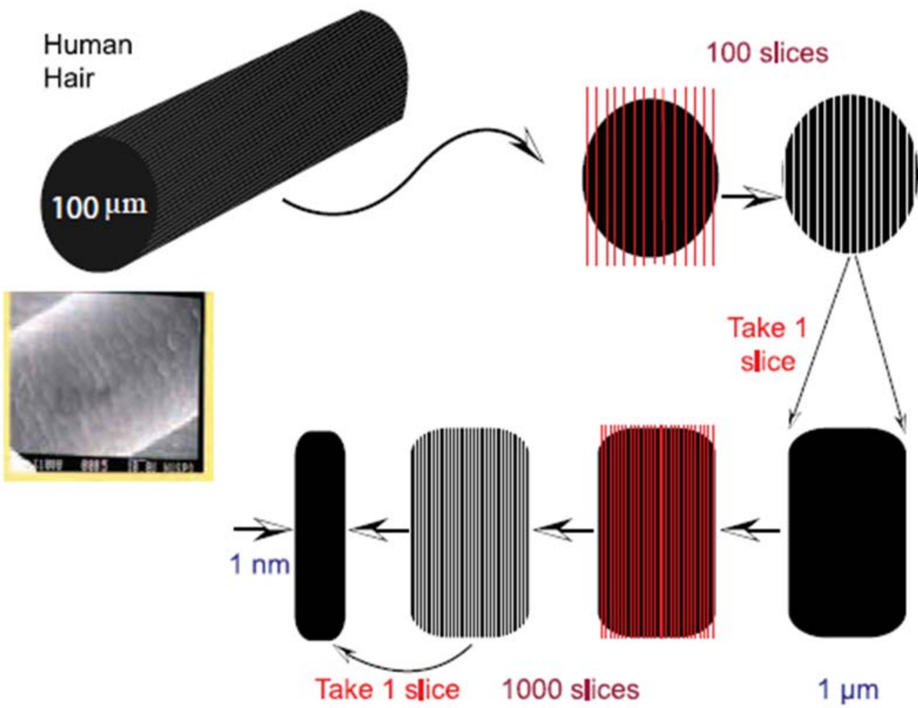
NANOCHEMISTRY

1 nm = 10^{-6} millimeter (mm) = 10^{-9} meter (m)

1 nm = 10 Angstrom

Nanoscience

A discipline concerning with making, manipulating and imaging materials having at least one spatial dimension in the size range 1–100 nm



Cross section of human hair

Nanotechnology

A device or machine, product or process based upon individual or multiple integrated nanoscale components

• The decorative glaze known as luster. Ruby Red glass pot (entrapped with gold nanoparticles)

• Nano-materials: Used by humans for 100 of years, the beautiful ruby red color of some glass is due to gold Nano particles trapped in the glass (ceramic) matrix.

Nanochemistry

Utilization of synthetic chemistry to make nanoscale building blocks of different:

- Size and shape
- Composition
- Surface structure
- Charge
- Functionality.

Bulk. In bulk materials, only a relatively small percentage of atoms will be at or near a surface or interface (like a crystal grain boundary).	**Nano.** In nanomaterials, large no. of atomic features near the interface.

Effects of Nano size

- Properties depends on size, composition and structure
- Nano size increases the surface area
- Change in surface energy (higher)
- Change in the electronic properties
- Change in optical band gap
- Change in electrical conductivity
- Higher and specific catalytic activity & chemical reactivity
- Change thermal and mechanical stabilities
- Different melting and phase transition temperatures

Various size of CdSe nanoparticles and their solution. The bulk CdSe is black

Properties of Nanomaterials

- **Surface area:** Large.
- **Reactivity:** High due to the unsaturated bonds on their pristine surfaces.
- **Basic properties:** Properties of materials change as:
  - their size approaches the nanoscale.
  - percentage of atoms at the surface of a material becomes significant.

  Example- Gold nanoparticles melt at much lower temperatures (~300 °C for 2.5 nm size) than the gold slabs (1064°C).
- **Optical properties:** Often possess unexpected optical properties as they are small enough to confine their electrons and produce quantum effects. Example- Gold nanoparticles appear deep red to black in solution.

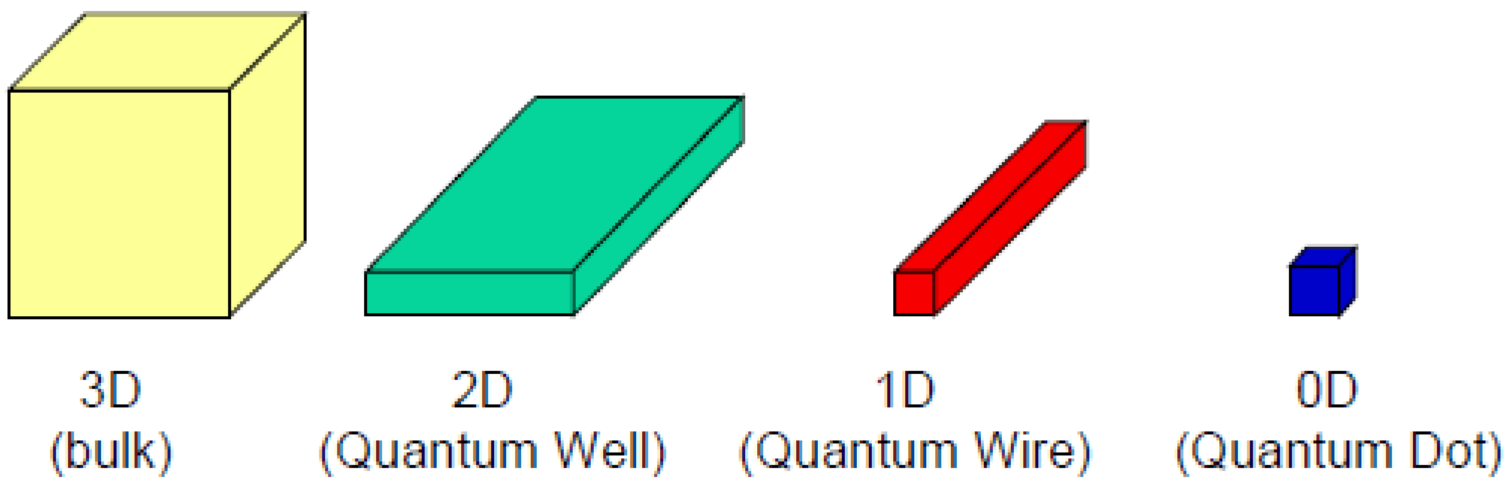
Applications of Nanomaterials

- Medicine
- Diagnosis
- Drug delivery
- Tissue engineering
- Environment
- Catalysis
- Filtration
- Energy

- Computers
- Aerospace
- Refineries
- Vehicle manufacturing
- Food packaging
- Optics
- Textiles
- Cosmetics

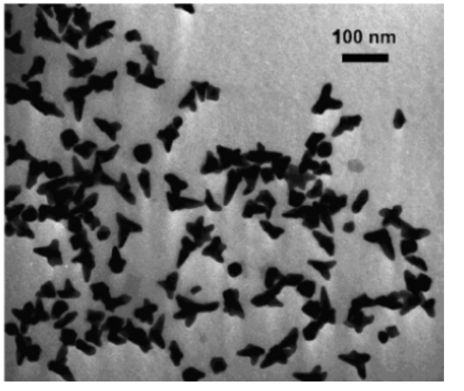
Few basic types

- Nanocrystals
- Nanotubes
- Nanowires
- Nanocomposites



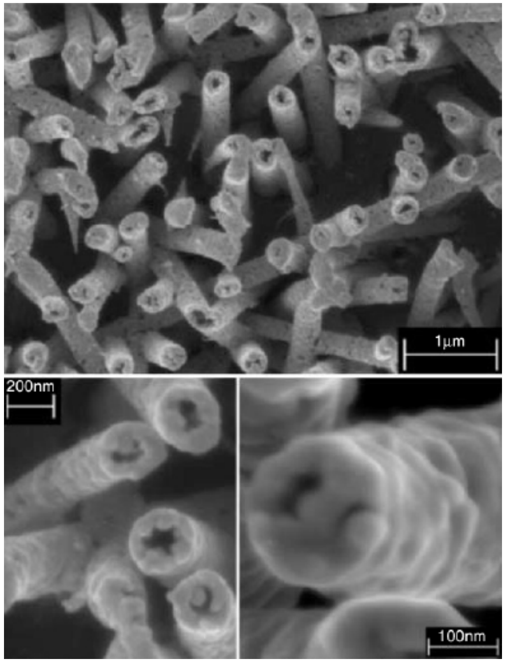
Nanocrystals

- Crystals of nanometer dimensions.
- Typical dimensions of 1 to 50 nanometers (nm), intermediate in size between molecules and bulk materials.
- Exhibit intermediate properties.
- Applications as:
  - o Biochemical tags
  - o As laser and optical components
  - o For the preparation of display devices
  - o For chemical catalysis.

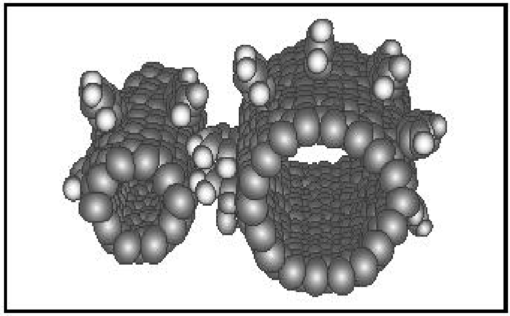


Au - Nanocrystals

Nanotubes

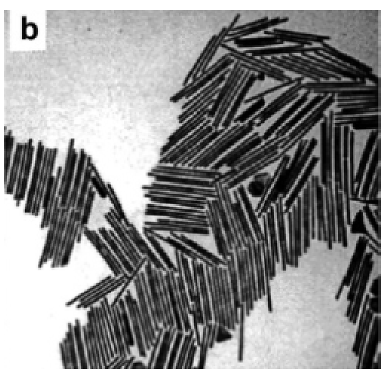


- Hollow carbon tubes of nanometer dimensions.
- Constitute a new form of carbon, configurationally equivalent to a graphite sheet rolled into a hollow tube.
- May be synthesized, with sizes ranging from a few microns to a few nanometers and with thicknesses of many carbon layers down to single-walled structures.
- The unique structure of these nanotubes gives them advantageous behavior relative to properties, such as electrical and thermal conductivity, strength, stiffness and toughness.

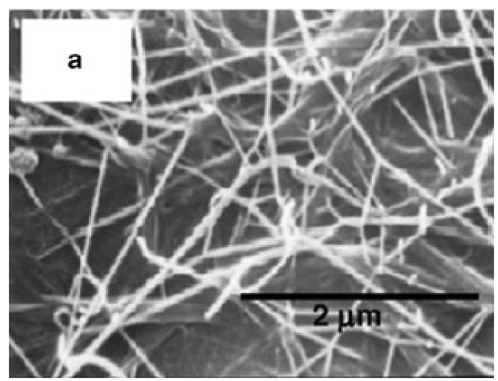


Nanowires

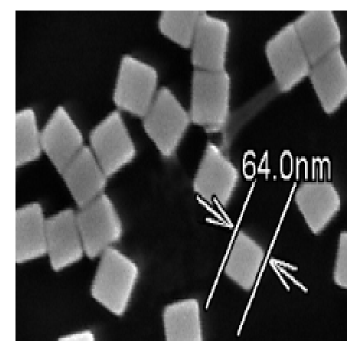
- Very small rods of atoms.
- Solid, dense structures, much like a conventional wire.
- Offer the potential for creating very small IC components.



Au - Nanorods



Silver nanowires



Silver nanocubes

Nanocomposites

- Encompass a large variety of systems composed of dissimilar components that are mixed at the nanometer scale.
- Can be one-, two-, or three-dimensional; organic or inorganic; crystalline or amorphous.
- Behavior is dependent on not only the properties of the components, but also morphology and interactions between the individual components, which can give rise to novel properties not exhibited by the parent materials.
- Size reduction from microcomposites to nanocomposites yields an increase in surface area that is important in applications, such as mechanically reinforced components, nonlinear optics, batteries, sensors and catalysts.

Methods of Preparation

There are many methods to synthesize nanoparticles, which can be classified as per following three criteria:

- By synthesis strategy
- By nature of process
- By medium of synthesis

Any Preparation technique should provide:

1. Identical size of all particles (mono sized or uniform size distribution).
2. Identical shape or morphology.

3 Identical chemical composition and crystal structure.

4 Individually dispersed or mono dispersed i.e., no agglomeration.

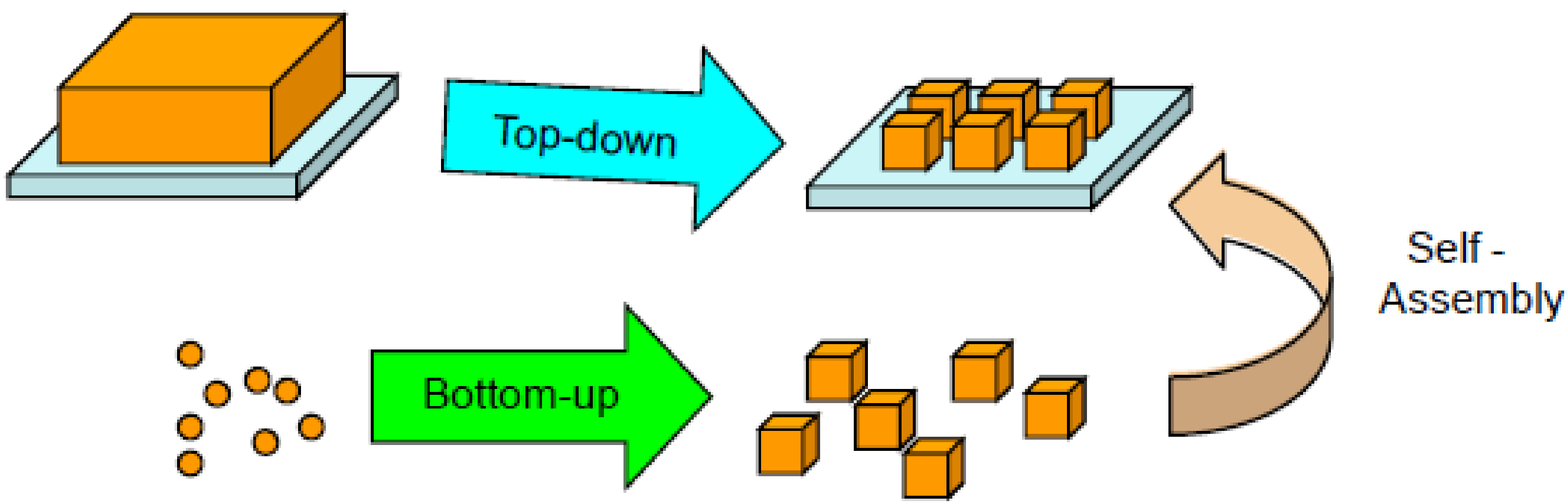
1. By synthesis strategy

a. Bottom-Up Strategy:

By the agglomeration of atoms or particles.

b. Top-Down Strategy: (Attrition)

- By breaking the larger particles to the nano size.
- Generally done by high energy ball milling.



2. By nature of process

a. Physical methods:

- Only the size of the particles can be reduced mechanically.
- Physical properties will be changed.
- No change in chemical properties.
- Just the increase in chemical reactivity due to increase in surface area.

b. **Chemical methods:**

- Chemical properties get change according to the chemical route.

3. By medium of synthesis

(i) Gas phase synthesis
(ii) Liquid phase synthesis
(iii) Solid phase synthesis

Different Methods of Preparation

Nanomaterials preparation

Physical Methods

- Ball milling
- Gas condensation processing (GPC)
- Laser ablation
- Ion beam
- Electron beam
- Nanolithography

Chemical Methods

- Sol-gel synthesis
- Wet chemical synthesis
- Precipitation method
- Chemical vapour condensation
- Catalytic chemical vapour deposition
- Template assisted CVD
- Electrochemical method
- Reverse micelles

Ball Milling :

Physical method

Solid state

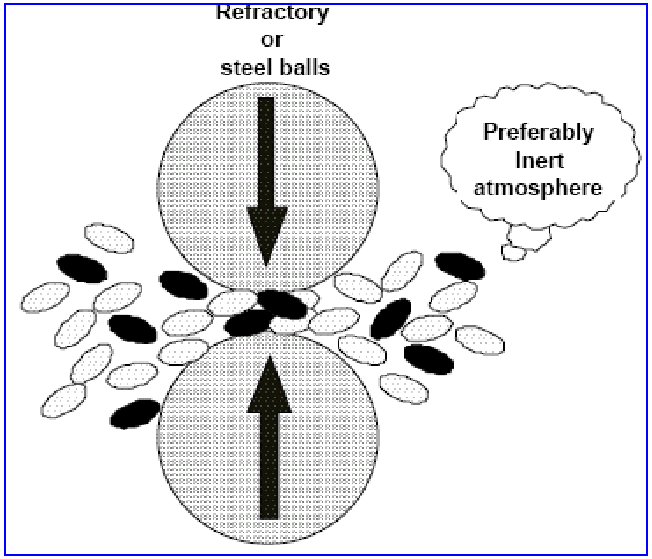
Top down approach

*Interest in the mineral, ceramic processing, and powder metallurgy industry.

* Involves milling process include particle size reduction (Fig.3).

* Restricted to relatively hard, brittle materials which fracture and/or deform during the milling operation.

* Different purposes including; tumbler mills, attrition mills, shaker mills, vibratory mills, planetary mills, etc.



Violent or agitation,

~50 μm $\rightarrow$ nm

Schematic representation of the principle of mechanical milling.

- **Limitations**
- Generation of high temperature leads thermal decomposition or evaporation of some materials.
- Difficulty in broken down to the required particle size.
- Contamination by the milling tools (Fe, Steel, Ceramic).

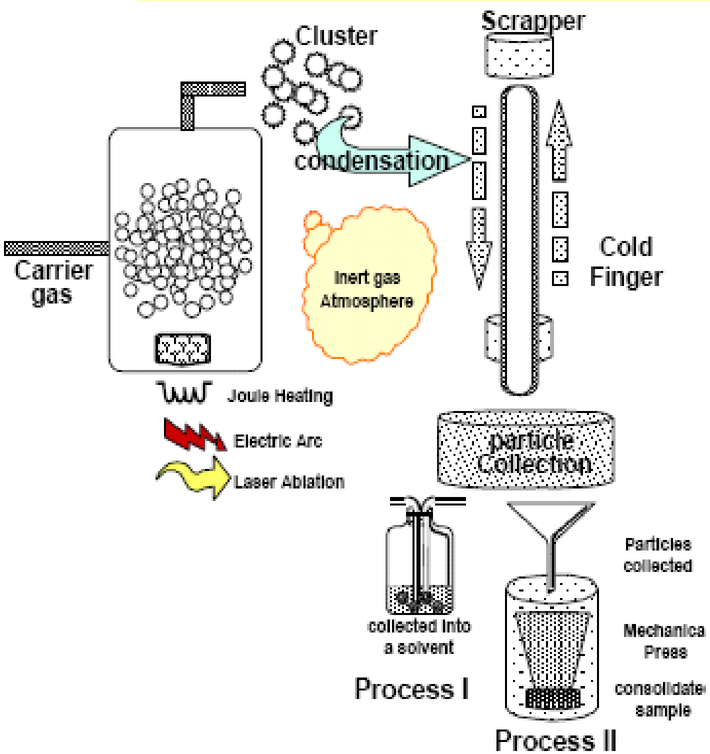
Gas Condensation Processing (GPC):

Physical method

Vapor Phase

Bottom-Up approach

Metal in crucible → **Thermal or electric evaporation** / **Homogenous nucleation in gas phase** → **Metal cluster (gaseous state)** → **Cooling (Rotating cylinder) Liquid N_2 (-80°C)** → **Nanoparticles deposits (2-50nm)**



Advantage:-

Major advantage is control of particle size.

These methods allow for the continuous operation hence suitable for large scale producction.

Limitation:-

Oxide impurities are often formed.

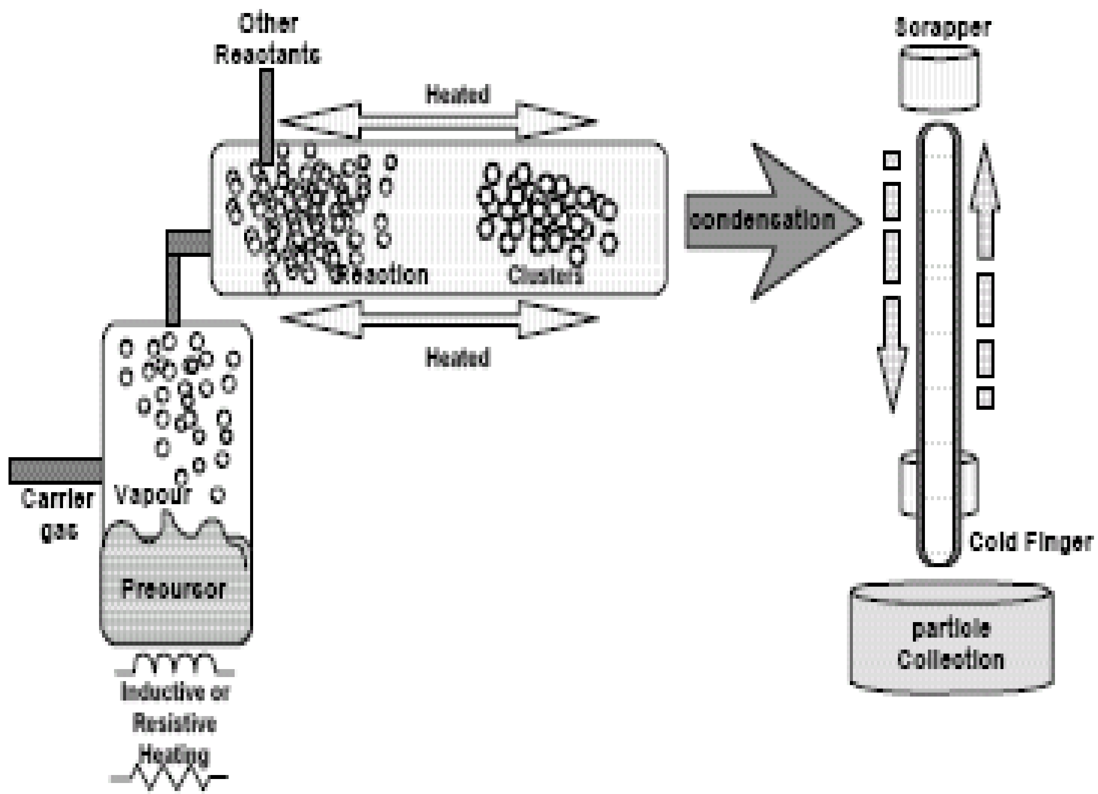
The method is extremely slow.

set-up for gas condensation synthesis of nanomaterials

Chemical Vapour Condensation (CVC) :

Chemical method
Vapor Phase
Bottom-Up approach

- Involves heat treatment of vapors of starting materials.
- Precursor residence time is the key parameter to control the size of nanoparticle .
- Other procedure similar to GPC.
- Production capabilities are much larger than in the GPC processing.

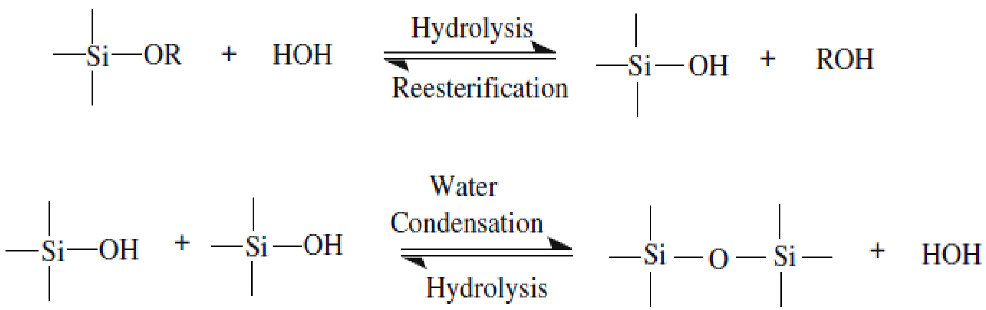


A schematic of a typical CVC reactor

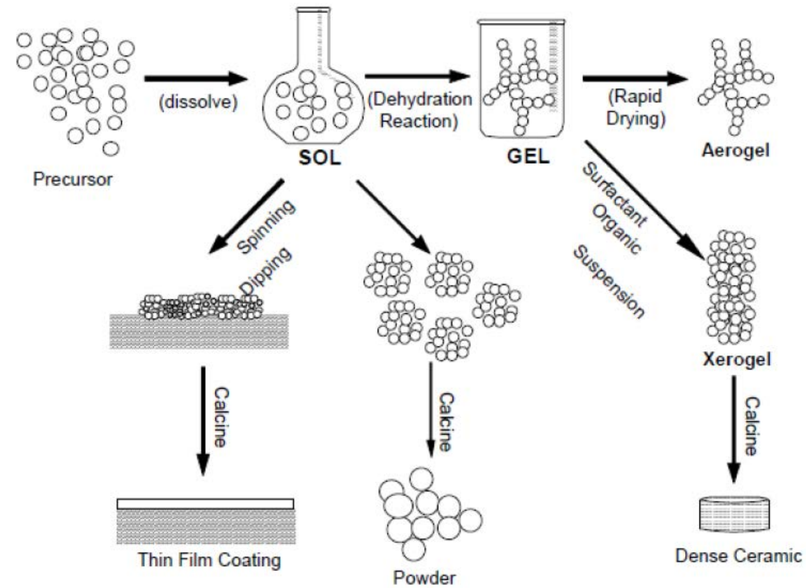
Sol-Gel Method:

Chemical method
Solution Phase
Bottom-Up approach

Sol-gel processing refers to the hydrolysis and condensation of alkoxide-based precursors such as $Si(OEt)_4$ (tetraethyl orthosilicate, or TEOS).



Classic sol-gel reaction scheme



- <u>**Over all Steps:**</u>
- **Step 1:** Formation of different stable solutions of the alkoxide (the sol).
- **Step 2:** Gelation resulting from the formation of an oxide- bridged network (the gel) by polycondensation reaction
- **Step 3:** Aging of the gel, during which the polycondensation reactions continue until the gel transforms into a solid mass.
- **Step 4:** Drying of the gel, when water and other volatile liquids are removed from the gel network.
- **Step 5:** Dehydration, during which surface- bound M-OH groups are removed, there by stabilizing the gel against rehydration. This is normally achieved by calcination at temperatures up to 800^0C.
- **Step 6:** Densification and decomposition of the gels at high temperatures ($T>800^0$C). The pores of the gel network are collapsed, and remaining organic species are volatilized.

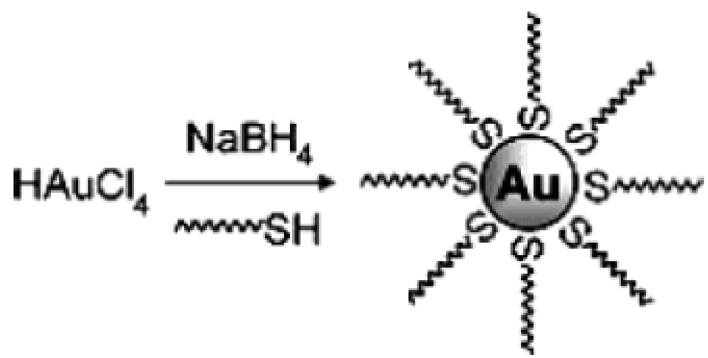
Wet chemical synthesis:

Chemical method
Solution Phase
Bottom-Up approach

Preparation of Gold nanoparticles

$HAuCl_4$ + Stabilizing agent + $NaBH_4$ $\longrightarrow$ Au nanoparticles

Stabilizing agents – Thiols, alkylammonium salts, surfactants etc

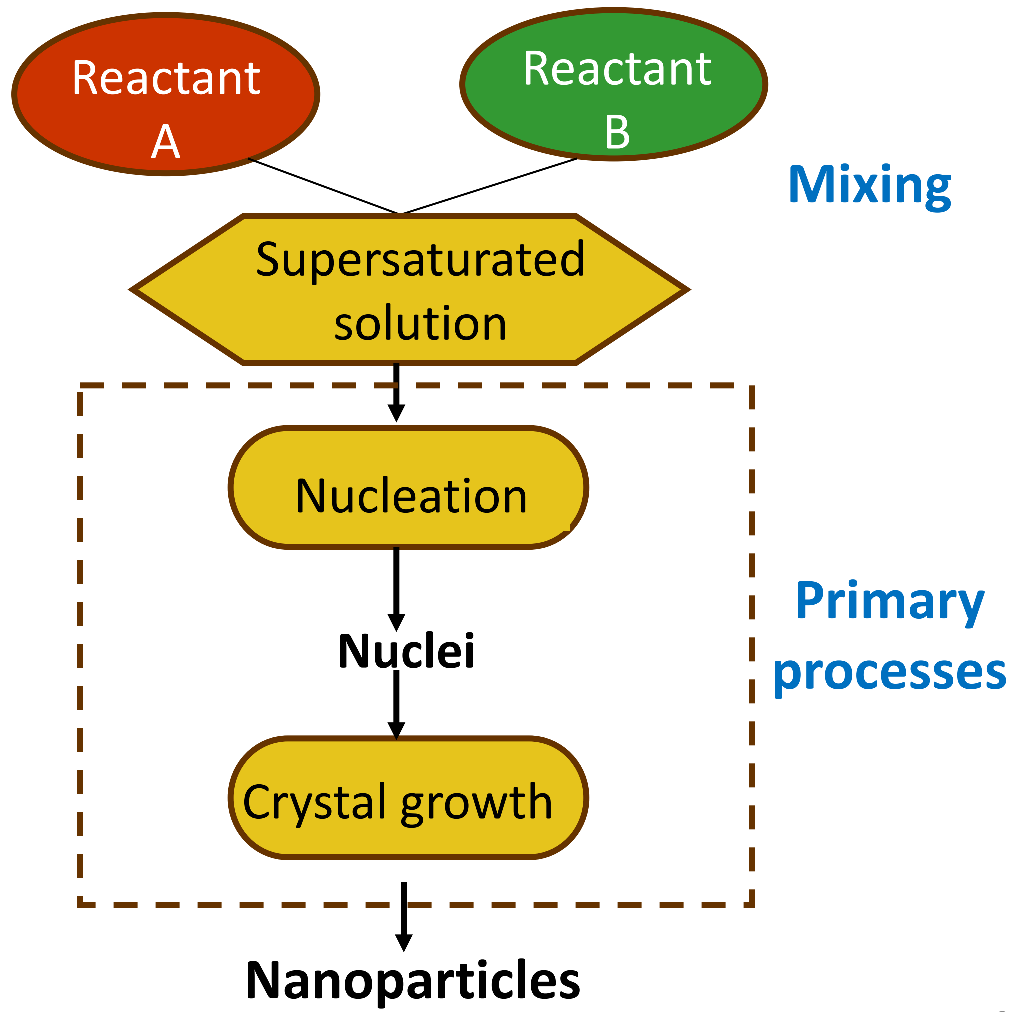


Stabilization with thiols involves two phase synthesis (Thiols bind strongly with gold due to soft character of Au and S)
This method give smaller particle size and reduced dispersity
The concentration of Au/thiol ratio determines the particle size
The stability of particles depends on the chain length of thiols

Chemical precipitation:

Chemical method
Solution Phase
Bottom-Up approach

Fast chemical reaction is required to obtain a high degree of super-saturation of the product to favor homogeneous nucleation.



Scheme of precipitation process.

Hydrothermal synthesis (Thermal hydrolysis):

Chemical method
Solution Phase
Bottom-Up approach

- Aqueous solutions of metal salts or gels are treated at elevated temperatures (100-300˚C) and pressures above 1 atm.
- Size and shape of nanoparticles can be controlled by changing the conditions of the solutions:
  - pH
  - Concentration
  - Solvent and process conditions (temperature, duration, etc.).

Micro-emulsion synthesis (reverse micelles method):

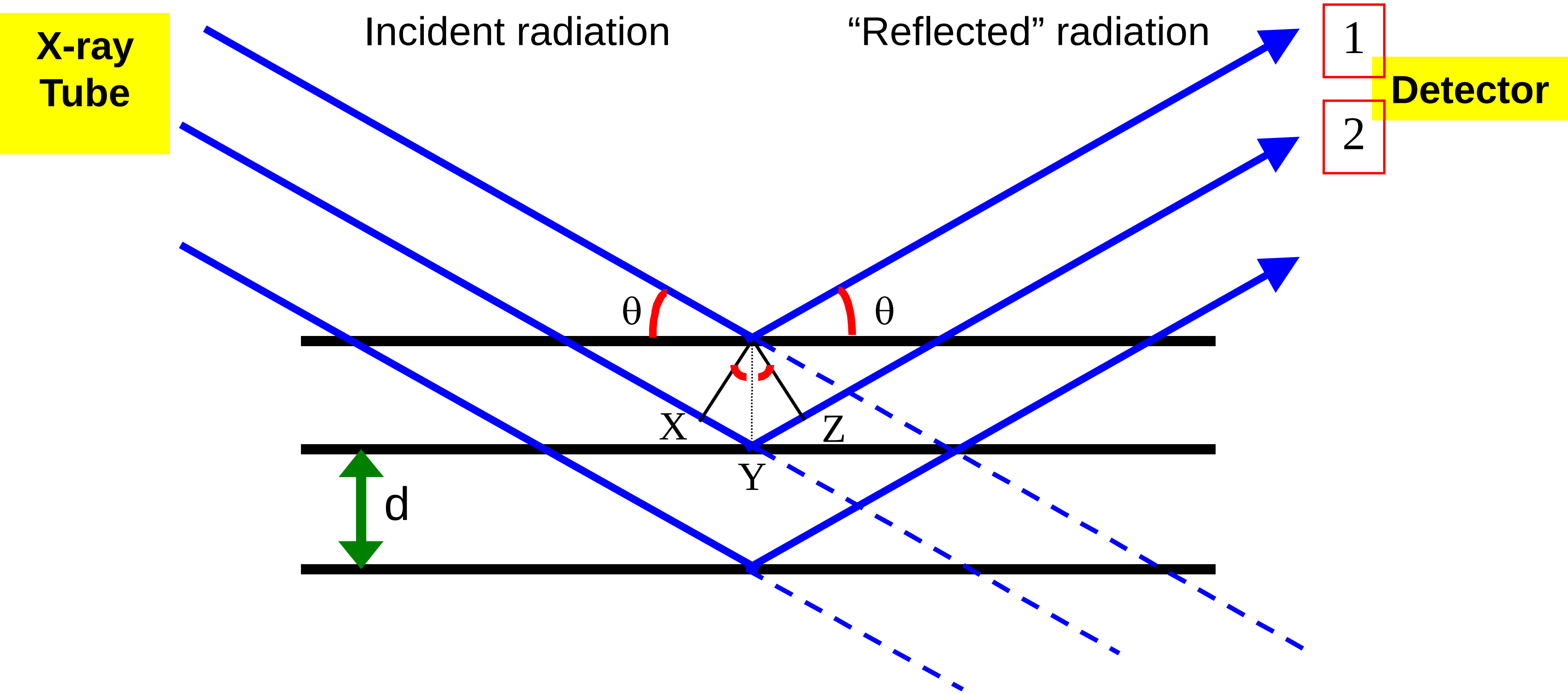
Chemical method
Solution Phase
Bottom-Up approach

- **Microemulsions:** Thermodynamically stable, optically clear dispersions of two immiscible liquids, such as water and oil.
- They are formed, when a surfactant lowers the oil/water interfacial tension allowing thermal motions to spontaneously disperse the two immiscible phases.
- Reverse micelles are molecular self assemblies from surfactants which have a spherical shape with a hydrophillic core and a hydrophobic tail on the sphere surface.
- Most popular method to prepare nanosized inorganic particles as oxides.

Techniques to Characterize Nanomaterials

- Scanning tunneling microscope (STM)
- Atomic force microscope (AFM)
- Scanning electron microscopy (SEM)
- Transmission electron microscopy (TEM)
- X-ray diffraction (XRD)

BRAGG'S EQUATION



Beam 2 lags beam 1 by XYZ = 2d sin θ

so $$2d \sin \theta = n\lambda$$ **Bragg's Law**

Remember the **'n'** may assume values **1, 2, 3...** and so on for **first, second** and **third** order diffraction events respectively.

QUESTION:

The diffraction pattern of copper metal was measured with X-ray radiation of wavelength of 1.315 Å. The first order Bragg diffraction peak was found at an angle 2Ө of 50.5 °. Calculate the d-spacing between the diffracting planes in the copper metal.

HINT:

$\lambda = 1.315$ Å.

$2\theta = 50.5^\circ$

$\rightarrow \theta = 25.25^\circ$

Bragg's law $n\lambda = 2d\sin\theta$

$d = \lambda / 2\sin\theta$

$d = 1.54$ Å

QUESTION:

Inter planar distance between two layers is 4Å in a crystal. Calculate the angle of reflection for first order reflection. X-rays of wavelength 1.54Å are diffracted by the crystal.

HINT:

$$\text{Solution: Since}, n\lambda = 2d\sin\theta$$

$$(1)(1.54\mathring{A}) = (2)(4\mathring{A})\sin\theta$$

$$\text{or}, \sin\theta = \frac{1.54}{8} = 0.1925$$

$$\text{or}, \theta = \sin^{-1} 0.1925$$

$$\text{or}, \theta = 11.1^0$$