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Nanotechnology

Nanotechnology deals with technology based on phenomenon exhibited by particles of very small size i.e. of the order of 10^{-9}m (nm) (Nanometer).

Nanoparticles or nanomaterials are materials having very small dimensions i.e. of the order of few nanometers. If any one dimension of material (either length, width, height or diameter) is of the order of 1 to 100 nm then we call them as nanomaterials or nanoparticles. These nanoparticles may have different structures such as spherical, cubic, rod, wires, flowers, petals, tubes etc.

When material is in nano dimension then its properties are completely different as it shows in its bulk form (bigger size or normal dimensions). This is because, when size of the material is in nanometer (10^{-9}m), it is comparable with charactoristic length of material. Charactoristic length decides properties of the materials. So combined effect of charactoristic length of materials defines properties of bulk material. If size of material is comparable with charactoristic length, its effect on properties is completely different.

Let us take example of gold (Au). Gold apears yellow in its bulk form but if we reduce size of gold in nano dimensional form it appears reddish to purple colour with increasing size.

Use of nanomaterials in technology is very effective and efficient since it posseses extra-ordinary properties.

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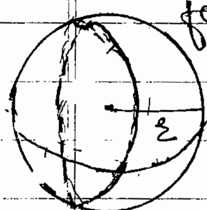
* Properties of the Nanoparticles :→

(1) Surface to volume ratio means ratio of surface area to volume of particle.

Let us calculate surface to volume ratio (SVR) for spherical shape of the particle.

$$SVR = \frac{\text{Surface Area}}{\text{Volume}} = \frac{4\pi r^2}{4/3 \pi r^3} = 3/r$$



for bulk particle of radius of 1cm
i.e. $r = 1cm = 1 \times 10^{-2}$ m.

$$SVR = 3/10^{-2} = 3 \times 10^{2} \text{ per meter.}$$

for nanoparticle of radius 10nm
i.e. $r = 10nm = 10 \times 10^{-9}$ m

$$SVR = \frac{3}{10^{-9}} = 3 \times 10^{9} \text{ per meter.}$$

Hence, for nanoparticles surface to volume ratio is very high means surface area is much higher as compared to volume of nanoparticle.

It means that number of atoms on the surface are much higher in nanoparticles or nanomaterials. This increases surface energy of the particle and hence surface becomes highly reactive.

High reactivity is very important for catalyst applications. Semiconductor nanoparticles are widely used in photocatalysis since its surface is highly reactive.

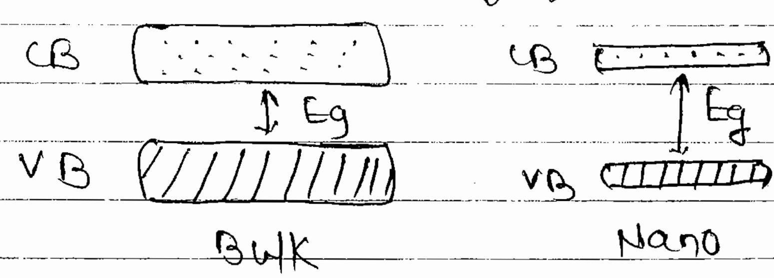
In photocatalysis, degradation of synthetic dyes are done with semiconductor nanoparticles in presence of visible and Ultraviolet light.

② When particle size decreases and it becomes comparable to characteristic length i.e. for semiconductor nanoparticle if size of nanoparticle is comparable with wavelength corresponding to band gap ($E = hc/\lambda$) or in metals if size of the particle is comparable with surface plasmon frequancy. Energy states get quantized (descrete) i.e. material shows quantization effect also called quantum quantization.

Descrete energy states affects electronic and optical properties of material.

③ Nanoparticles also shows blue shift in absorption wavelength. Blue shift means absorption wavelength is decreases i.e. absorption energy increases.

i.e. If particle size decreases, no. of atoms (atomic density) in particle decreases. hence energy states corresponding to atoms also decreases this causes narrowing of energy bands.



$$E_g = \frac{hc}{\lambda}$$

Hence band gap is increases in nanoparticles so wavelength corresponding to band gap decreases. It means wavelength shifted to Blue wavelength (towards left). This is called Blue shift.

Also for metal nanoparticles surface plasmon frequancy increases i.e. wavelength decreases it is also called blue shift.

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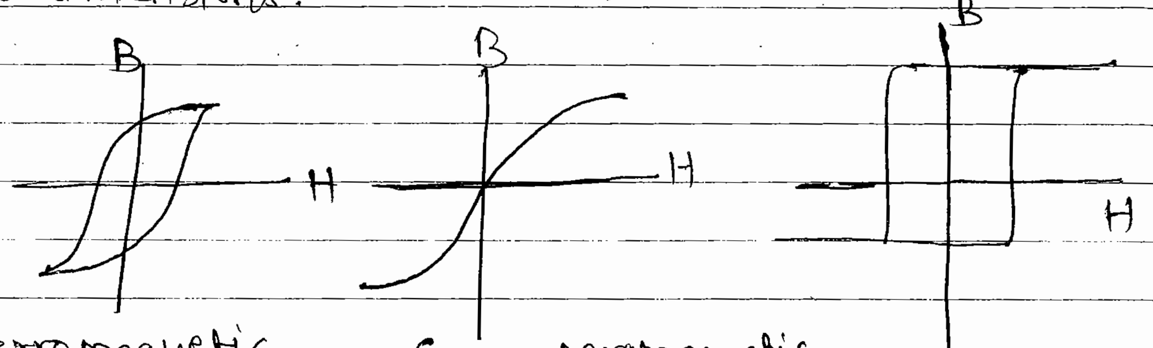
(4) Reduced in particle size causes bond weakening and Bond weakening gives lowering in melting point of nanomaterials.

(5) Ferromagnetic nature of bulk materials is transformed in to super paramagnetic and single domain nature when they are in nanodimensions.



ferromagnetic — Superparamagnetic (Used in hyperthermia for curing cancer) — Single domain (Used in memory devices)

(6) If size of the particles is reduced to nano form, surface defects such as vaccancies and interstitials (for doping) also increases on the surface, since area of surface is higher in nano form, electronic ~~and~~ properties of the material changes.
e.g. metal oxides are electrically insulator in bulk form but it shows conducting nature when ~~in~~ it is nanoform.

(7) It is also observed that mechanical strength of carbon nanotubes (carbon nano form) is 1000 times higher than stainless steel.

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* Applications of the nanoparticles :→

① Catalysis :→

High surface area as well as highly defective surface of the nanoparticles increases chemical activity of materials, so nanoparticles are used in catalysis in industry. e.g. photocatalysis.

② Chemical sensors :→

Due to high surface reactivity, nanoparticle based chemical sensors gives high sensitivity, fast responce and recovery.

③ Biomedical applications :→

Nanoparticles show superparamagnetic nature i.e. zero hysteresis loss. Hence nanoparticles give no heat dissipation in absence of Radio frequancy radiation. This phenomenon is very useful in hyperthermia i.e. cancer treatment.

[In hyperthermia, cancer cells are heated with magnetic nanoparticles by exposing it to RF radiation. Temperature of the cells is controlled in small regoin of the body where cancer cells are located. Healthy cells live up to 48 °C and cancer cells live up to 42 °C.]

Magnetic nanoparticles are also used in drug targeting. Drug is loaded / coated on nanoparticle and it is transported to perticular place or organ in the body by applying external magnetic field.

Magnetic nanoparticles are also used in M.R.I. (Magnetic Resonance Imaging)

Porous Nanoparticles are also used in susteined drug release (i.e. slow drug release with time).

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(4) Nano electronics :→

Nanoparticles based devices are used in NEMS i.e Nano - Electro - Mechanical - system. NEMS provides extremely small electronic devices such as transistors and diodes. (Miniaturization of technology)

NEMS works more efficiently and also takes small space and very small power.

(5) Energy Sector :→

Efficiency of the solar cells are ~~to~~ increased by using quantum dots (semiconductor nanoparticles such as CdTe, CdSe with size less than 10 nm)

Also efficiency of the fuel cells are increased by adding nanoparticles to electrodes as well as to proton exchange membrane.

(6) Cosmetics :→

Sun screens and Fairness creams prepared with addition of Zinc oxide (ZnO) and Titenium oxide (TiO_2) nanoparticles blocks ultravoilet rays from sun. Ultravoilet rays cause skin cancer.

(7) Self cleaning Glasses :→

If nanoparticles are coated on glass, structures of nanoparticles on glass surfaces gives super hydrophobic and super hydrophilic surfaces.

super hydrophobic surface (contact angle is $> 90^0$)

super hydrophilic surface (contact angle is zero)

Super hydrophobic surfaces repell water, so moisture is not get condensed on glass. As moisture is main reason to get glasses dusty. so glass remains clean without any cleaning.

Superhydrophilic surfaces attracts moisture and it helps to remove dust on the glass.

These surfaces are also used to condense water in dry regoins like desert.

Self cleaning glasses are widely used in eye glasses and in vehicle glasses. It is also used in optical instruments.

(8) Defence :-

Most light weighted bullet proof jackets are made up of composites. These composites are madeup of polymers and carbon nanotubes.

Metal Nano-structures are used in cloaking i.e. concept of invisibility. Metamaterials are used for cloacking. These metamaterials are consist of Gold and platinum nanostructures with negative refractive indices. Metamaterials completely absorb electromagnetic radiation or completely reflect electromagnetic radiations which is concept of cloaking.

* Synthesis of Nanoparticles / Nanomaterials :→

Nanoparticles are synthesized by various chemical, physical and hybrid methods but basically there are two approaches to synthesize nanoparticles. First one is Top-Down approach and second is Bottom-up approach. All the chemical, physical and hybrid methods are grouped in to these two approaches.

I] Top - Down approach :→

In top down approach, nanoparticles are synthesized from bulk materials. It is similar to create or design sclupture or statues from big stone

or rock. i.e. from big things, small things are made.
i) synthesis of nanoparticles by Ball milling is one of the example of top down approach.
Ball milling is physical method to synthesize nano-particle from microparticle powder of materials.
Ball milling consists of Hard stainless steel cylinder in which spheres of different radius made up from stainless steel is filled. Microparticle powder is then placed in cylinder and cylinder is rotated with different RPM (revolution per minute). Due to friction in the spheres, powder is grinded and takes nanosize. Size of the nanoparticle depends on speed of the rotation and duration of rotation.

ii) synthesis of graphene from graphite :→
This is also top down approach. This is chemical method in which graphite kept in concentrated hydrochloric acid (HCl) and sulphuric acid (H_2SO_4). It breaks interlayered bonds in graphene layer and separate them. Graphene is single layer hexagonal carbon which is highly electrically conductive.

iii) Synthesis of metal oxide nanoparticles from bulk powder is also similar approach. Bulk microparticles are kept in citric acid solution. citric acids breaks the bonding between atoms. This bonding is physical bonding (Vander Waals bonding). so particles get break in to nanoform.

iv) PLD (Pulsed Laser Deposition) :- PLD is physical technique used to deposit (coating) nanoparticles in thin film form. Sample in bulk is exposed to high energy density beam of pulsed Laser. This high energy melt the sample and form plum. This plum is condensed on substrate kept near to bulk sample. It forms thin film of nanoparticles on substrate. substrate means support on which film is formed.

II] Bottom - Up Approach :-

In bottom up approach, nanoparticles are synthesized with oxidation and reduction of ~~too~~ ionic solutions. It is similar to built building with small brick. means nanoparticles are formed with atoms with nuecleation and condensation process.

i) Chemical wet route is bottom up approach to synthesize nano particle. This method is also called colloidal route. In this method, ionic solution is prepared using salts such as chlorides, nitrides, sulphide, acetate in appropriate solvent such as water, ethanol or chloroform. Then capping agent such as thiols are added to solvent and finally either reducing agents such as sodium borohydrate is added drop by drop to get metal nanoparticles. or oxidizing agent is added such as sodium hydroxide (NaOH) and pottasium Hydroxide (KOH) to get metal oxide nanoparticles. Capping agent controls the size of nanomaterials and gives dispersed nanoparticles in solution due to electrostatic repulsion of similar charges of caping agents on the surface of nanoparticles.

ii) Co-precipitation method is also bottom up approach This is chemical method in which precipitation of ionic solution is prepared by adding ammonia.

Basic pH is maintained to ensure complete oxidation. The precipitate then washed and dried at appropriate temparature and nanoparticles get formed.

iii) Physical Vapour Deposition :- (PVD)
PVD is used to form thin film of nanoparticles perticularly for metals. 10^{-4} Torr vacuum is created in chamber and metal is evapourated by passing high current through metal. Vapours of the metal is condensed on cold substrate.

iv) Chemical Vapour Deposition (CVD) is hybrid method mostly used to synthesize carbon nanostructures such as graphene, fullerens and carbon nanotubes (CNT).

Vapours of alchols and alkanes such as methyl alcohol and methane is passed in tube furnace maintained at high temperature (above 1000°C) chemical reactions of these carbon compounds forms carbon nanostructures in tube furnace.

v) Spray Pyrolysis Technique (SPT) is used to form thin film of nanoparticles. Metal salts in ionic solutions are formed in methanol and distilled water and this solution is sprayed on hot substrate. pyrolysis means reaction / degradation using heat. On the substrate salt reacts with oxygen and forms metal oxide nanoparticles on the substrate.

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* Characterization Tools :-

To study shape and size (Morphology and topography) of the nanoparticles following tools are used.

(1) Scanning Electron Microscope (SEM) :-

(2) Transmission Electron Microscope (TEM) :-

(3) Scanning Tunneling Microscope (STM) :-

(4) Atomic Force Microscopy (AFM) :-

(1) Scanning Electron Microscope (SEM) :→

Optical microscopes give resolution of object up to micrometer range as wavelength of visible light is much larger. In order to observe objects smaller than micrometer, we have to use smaller wavelength. If source with very small wavelength i.e. in nanometer range or in Å range, one can observe nanoparticles or object with nano dimensions.

For such a small wavelengths, beam of electron from electron gun is used. The wavelength of electron beam is calculated with de Broglie hypothesis.

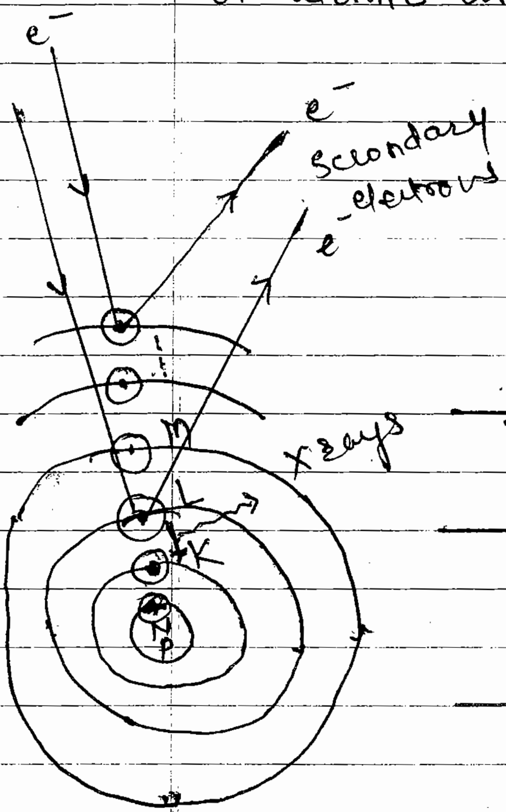
$$\lambda = h/p = \frac{h}{\sqrt{2meV}} = \frac{12.27}{\sqrt{V}} \text{Å}$$

where, V is applied potential.

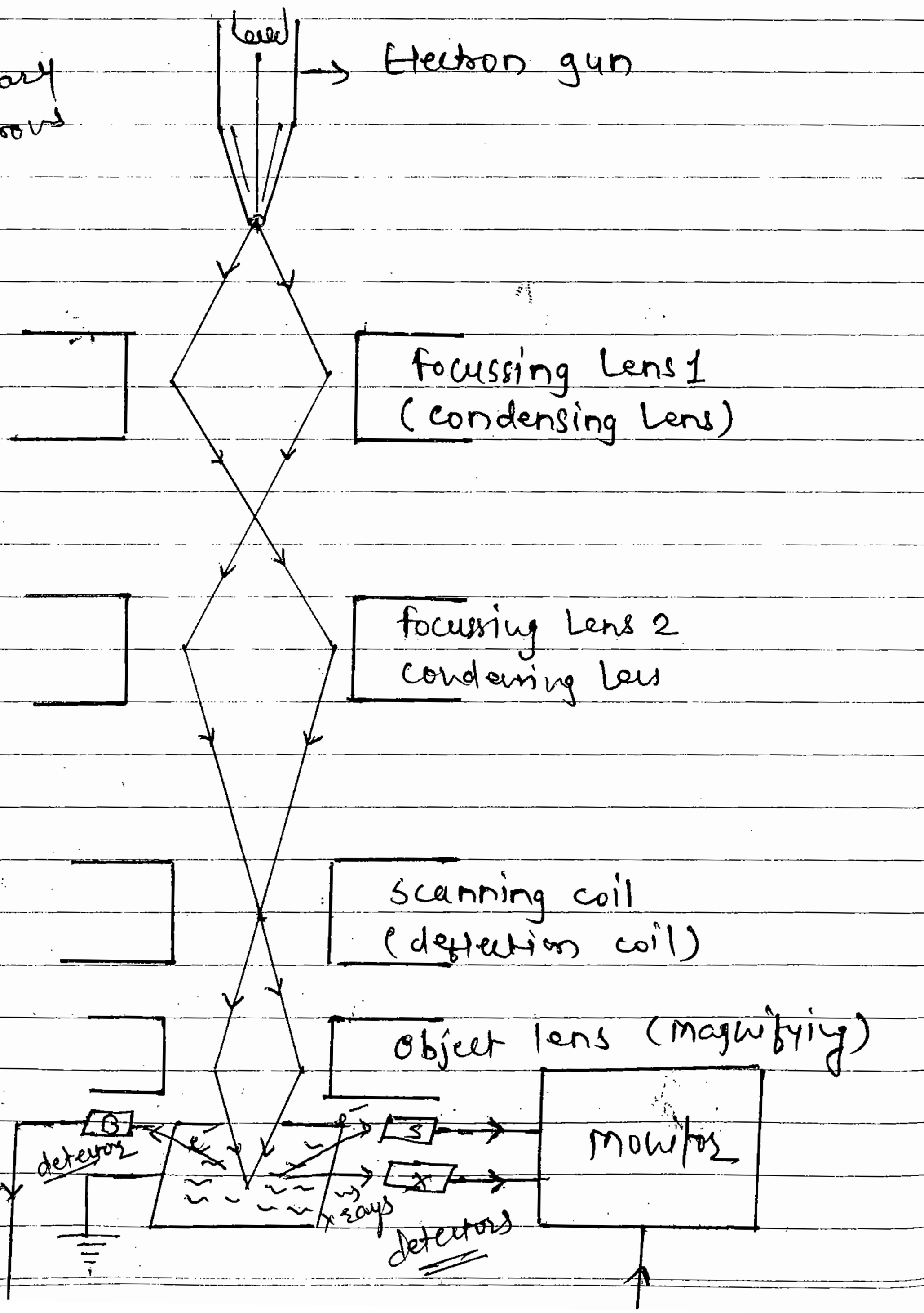
Scanning Electron Microscope consists of electron gun, focusing lenses (condensing lenses), scan coils, objective lens, sample holder and electron detectors.

* **Principle :-**

Beam of electron is incident on nanoparticles, scattered electrons from nanoparticles such as secondary electrons, backscattered electrons and x-rays are detected with respective detectors and morphology of the nanoparticles is formed on monitor by secondary and back scattered electrons. Chemical composition or atomic composition is analysed by x-ray detectors.



Atom



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* Working :- A beam of electron is produced from electron gun. This beam is focussed by two focussing lenses (electrostatic lenses) also called as condensing lenses. focussed beam of electron is moved over nanoparticles using scanning coils (deflection coils). scanning of beam over sample holder is used to observe complete view of the nanoparticles and also observe different regions of nanoparticles on sample holder. Finally beam is focussed on sample (nanoparticles) using objective lens. objective lens magnify image of the nanoparticles.

When beam is get incident on nanoparticles, beam get scattered. It gives two scatterings. scattered beam of electrons consist of back scattered electrons i.e. electrons get scattered elastically (with same energy) by repulsion from inner shell electrons. scattered beam of electron also consist of secondary electrons i.e. electrons from the sample. This is inelastic scattering (less energy than incident beam). Energy of the beam is transfered to electrons in the nanoparticle and it eject electrons, these are secondary electrons. If incident energy is smaller, then mostly secondary electrons are from outer shells of atom. If incident energy of the beam is higher then secondary electrons are from core shells (inner shells).

Back scattered electrons and secondary electrons form image. Also high energy electron beam produces characteristic X rays from nanoparticles. These X-rays provide chemical composition (atomic composition) of nanoparticles.

To observe nanoparticle under electron microscopes, it must be conducting and must be grounded in order to avoid electron loss in nano-particles due to ejection of secondary electrons. If nanoparticles are insulating then they are coated with fine layer of conducting metal nanoparticles such as Platinum (Pt) and Aluminium (Al).

SEM gives image resolution upto 50 nm. Below, 50 nm, it does not give good contrast in image formation.

Transmission Electron Microscopes are used to observe particles below 50 nm.

② * Transmission Electron Microscopes :→

The working of Transmission Electron microscope is similar to scanning electron microscope. Only difference is beam of electron is transmitted through nanoparticles dispersed on thin copper grid (foil of copper).

Transmitted electron beam from nanoparticles is magnified with magnetic lenses and final image is detected with electron detector.

Transmitted electron beam also gives diffraction pattern due to diffracted electron beam from nanoparticles. This helps to study crystal structure of material.

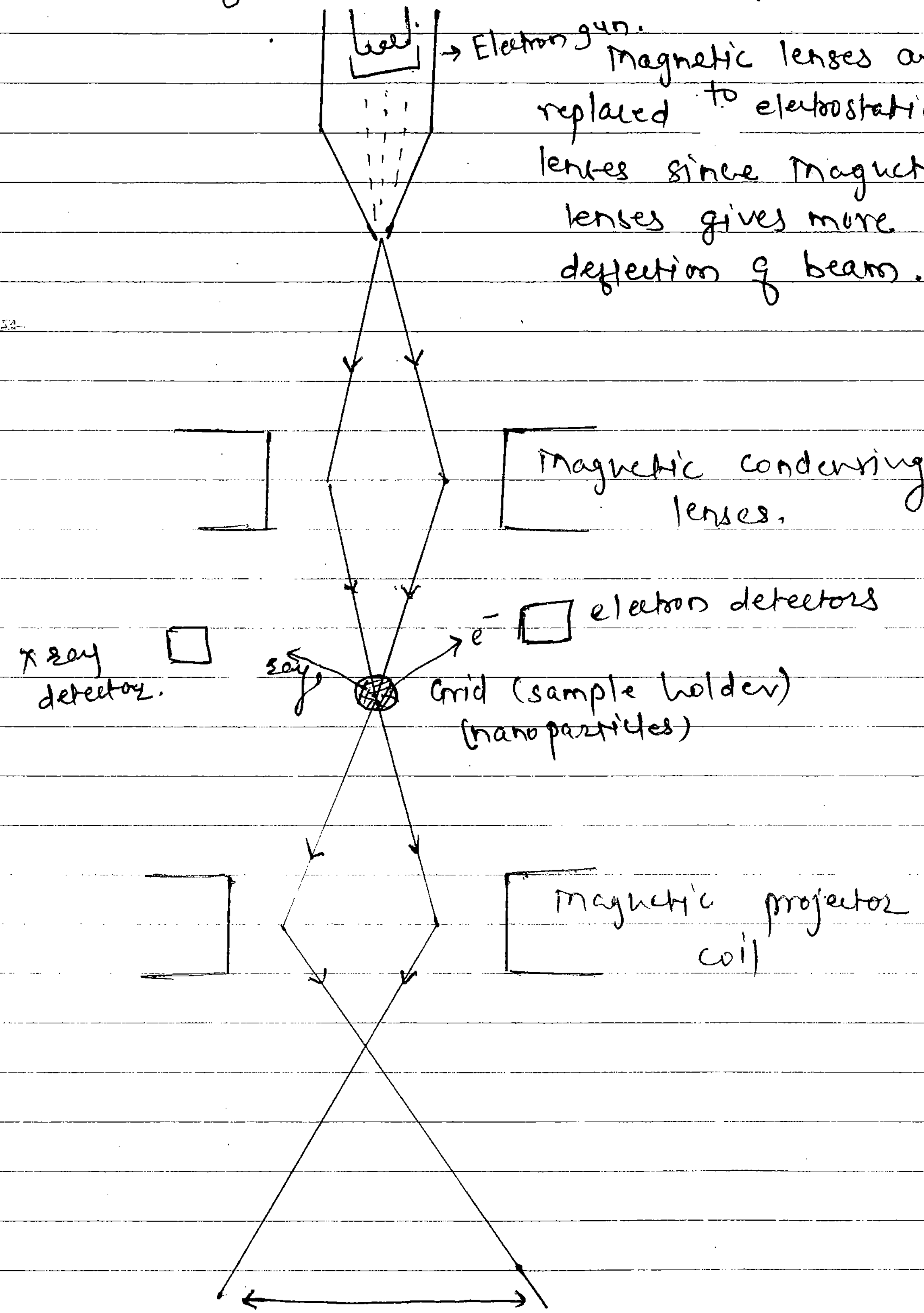
Since energy is higher, resolution of TEM images is much higher than SEM. Particle size upto few nanometers can be observed using TEM.

High Resolution TEM (HR-TEM) gives atomic arragement of the materials. It helps to study defects in materials.

Since electron beam is transmitted through material, electron densities difference in nanoparticle and its capping clearly seen in TEM images.

construction of TEM is as shown in figure.

Magnetic lenses are replaced to electrostatic lenses since magnetic lenses gives more deflection of beam.



Final image of Nanoparticles.

Electron detector and photographic plate (diffraction pattern)

TEM.

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③ Scanning Tunneling Microscope :- (STM)

Scanning Tunneling microscope is used to study surface morphology and electronic properties of the nanoparticles. It works on quantum mechanical phenomenon called tunneling. Tunneling is probability to cross potential barrier by electron even though electron has low energy than potential barrier.

If we maintain potential borrier (gap) between two atoms, tunneled electrons give current (tunneling current) and this tunneling currents is used to study surface morphology and local density states of atom (or nanoparticles). since STM works on tunneling current only conducting particles are studied under STM.

Nanoparticles or thin film of nanoparticles are kept on horizontal sample holder and probe i.e. needle of very small diameter (order of few atoms) is aligned on nanoparticles. Very small distance (4 to 7 Å) is maintained between probe and nanoparticles. (i.e. small gap of 4 to 7 Å is maintained between probe and nanoparticles).

Current is passed through needle (or probe) and nanoparticles are grounded. Electrons are tunnelled in to nanoparticles and grounded and hence completed the circuit. This tunneling currents on different locations of nanoparticles gives morphology (shape) and local density states of nanoparticles. From density states, conductivity and defects on the surface are studied.

Amount of tunneling current is of the order of nano Ampere (nA).

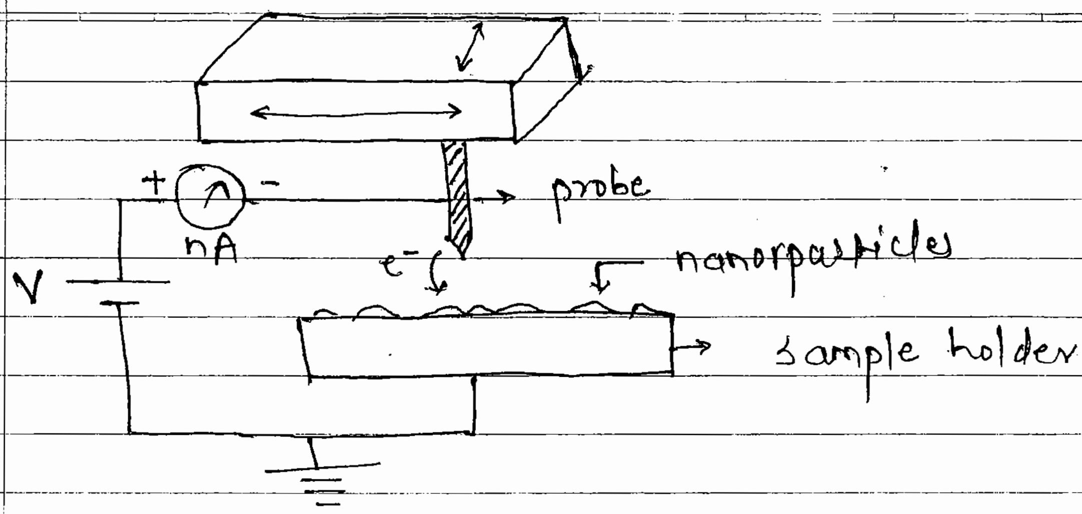

fig. Scanning Tunneling Microscope.

Atomic arrangement in nanoparticles is also observed in STM.

STM works in two modes :-

① constant current mode — current is kept constant by varrying distance between probe and nanoparticles

② constant Height mode — Height of the probe is kept fixed and varrying tunneling current is recorded on different locations of the nanoparticles.

In STM, vacuum is very important since tunneling of electron takes place. so tunneling may affected due to collision between air molecules and electrons.

Also nanoparticles must be conducting. Insulating nanorpticles can not be studied in STM.

(4) Atomic Force Microscopy (AFM) :→

Atomic force microscopy is invented to overcome non-conducting nature of nanoparticles in STM.

It works on intermolecular forces between two atoms. If atoms are very close to each other, they experience either repulsive or attractive forces depending upon distance of separation.

Net force is given by,

$$F = \frac{A}{R^{12}} - \frac{B}{R^{6}}$$

If R is very small, force is repulsive and repulsive force is due to repulsion between electrons of two atoms.

$$\therefore F = \frac{A}{R^{12}} \text{ is dominating term.}$$

If R is slightly larger, force is attractive

$$\therefore F = -\frac{B}{R^{6}} \text{ is dominating term.}$$

Atomic force Microscope consists of atomically sharp and hard tip made from silicon Nitride (Si_3N_4) or silicon mounted on head of the cantilever. This tip is moved over surface of nanoparticles. Force experienced by tip is used to study surface morphology of nanoparticles.

Feedback mechanism is provided with piezo-electric sensor to maintain tip at constant height from the sample (nanoparticle).

Deflection of cantelever due to attractive and repulsive force is detected by laser beam focused on head of cantelever and further beam incident on photodiode (photodetector). Variation in current of photodiode is feedback to peizosensor to maintain hiegut and variation in current is also used to study surface morphology of nanoparticles.

AFM works in to two modes :-

(1) Contact mode :→ In contact mode force experienced by tip is repulsive force.

② Non-contact mode :- In non-contact mode, force experienced by tip is attractive.

Different intensities of laser beam detected by photo diodes is used to study surface morphology of nanoparticles.

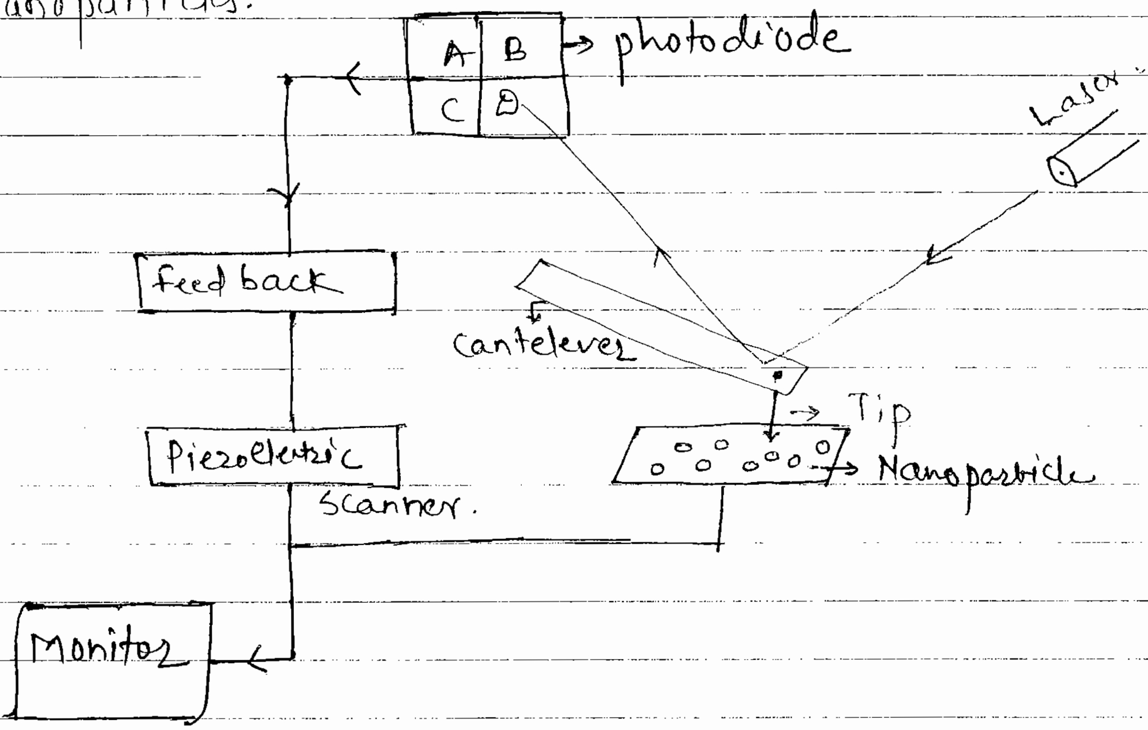

fig. Atomic Force Microscope.

Advantages of AFM :-

① Any sample, either conducting or non conducting can be scanned by AFM.

② Atomic resolution is obtained by AFM.

③ AFM does not require vacuum, so more easy to mount sample.

④ AFM gives 3-D topography of surface of nanoparticles.