나노소재합성개론

2025-2

4. Synthesis of Nanomaterials - II
(Chemical Methods)

4. Synthesis of Nanomaterials II (Chemical Methods)

4.4 Synthesis of Metal Nanoparticles by Colloidal Route

- Colloidal metal nanoparticles are often synthesized by reduction of some metal salt or acid
- **Example**: highly stable gold particles can be obtained by reducing chloroauric acid ($HAuCl_4$) with tri sodium citrate ($Na_3C_6H_5O_7$)

$$HAuCl_4 + Na_3C_6H_5O_7 \rightarrow Au^+ + C_6H_5O_7^- + HCl + 3NaCl$$

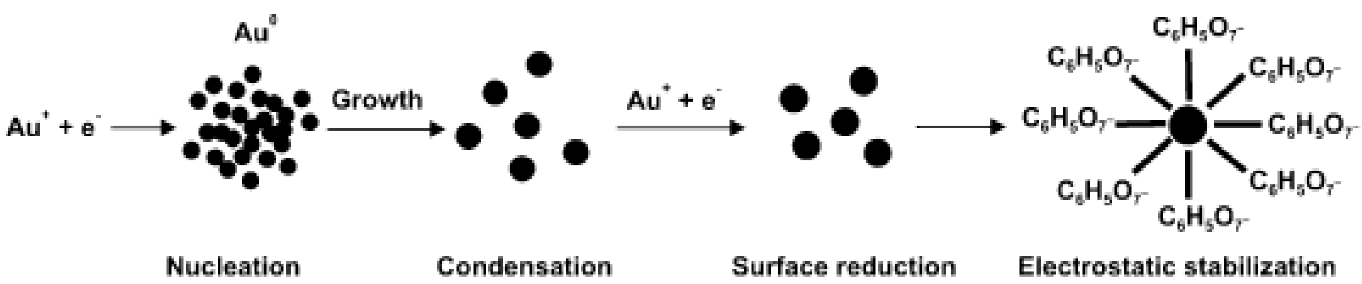

Fig. 4.17 Stabilization by electrochemical double layer formation

4. Synthesis of Nanomaterials II (Chemical Methods)

4.4 Synthesis of Metal Nanoparticles by Colloidal Route

- Metal gold nanoparticles exhibit intense red, magenta and other colors, depending upon the particle size.
- Gold nanoparticles discussed above are stabilized by repulsive Coulombic interactions
- It is also possible to stabilize gold nanoparticles using thiol or some other capping molecules
- In a similar manner, silver, palladium, copper and other metal nanoparticles can be synthesized using appropriate precursors, temperature, pH, duration of synthesis etc.

4. Synthesis of Nanomaterials II (Chemical Methods)

4.5 Synthesis of Semiconductor Nanoparticles by Colloidal Route

- Compound semiconductor nanoparticles can be synthesized by wet chemical route using appropriate salts

- Sulphide semiconductors like CdS and ZnS can be synthesized as nano-particles simply by coprecipitation

- **Example**: to obtain ZnS nanoparticles any zinc salt like zinc sulphate ($ZnSO_4$), zinc chloride ($ZnCl_2$), zinc nitrate ($ZnNO_3$) or zinc acetate ($Zn[CH_3COO]_2$) can be dissolved in aqueous medium and Na_2S is added to the solution. (One can even dissolve H_2S gas in the Zn salt solution).

$$ZnCl_2 + H_2S \rightarrow ZnS + 2HCl$$

- To obtain zinc oxide particles one can use NaOH.

$$ZnCl_2 + 2NaOH \rightarrow Zn(OH)_2 + 2NaCl$$
$$Zn(OH)_2 \rightarrow ZnO + H_2O$$

4. Synthesis of Nanomaterials II (Chemical Methods)

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4. Synthesis of Nanomaterials II (Chemical Methods)

4.5 Synthesis of Semiconductor Nanoparticles by Colloidal Route

- Once we get our desired nanoparticles, they need to be surface passivated as colloids formed in liquids have a tendency to coagulate or ripen due to attractive forces existing between them.

  ➡ "Chemical capping"

- Advantage with this chemical route is that, one can get stable particles of variety of materials not only in the solution, but even after drying off the liquid.

  - Possible to make thin films of the capped particles by spin coating or dip coating techniques

- The coating, however, has to be stable and noninteractive with the particle itself except at the surface

  - If it is a part of the synthesis reaction, the concentration of capping molecules can be used in two ways i.e. <u>to control the size as well as to protect the particles from coagulation</u>.

4. Synthesis of Nanomaterials II (Chemical Methods)

4.5 Synthesis of Semiconductor Nanoparticles by Colloidal Route

- Chemical capping can be carried out at high or low temperature depending on the reactants

- In high temperature reactions, cold organometallic reactants are injected in some solvent like trioctylphosphineoxide (TOPO) held at a temperature of 300 ~ 400 °C

- **Example**: when dimethyl cadmium [$Cd(CH_3)_2$] and Se powder were injected in TOPO, CdSe nanoparticles capped with PO_4 groups were obtained.

- Although, this is a very good route of synthesizing the nanoparticles, most of the organo-metallic compounds are prohibitively expensive.

-> Besides they are also toxic and difficult to handle

"expert guidance"

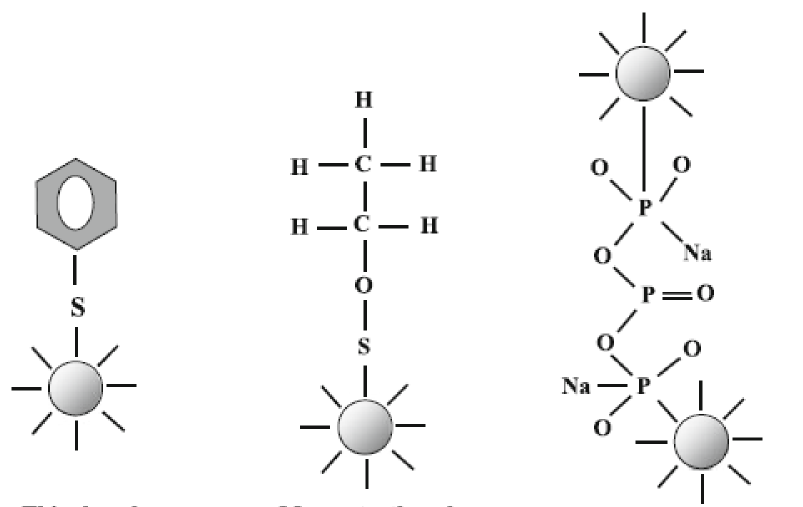
4. Synthesis of Nanomaterials II (Chemical Methods)

4.5 Synthesis of Semiconductor Nanoparticles by Colloidal Route

- A wide range of metal oxides and other insulators with wide band gap can be synthesized by chemical precipitation method along with suitable surface passivant

Chemical Capping of Nanoparticles

A variety of molecules can be used to cap the nanoparticles. For example capping of metal-sulphide nanoparticles by few organic and inorganic molecules



Thiophenol (C_6H_5SH)

Mercaptoethanol (C_2H_5OSH)

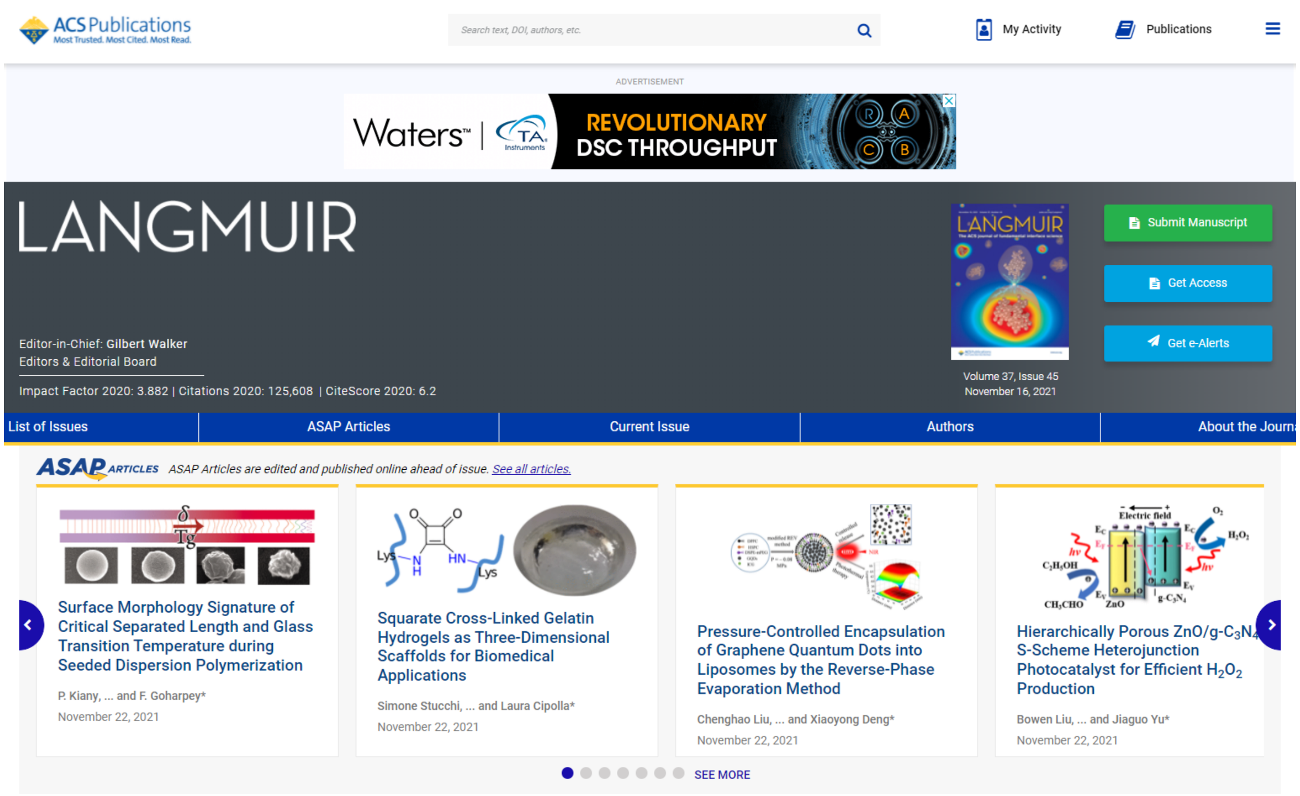
Sodium Hexametaphosphate $(NaPO_3)_6$

4. Synthesis of Nanomaterials II (Chemical Methods)

4.6 Langmuir-Blodgett (LB) Method

- This technique to transfer organic overlayers at air-liquid interface onto solid substrates is known for nearly 70 years.

developed by two scientists *Langmuir* and *Blodgett*



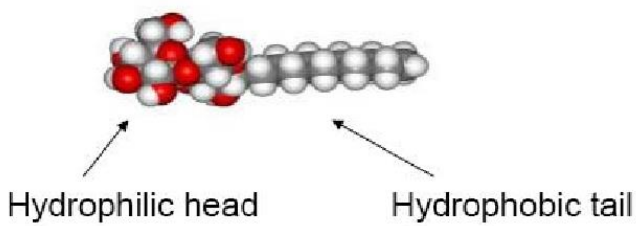
4. Synthesis of Nanomaterials II (Chemical Methods)

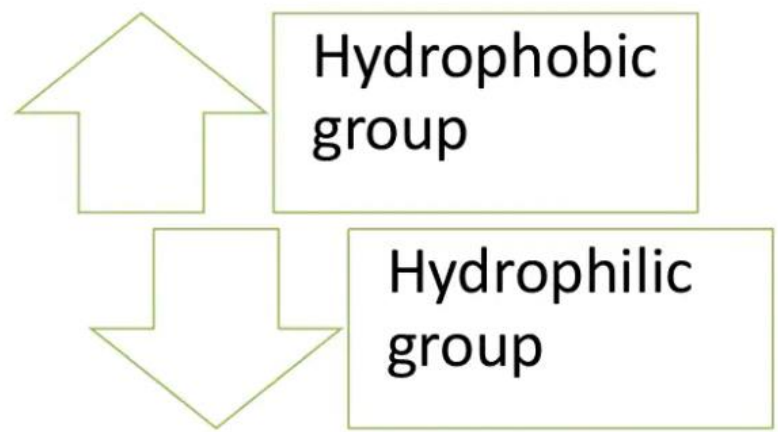
4.6 Langmuir-Blodgett (LB) Method

- In this technique, one uses <u>amphiphilic long chain molecules</u> like that in fatty acids.

<u>Amphiphilic (양친매성) structure</u>

An *amphiphile* is a chemical compound possessing both *hydrophilic* (water-loving, polar) and *lipophilic* (fat-loving) properties





4. Synthesis of Nanomaterials II (Chemical Methods)

4.6 Langmuir-Blodgett (LB) Method

- An amphiphilic molecule (see Fig. 4.19) has a hydrophilic group (water loving) at one end and a hydrophobic group (water hating) at the other end
- **Example**: the molecule of arachidic acid, which has a chemical formula [$CH_3(CH_2)_{16}COOH$]. There are many such long organic chains with general chemical formula [$CH_3(CH_2)_nCOOH$], where n is a positive integer. In this case –CH_3 is hydrophobic and –COOH is hydrophilic in nature.

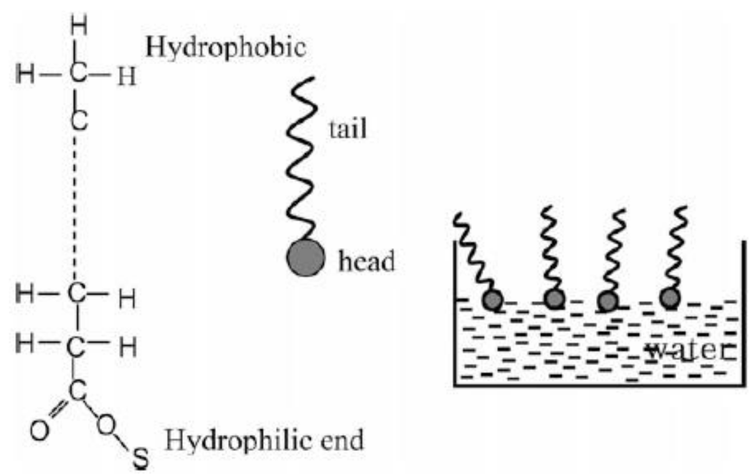


Fig. 4.19 Amphiphilic molecules with hydrophilic and hydrophobic ends to stay with head group immersed in water and tail group in air

4. Synthesis of Nanomaterials II (Chemical Methods)

4.6 Langmuir-Blodgett (LB) Method

- Usually molecules with n>14 are candidates to form L-B films. This is necessary in order to keep hydrophobic and hydrophilic ends well separated from each other.
- When such molecules are put in water, the molecules spread themselves on surface of water in such a way that their hydrophilic ends, often called as 'heads' are immersed in water, whereas the hydrophobic ends called as 'tails' remain in air.
- They are also surface active agents or surfactants.
- Surfactants are amphiphilic molecules that is an organic chain molecule in which at one end there is a polar, hydrophilic (water loving) and at the other a nonpolar, hydrophobic (water hating) group of atoms.

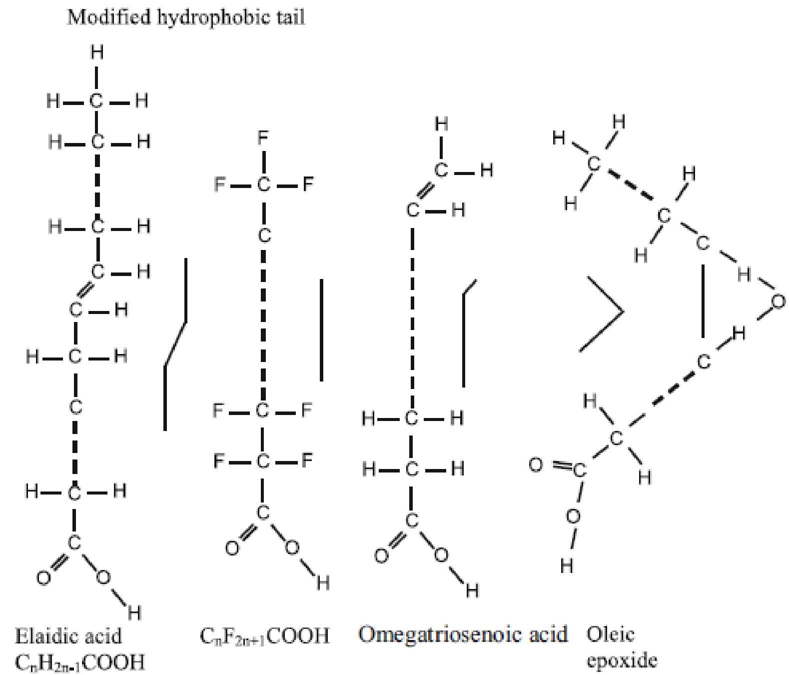
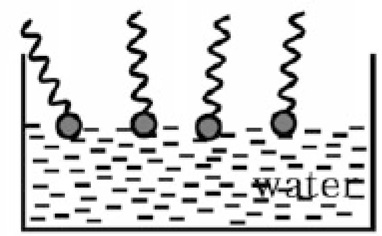


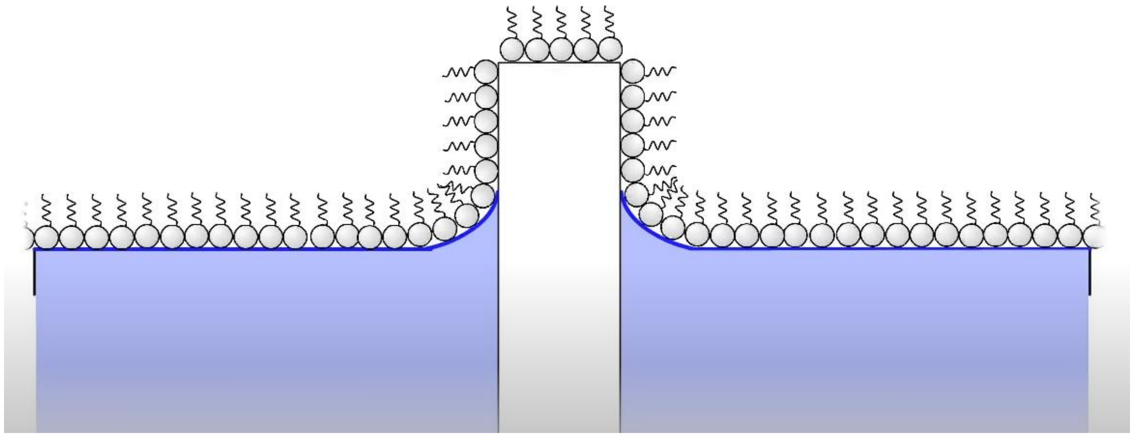
Fig. 4.20 A variety of organic molecules used for L-B thin film deposition

4. Synthesis of Nanomaterials II (Chemical Methods)

4.6 Langmuir-Blodgett (LB) Method



- Using a movable barrier, it is possible to compress these molecules to come closer together to form a 'monolayer' and align the tails.
- Such monolayers are two dimensionally ordered and can be transferred on some suitable solid substrates like glass, silicon etc.



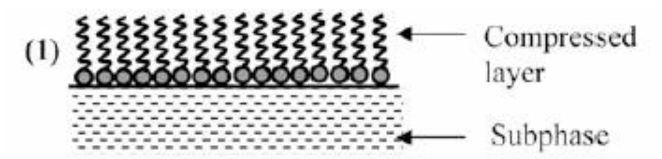
https://youtu.be/j8yqyRr2VQg

Fig. 4.20 A variety of organic molecules used for L-B thin film deposition

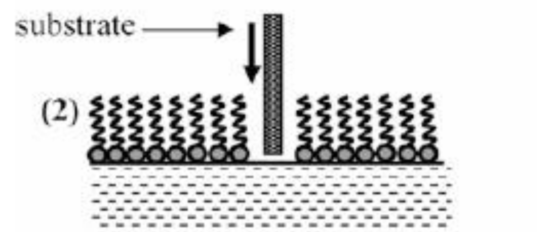
4. Synthesis of Nanomaterials II (Chemical Methods)

4.6 Langmuir-Blodgett (LB) Method

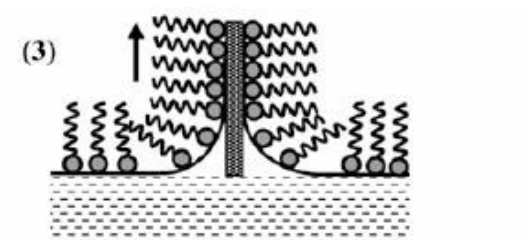
- This is done simply by dipping the solid substrate inside the liquid in which ordered organic molecular monolayer is already formed. (Fig. 4.21.)



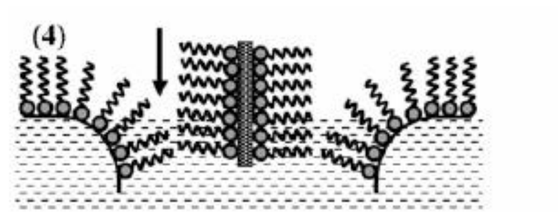
(1) A monolayer of amphiphilic molecules is formed.



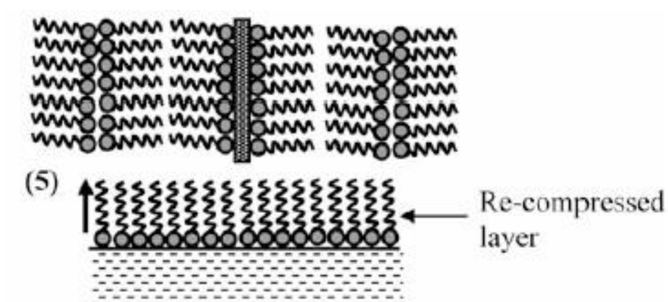
(2) A substrate is dipped in the liquid.



(3) The substrate is pulled out, during which ordered molecules get attached to the substrate.



(4) When the substrate is again dipped, molecules again get deposited as the substrate forming a second layer on the substrate.



(5) As the substrate is again pulled out, a thin layer gets deposited. By repeating the procedure a large number of ordered layers can be transferred on a substrate

4. Synthesis of Nanomaterials II (Chemical Methods)

4.6 Langmuir-Blodgett (LB) Method

- Depending upon the nature of substrate material i.e. whether hydrophobic or hydrophilic, layers are transferred on the solid substrates
- A glass slide when dipped in the solution becomes wet with water. Therefore, while it is withdrawn from the liquid the head groups can be easily attached to glass surface.
- As a result the whole monolayer gets transferred in a manner as if a carpet is pulled.
- Now the glass substrate has tail groups, which are hydrophobic on outer side.
- Therefore as it is dipped in the liquid again, it acquires a second layer with tail-tail coming closer together and while it is pulled back to air, another monolayer of molecules with head-head groups coming together is pulled.
- The process of dipping-pulling the substrate can be repeated several times to obtain ordered multilayers of molecules. However to keep ordered layers available on water surface, it is necessary to keep constant pressure on the molecules.

4. Synthesis of Nanomaterials II (Chemical Methods)

4.6 Langmuir-Blodgett (LB) Method

- Type of L-BN films (X, Y and Z type)

  - Y types of films are most commonly found. Although the layers are ordered, there is only the weak Van der Waals interaction between different layers

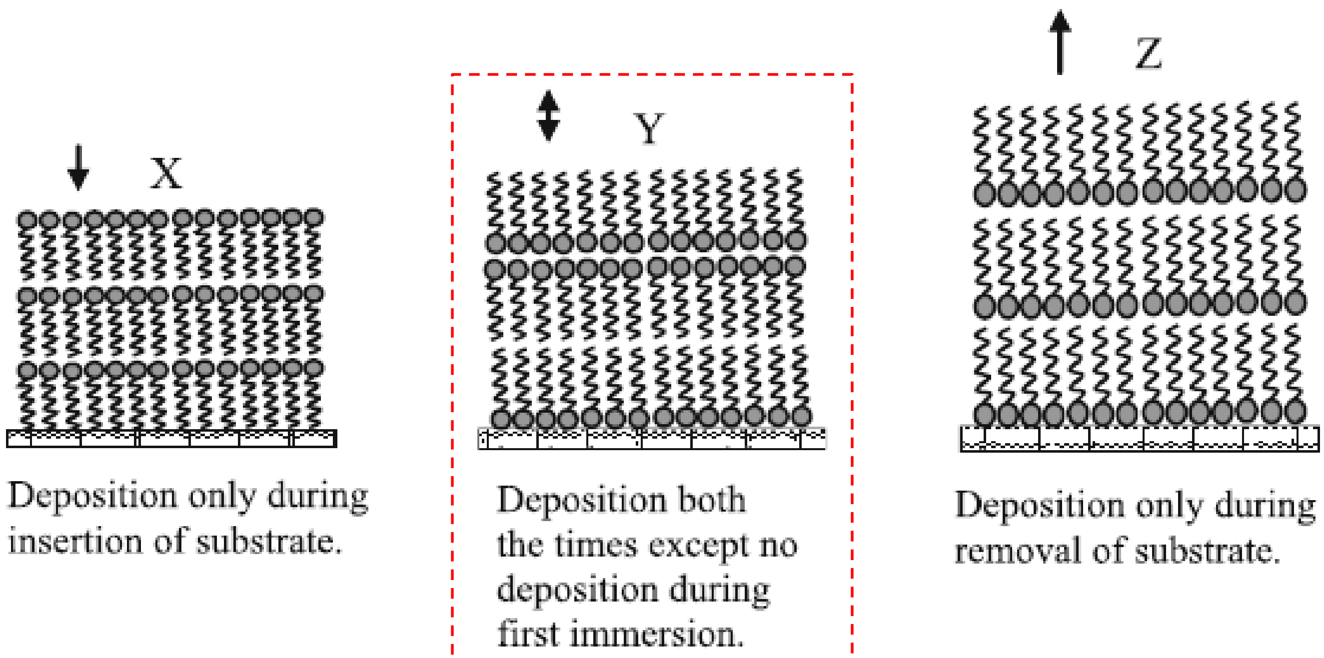


Fig. 4.22 X, Y and Z type L-B films

4. Synthesis of Nanomaterials II (Chemical Methods)

4.7 Microemulsions

- Whenever two immiscible liquids are mechanically agitated or stirred together, they are known to form an ‘emulsion’.
- The tendency of the liquids is such that the liquid in smaller quantity tries to form small droplets, coagulated droplets or layers so that they are all separated from the rest of the liquid in large quantity (for example droplets of fat in milk).
- The droplet sizes in emulsions are usually larger than 100 nm upto even few millimetres. Emulsions are usually turbid in appearance.

4. Synthesis of Nanomaterials II (Chemical Methods)

4.7 Microemulsions

- Amphiphilic Molecules in Liquids (**Micelles and Inverse-micelles**)

  - Consider now a situation in which a hydrocarbon molecule solution is put in an aqueous medium.

  - The hydrocarbon solution itself would be separated from aqueous solution and float on it.

  - When surfactant molecules are mixed in large quantity in aqueous solution, they would try to form what are known as 'micelles' and 'inverse-micelles' when aqueous solution is mixed in oil.

  - In micelles, the head groups float in water and tails are inside, whereas tails point outwards in case of inverse micelles

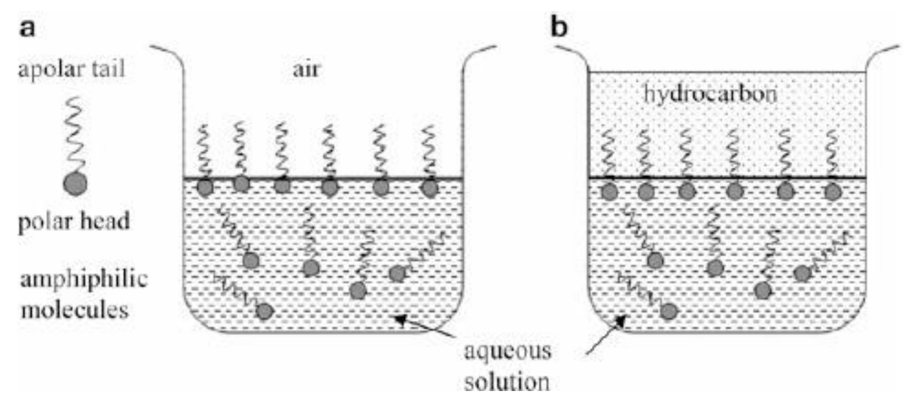


Fig. 4.24 Amphiphilic molecules in aqueous solutions

4. Synthesis of Nanomaterials II (Chemical Methods)

4.7 Microemulsions

- Microemulsions are stabilized using surfactants (surface stabilized active agents).

- When an organic liquid or oil (O), water (W) and surfactant (T) are mixed together, under some critical concentration, 'micelles' or 'inverse micelles' are formed, depending upon the concentrations of water and organic liquid.

- micelles are formed with excess water and inverse micelles are formed in excess of organic liquid or oil.

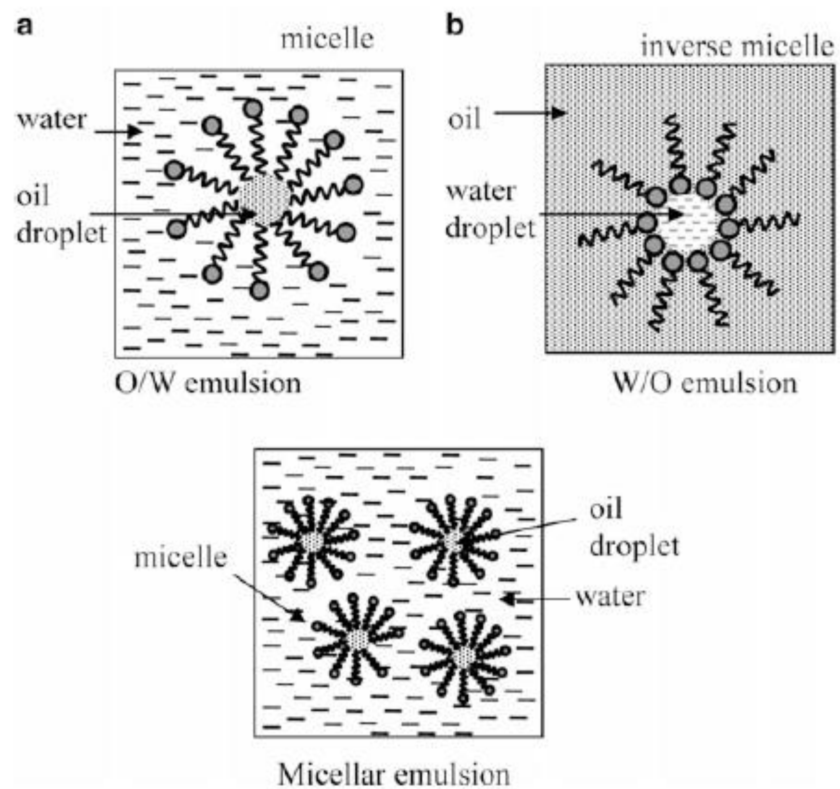


Fig. 4.26 Formation of micelles and inverse micelles

4. Synthesis of Nanomaterials II (Chemical Methods)

4.7 Microemulsions

- The shape of Micelles

  - Different shapes taken by micelles under different synthesis conditions

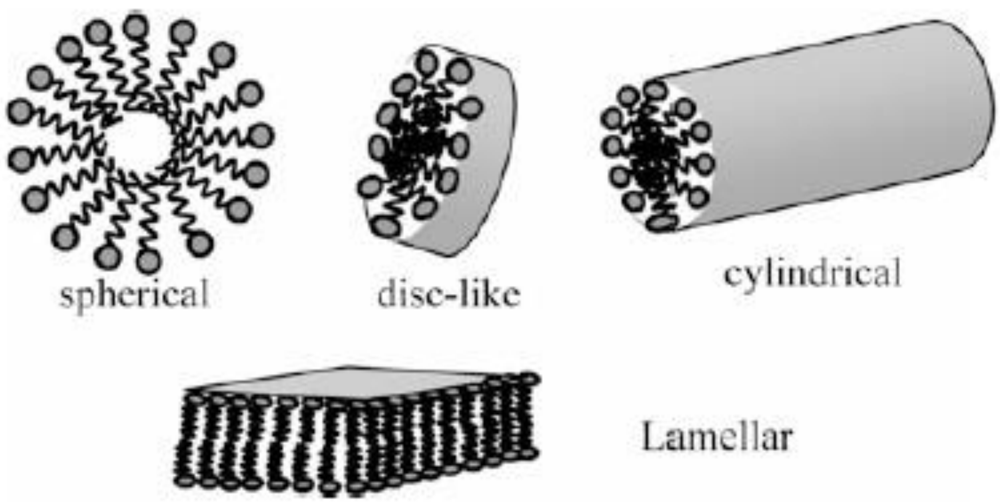


Fig. 4.27 Different shapes of micelles

4. Synthesis of Nanomaterials II (Chemical Methods)

4.7 Microemulsions

- The ratio of water (W), oil (O) and surfactant (T) is important to decide which type of micelle will be formed and can be represented in a ternary phase diagram

- Composition can be determined by drawing lines parallel to all three sides of the triangle

Point *P*

60 % of water

26 % of oil

14 % of surfactant

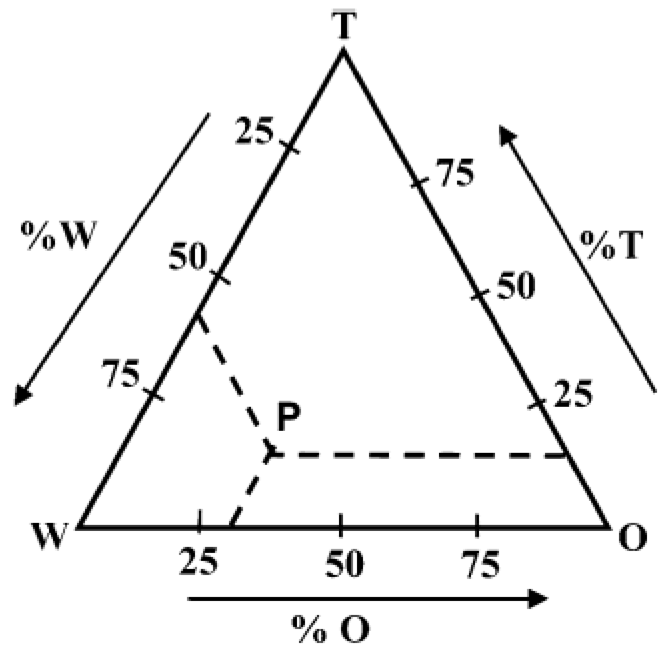
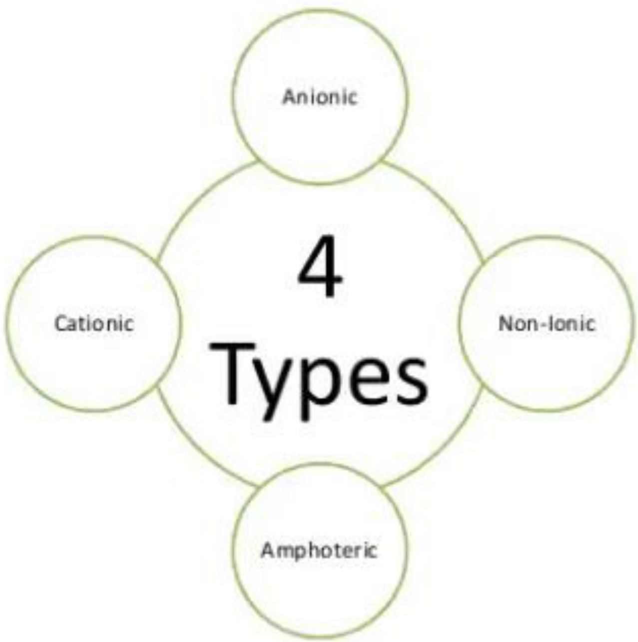


Fig. 4.28 Ternary phase diagram of water (W), oil (O) and surfactant (T) mixture

4. Synthesis of Nanomaterials II (Chemical Methods)

4.7 Microemulsions

- Type of Surfactants



1. **Cationic** – For example CTAB, $_{16}H_{33}N(CH_3)_3^+Br^-$
2. **Anionic** – For example sulphonated compounds with general formula $R–SO_3^+Na^-$ where R is C_nH_{2n+1}
3. **Nonionic** – For example $R–(CH_2–CH_2–O)_{20}–H$
4. **Amphoteric** – Some properties are similar to ionic and some to nonionic surfactants as in betaines.

4. Synthesis of Nanomaterials II (Chemical Methods)

4.8 Sol-Gel Method

- As the name suggests sol gel involves two types of materials or components, ‘sol’and ‘gel’.

- Sols are solid particles in a liquid (see Fig. 4.30). They are thus a subclass of colloids.

- Gels are nothing but a continuous network of particles with pores filled with liquid (or polymers containing liquid).

  - A sol gel process involves formation of ‘sols’ in a liquid and then connecting the sol particles (or some subunits capable of forming a porous network) to form a network

  - By evaporating the liquid, it is possible to obtain powders, thin films or even monolithic solid.

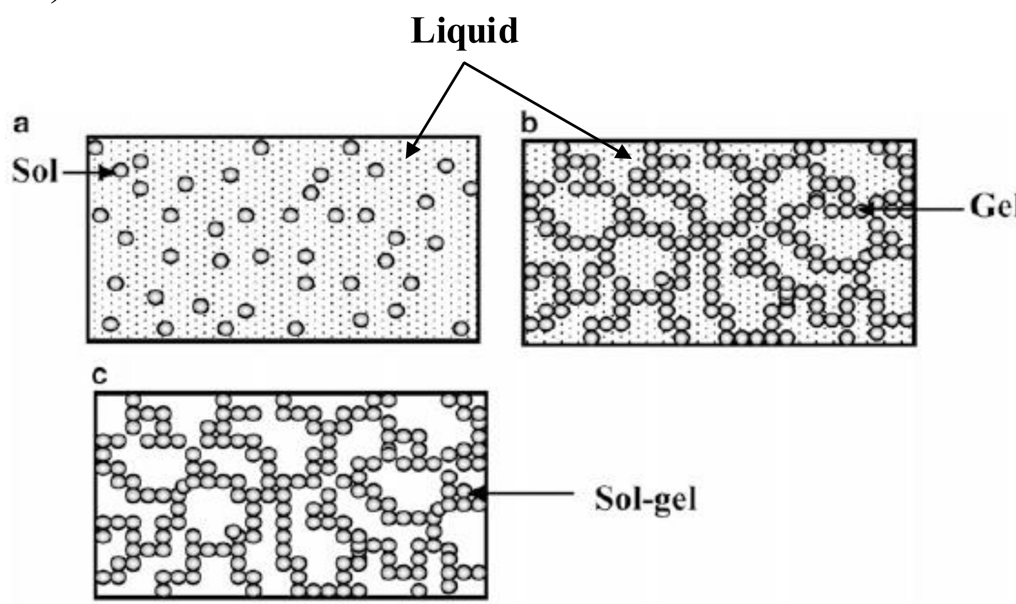


Fig. 4.30 Sol (**a**), gel (**b**) and sol-gel (**c**) monolithic solid

4. Synthesis of Nanomaterials II (Chemical Methods)

4.8 Sol-Gel Method

- Sol-gel method is particularly useful to synthesize ceramics or metal oxides although sulphides, borides and nitrides also are possible.

- Advantage

  - Sol gel formation is usually a low temperature process. This means less energy consumption and less pollution too

  - It competes with other processes like CVD or metalloorganic vapours derived ceramics

  - It is also possible to synthesize nanoparticles, nanorods or nanotubes using sol-gel

4. Synthesis of Nanomaterials II (Chemical Methods)

4.8 Sol-Gel Method

- Synthesis

  - Synthesis of sol-gel in general involves hydrolysis of precursors, condensation followed by polycondensation to form particles, gelation and drying process

  - Precursors (starting chemicals) are to be chosen so that they have a tendency to form gels.

  - Both alkoxides or metal salts can be used

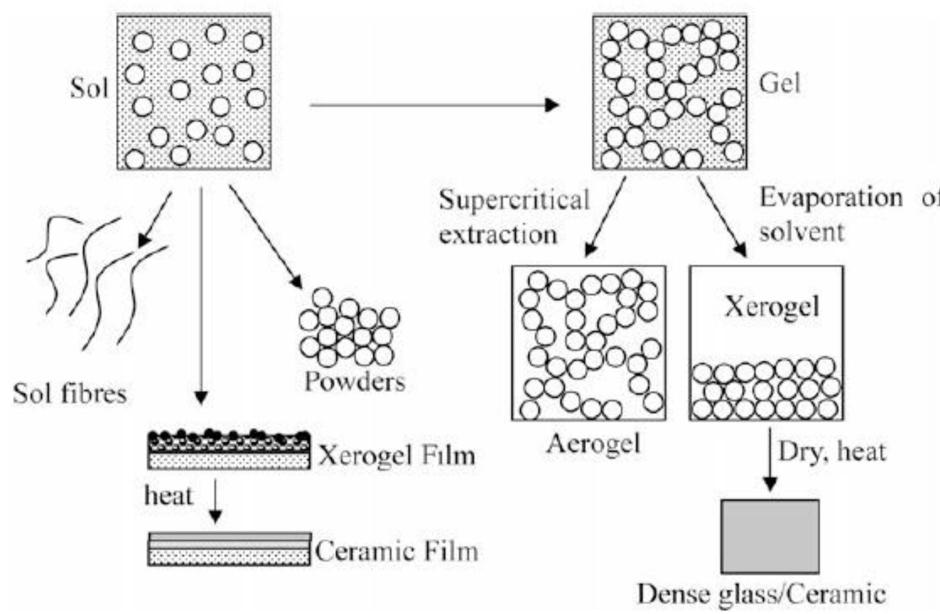


Fig. 4.31 Sol-gel options

4. Synthesis of Nanomaterials II (Chemical Methods)

4.9 Hydrothermal Synthesis

- This synthesis method is useful to make a large scale production of nano to micro size particles
- In this technique adequate chemical precursors are dissolved in water and placed in vessel made of steel or any other suitable metal which can withstand high temperature typically upto 300 °C and high pressure above 100 bars.

  ➡ The vessel, known as *Autoclave*

- The technique was later used mostly by geologists and has become popular amongst nanotechnologists due to the advantages like large yield and novel shapes and sizes that can be obtained using this technique.
- It is also advantageous to use the technique to grow nanoparticles if the material has a high vapour pressure near its melting point or crystalline phases are not stable at melting point.

4. Synthesis of Nanomaterials II (Chemical Methods)

4.9 Hydrothermal Synthesis

- The uniformity of shapes and sizes of the nanoparticles also can be achieved by this technique. Various oxide, sulphide, carbonate and tungstate nanoparticles have been synthesized by the hydrothermal synthesis.

  ➡ For example, Copper nanosheets in Prof. Kim's Lab

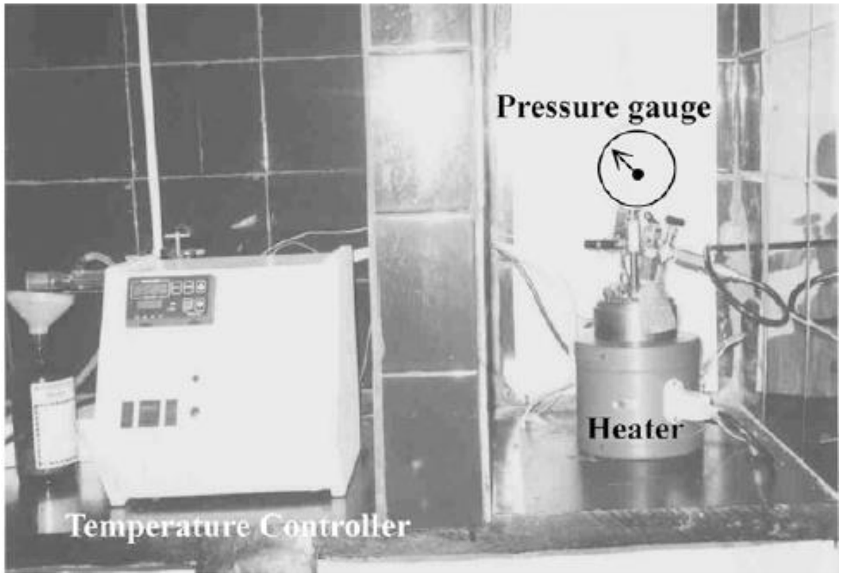


Fig. 4.32 Photograph of an autoclave set up

4. Synthesis of Nanomaterials II (Chemical Methods)

4.10 Sonochemical Synthesis

- In this technique the reactivity of the precursors is enhanced by taking the advantage that large amount of energy can be released when bubbles burst in a liquid.

- Bubbles are formed (see Fig. 4.33) by using ultrasonic waves in a frequency range of ~ 20 kHz – 2 MHz. It can be considered as an alternative method to enhance the chemical reactions in liquids by heating and/or pressurizing.

- The creation, growth and collapse of bubbles in liquids is most important pathway of causing the reactions.

  - The ultrasonic waves while passing through the liquids create very small bubbles which keep on growing until they reach a critical size and then burst, releasing very high energy to locally reach a temperature of 5,000 °C and a pressure of few hundred times that of atmospheric pressure.

  - The reaction can also occur in the liquid phase at exploding bubble where in the interfacial region surrounding the bubble (200 nm distance) the temperature as high as 1,600 °C can be reached.

4. Synthesis of Nanomaterials II (Chemical Methods)

4.10 Sonochemical Synthesis

- Careful use of the solvents and solutes are very important.

  - Non-volatile liquids would prevent formation of bubbles, which is desired, as only reactants should find their place inside the bubble in the form of vapour. Solvents should be inert and stable to ultrasonic irradiation.

- Various nanoparticles like ZnS, CeO_2 and WO_3 have been synthesized using sonochemical method.

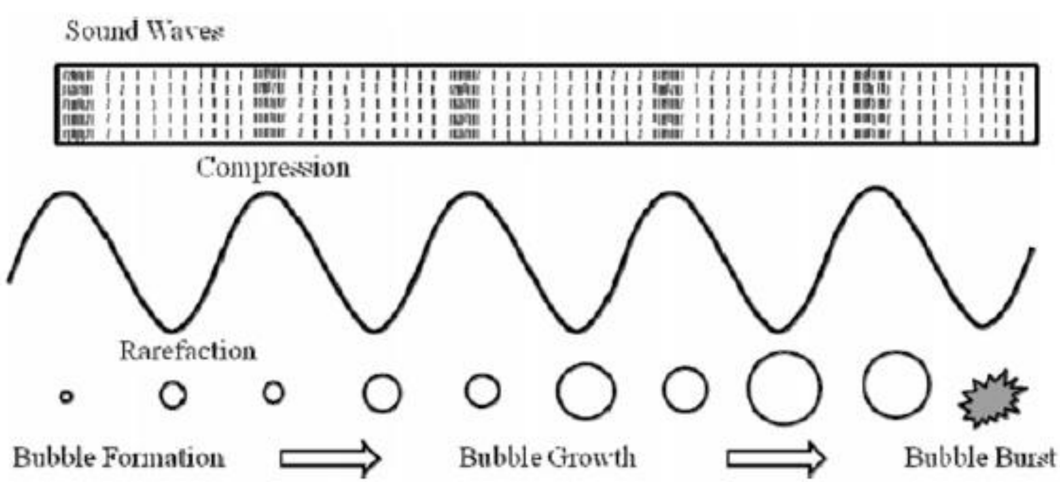


Fig. 4.33 Ultra-sound waves form compressions and rarefactions, shown as a sine wave

4. Synthesis of Nanomaterials II (Chemical Methods)

4.11 Microwave Synthesis

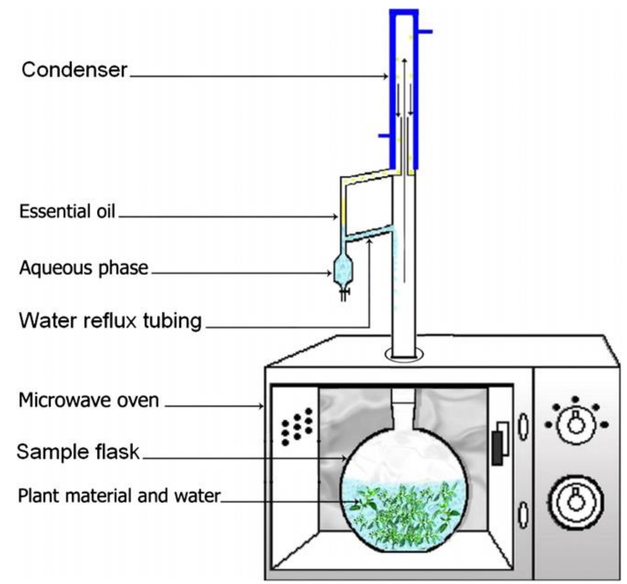
- Use of microwave ovens for heating or cooking food is very common.
- Due to its several advantages microwave synthesis has been used in research laboratories with equipment capable of controlling various parameters.

➡ Parameters: stirring, temperature or power

- A microwave has oscillating electric and magnetic fields associated with it which produces nodes and antinodes and correspondingly hot and cold spots in a vessel.

➡ Non-uniformities.

- Several types of oxide, sulphide and other nanoparticles have been synthesized to obtain various shapes and sizes.



4. Synthesis of Nanomaterials II (Chemical Methods)

4.12 Synthesis Using Micro-reactor or Lab-On-Chip

- Micro-reactor or lab-on-chip is a relatively new method of synthesizing nanoparticles in small quantities

- Very narrow channels (less than about 100 μm upto few tens of nm in width and depth) are made in some suitable substrates like glass, silicon or polymers like poly-dimethylsiloxane (PDMS) using lithography techniques.

  - Similar to an electronic circuit in a semiconductor chip, these channels make some circuit where the fluids can mix.

  - There can be some mixer regions where stirring takes place with the help of magnetic or some other actuation.

  - The channels can be of short or long length depending upon the requirements and are designed to suit a particular requirement.

➡ The size of the whole reactor can be as small as ~10 cm^2.

4. Synthesis of Nanomaterials II (Chemical Methods)

4.12 Synthesis Using Micro-reactor or Lab-On-Chip

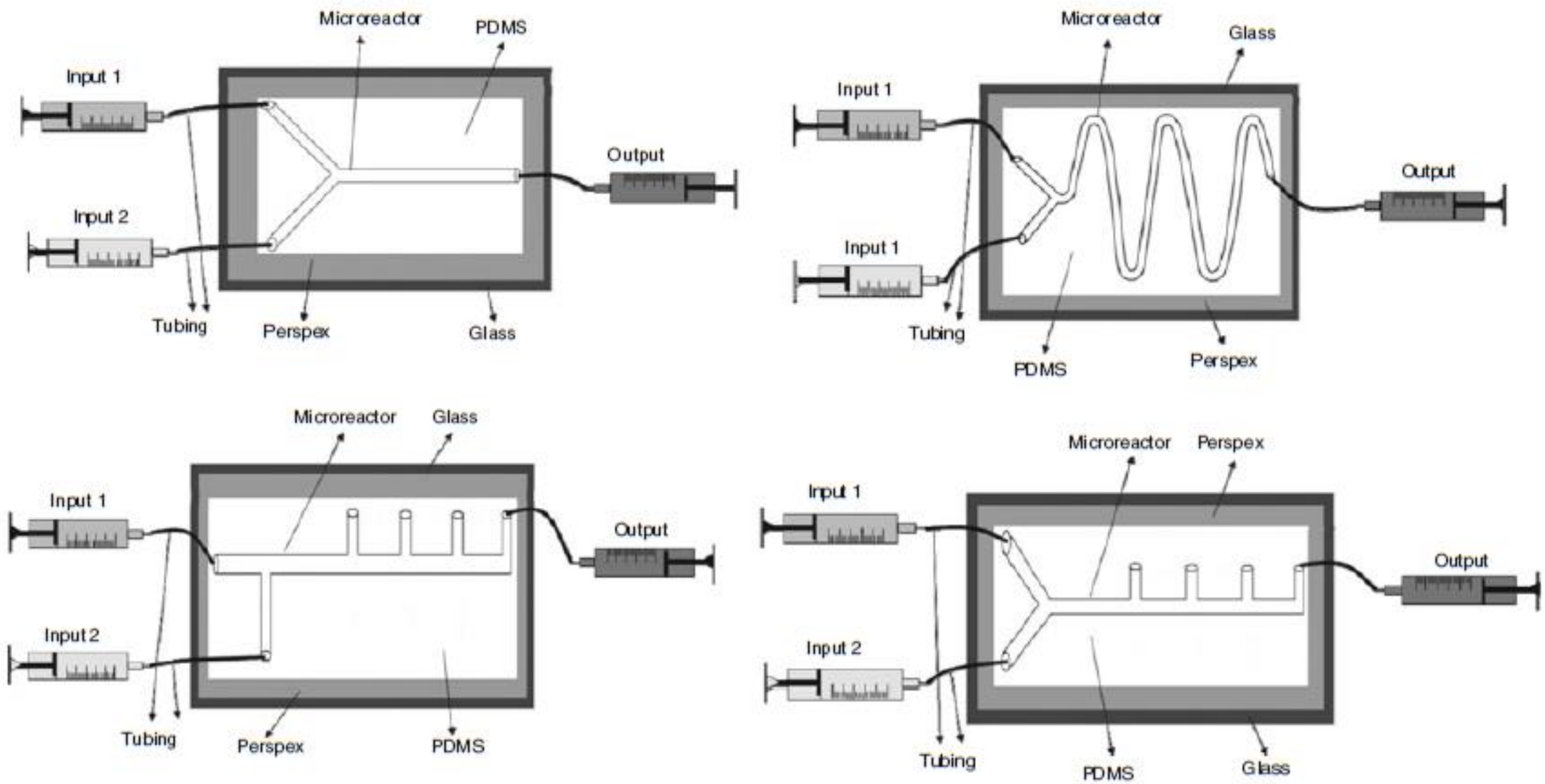


Fig. 4.34 Schematic of microreactor set up

4. Synthesis of Nanomaterials II (Chemical Methods)

4.12 Synthesis Using Micro-reactor or Lab-On-Chip

- The liquids may be aqueous or non-aqueous and suitable reactor will have to be chosen according to the reactions to be carried out.

- It is also possible to heat some of the reactors to enhance the rates of reaction

- The liquids should not react with the reactor material or percolate inside its body. The liquids are injected inside the channels using syringe pumps

• Advantage

- Reactions can be carried out in a very short time using small amounts of reactants.
- Expensive or toxic reactants are to be used
- Due to small amounts involved, the risk of pollution is minimized
- Short synthesis time enables many reactions to be carried out in a short time
- Optimization of reaction parameters can be done very quickly

4. Synthesis of Nanomaterials II (Chemical Methods)

4.12 Synthesis Using Micro-reactor or Lab-On-Chip

- Disadvantage
  - Due to small channel size, the fluid flow in channels and in large glass flask reactor may differ
  - If the particles grow to large size they may clog the channels
  - Cleaning of the channels also can pose problems (cross-contamination)

- There are many reports now which show that TiO_2, ZnS, CdSe, Au, Ag etc.

- Doping of nanoparticles also is possible in microreactors

Next

5. Self Assembly & Some special nanomaterials