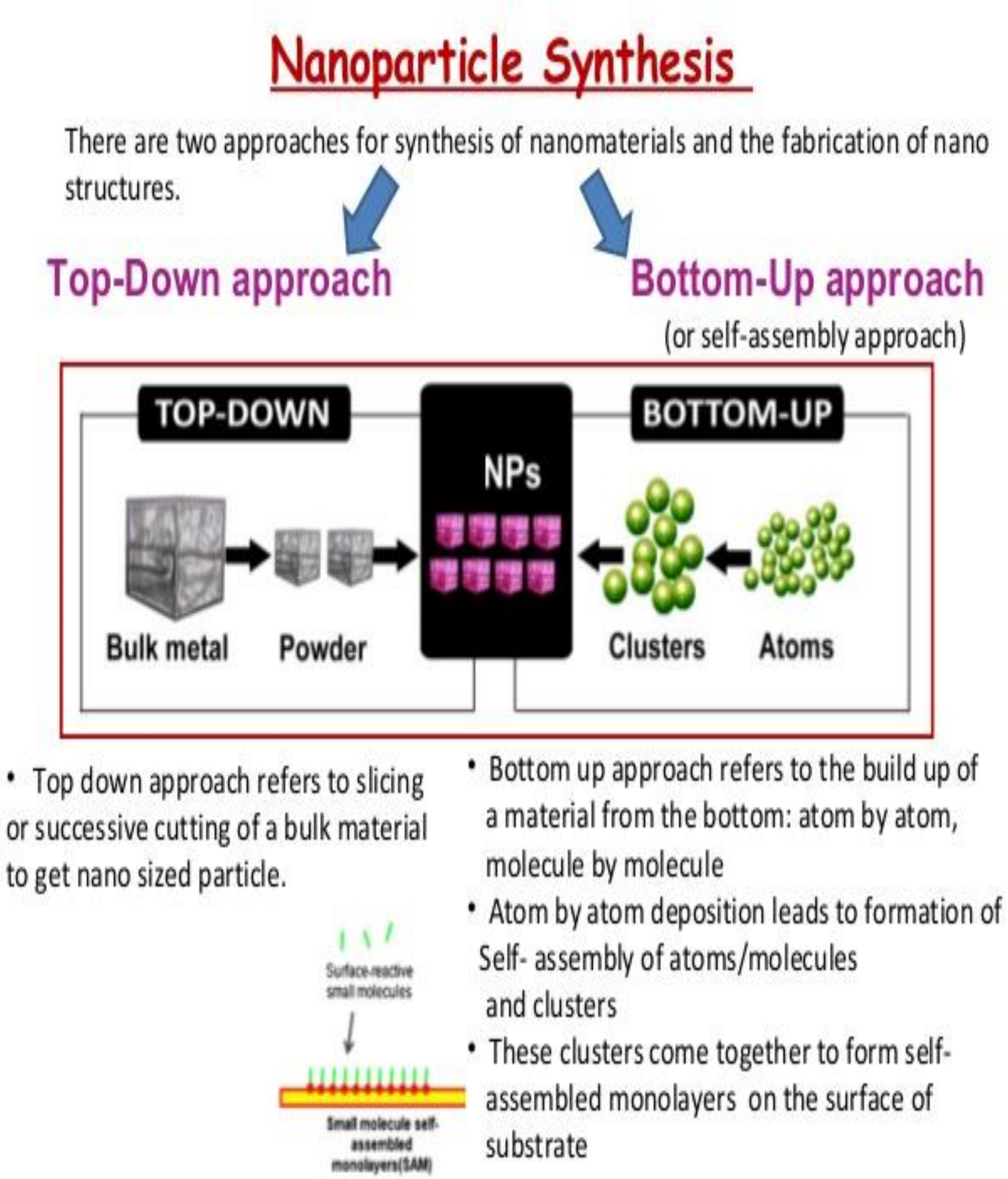
Synthesis of Nanostructured Materials (NSMs)......continued



Nanoparticle Synthesis

There are two approaches for synthesis of nanomaterials and the fabrication of nano structures.

Top-Down approach

Bottom-Up approach

(or self-assembly approach)

- Top down approach refers to slicing or successive cutting of a bulk material to get nano sized particle.

- Bottom up approach refers to the build up of a material from the bottom: atom by atom, molecule by molecule
- Atom by atom deposition leads to formation of Self- assembly of atoms/molecules and clusters
- These clusters come together to form self-assembled monolayers on the surface of substrate

All the synthesis/deposition techniques are divided into two categories based on the phase of starting material

Top-Down approach

In Top-down techniques,
the starting material is solid state

Physical processing methods:

- ✓ Mechanical methods :
  - cutting , etching, grinding
  - ball milling
- ✓ Lithographic techniques:
  - Photo Lithography
  - Electron Beam Lithography

Bottom-Up approach

All the Bottom-up techniques, the starting material is either gaseous state or liquid state of matter

- Physical and chemical processing methods:

Physical techniques-

Physical Vapor Deposition (PVD): involves condensation of vapor phase species

- Evaporation (Thermal , e-beam)
- Sputtering
- Plasma Arcing,
- Laser ablation,

Chemical techniques-

CVD: Deposition of vapor phase of reaction species

- PECVD(RF-PECVD,MPECVD)

Self-assembled Monolayer :

Electrolytic deposition, Sol-gel method, Microemusion route, pyrolysis.

Bottom – Up Synthesis

- Two approaches
  - Physical Processing : thermodynamic equilibrium approach
    - generation of supersaturation
    - nucleation
    - subsequent growth
  - Chemical Processing: kinetic approach
    - limiting the amount of precursors for the growth confining in a limited space

Bottom – Up Synthesis

Phase Classification:

I. Gas (Vapor) Phase Fabrication:

- PVD:
  - Inert Gas Condensation,
  - Evaporation (Thermal , e-beam)
  - Plasma Arcing,
  - Laser ablation,
  - Sputtering
- CVD: (PECVD and Microwave-PECVD)

II. Liquid Phase Fabrication:

- Wet chemical synthesis,
- Sol-gel,
- Self assembled Monolayer(SAM)
- Microemulsion method
- Spray Pyrolysis

Cluster beam evaporation
(for deposition of nanostructured thin films)
Physical Vapor Deposition (PVD)

Thin Films: Introduction

- Each solid material builds up by atomic/molecular aggregation layer by layer.

- When solid is only a few layers thick, its periodicity/ spacing etc. is different than bulk and its property may be different.

- In general, most properties vary with thickness (and also with the method of preparation and its associated process parameters).

- Approximately, for thickness greater or equal to 1000A° the bulk and film properties are same. Scientifically; it is convenient to call films from monomolecular layer (~5-10A°) to1000A° as thin films and beyond this it is thick film regime followed by real bulk material.

The broad categories in which film deposition techniques can be put are as follows:

1. Physical Methods
Physical Vapor Deposition (using different heating techniques)
(a) Resistive heating
(b) Laser heating
(c) Electron beam heating
(d) Induction heating
2. Chemical Methods
(e) Screen printing
(f) Chemical Vapour deposition(CVD)
(g) Solution Growth or electroless deposition.
(h) Electrochemical deposition.

Here, we will discuss, Cluster beam evaporation for deposition of nanostructured thin films. Its fall under Physical Vapor Deposition (PVD) as a Bottom-up approach.

PVD involves generation and condensation of vapor phase species (Growth species) via thermal evaporation (mainly using resistive heating, Electron beam heating, Laser Beam heating).

- This technique is based in the heat produced by high energy electron beam bombardment on the material (Source material) to be deposited as a film on a substrate (may be glass, quartz, silicon etc).

- A high dc voltage is applied to a tungsten filament that causes electrons to be emitted out. These emitted electrons are accelerated to excites the solid target (Source material) and produces vapors, which travels to the substrate in ultra high vacuum chamber. As these vapors (growth species) reach the surface, they condense and form a thin film coating on the substrate.

- The nature (crystalline or amorphous) and material of substrate play a very important role in deciding the properties of the film.

Experimental set up:

  - Figure below shows an apparatus of the cluster-beam evaporation technique equipped with a crucible (a vessel in which solid material is feeded) machined from a carbon rod.

- ✓ The cap of the crucible is 1mm thick and has a fine nozzle hole with a diameter approx of 1 mm.

- ✓ The crucible loaded with small pieces of solid metal material (Film material) is heated by electron bombardment as shown in Figure.

- ✓ During the deposition, the temperature of the crucible is kept as high as Melting point of solid material feed in crucible.

- ✓ The chamber is evacuated with high vacuum (of the order of 10^{-6} torr) to minimize the impurities and increase the mean free path for getting good quality film.

- ✓ The substrate temperature: Either Room or liquid nitrogen temperature (low as -196^{o}C).

- ✓ The classical nucleation theory predicts that the size of nanostructures formed by cluster beam evaporatimuch on technique would be much smaller than those by conventional thermal vacuum evaporation technique.

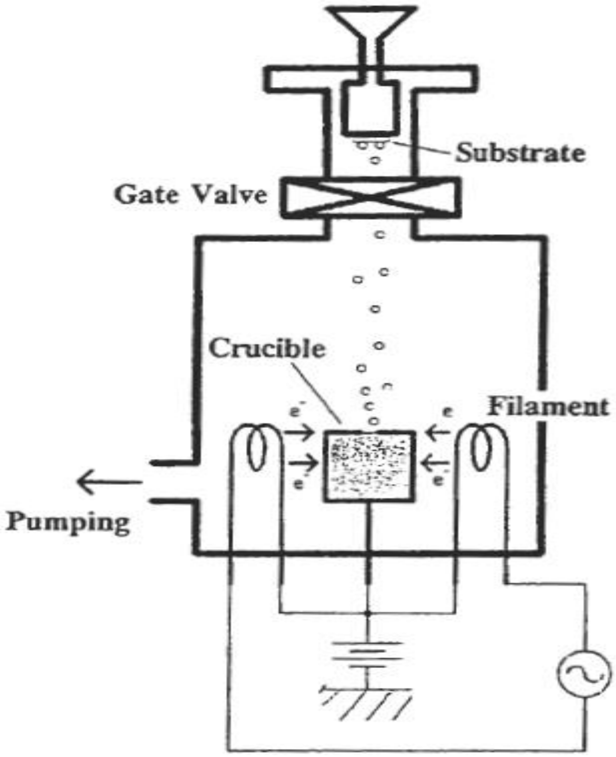


Fig.1 Apparatus of the cluster-beam evaporation technique.

Top Down Approach:

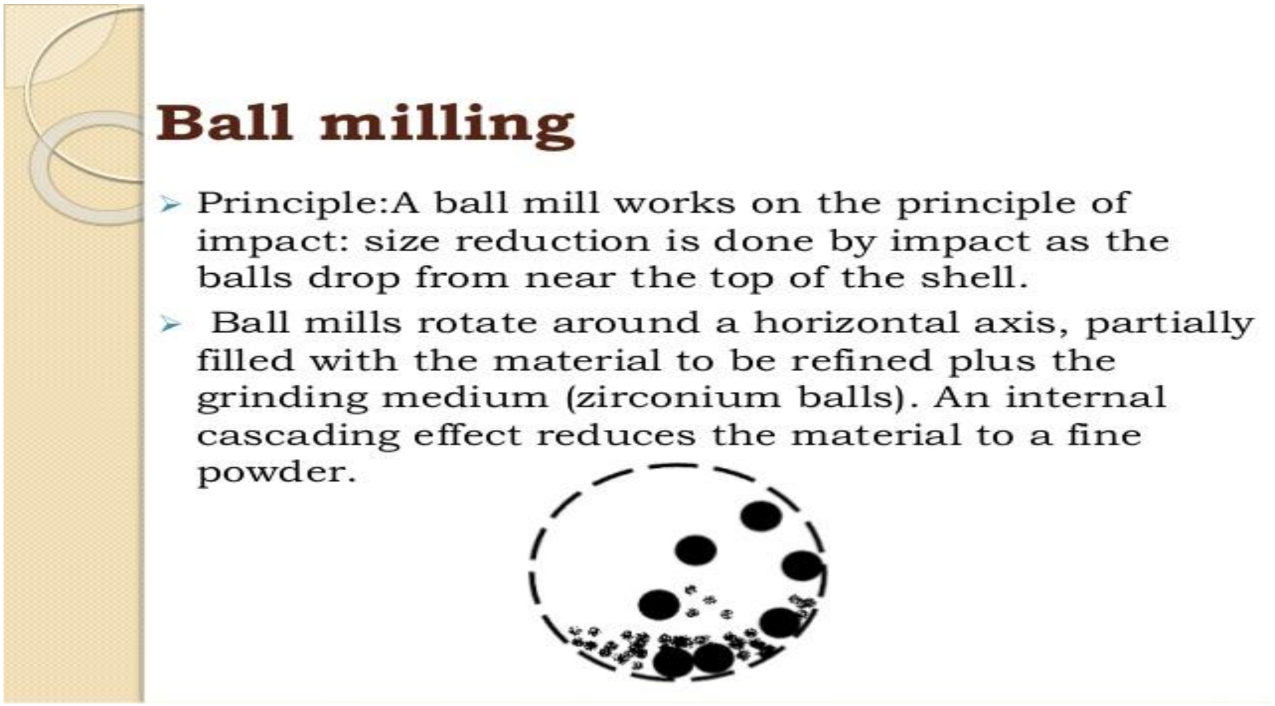
Mechanical Milling (Ball milling) : a Top Down Approach for the Synthesis of Nanomaterials and Nanocomposites

(A ball mill is a type of grinder used to grind the materials.)

- Synthesis of nanomaterials by a simple, low cost and in high yield has been a great challenge.
- Various bottom and top down approaches have been developed so far, for the commercial production of nanomaterials.
- Among all top-down approaches, high energy ball milling, has been widely exploited for the synthesis of various nanomaterials, nanograins, nanoalloy, and nanocomposites materials.
- In Ball milling process, a powder mixture is placed in the ball mill is subjected to high-energy collision from the balls. This process was developed by Benjamin and his coworkers at the International Nickel Company in the late of 1960.

- Mechanical alloying techniques have been utilized to produce amorphous and nanocrystalline alloys as well as metal/non-metal nanocomposite materials by milling and post annealing, of elemental or compound powders in an inert atmosphere.
- Mechanical alloying is a non-equilibrium processing technique in which different elemental powders are milled in an inert atmosphere to create one mixed powder with the same composition as the constituents.
- In high-energy ball milling, plastic deformation, cold-welding and fracture are predominant factors, in which the deformation leads to a change in particle shape, cold-welding leads to an increase in particle size and fracture leads to decrease in particle size resulting in the formation of fine dispersed alloying particles in the grain-refined soft matrix.
- By utilizing mechanical milling various kind of aluminium/ nickel/ magnesium/ copper based nanoalloys, wear resistant spray coatings, oxide and carbide strengthened aluminium alloys, and many other nanocomposites have been synthesized in very high yield.
- The mechanical milling has been utilized for the synthesis of nanomaterials either by milling and post annealing or by mechanical activation and then applying some other process on these activated materials.

Mechanical Milling

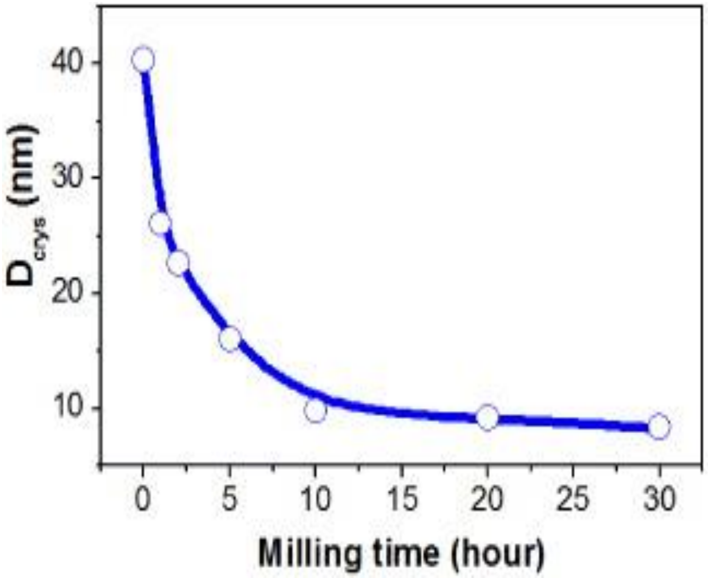


Ball milling

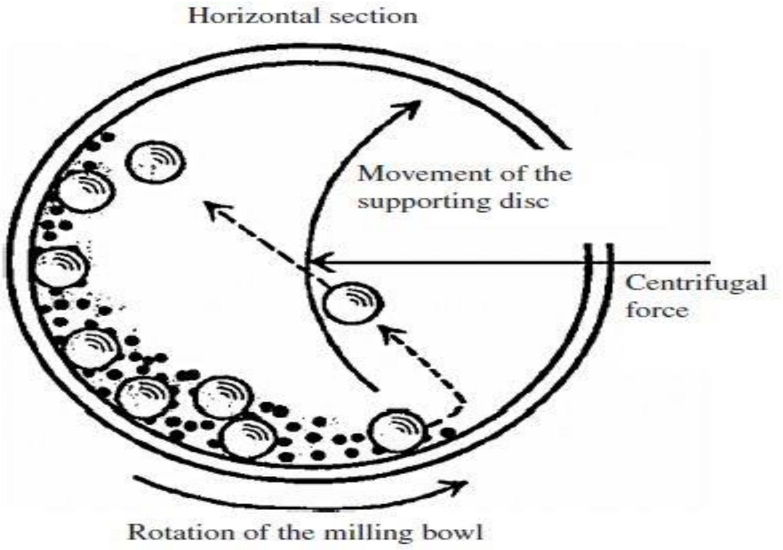
- Principle:A ball mill works on the principle of impact: size reduction is done by impact as the balls drop from near the top of the shell.
- Ball mills rotate around a horizontal axis, partially filled with the material to be refined plus the grinding medium (zirconium balls). An internal cascading effect reduces the material to a fine powder.

- ✓ For large scale production with nano size grain, mechanical millings are more economical processes.
- ✓ In mechanical milling (MM), a suitable powder charge (typically, a blend of elemental) is placed in a high energy mill, along with a suitable milling medium.
- ✓ The objective of milling is to reduce the particle size and blending of particles in new phases.
- ✓ The different type of ball milling can be used for synthesis of nanomaterials in which balls impact upon the powder charge.
- ✓ The balls may roll down the surface of the chamber in a series of parallel layers or they may fall freely and impact the powder and balls beneath them.
- ✓ The kinetics of mechanical milling or alloying depends on the energy transferred to the powder from the balls during milling.
- ✓ The energy transfer is governed by many parameters such as the type of mill, the powder supplied to drive the milling chamber, milling speed, size and size distribution of the balls, dry or wet milling, temperature of milling and the duration of milling.
- ✓ Since the kinetic energy of the balls is a function of their mass and velocity, dense materials (steel or tungsten carbide) are preferable to ceramic balls, and the size and size distribution should be optimized for the given mill.
- ✓ The temperature during milling can depend on the kinetic energy of the ball and the material characteristics of the powder and milling media.
- ✓ The temperature of the powder influences the diffusivity and defect concentration in the powder influencing the phase transformations induced by milling.

The particles size (nm) reduced with milling time (hrs) as follows:



The figure below shows the motions of the balls and the powder. Since the rotation directions of the bowl and turn disc are opposite, the centrifugal forces are alternately synchronized. Thus friction resulted from the hardened milling balls and the powder mixture being ground alternately rolling on the inner wall of the bowl and striking the opposite wall. Hence, the planetary ball mill can be used for high-speed milling.



BALL MILLING

- The balls rotate with high energy inside a container and then fall on the solid with gravity force and kinetic and hence crush the solid into nano crystallites.

Bottom-Up approach

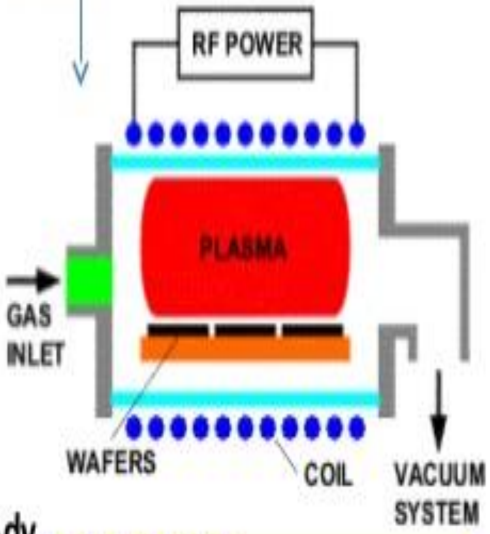
Chemical vapor Deposition:

Chemical vapour deposition (CVD) is a chemical process used to produce high-purity, high-performance solid materials. The process is often used in the semiconductor industry to produce thin films. In a typical CVD process, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit.

Plasma Enhanced CVD-

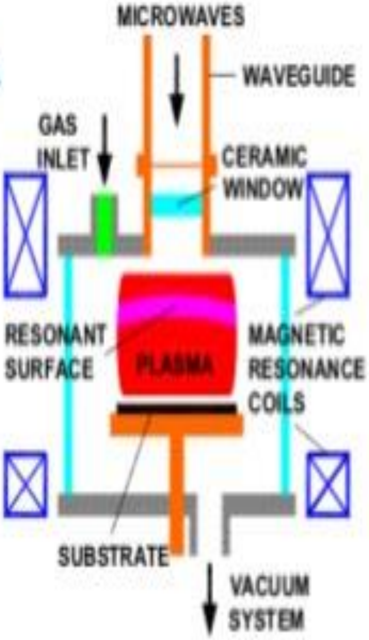
The energy source (RF/ Microwave power) is intended to generate a plasma in which the gases are broken down to form reaction species.

- RF-plasma enhanced CVD
- Microwave Plasma Enhanced CVD



Adv.

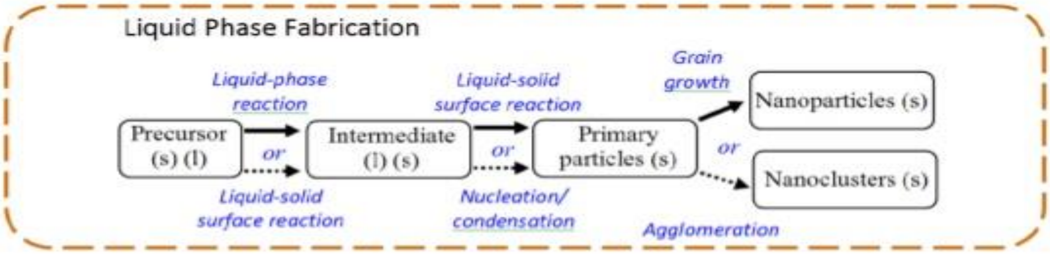
- High Purity
- Low Temperature Process
- Controlled Synthesis
- High Productivity, large scale deposition



Bottom – Up Synthesis

Chemical Methods:

with starting phase as Liquid phase



Wet Chemical Synthesis technique:

wet chemical approaches for the production of inorganic nanoparticles are important for large scale production of nanoparticles

Colloidal Synthesis: Self Assembled Monolayers

Colloidal methods are simple and well established wet chemistry precipitation processes in which solutions of the different ions are mixed under controlled temperature and pressure to form insoluble precipitates.

Micro-emulsion method Reverse-Micelle structures

langmuir-blodgett films

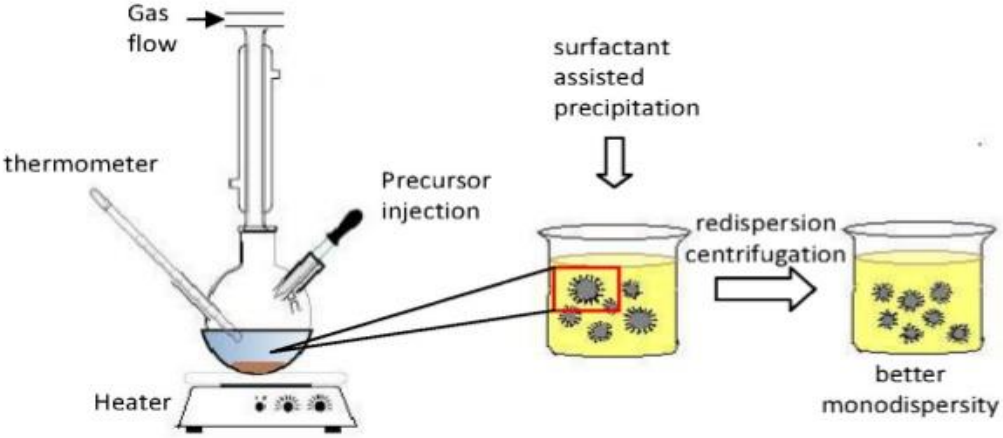
Sol-gel method:

Dip coating method

Spin coating method

Spray pyrolysis method:

Colloidal Synthesis of Semiconducting Quantum Dots



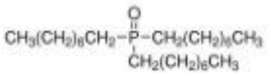
Colloidal Synthesis of CdSe (semiconducting) Quantum Dots:

Chemicals used:

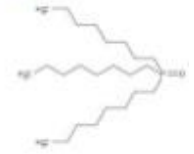
CdO - Cadmium Oxide
TOP - Trioctylphosphine
TDPA - Tetradecylphosphonic Acid
Se - Selenium Powder

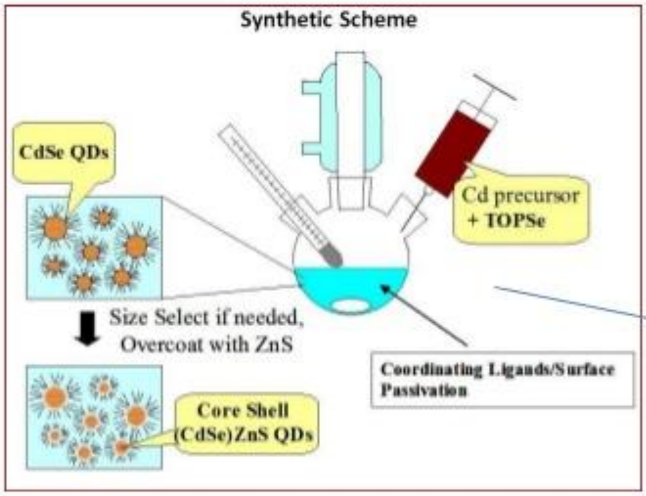
Surfactant/ Capping agent used:

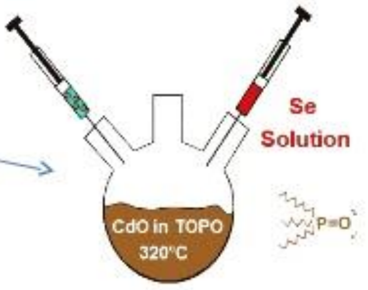
Trioctylphosphine Oxide (TOPO)



$$CH_3(CH_2)_6CH_2-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_2(CH_2)_6CH_3}{|}}{P}}-CH_2(CH_2)_6CH_3$$







Capping agents and their roles in synthesis of nanomaterials:

Capping agents are the stabilizing agents (mostly organic compounds or biomolecules) used to control the growth of nanoparticles hence nanoparticle size.

- The preparation of nanomaterials by organometallic precursors require a capping agent, which primarily acts as stabilizing agent and provide colloidal stability along with preventing agglomeration and stopping uncontrolled growth.
- Final morphology of nanocrystal largely depends on the type of capping agent which is adsorbed on the surface of nanocrystal.
- Thus capping agents are the keys to obtain the small-sized nanoparticles and are very frequently used in colloidal synthesis of nanoparticles to avoid its overgrowth.

A capping agent is an amphiphilic molecule consisting of polar head group and a nonpolar hydrocarbon tail and the functionality of the capping agent depends upon both the parts. The non-polar tail interacts with surrounding medium whereas polar head coordinates to the metal atom of the nanocrystals.

Examples:

N-TERMINATED LIGANDS:

The ligands which involves coordinating ligands like hexadecylamine, (HDA), octadecylamine, (ODA), oleyamine, (oAm), quinolone and pyridine etc

O-TERMINATED LIGANDS:

Solvents like oleic acid and linolinic acid contribute to this category by forming coordination bonds through their oxygen end.

P-TERMINATED LIGANDS:

Typical examples of P-terminated capping agents are tri-n-octylphosphene oxide (TOPO), tri-n-octylphosphine (TOP) and triphenylphosphene (TPP). TOPO is the most frequently used capping agent for the production of CdSe quantum dots.

S-TERMINATED LIGANDS:

It involves ‘S’ containing hydrophilic molecules for example thiols and form an important class of capping agents. Thiols with polar head groups are used to synthesize biocompatible quantum dots which do not need any ligand exchange process. The common thiols used as capping agents are 2-mercapto ethanol, 1-thioglycerol, thioglycolic acid (TGA) and thiolactic acid

GREEN CAPPING AGENTS:

Metal nanoparticles and nanocomposites have been successfully used with a variety of applications in electronics, biology and biomedicines, physical sciences and other various interdisciplinary fields.

The functional groups of a capping polymer stabilize the nanoparticles by steric or electrostatic repulsions. Polymers like poly(ethylene glycol), poly(vinyl alcohol), poly(vinyl pyrrolidine) and nonionic surfactants like Triton X-100 stabilizes the nanoparticles by steric interaction whereas ionic surfactant like sodium dodecyl sulphate, cetyltrimethyl ammonium bromide provides electrostatic stabilization to the nanoparticles, whereas simultaneous stabilization is provided by a poly electrolyte.

Conjugating polymers: Conjugating polymers are organic macromolecules that are characterized by a chain of alternating single and double bonds. Some commonly used conjugated polymers are polyacetylene (PA), polythiophene (PT), polyparaphenylene (PPP), poly(3-hexyl)thiophene (P3HT), polyparavinylene (PPV) etc.

Block copolymers: Block copolymers have an ability to form micro domains and micelles of well-defined and nanosized volumes, inside which particles of a finite size can be generated and stabilized. Poly (ethylene oxide)-Poly (propylene oxide)-Poly (ethylene oxide), (PEP-PPO-PEO) block copolymer can act as reductant and as well as stabilizer.

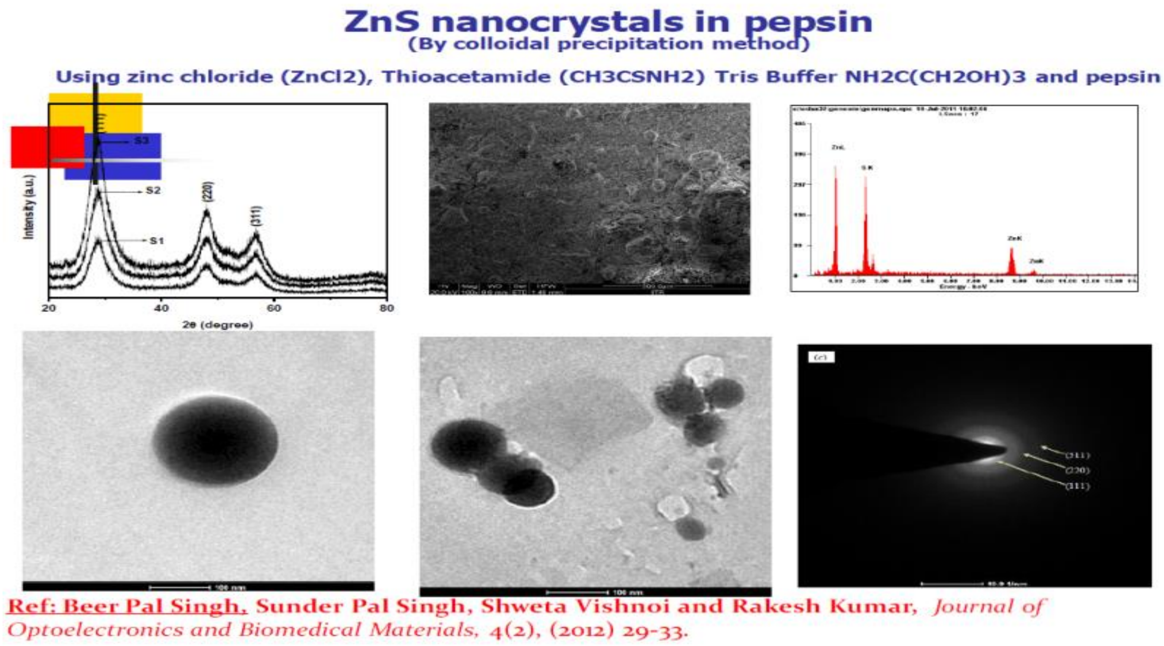
(Reading Optional)

Green nanotechnology: Current issues in synthesis of Nanomaterials

Green synthesis of NSMs

- ✓ Green nanotechnology produces nanomaterials and nanomaterials-based products without harm the environment and living organism.
- ✓ The production of nanomaterials from biological methods using various biological systems can be considered a superior biomimetic engineered methodology for synthesis of nanostructured materials.
- ✓ Currently, green nanotechnology is an multidisciplinary field that has come out as a safe and rapidly emergent research area.
- ✓ Various kinds of biological systems such as plants, phototrophic eukaryotes namely algae, microbes, bacteria, actinomycetes, fungi, yeasts, virus and many biocompatible agents which are capable of reducing the metal ions to metal nanoparticles.
- ✓ Green synthesized various kind of nanomaterials have been effectively utilized in different nano-products.

The following novel techniques has been developed in our research laboratories for synthesis of nanoparticles:



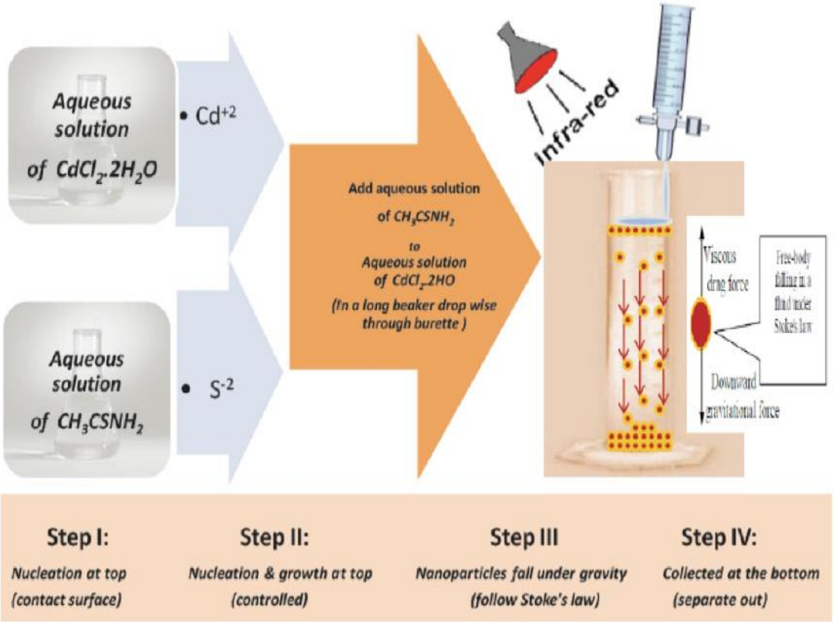
ZnS nanocrystals in pepsin

(By colloidal precipitation method)

Using zinc chloride ($ZnCl_2$), Thioacetamide (CH_3CSNH_2) Tris Buffer $NH_2C(CH_2OH)_3$ and pepsin

Ref: Beer Pal Singh, Sunder Pal Singh, Shweta Vishnoi and Rakesh Kumar, *Journal of Optoelectronics and Biomedical Materials*, 4(2), (2012) 29-33.

Gradation of Nanoparticle Size by Stokes' Law: A New Approach for Synthesis of CdS Nanoparticles



Research Article

Infrared Radiation Assisted Stokes' Law Based Synthesis and Optical Characterization of ZnS Nanoparticles

Beer Pal Singh,[1] Ravish Kumar Upadhyay,[1] Rakesh Kumar,[1]
Kamna Yadav,[2] and Hector I. Areizaga-Martinez[3]

The strategy and technique exploited in the synthesis of nanostructure materials have an explicit effect on the nucleation, growth, and properties of product materials. Nanoparticles of zinc sulfide (ZnS) have been synthesized by new infrared radiation (IR) assisted and Stokes' law based controlled bottom-up approach without using any capping agent and stirring. IR has been used for heating the reaction surface designed in accordance with the well-known Stokes law for a free body falling in a quiescent fluid for the synthesis of ZnS nanoparticles. The desired concentration of aqueous solutions of zinc nitrate ($Zn(NO_3)_2{\cdot}4H_2O$) and thioacetamide (CH_3CSNH_2) was reacted in a controlled manner by IR radiation heating at the reaction area (top layer of reactants solution) of the solution which results in the formation of ZnS nanoparticles at ambient conditions following Stokes' law for a free body falling in a quiescent fluid. The phase, crystal structure, and particle size of as-synthesized nanoparticles were studied by X-ray diffraction (XRD). The optical properties of as-synthesized ZnS nanoparticles were studied by means of optical absorption spectroscopic measurements. The optical energy band gap and the nature of transition have been studied using the well-known Tauc relation with the help of absorption spectra of as-synthesized ZnS nanoparticles.

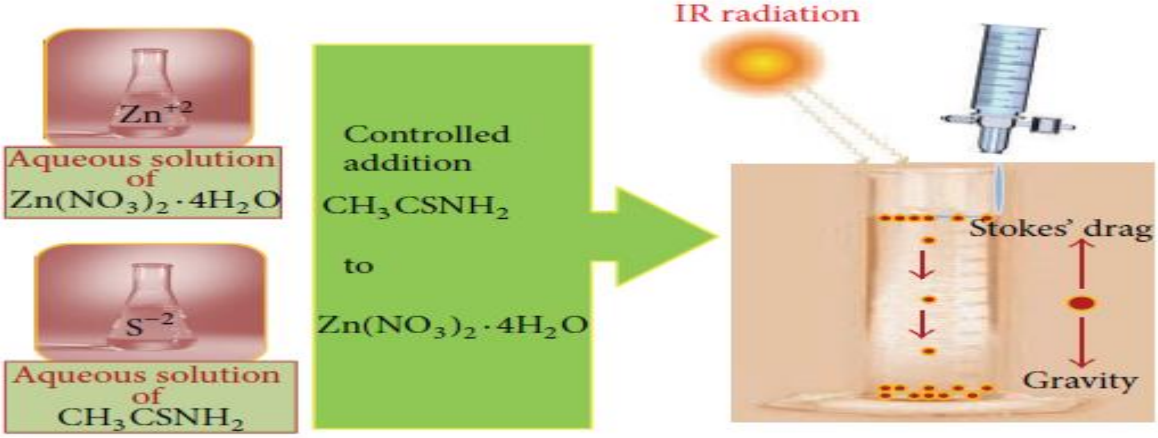


FIGURE 1: Schematic illustration of controlled IR assisted chemical precipitation method based on Stokes' law for a free body falling in a quiescent and viscous fluid as used for synthesis of ZnS nanoparticles.

ZnS nanoparticles were effectively synthesized by an infrared (IR) radiation assisted and Stokes' law based new controlled bottom-up approach without using any capping agent or stirring. The reaction is controlled by the IR radiation surface heating and consequently the synthesis mechanism is based on the physics of the well-known Stokes' law for a free body falling in a quiescent and viscous fluid. The structural and