

Bottom up Synthesis of Nanomaterials

Design and preparation of nanoparticles with high functionality i.e., to fabricate nanomaterials which have the suitable properties for applications.

The fabrication of nanomaterials of tailored properties involve the control of Size, shape, structure, composition and purity of their constituents.



- **Different Methods (Top-down and Bottom up approaches)**
- **Growth Kinetics (Cluster Formation followed by Nucleation and Growth)**

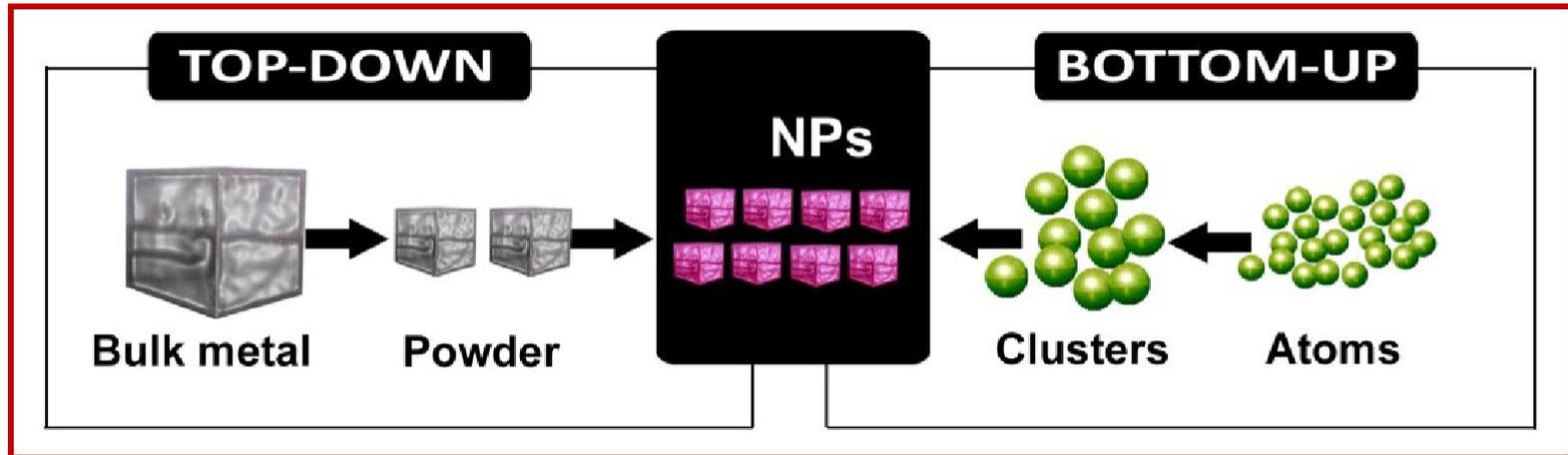
Nanoparticle Synthesis

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.
- tom 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- ass

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,

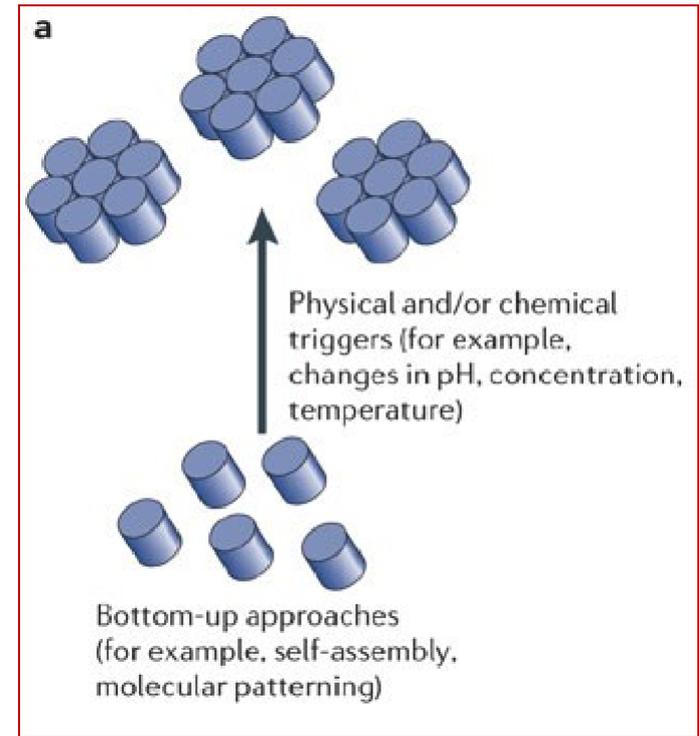
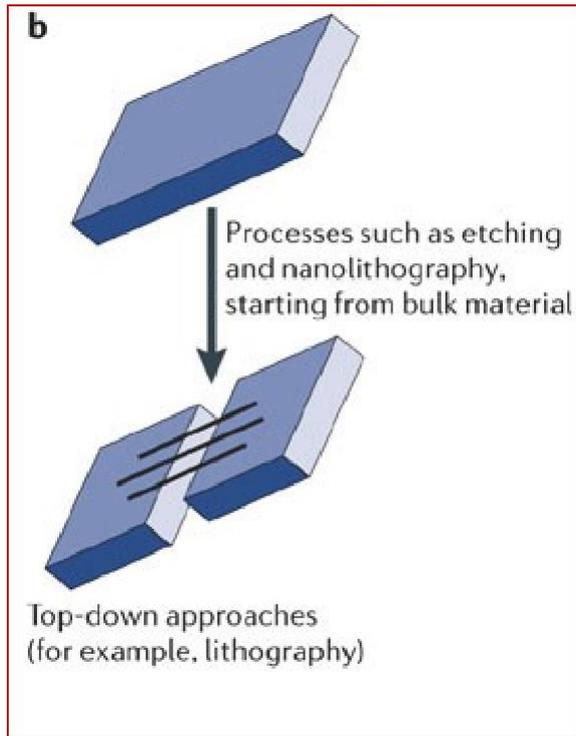
Chemical techniques-

CVD: Deposition of vapor phase of reaction species

- PECVD(RF-PECVD,MPECVD)

Self-assembled Monolayer :

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



How to synthesize nanoparticles?

The key to make nanoparticles is how to control and stop the reaction to make nano-size products because the properties of nanoparticles depend on their size and morphology.

Top-down refers to the traditional workshop or microfabrication method where tools are used to cut, mill and shape materials into the desired shape and order.

Bottom-up refers to methods where devices 'create themselves' by self-assembly. Chemical synthesis is a good example. Bottom-up should broadly speaking be able to produce devices much cheaper than top-down methods, but getting control over the methods is difficult when things become larger and more bulky than what is normally made by chemical synthesis. Of course nature has had time to evolve and optimize self-assembly processes that can do wonders.

Top-down Versus Bottom-up

Top Down Process



Start with bulk wafer



Apply layer of photoresist



Expose wafer with UV light through mask and etch wafer



Etched wafer with desired pattern

Bottom Up Process



Start with bulk wafer



Alter area of wafer where structure is to be created by adding polymer or seed crystals or other techniques.



Grow or assemble the structure on the area determined by the seed crystals or polymer. (self assembly)

Top-Down approach

ADVANTAGES

- Large scale production: deposition over a large substrate is possible
- Chemical purification is not required

DISADVANTAGES

Yields:

- broad size distribution (10-1000 nm)
- varied particle shapes or geometry
- Control over deposition parameters is difficult to achieve
- Impurities: stresses, defects and imperfections get introduced
- Expensive technique

Bottom-Up approach

ADVANTAGES

- Ultra-fine nanoparticles, nanoshells, nanotubes can be prepared
- Deposition parameters can be controlled
- Narrow size distribution is possible (1-20 nm)
- Cheaper technique

DISADVANTAGES

- Large scale production is difficult
- Chemical purification of nanoparticles is required

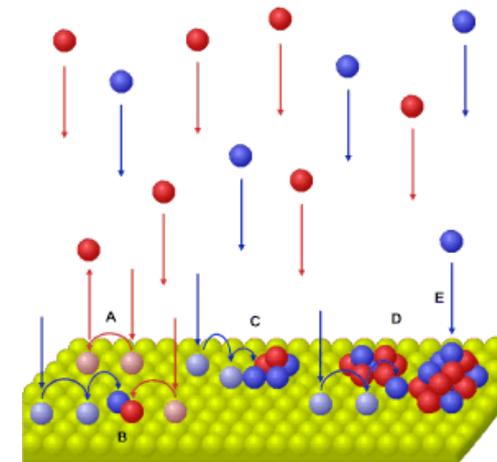
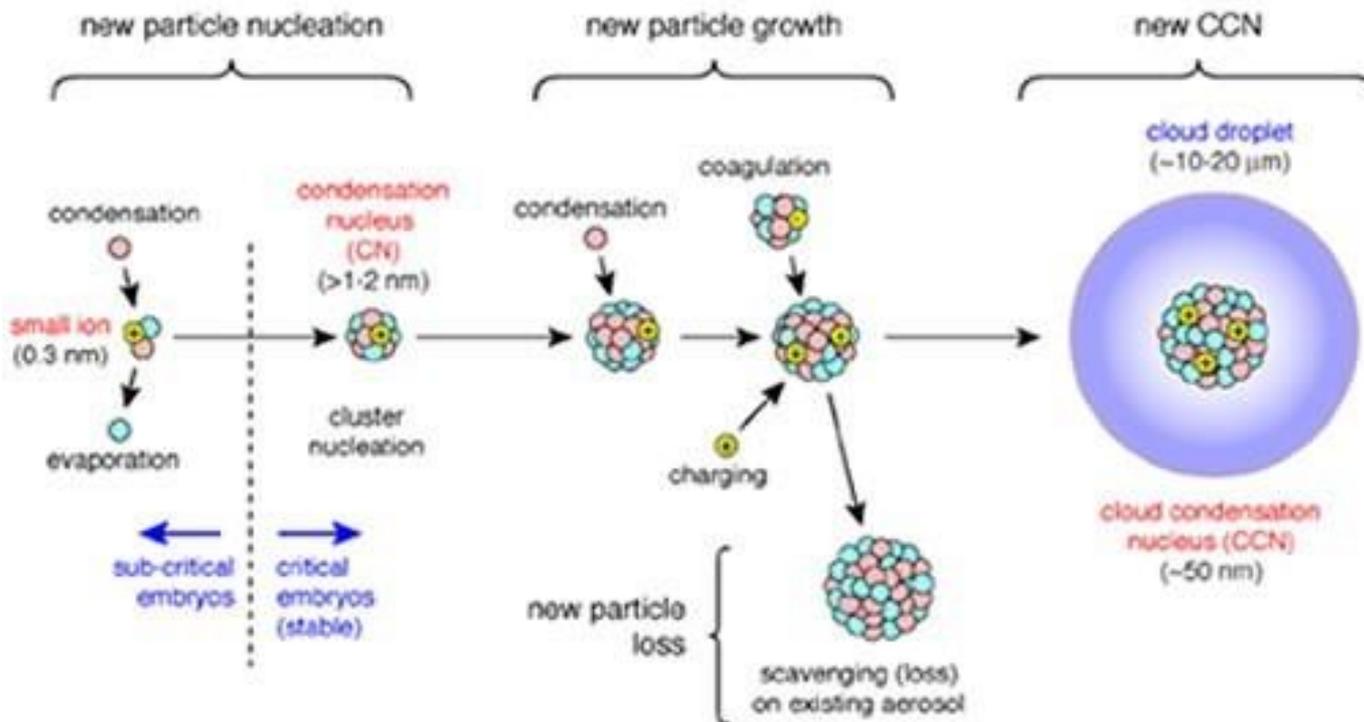
Bottom – Up Synthesis

- 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

Growth Kinetics: Nucleation and Growth processes

Synthesis of nanoparticles is a combination of two stage process, nucleation and growth.

- Most phase transformations begin with the formation of **numerous small particles (clusters)** of the new phase that increase in size until the transformation is complete.
- Nucleation** is the process whereby nuclei (seeds) act as templates for crystal **growth**.



Phase Transformations

- Transformation rate
- Kinetics of Phase Transformation
 - Nucleation: homogeneous, heterogeneous
 - Free Energy, Growth

Nucleation

Nucleation is the first step in the formation of either a new thermodynamic phase or a new structure via self-assembly or self-organisation.

Nucleation is typically defined to be the process that determines how long we have to wait before the new phase or self-organised structure, appears. Nucleation is often found to be very sensitive to impurities in the system.

There are two different categories of Nucleation:

Heterogeneous nucleation –

The nucleation of critical nuclei forming at defects such as surface imperfections, grain boundaries is called *heterogeneous nucleation*. Nucleation is much easier since stable “nucleating surface” is already present; requires slight supercooling (0.1-10°C).

Homogenous nucleation – this happens spontaneously! nucleation

that randomly occurs away from a surface.

nuclei form uniformly throughout the parent phase ; requires considerable supercooling (typically 80-300°C)

Supercooling

- During the cooling of a liquid, solidification (nucleation) will begin only after the temperature has been lowered below the equilibrium solidification (or melting) temperature T_m . This phenomenon is termed **supercooling** (or **undercooling**).
- The **driving force** to nucleate increases as ΔT increases
- Small **supercooling** □ slow nucleation rate - few nuclei - large crystals
- **Large** supercooling □ **rapid nucleation rate** - many nuclei - small crystals

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:

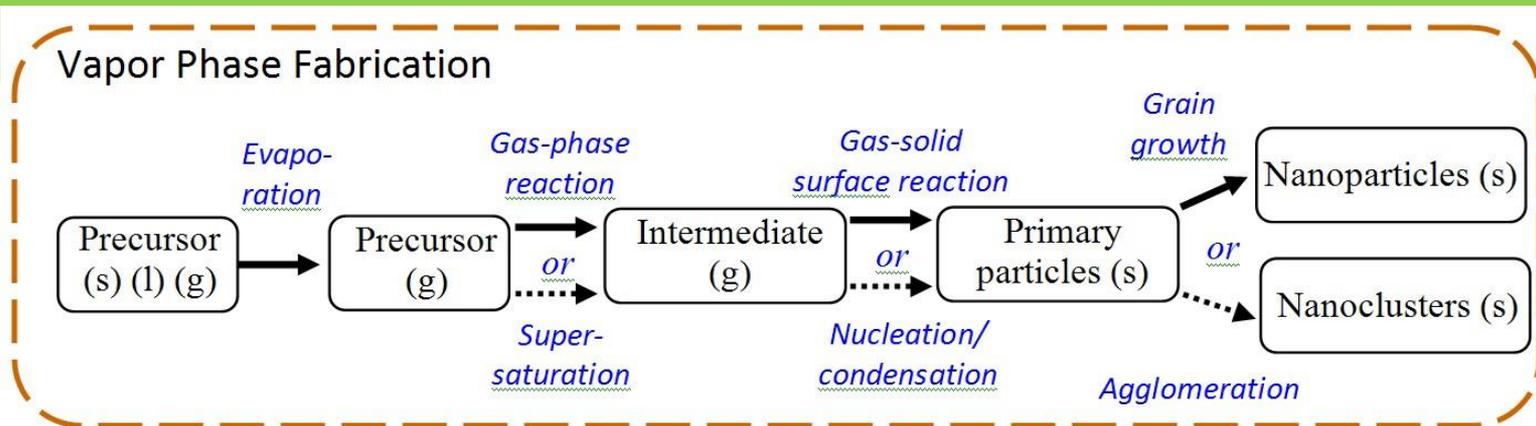
- Wet chemical synthesis,
- Sol-gel,
- Self assembled Monolayer(SAM)
- Microemulsion method
- Spray Pyrolysis

Bottom – Up Synthesis

Physical Methods:



with starting phase as Gas (Vapor) phase



- (i) precursor vaporization (typically involves a catalyst)
- (ii) nucleation, and
- (iii) growth stage

Bottom-Up approach

Physical Vapor Deposition (PVD):

- involves generation and condensation of vapor phase species via thermal evaporation, sputtering or laser ablation

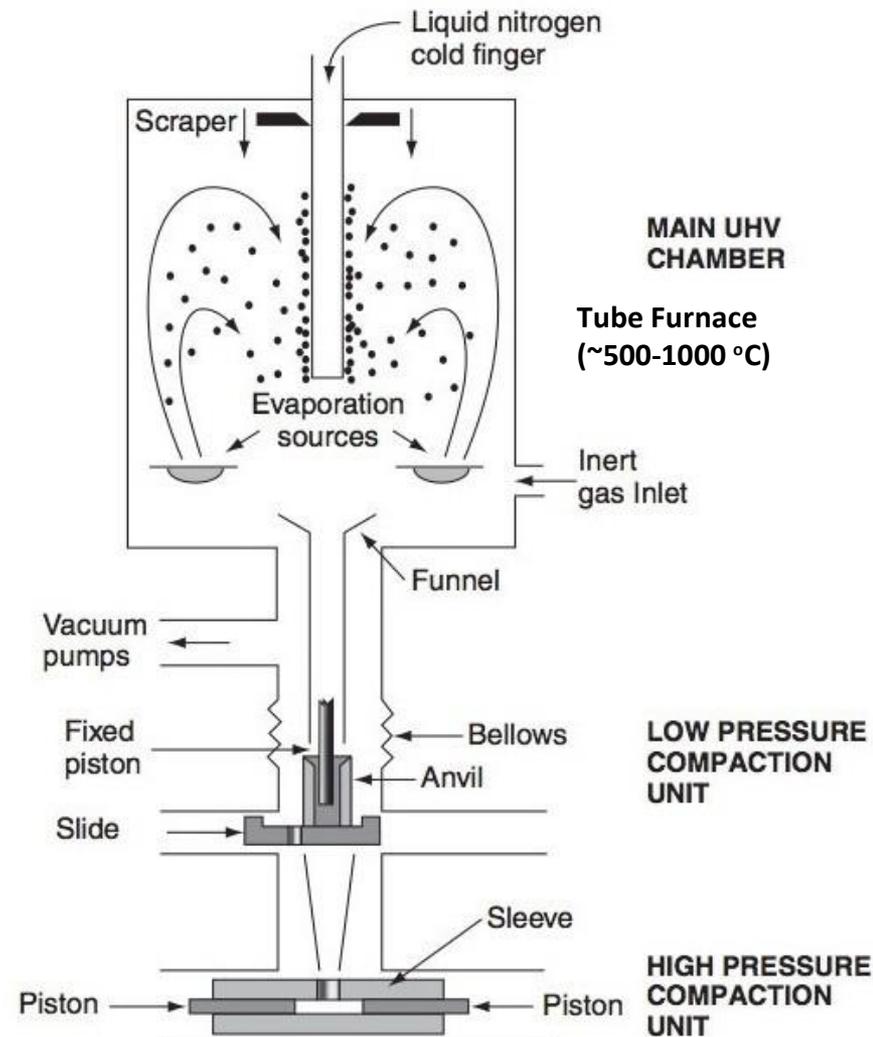
- **Inert-gas condensation:**

The inert gas evaporation–condensation (IGC) technique, in which nanoparticles are formed via the evaporation of a metallic source in an inert gas, has been widely used in the synthesis of ultrafine metal particles

In this process, a metal is evaporated inside an ultra-high vacuum (UHV) chamber filled with inert gas (He). The vaporized species collide with Helium molecules thus losing kinetic energy. As collisions limit the mean free path, supersaturation can be achieved above the vapors source.

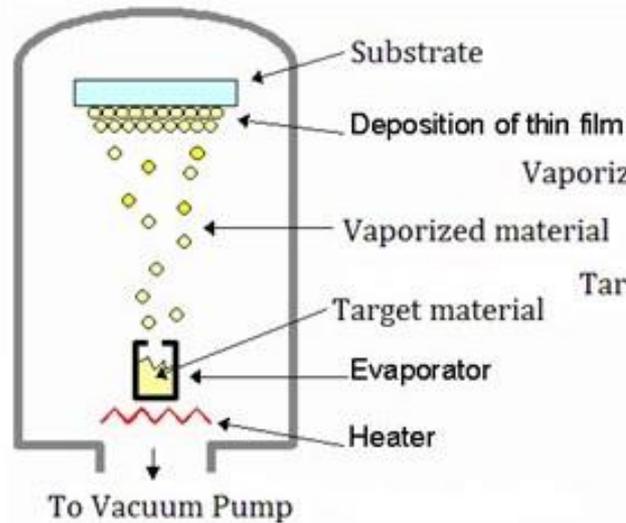
At high supersaturation, the vapors rapidly form no. of clusters that grow via coalescence and agglomeration. These clusters get condensed on liquid nitrogen cooled surfaces to form nanoparticles.

The size, morphology, and yield of the NPs should be controlled

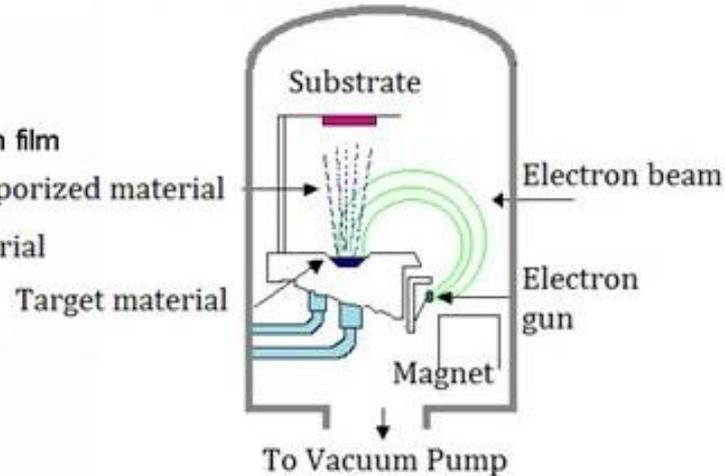


Evaporation technique

Resistance heating evaporation



Electron beam evaporation



Thermal evaporation

Thermal deposition inside a vacuum chamber where the material, usually in a boat is heated typically to its melting point and the substrate to be deposited on is positioned facing the source. A high current flowing through the boat heats it up and causes evaporation. A crystal monitor is mounted close to the substrate, which provides an estimate of how much and how fast the material is being deposited.

Limitations-

- High temperature process (500-1200°C)
- Ultra high vacuum(10^{-6} torr)
- High cost

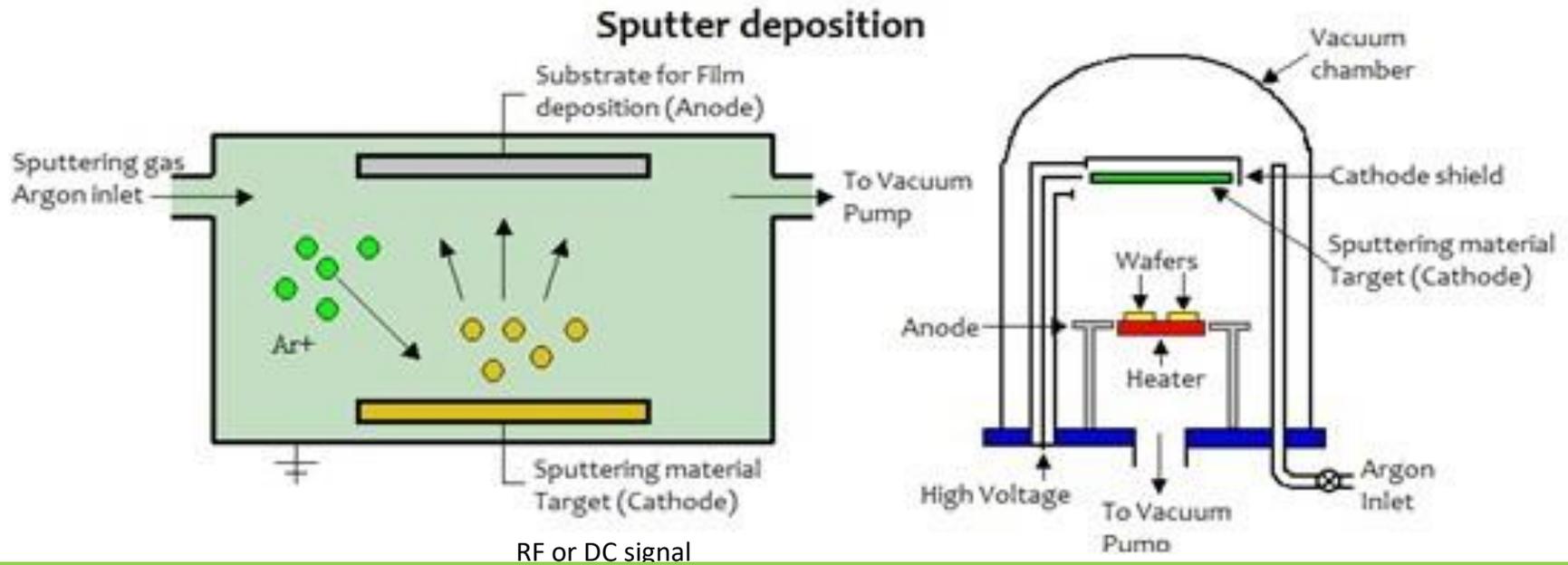
Electron-beam evaporation

This technique is based in the heat produced by high energy electron beam bombardment on the material to be deposited. 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 target solid and produces vapors, which travels to the substrate. As they reach the surface, they condense and form a thin film coating.

- Used for depositing materials with high melting point (W, Ta, C, etc.)
- As electrons can be focalized, it is possible to obtain a very localized heating on the material to evaporate, with a high density of evaporation power (several kW)

• Sputtering →

Sputter deposition are methods of depositing thin films by sputtering. They involve ejecting material from a “target” that is a source onto a “substrate” such as a silicon wafer.



Atoms of Target (source) materials are ejected or sputtered by high energy ion bombardment of high-energy noble gas atoms, commonly Argon, produced by a high voltage DC or RF glow discharge. These ejected sputtered atoms (due to momentum transfer) form a thin film coating after condensing on substrate kept as anode plate

Sputtered atoms ejected from the target have a wide energy distribution, typically up to tens of eV.

Advantages-

- Non-thermal process, no heating reqd.
- low vacuum(10^{-3} torr) is needed.

Limitations-

- controlling Deposition parameters is difficult
- High cost

Thin Film Deposition by sputtering process

The sputtering process consists of the bombardment of the target material by fast moving, heavy, inert gas ions from a plasma. The bombarding ions cause atoms to be ejected from the target material by momentum transfer between the colliding ions and the target atoms. The process is schematically shown in Figure 3.1a, where a number of processes are shown to occur when the ions collide with the target material. Some of the bombarding ions are reflected back and are neutralized, but may still be sufficiently energetic to reach the substrate where the film is being deposited. This can be a source of substrate bombardment (back scattering) which can effect the resulting properties of the film. The majority of the colliding ions tend to induce sputtering by ejecting atoms of the target material by momentum transfer. This is a secondary collision process, as shown schematically in Figure 3.1a. The ejected atoms will have random directions but, as discussed in Chapter 4, the sputtering process can induce texture in the resulting films due to the sputtering conditions. Secondary electrons which are emitted either join the oscillating plasma gas, which cause the continuous ionization of the gas to sustain the incident ions needed for sputtering, or they liberate their energy in the form of heat on colliding with the substrate or other parts of the chamber. The sputtered target atoms which are deposited at the substrate form the resulting thin film. The basic processes occurring at the surface of the substrate are shown in Figure 3.1b.

The mobility of the incident atoms arriving at the substrate is highly dependent upon the sputtering parameters (pressure and power), the temperature of the substrate, the distance between target and substrate, and the surface.

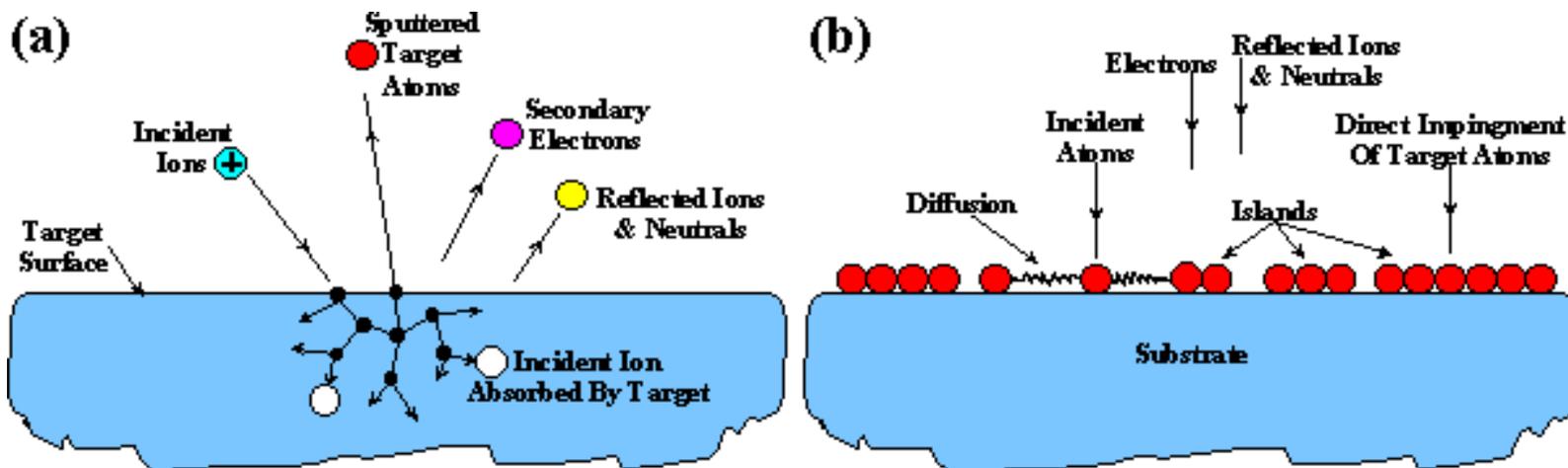
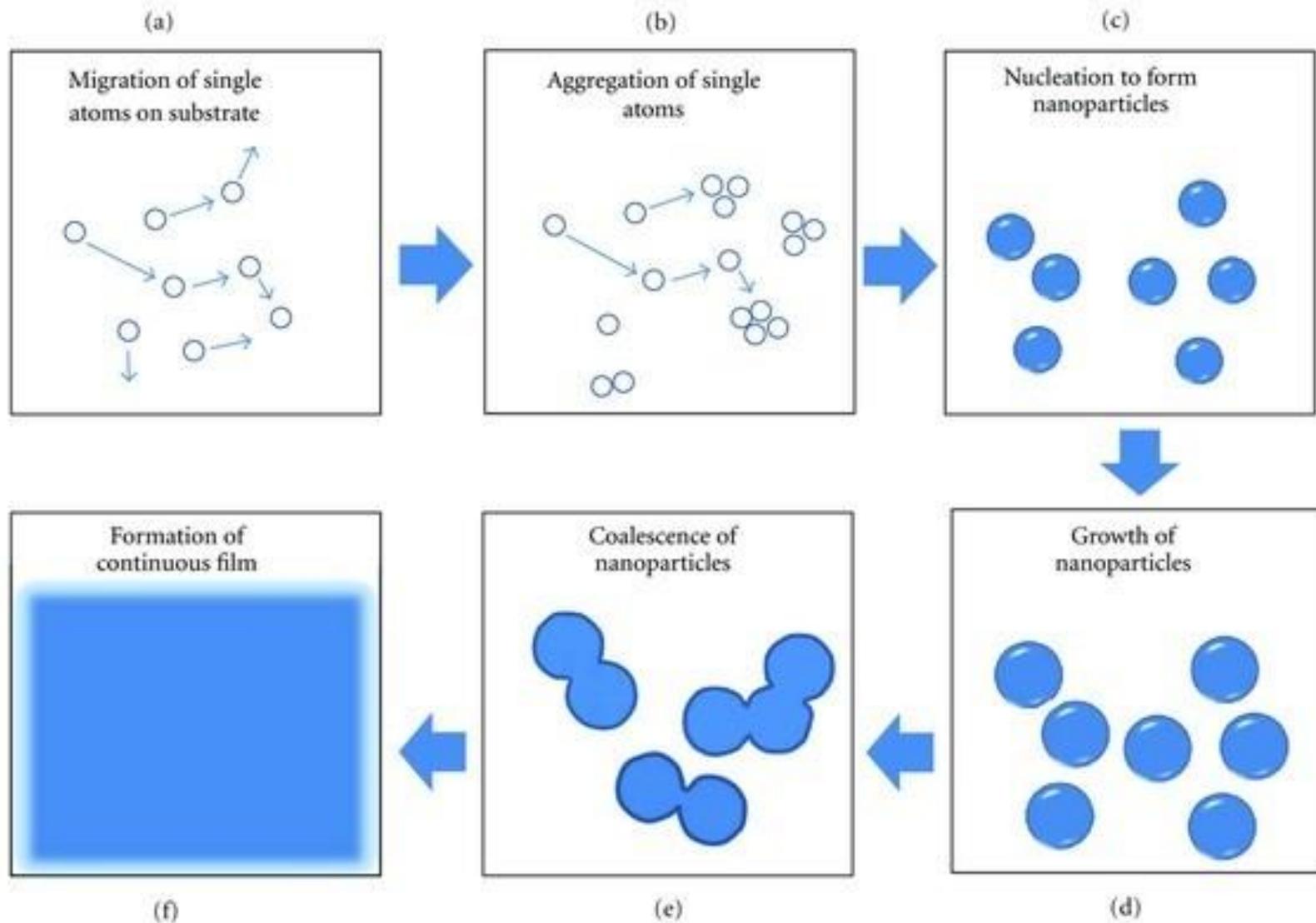


Figure 3.1: An illustrative diagram showing the sputtering process at the target (a), and film formation at the substrate (b).



Schematic of thin-film growth based on DC sputtering technique. The processes include (a) migration of single atoms on substrate, (b) aggregation of single atoms, (c) nucleation to form nanoparticles, (d) growth of nanoparticles, (e) coalescence of nanoparticles, and (f) formation of continuous film.

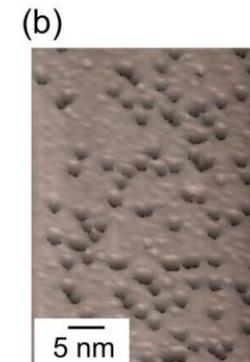
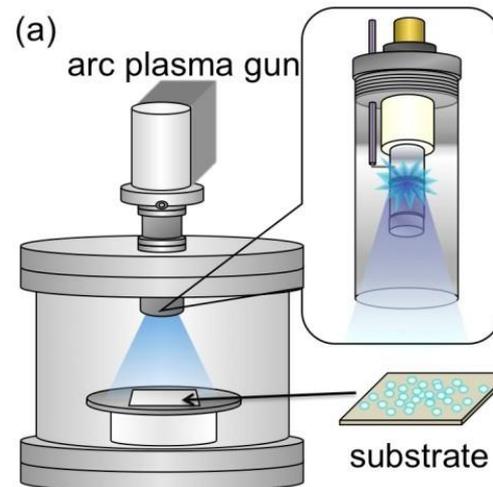
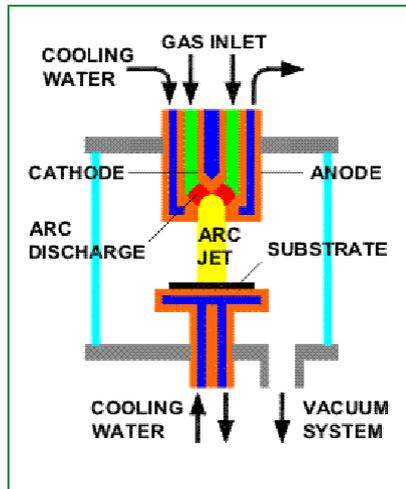
Plasma Processing methods



In general, plasma processing involves chemical and physical reactions between particles and solid surfaces in contact with the plasma. Some examples are plasma etching, thin film deposition, protective coating, surface hardening, ion implantation etc.

- Arc discharges technique:**

plasma of inert gases is produced by DC (direct current) glow or arc discharges,



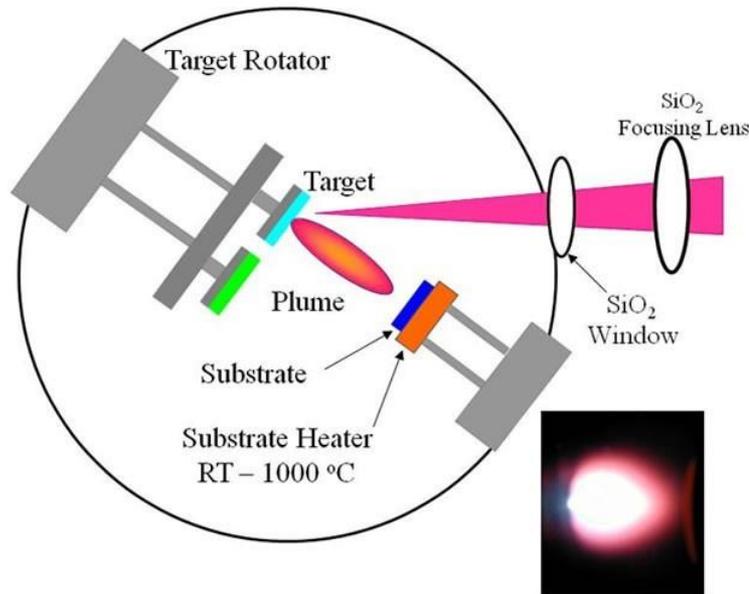
In this electric arc discharge method, material is vaporized between two electrodes by arc produced by applying very high voltage (50-100V) across the electrodes. This ionizes the inert gas and plasma is generated (temperature 6000°C), due to which metal atoms are evaporated and get condensed on water cooled substrate. Later the substrate is heated to remove the impurities.

Carbon nanotubes are prepared by graphite as cathode.

Nanotubes of dichalcogenides are prepared by such as MoS₂, WS₂ are prepared are prepared by starting with MoO₃ and WO₃.

- Laser ablation  pulsed laser deposition system

This method is applicable for high melting point elements and transition metals.



In this method, a solid metal rod is ablated using a Nd:YAG laser (high Power) in a chamber containing Ar gas. In the plasma that results from the laser ablation, metal atoms are evaporated and condensed on water cooled substrate.

Later the substrate is heated to remove the impurities.

NPs of Iron, gold, palladium, and compounds of sulphide are prepared by this method.

Advantage:

- capable of High deposition rate of 2-3 g/min

Disadvantage:

- High temperature method
- low quality of material deposited

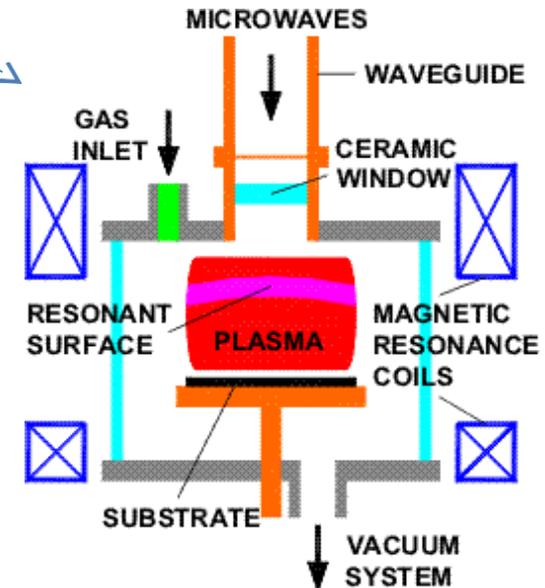
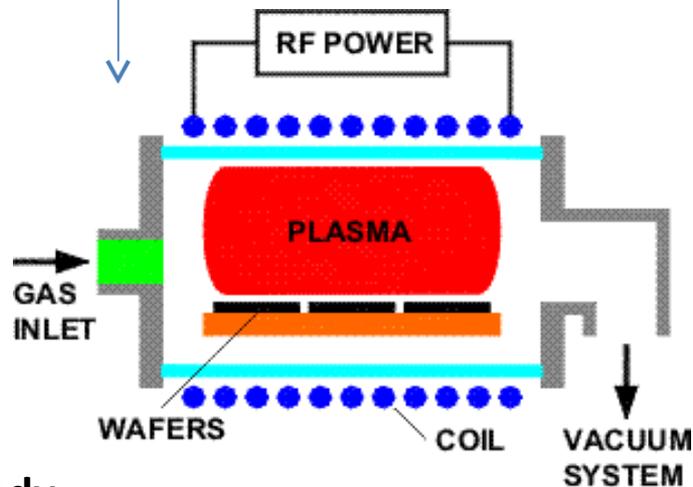
Chemical vapor Deposition:

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-

- RF-plasma enhanced CVD
- Microwave 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.



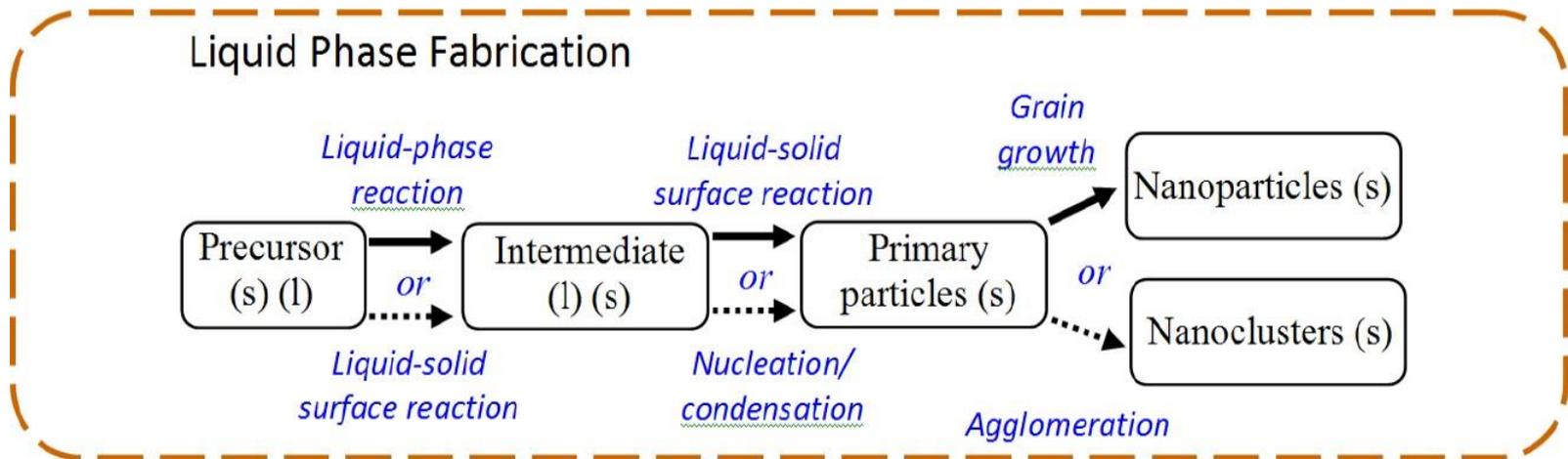
Adv.

- 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:

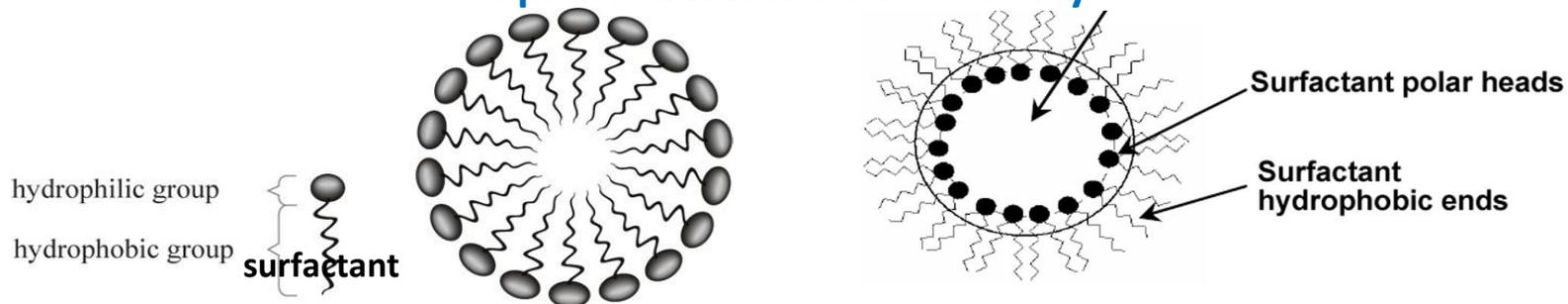
Dip coating method

Spin coating method

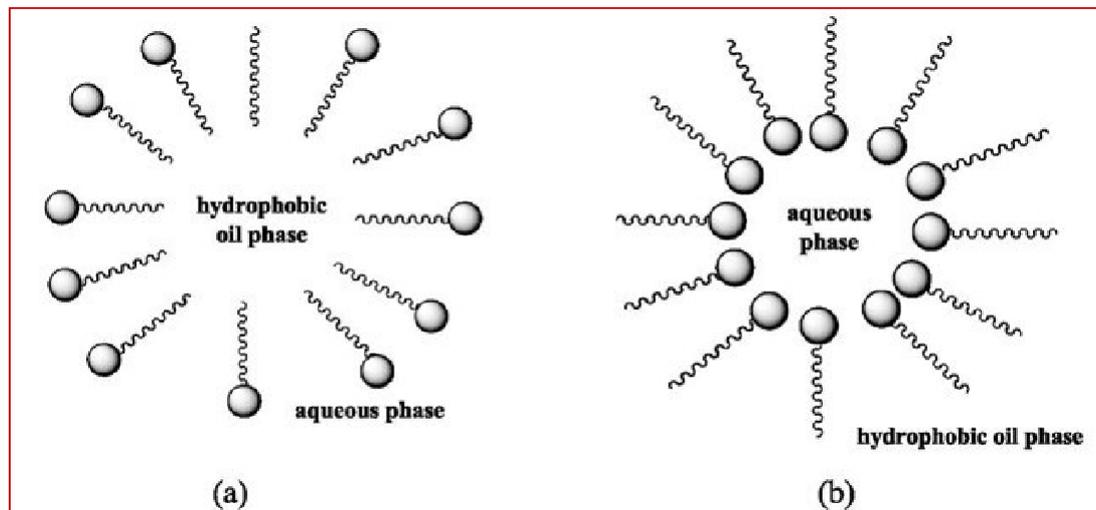
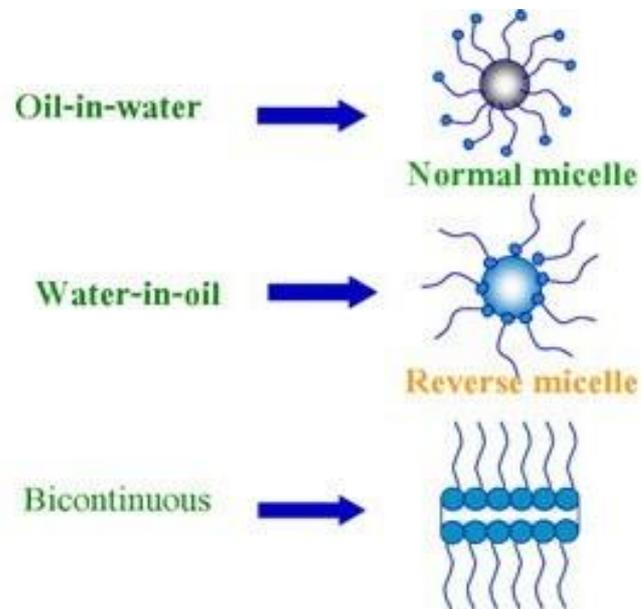
Spray pyrolysis method:

• Microemulsion method

Spherical micelle structure layout:



amphiphilic molecules



Micelle structure

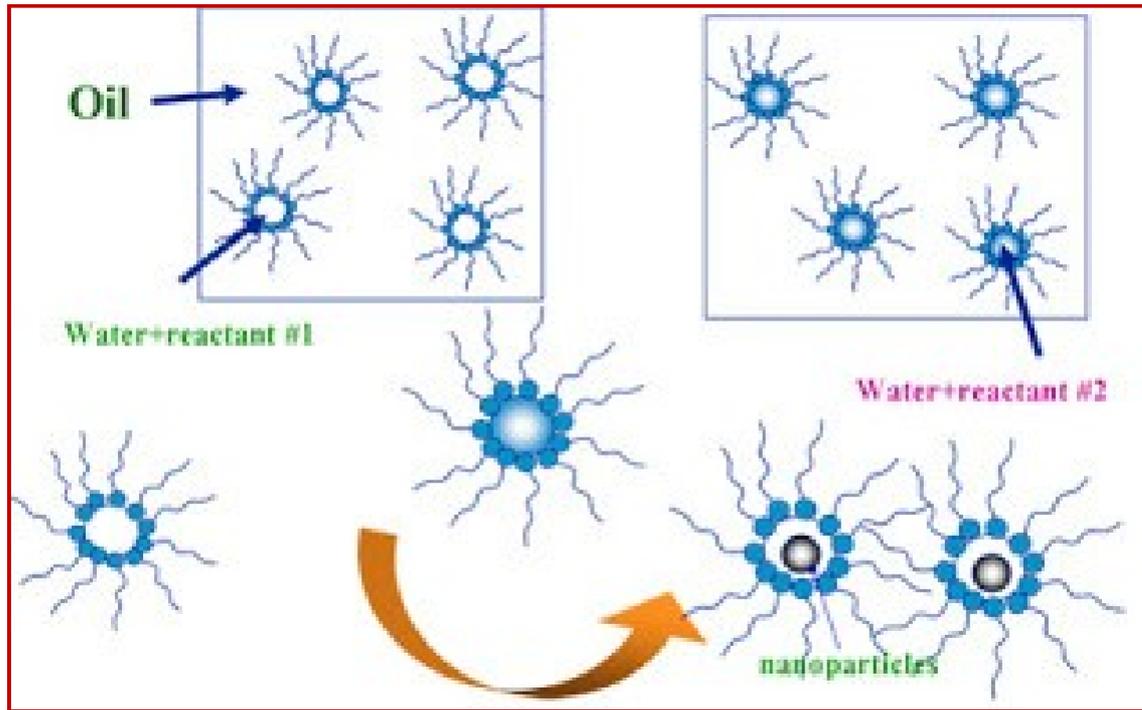
Reverse Micelle structure

If the dispersion medium is aqueous solvent, several molecules aggregate in such a manner that hydrophobic radicals form a core (inner element), while hydrophilic groups form the surface layer of a micelle (a micelle structure develops)

If the dispersion medium is an organic liquid, molecules in a micelle may have a reverse orientation, when the core is made up of polar groups, and hydrophobic radicals are turned inwards (reverse micelle structure develops)

• Microemulsion method

An example of self-assembly that achieves a limited degree of control over both formation and organization is the growth of quantum dots.



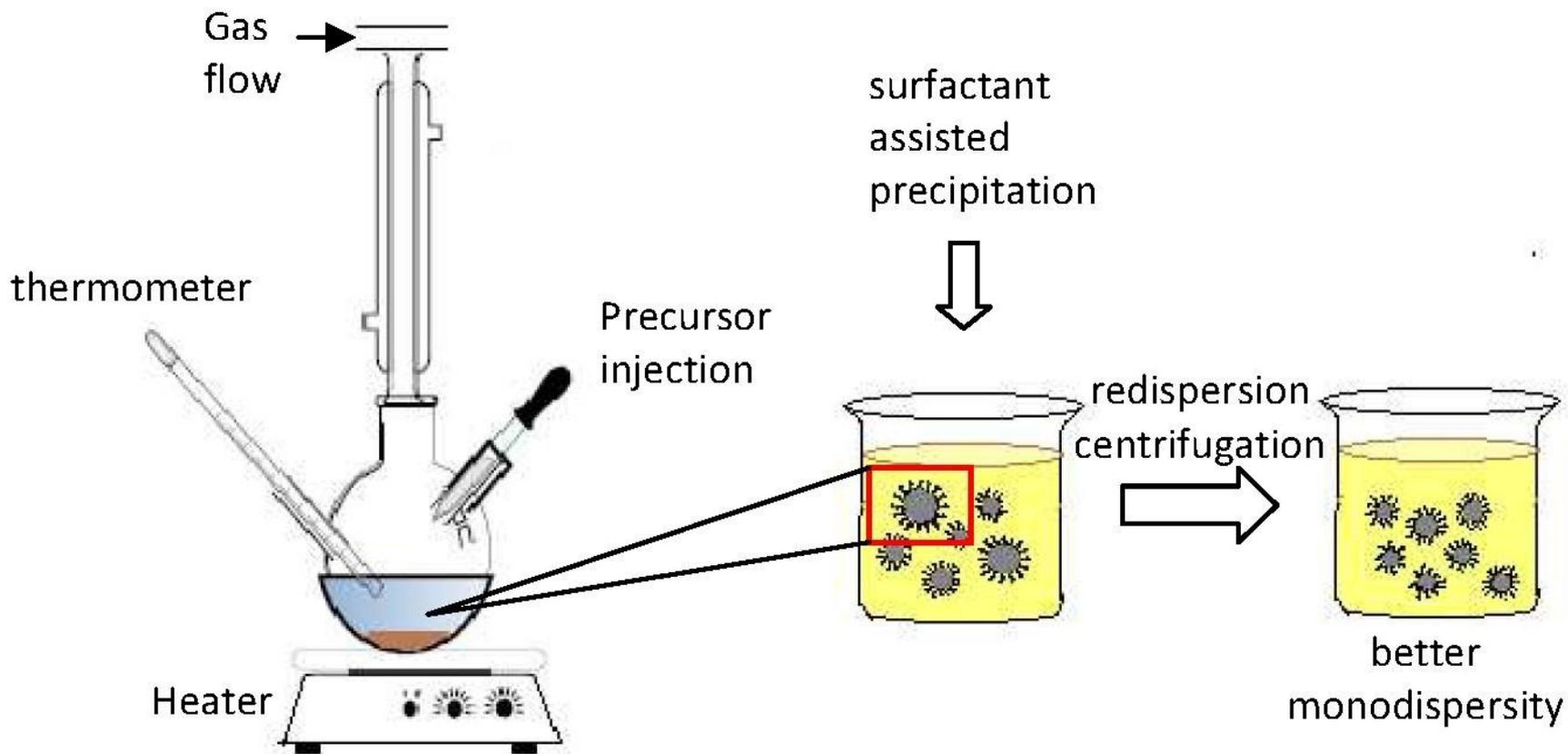
Microemulsions are isotropic, thermodynamically stable dispersion of oil, water, surfactant and often cosurfactant. Microemulsion can be characterized as oil-in-water (O/W), water-in-oil (W/O) and bicontinuous system. Water-in-oil microemulsions are composed of nanometer-sized water droplets that are dispersed in a continuous oil medium and stabilized by surfactant molecules. These droplets can serve as nanoreactors for producing nanoparticles

Several parameters, such as the concentration of the reactive precursor in the micelle and the weight percentage of the aqueous phase in the microemulsion, affect the properties including particle size, particle size distribution, and phases of the final particles formed.

There are several advantages to using this method—
the preparation of very small particles and
the ability to control the particle size.

Disadvantages - include low production yields and
the need to use large amount of liquids.

Colloidal Synthesis of Semiconducting Quantum Dots



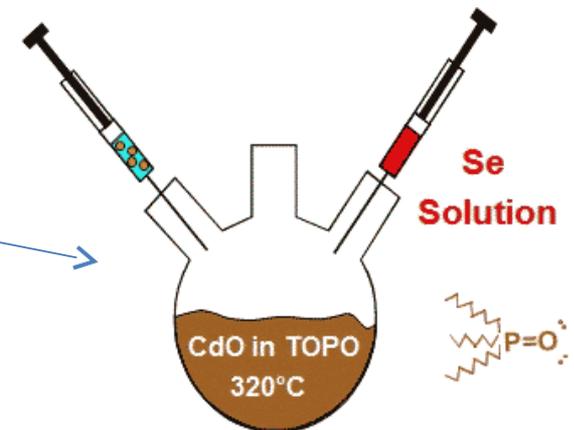
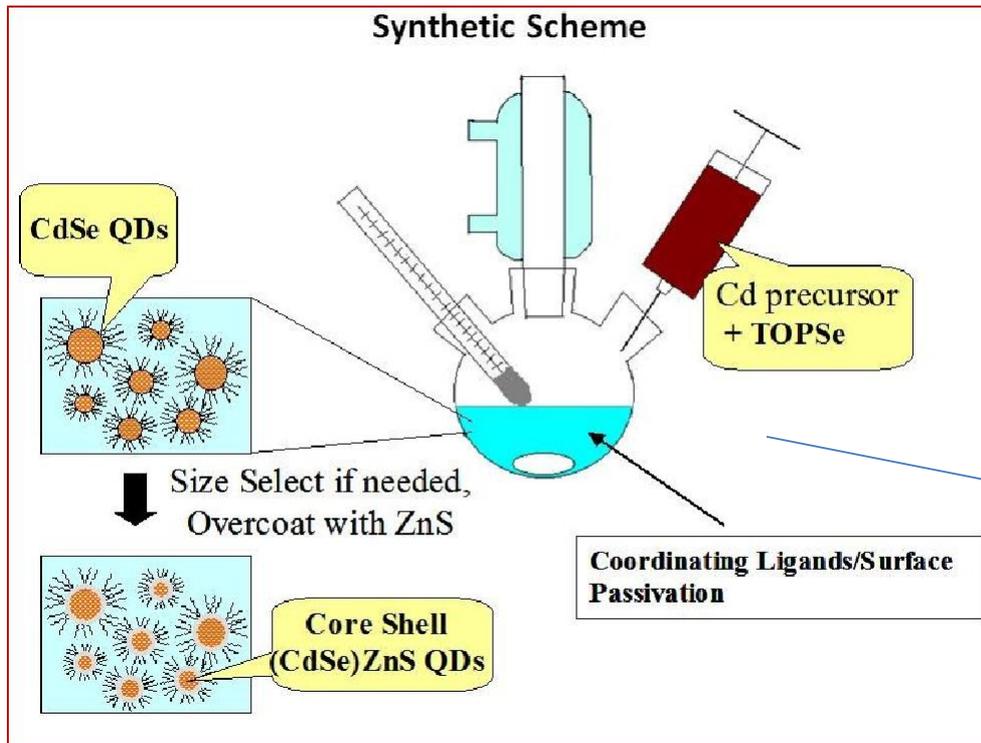
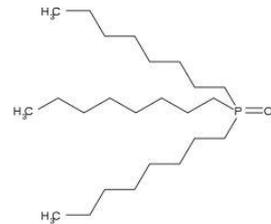
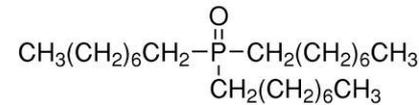
Colloidal Synthesis of CdSe (semiconducting) Quantum Dots:

Chemicals used:

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

Surfactant/ Capping agent used:

Trioctylphosphine Oxide (TOPO)



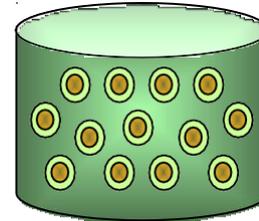
Colloidal Synthesis of CdSe (semiconducting) Quantum Dots:

Synthesis Approach →

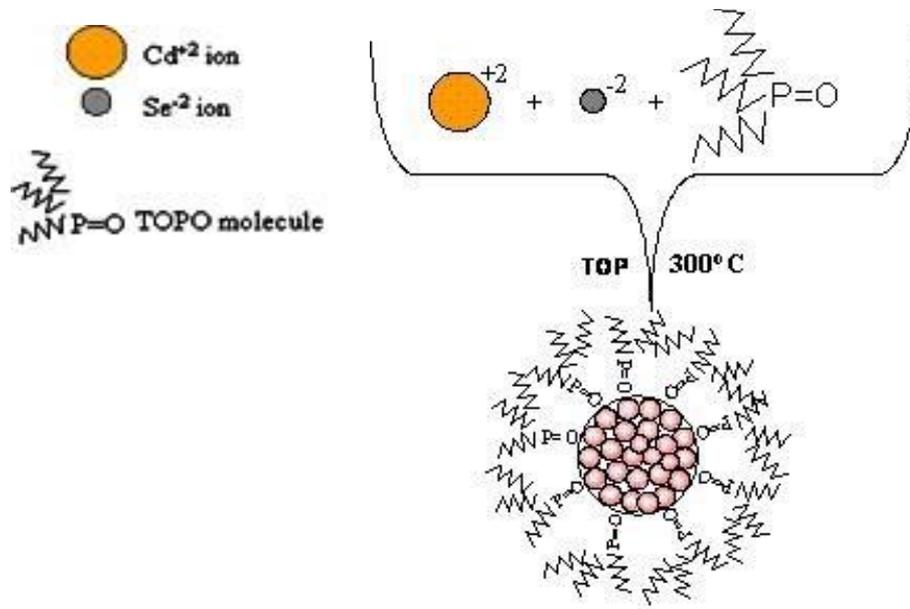


TOP-Se/Ar gas

> 300° C



TOPO- capped CdSe



TOPO capped CdSe nanoparticle

A Monodisperse Colloid Growth (La Mer)

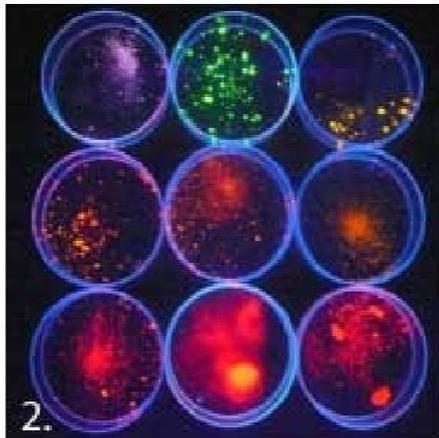
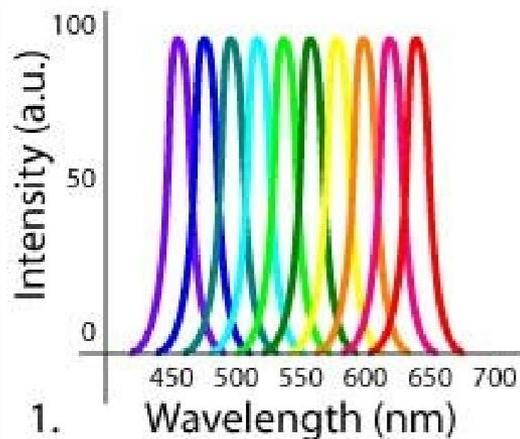
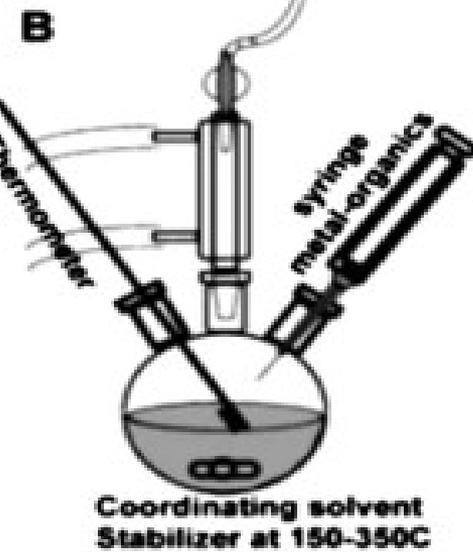
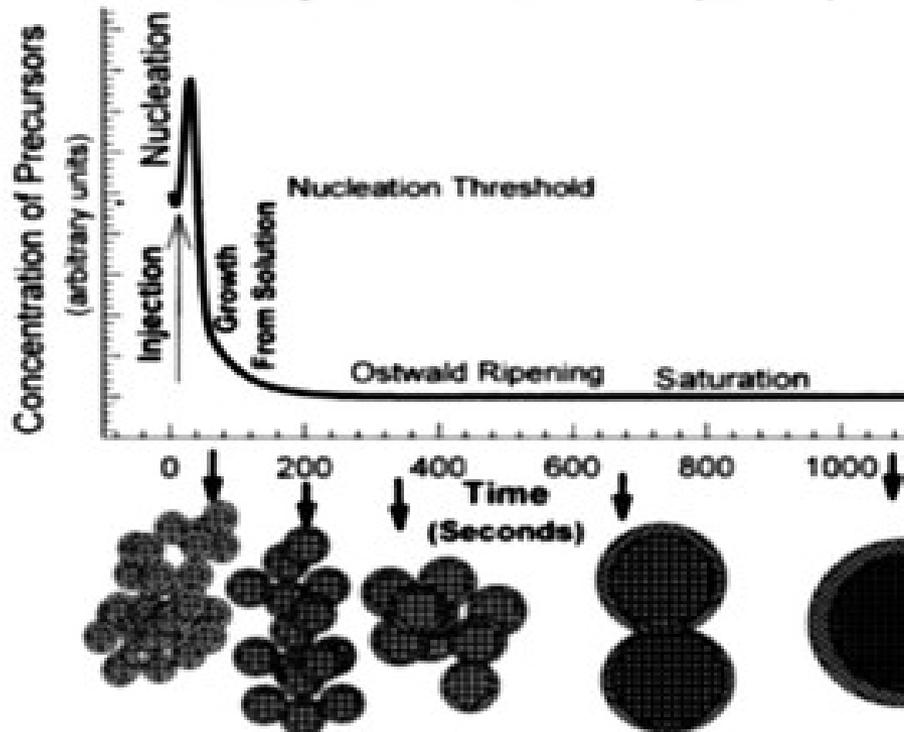


Figure1. Photoluminescence spectra of the quantum dots at wavelength of emission.

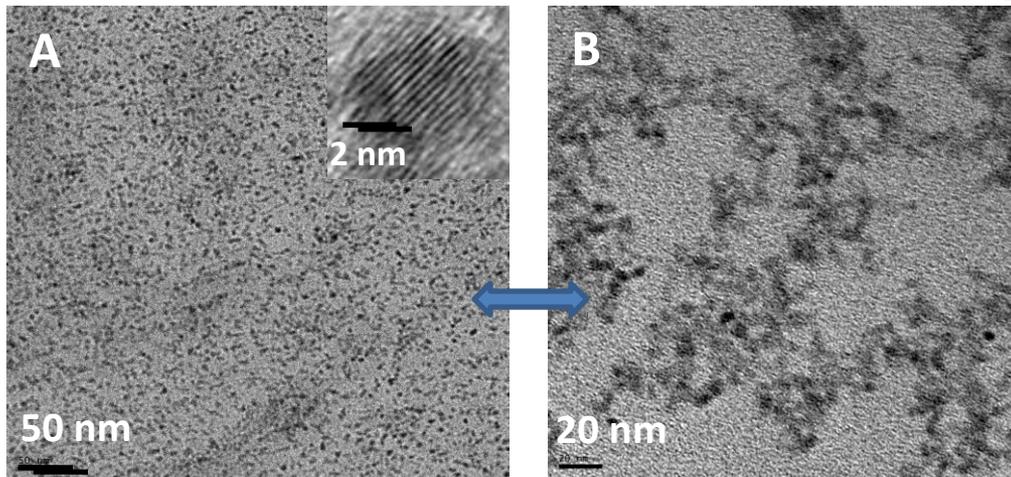
Figure2. Ocean's quantum dots in powder form.

Figure3. TEM of Ocean's quantum dots and their corresponding colors at the wavelength of emission.

Colloidal Synthesis of CdSe (semiconducting) Quantum Dots:

TEM Studies

Nearly monodispersed and highly crystalline CdSe quantum dots can be synthesized by colloidal synthesis

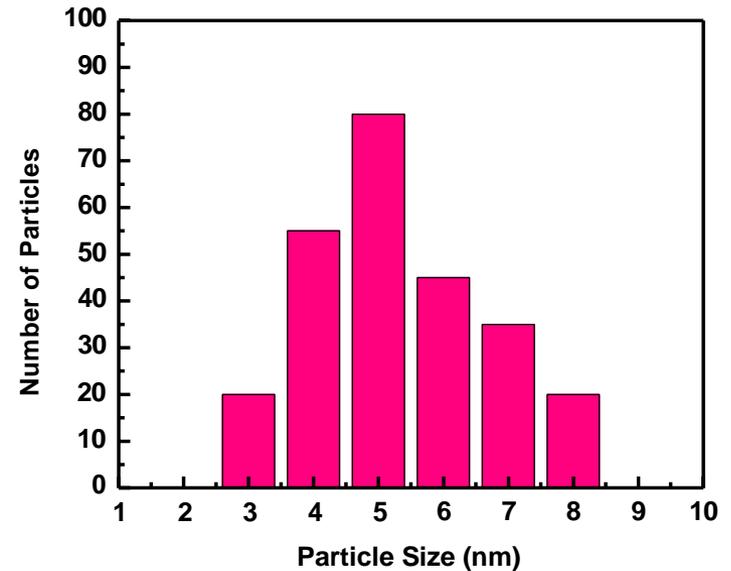


Size ~ 5 nm

CdSe/TOPO QDs

CdSe QDs
(After Pyridine Treatment)

Size distribution of nanoparticles formed



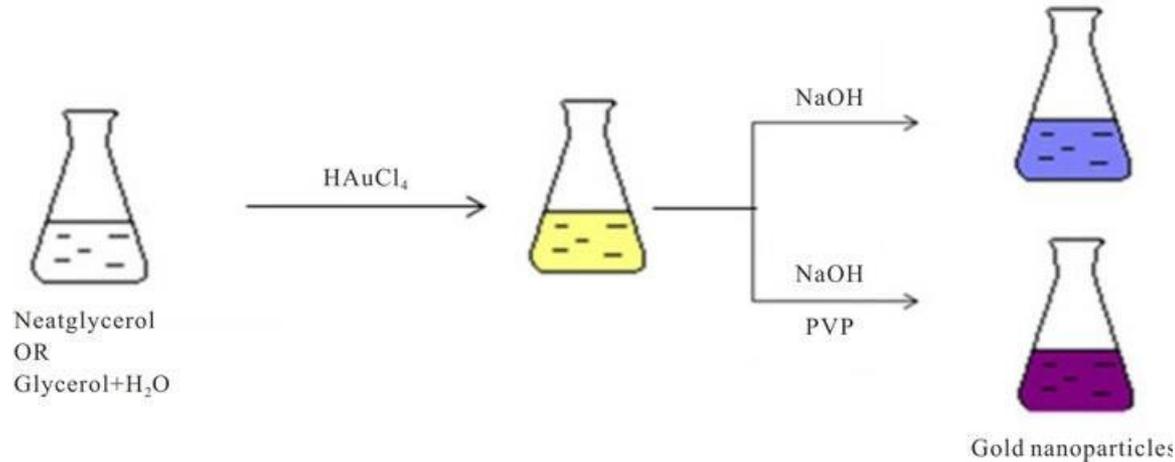
Advantages:

- Greener technique (environment friendly)
- cheaper and effective
- Narrow size particles(2-10 nm) can be synthesized

Disadvantage:

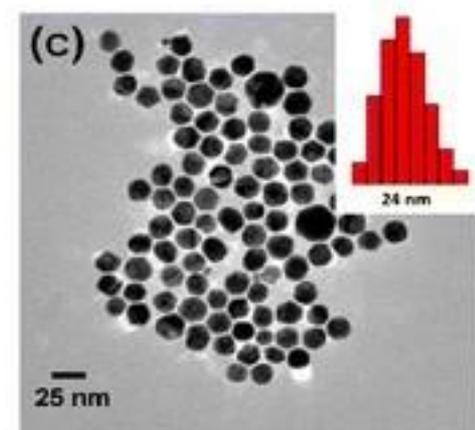
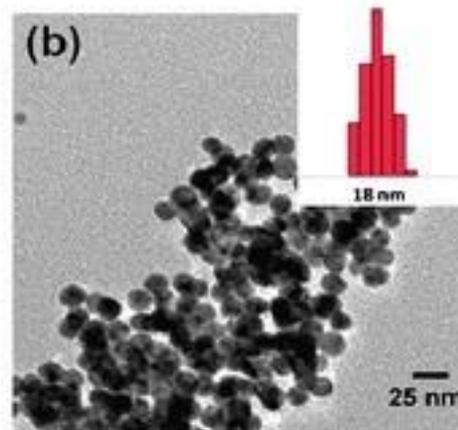
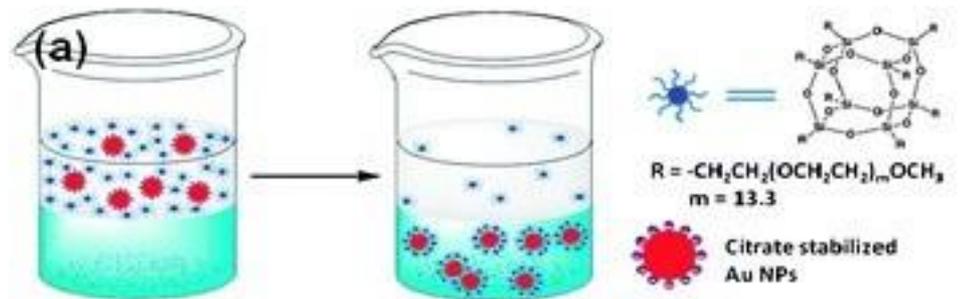
- controlling time and precursor is critical

Green Synthesis of Gold nanoparticles (Au NPs):



Gold sol was prepared by mixing the required concentration of NaOH (5×10^{-4} M) and chloroauric acid solution (1×10^{-4} M) in either neat glycerol or glycerol-water mixtures [80 to 20% (v/v) glycerol in water] at room temperature in the absence or presence of PVP [0.05% - 0.1% (w/v)].

Gradual formation of different color with time indicates the formation of Au NPs (Scheme 1). The experiments were repeated at least three times and found to be within the experimental error of $\pm 5\%$.



Spray pyrolysis



Spray pyrolysis is a process that atomizes a precursor solution with the help of a spray nozzle, and heats the droplets to form solid particles on the substrate

In spray pyrolysis, the source is deposited to the substrate in droplets of liquid sprayed onto the surface of the substrate to form a coating. The substrate is heated to about 350-500°C, which results to film formation. The liquid that is sprayed is made of the material diluted in either water or alcohol, or both.

