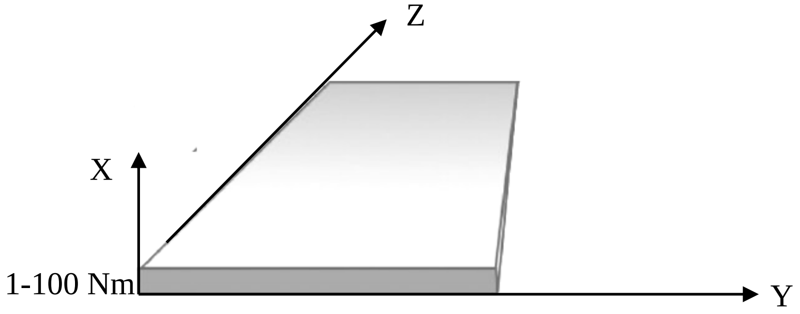
1. One dimensional Nanomaterials
2. Two dimensional Nanomaterials
3. Three Dimensional Nanomaterials

1. **One dimensional Nanomaterials:-**

Materials whose grain size is of the order of 1-100 nm along only in one dimension are known as 1-dim Nanomaterials

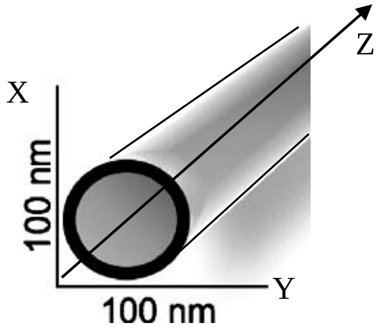
Example:

Thin films, Surface coatings, etc.,



2.Two dimensional Nanomaterials:-

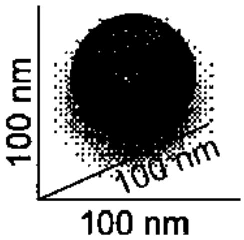
Materials whose grain size is of the order of 1-100 nm along any two dimensions are known as 2-dim Nanomaterials



Example: Nanowires , Carbon Nanotubes , Nanofibers etc.,

3.Three dimensional nano materials:-

Materials whose grain size is of the order of 1-100 nm along all the dimensions are known as 3-dim Nanomaterials



Examples: Precipitates, colloids and quantum dots…

Basic principles of Nanomaterials:

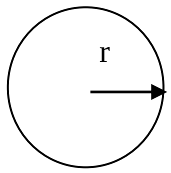
The properties of Nanomaterials s are different from those of bulk materials.
Two important factors that make the Nanomaterials to differ significantly from other materials are due to

1. **Large Surface to volume ratio**
2. **Quantum Confinement**

1. Increase in surface area to volume ratio:

Nanomaterials have a relatively larger surface face area compare its volume for example

Example-1



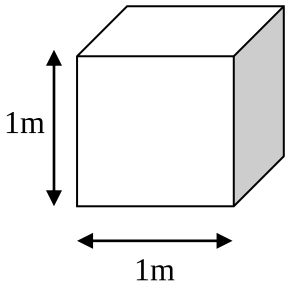
Let us consider a sphere of radius 'r'
its Surface area = $4\pi r^2$
and
Volume = $\frac{4}{3}\pi r^3$

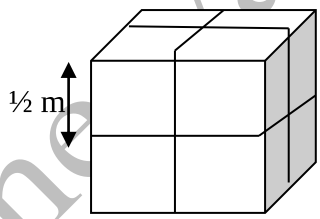
Therefore , Surface area to volume ratio = $\frac{surfacearea}{Volume} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}$

Thus, when the **radius of the sphere decreases its surface area to volume ratio increases**

Example-2

Let us consider another example.
For a cube of 1 unit volume shown in figure
the surface area is $6m^2$
When it is divided into eight pieces its suface area becomes $12m^2$.
When the same volume is divided into 27 pieces its surface ares becomes $18m^2$
When a given volume is divided into smaller pieces the surface area increases.





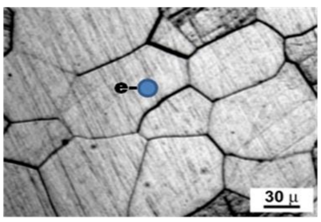
Surface area of each face of the cube =1mx1m=1 m^2
Surface area of the cube with 6 faces = $1m^2$ x 6= **$6m^2$**

Surface area of each face = 1/2m X 1/2m = ¼ m^2
Surface area of the cube with 6 faces =1/4x6
Surface area foe 8 cubes = 8x6x1/4 = **12 m^2**

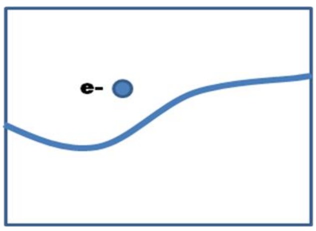
From the above it is clear that , as size of the particle reduces , surface area increases
As **particle size decreases, a greater proportion of atoms are found at the surface** compared to the atoms inside the material
For example a particle of size 30nm has 5% of its atoms on its surface at 10nm 20% of its atoms, and at 3nm 50% of its atoms on its surface.
Due to this, Nanomaterials are more **chemically reactive**.

<u>Quantum confinement:</u>

Electrons movement restricted in Nanomaterials compare to bulk material



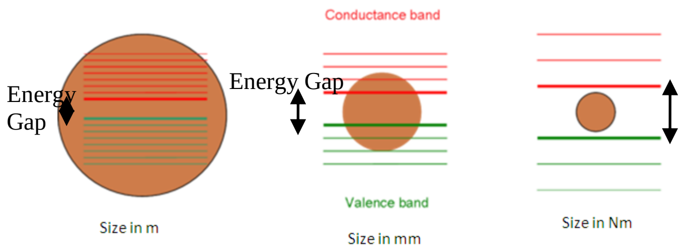
Bulk material



Nanomaterial

The bulk material consists of various many grain structure separated by grain boundaries. So electrons are very free to move. But the same material, as it goes to nanoform, the no of grains are reducing and the grain boundary increases in area. So the electrons movements are restricted. So heir allowed energy levels reduces and hence energy gap increases. This is known as quantum confinement.

Due to this, the electrical, optical and magnetic properties of Nanomaterials changes



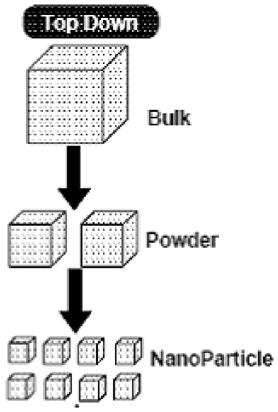
<u>Fabrication of Nanomaterials</u>:-

The Nanomaterials can be synthesized by two techniques namely

1. Top-down Method
2. Bottom up Method

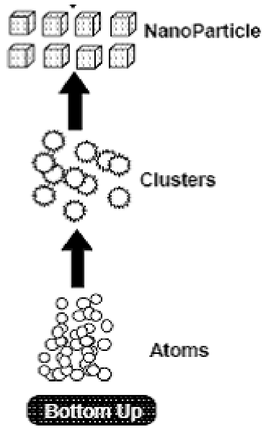
Top-down Method

In the top-down approach the bulk solids are disassembled (broken down to pieces) into finer pieces until the particles are in the order of nanoscale



Bottom up Method

In the bottom-up approach, the Nanomaterials are synthesized by assembling the atoms or molecules together to form the Nanomaterials

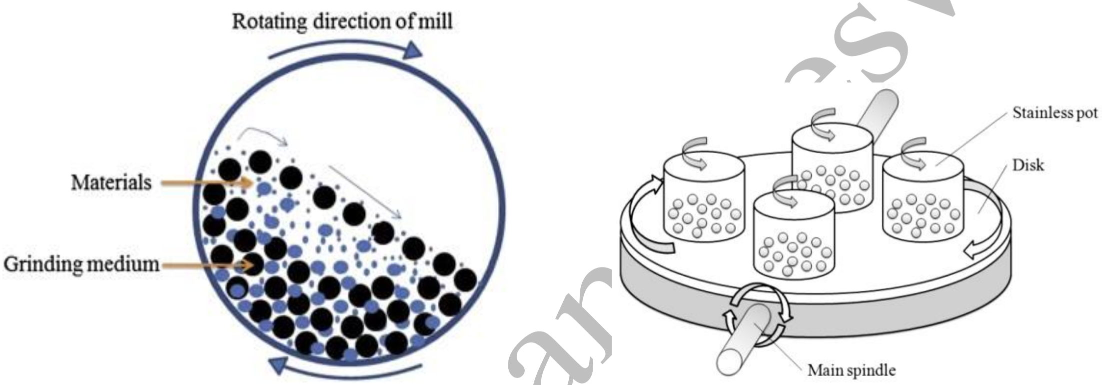


For example **Ball milling and sol-gal** are the methods used for fabricating Nanomaterials in top-down approach

The chemical vapor disposition method and plasma arching methods are the methods employed in the fabrication of Nanomaterials in bottom up

Ball milling method

1. Ball milling method is a **Top Down** method.
2. It is also known as **Mechanical Crushing or Mechanical Attrition**.
3. This is a **simple method** and **low temperature** method
4. This method is used **of synthesis all classes** of Nanomaterials.
5. This method is used to produce **Nano crystalline or amorphous** materials.



6. The Nanomaterials of **single phase or dissimilar powders** can be prepared by this method.
7. Ball milling is a process used for the production of Nanomaterials. In his method, **balls rotate with high energy inside a container** and then fall on the solid with gravity force and hence crush the solid into nanocrystallites.
8. Depending on the material to be synthesized **Steel, Iron, plastic, α-alumina and zirconium** balls are used.
9. Here the nanoparticles are produced due to **shear action** between the balls and the material.
10. Depending upon our requirement, the **rotational speed , size of the ball, the number of balls, milling time and milling atmosphere** can be varied.
11. By using a **cryogenic liquid** the brittleness of the particles can be increased.
12. **Care should be taken to prevent oxidation** during the process of milling.
13. In this method **scaling can be achieved up to tonnage quantity** of materials.

Advantages of ball milling process:

1. Nanopowders of **2 to 20 nm** in size can be produced. The size of nanopowder also depends upon the speed of the rotation of the balls.
2. It is an **inexpensive** and easy process.
3. It is a low temperature technique

Disadvantages:

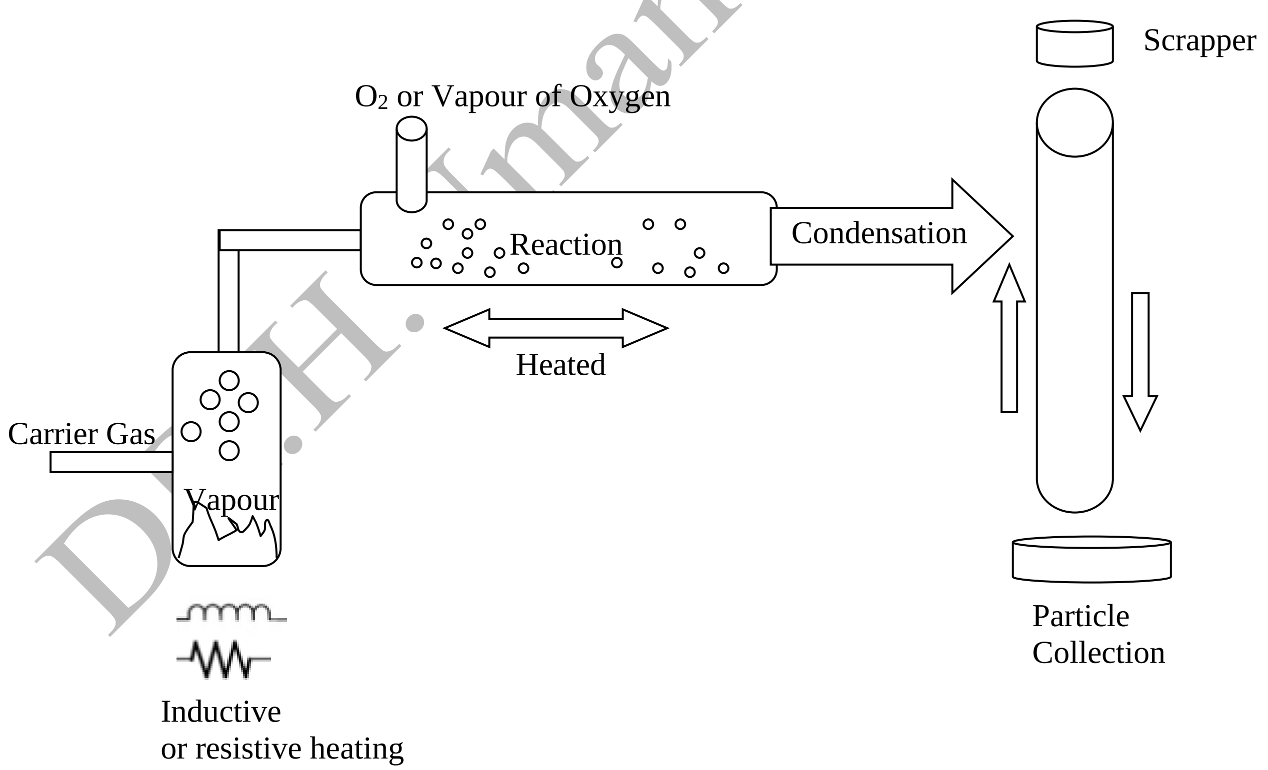
1 Shape of the Nanomaterial is **irregular**.

2. There may be **contaminants inserted** from ball and milling additives.

3. This method produces **crystal defects**.

Chemical Vapor Deposition Method:

1. In a chemical vapor deposition (CVD) the atoms or molecules which are in gaseous state are allowed to react **homogenously of heterogeneously**.
2. In a homogenous CVD, the particles or atoms or molecules in the gas phase are **diffused** towards the cold surface by **Thermophoresis action**.
3.



4. The **diffused particles can be scrapped** from the cold surface to get nanopowder
5. The particles are deposited into a subtract to form a film know as **Particulate Film**.

6. In a heterogeneous CVD, a **dense film of nanoparticles** is obtained on the surface of substrate
7. In CVD method **particle size, crystal structure and chemical composition** can be controlled
8. The **metal organic precursor** is introduced into the hot zone of the reactor with flow controller.
9. The precursor is vaporized by using **inductive heating or resistive heating**.
10. An **inert gas like argon or neon is used as carrier gas**,
11. The evaporated matter consists of hot atoms which undergo condensation in to small clusters .The cluster size is controlled by controlling **rate of evaporation rate of condensation and rate of gas flow. The clusters together produces nanoparicles**
12. The nano particles are collected by using a **scrapper** from the cold surface
13. The CVD method is **pure method** and also can produce defect free nanoparticles.

Advantages of CVD:

1. Pure methods , Contaminations can be avoided
2. Defect free material
3. Better film quality

Disadvantages

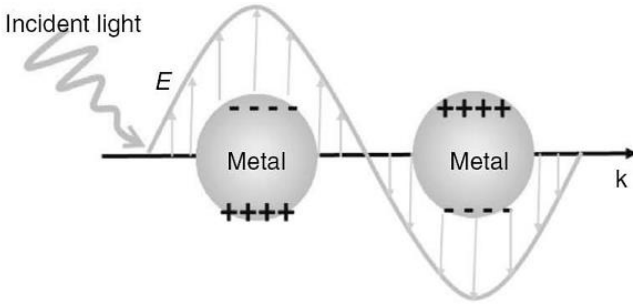
1. High process temperatures.
2. Complex processes,
3. Toxic and corrosive gasses.

Properties of Nanomaterials

OPTICAL PROPERTIES OF NANOMATRERILAS

Nanocrystalline systems have **novel optical properties**. If semi conductor particles or metallic particles are made small enough then **quantum effects** come into play

2. As the bulk materials go to nano level , **its allowed energy levels are reducing and hence he energy gap increasing** , this is called quantum confinement.
3. This drastically changes the optical properties of nanoparticles. In the nano level, the electron cloud on the surface of the Nanomaterial absorbs the visible light and starts oscillate and emit different wavelengths which are known as **surface Plasmon**. As the material goes to nanoscale even ultraviolet range absorption will be promoted.



For example

Golden nano spheres of 100nm size appears orange in **colour**

Gold nano spheres of 50nm size appear **green** in colour.

Gold spheres of **10-20nm** exhibit **red color**

Gold spheres of **2-5nm** exhibit **yellow color**.

Gold spheres of >20nm exhibit **purple color**

Similarly,

Silver particles of **40nm** exhibit **blue color**

Silver particles of 1**00nm** exhibit **yellow color**

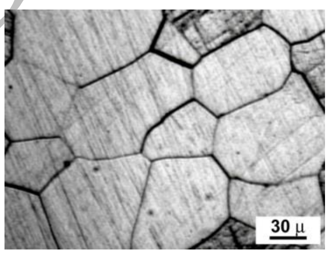
Prism shaped Silver particles **red color**.

Therefore the optical properties can be changes by controlling the particle size and even shape of the particle. Semiconductors and many metals show large changes in optical properties such as colour, as a function of particle size.

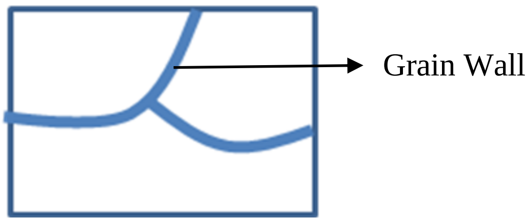
Mechanical Properties

Due to the nanometer size, many of the mechanical properties of the nanomaterials are modified to be different from the bulk materials including the hardness, elastic modulus, fracture , toughness, scratch resistance and fatigue strength etc

Most metals are made up of small crystalline grains. If there grains **are nanoscale in size the interface area within the material greatly increases**, which enhances its strength of the Nanomaterials.



Bulk material



Nanomaterial

According to Vicker's Law, Hardness is inversely proportional to grain size

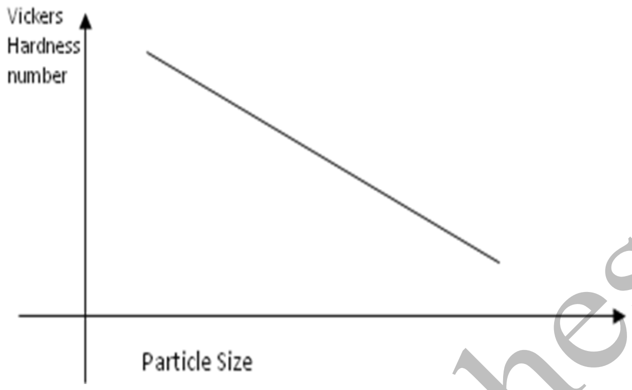
$$H = H_i + \frac{K}{\sqrt{d}}$$

H= Hardness.

H_i = Vickers hardness

K= Constant of Proportionality.

d= Average grain size.



Since the grain boundary increases it resists the defects and damages. In bulk material there is more possibility of crystal imperfections such as point defects, line defects, surface defects and volume defects, etc., The mechanical properties of nanomaterials increase with decrease in size, because smaller the size, lesser is the probability of finding imperfections.

The Strength of material improves significantly as the particle size decrease due to perfect defect free surface. Elastic modulus and toughness of material also increases as particle size is decreased

At high temperatures, the nanonmaterials behave like superplasitc materials. Super plastic materials will have extensive tensile deformation without fracture. In nanonmaterial's the occurrence of super plastic temperature decreases due to the decrease in grain size.

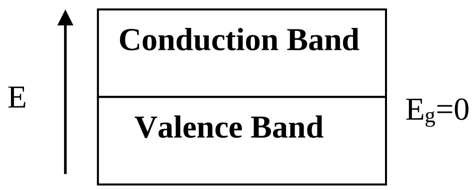
Example:

1. Nanocrystalline **nickel is as strong as hardened steel**.
2. The amorphous carbon which is having very poor mechanical strength, when goes to nano size known as carbon nanotube, gains mechanical strength which is equal to hard steel

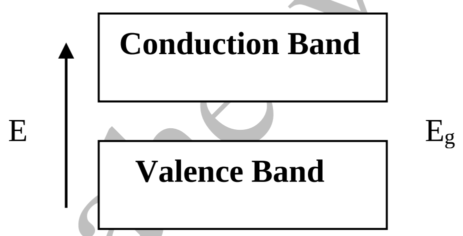
Electrical properties:--

The ionization potential at small sizes is higher than that for the bulk materials. This is because of quantum confinement effect. Quantum Confinement which is a fundamental characteristic effect in a nanomaterial as a result of size reduction. The free electrons present in such a size-reduced system gets confined due to quantum effects thereby leading to drastic effects on several electrical of Nanomaterials

In bulk materials, the electrons have more allowed energy levels, for example in metal, the valence band and the conduction band overlap, but in nanoscale due to quantum confinement, the allowed energy values of electron reduces , so the overlapping of energy bands disappears and it will be transformed into energy gap.



Bulk Metal



Nano Metal

Example:

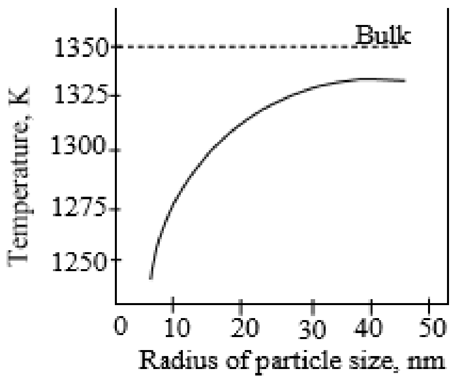
In nanoceramics and magnetic composites the electrical conductivity increases with reduction in particle size.

1. Bulk silicon is an insulator which becomes a conductor in nano phase.
2. The carbon nanotubes can act as conductor or semiconductor in behaviour but we all know that large carbon (graphite) is good conductor of electricity.

<u>Thermal Properties:</u>

1. The **melting point of a material directly correlates with the bond strength**. In bulk materials, the surface to volume ratio is small and hence the surface effects can be neglected.
2. In bulk materials the no,of atoms surrounding a particular atom is more compare to nano materials.
3. For example if an atom is surrounded by 7 atoms in a bulk materials , as it go to nano level, it will be surrounded by only three atoms.
4. Therefore the mount of energy required to make the solid in to individual atoms decreases , when the material goes from bulk to nano
5. So, Decrease in phase transition temperature
6. Example: Bulk gold is solid, as it goes to nano level it becomes liquid

7. Therefore , in nanomaterials the melting temperature is size dependent and it decreases with the decrease particle size diameters. The reason is that in nanoscale materials, surface atoms are not bonded heavily and hence has more freedom to move. Thermal conductivity increases with decrease in size of particle.
8. Melting point of gold decreases from 1200K to 800K when the size decreases from 30 nm to 20 nm size.



__Application of Nanomaterials__

MATERIALS TECHNOLOGY:-

1. Nanoscale additives in polymer composite materials for baseball bats, tennis rackets, motorcycle helmets, automobile bumpers, luggage, and power tool housings can make them simultaneously lightweight, stiff, durable, and resilient.
2. Nanoscale additives to or surface treatments of fabrics help them resist wrinkling, staining, and bacterial growth, and provide lightweight ballistic energy deflection in personal body armor.
3. Nanoscale thin films on eyeglasses, computer and camera displays, windows, and other surfaces can make them water-repellent, antireflective, self-cleaning, resistant to ultraviolet or infrared light, antifog, antimicrobial, scratch-resistant, or electrically conductive.
4. Nanoscale materials in cosmetic products provide greater clarity or coverage; cleansing; absorption; personalization; and antioxidant, anti-microbial, and other health properties in sunscreens, cleansers, complexion treatments, creams and lotions, shampoos, and specialized makeup.
5. Magnets made of nano crystalline yttrium- samarium-cobalt grains possess unusual magnetic properties. This is because they are having large interface area. Nono magnetic crystals will have high coactivity .they are used in motors and analytical instruments like

magnetic resonance imaging (MRI)

6. Nano sized titanium diozide and zincoxide are currently used in sunscreens. They absorb and reflect ultra violet rays (UV). They are transparent to visible light.
7. Nano engineered membrane could potentially lead to more energy- efficient water purification processes. They are used in desalination water plants by reverse osmosis.
8. Nano sized iron oxide is used in lipsticks as a pigment
9. Carbon nano particle act as fillers in a matrix. They are used as a filter to reinforce car tires.
10. Clay particles based composites containing plastics and nano-sized flakes of clay also used in the fabrication of car bumpers.
11. Improved control porosity at the nanoscale has applications in textiles. Breathable water proof and stain resistant fabrics can be fabricated using nano materials.
12. Nano particles are having high surface area. They can be used as catalytically active agents.
13. Unusual color paints can be prepared by using nano particles; this is because nano particles exhibit different optical properties.

INFORMATION TECHNOLOGY:-

1. Nano scale fabricated magnetic materials are used in storage of data.
2. Nano crystalline zinc selenide, zinc sulphide, cds and telluride fabricated by sol-gel technique are the materials for high emitting phosphors and are used in flat panel displays.
3. Nano particles are used for information storage.
4. Nano dimensional photonic crystals are used in chemical/optical computer.

Coatings with thickness controlled at the nano scale are used in optoelectronic devices.

BIOMEDICALS:-

1. Nano crystalline silicon carbide is used for artificial values of heart because of low weight high strength and inertness
2. Biosensitive nano particles are used for tagging of DNA and DNA chips.
3. Nano structured ceramics readily interact with bone cells and hence are used as implant material
4. Controlled during delivery and controlling the decrase are possible with nano technology.
5. Nano materials are used as agents in cancer therapy

ENERGY STORAGE:-

1. Addition of nano particles (Cerium oxide) to diesel fuel improves fuel economy by reducing the degradation of fuel consumption over time
2. Nano particles are having high absorbing capacity nano particles of nickel, platinum are used in hydrogen storage devices
3. Nano particles are used in magnetic refrigeration
4. Metal nano particles are very useful in the fabrication of Ionic batteries.