Unit V – Nanochemistry

5.1 BASICS

NANOSCIENCE:

According to the UK Royal Society, nanoscience is defined as "the study of phenomena and manipulation of materials at atomic, molecular, and macromolecular scales, where properties differ significantly from those at a larger scale".

NANOTECHNOLOGY:

Nanotechnologies are the design, characterization, production, and application of structures, devices, and systems by controlling shape and size at the nanoscale.

NANOCHEMISTRY:

Branch of nano science dealing with the study and application of extremely small sized materials with at least one dimension in the 1-100 nm range.

Nanomaterials cross the boundary between nanoscience and nanotechnologies and link these both areas together. Generally, nanomaterials deal with sizes of 100 nm or smaller in at least one dimension. The material properties of nanostructures are different from the bulk due to ***the high surface area over volume ratio*** and possible appearance of ***quantum effects*** at the nanoscale.

5.2 CLASSIFICATION OF NANOMATERIALS:

i. **Zero dimensional:** All dimensions (x, y, z) at nanoscale. Eg: nanoparticles, nanoclusters and nanocrystals
ii. **One dimensional:** Two dimensions at nanoscale. Another dimension exceeds in nanometer scale. Eg: nanofibre, nanorod, nanotube.
iii. **Two dimensional:** One dimension at nanoscale and two dimensions exceeds in nanometer scale. Eg: films and coatings with nanometer thickness.
iv. **Three dimensional:** Three dimensions exceeds in nanometer scale. Eg: powders, multilayer materials.

5.3 DISTINCTION BETWEEN MOLECULES, NANOPARTICLES AND BULK MATERIALS:

In general, **Nanomaterials Vs Bulk materials:**

Nanomaterials possess:

1. Hardness : 5 times more
2. Wear resistnce : 200 times more
3. Electrical resistivity : 3 times more
4. Optical : unexpected property
5. Mechanical : less defects and hence more mechanical strength

S.No	Property	Molecules	Nanoparticles	Bulk materials
1	Constitution	collection of atoms	collection of few molecules	collection of thousands of molecules.
2	Size	in the range of picometer (10^{-12} m)	less than 100 nm	range in microns
3	Geometrical structure	well defined structures	well defined structures	depends on the crystalline lattices.
4	Physical properties (eg: melting point, boiling point etc.)	constant	Not constant	Constant
		Eg: Gold sheet melting point = 1064 °C Gold nanoparticles melting point = 300 °C		
5	Surface area	NA	Very high compared to bulk materials	Low compared to nanomaterials

5.4 SIZE DEPENDENT PROPERTIES OF NANOMATERIALS:

Significant change in the following properties are observed for nanomaterials compared to their bulk counterparts, due to the reduction in size, without change in chemical composition.

i. Nanomaterials have extremely large surface area to volume ratio.
ii. They have large fraction of surface atoms, high surface energy, spatial confinement and reduced imperfections.
iii. These enhance the following properties:

a) Melting points:

Significantly lower for nanomaterials, because most of the atoms in the material are at the surface.
Eg : Gold – bulk gold has a melting point of 1064 ºC while 100 nm gold particles have a melting point of 300 ºC.

b) **Optical Properties**:

1. Quantum confinment & 2. Surface plasma resonance--- responsible for a change in optical properties of materials in nm scale.

Eg : 1. Ag : 40 nm size : blue — 2. Gold: 25 nm: red
Ag: 100 nm size: yellow — Gold: 50 nm: green
Prism shaped Ag nano: Red — Gold :100 nm: orange

c) Mechanical Properties:

Nanomaterials have lesser voids and defects compared to bulk materials. Therefore, they impart very good mechanical properties.

Compared to bulk materials, for nanomaterials, Hardness: 5 times more; Wear resistance: 200 times more; Corrosion resistance : higher ; Toughness and ductility : can be varied according to requirement.

Eg: Nanocomposites of polymers metals and ceramics.

d) Electrical Properties:

Conductivity decreases with decrease in size due to increased surface scattering. But better ordering of the particles in micro structure can enhance the conductivity. Therefore, nanomaterials with the same chemical composition but different conductivities can be prepared.

Eg:

1. Metals --- become non-metallic when the diameter of the nano crystals is in 1-2 nm range.
2. Hg clusters --- shows non-metallic band gap but with the addition of more Hg atom to clusters , band gap can be decreased to metallic range.

e) Magnetic properties:

With most of the atoms on the surface, the coupling of magnetic moments of atoms leads to an entirely different set of magnetic properties for nanomaterial.

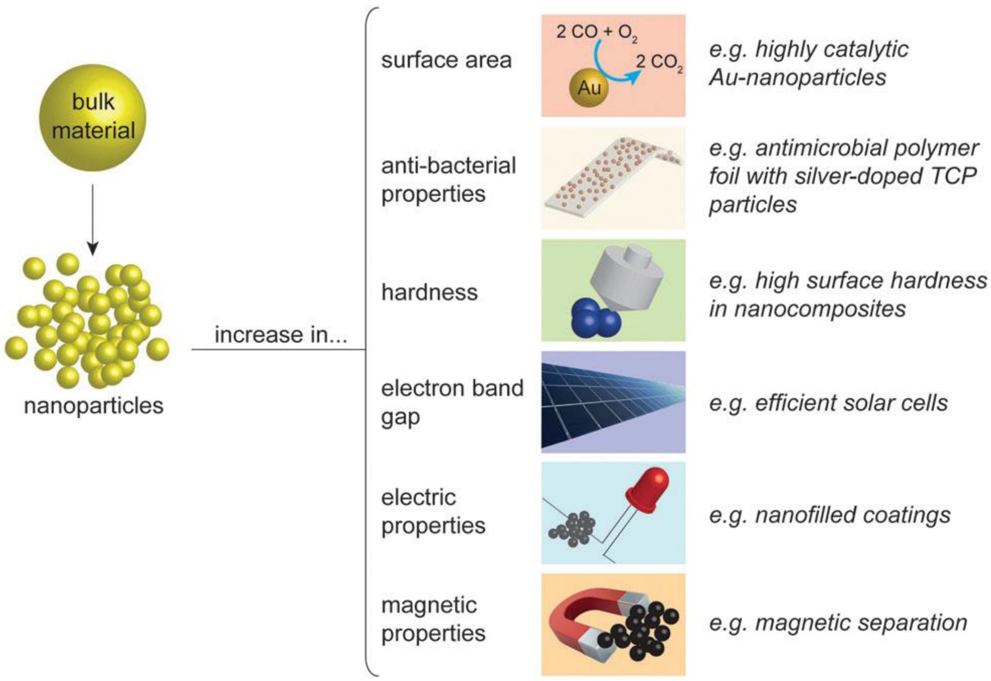
Eg : Bulk Au & Pt --- non-magnetic
50 nm Au & Pt --- magnetic
25 nm capping --- ferromagnetic
< 25 nm --- superparamagnetic

f) Catalytic properties :

Larger surface area : 1000 times more catalytic efficiency

g) Self-purification is an intrinsic thermodynamic property of nanostructures and nanomaterials due to enhanced diffusion of impurities/defects/dislocations to the nearby surface.

h) Increased perfection enhances chemical stability.



In general,

Increases hardness, strength, toughness and catalytic properties.

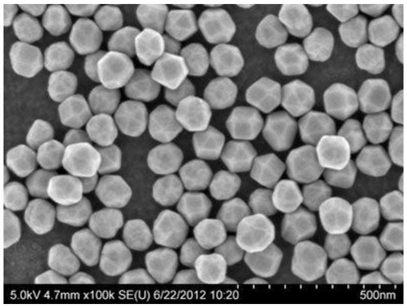
Particle Size reduction →

Decreases conductivity, melting point, density, electrical properties.

5.5 TYPES OF NANOMATERIALS – DEFINITION, CHARACTERISTICS AND USES:

1. Nanoparticles:

Nanoparticles are generally 0D nanostructures with a structural radius of <100 nm. They are discrete nano-objects where all the Cartesian dimensions are less than 100 nm.



SEM of Gold nano-particles

Characteristics:

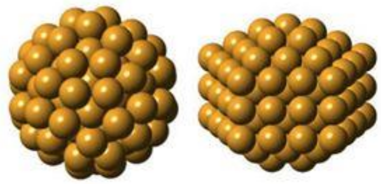
- Zero dimentional nanostructures
- Most of their physical properties are not constant
- Have peculiar optical properties. They are small enough to limit the thickness of common electron layer metals leading to quantum effects

Uses:

1. Pd nanoparticles are used as H_2 storage materials.
2. Ag & Au nanoparticles – transmit brilliant coloured light through glass windows.
3. Gold and nanopolymer composites are used for cancer detection and treatment
4. Cu & Ag nanoparticles are used in PCBS in electronics
5. <100 nm sized Ag & TiO_2 are used in surgical masks due to their antimicrobial properties
6. Ag & AgO nanoparticles are used in air filters in air conditioners, sweat-free textiles & sports wears.
7. TiO_2 nanoparticles added in paints and sunscreen lotions.

2. Nanoclusters :

They are zero dimensional nanomaterials with dimension 1 – 10 nm and narrow size distribution. They are formed by the aggregation of atoms (or) molecules by : i) Van der Waals, ii) Metallic, iii) Ionic (or) iv) Networking types of interaction. Eg., Nanocarbon clusters, Au clusters.



Characteristics:

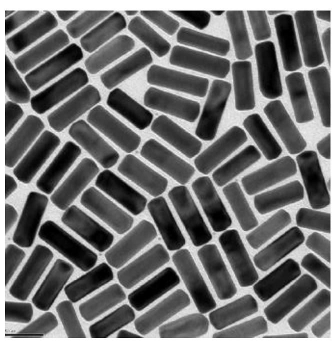
1. They exhibit quantum electronic properties such as i) photoluminescence, ii) ferromagnetism, iii) semiconduction, iv) photoconductivity.
2. The growth of nanoclusters proceeds through the formation of "magic no" clusters that exhibit usual electronic properties.

Uses:

1. Si nanoclusters embedded in wide band gap materials are used for the construction of microelectronic and optical devices.
2. Core-shell nanoclusters with tunable properties are used for magnetic recording, magnetic sensor, bioseparation & drug delivery applications.

2. <u>Nanorods :</u>

<u>Nanorods</u> are one morphology of nanoscale objects (1D nanostructures). Each of their dimensions range from 1–100 nm. They may be synthesized from metals or semiconducting materials. Standard aspect ratios (length divided by width) are 3-5.



TEM of 25nm Au nanorods

Characteristics:

1. One dimensional cylindrical solid nano structures.
2. Exhibit optical absorbance, luminescence of photodetection property.
3. Have anisotropic magnetic properties.
4. Many of them can be prepared as conducting and superconducting material.

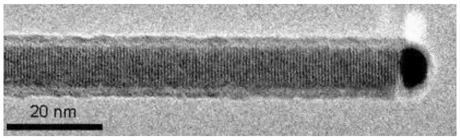
Uses:

1. Au nanorods are used for detecting target sequences in disease like HIV-1, cancer.
2. MnO_2 rods of 5-6nm dia and 20-40nm length are excellent electrochemical capacitors.
3. ZnO nanorods are used in optoelectronic devices as UV light emitters.
4. MgO nanorods are used in high temperature superconductors.
5. ZnO nanods arrays are used as gas sensors.

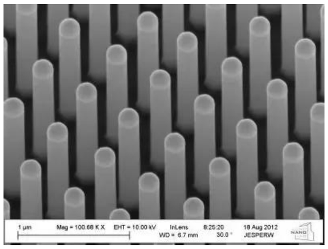
3. Nanowires :

Nanowires are cylindrical, solid 1D nanostructures with diameter in the 10 – 100 nm range and length in μm dimension. Aspect ratio is greater than 10.

It can also be defined as the ratio of the length to width being greater than 1000.



TEM of GaAs nano-wire in Wurtzite phase



SEM of Indium phosphate nano-wires

Properties:

1. One dimensional nanostructures.
2. Electrical conductivity is less than that of bulk materials.
3. High aspect ratio, enhances physical properties.

Uses:

1. Nanowires of Ag, Au, Ni, Pd, etc are used as barcode tags.
2. Semiconductor nanowires are used as junction in LEDs, transistors, invertors, switches & memory cells.
3. In_2O_3 nanowires are used as chemisensors at room temperature.

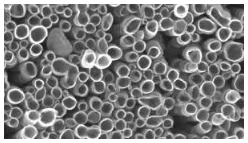
Nanowires and nanorods are very similar, and in most synthesis produced together. The difference lies in the length to diameter ratio of the two. Nanorods are thicker in comparison to nanowires, the latter thus having greater flexibility (And both of them having greater flexibility than nanotubes).

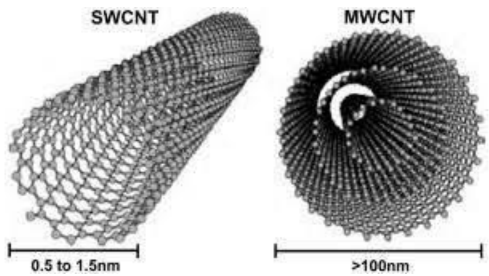
3. Nanotubes:

A **nanotube** is a nanometer-scale tube-like structure, which are also like nanowires, in terms of aspect ratio; but unlike wires, tubes are hollow! Nanotubes maybe single-walled or multi-walled.

Nanotubes are long, hollow solid structures with the walls formed by one atom thick sheets of materials. They can be metallic, semiconducting (or) semiconducting depending on the diameter, length and chirality (twist).

- Generally nanotubes are mainly made of carbon
- Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure.
- Owing to the material's exceptional strength and stiffness, nanotubes have been constructed with length-to-diameter ratio of up to 132,000,000:1, significantly larger than for any other material.





Properties

- CNTs are flexible & do not break on bending
- Thermal conductivity of CNTs is several times higher compared to graphite and bulk materials
- CNTs are 100 times stronger than steel even though they are 6 times lighter.
- Metallic or semiconducting property of CNTs is determined by its helicity

Uses

1. Used for H_2 storage in fuel cells
2. In field emission array for flat-panel display in mobiles & laptops
3. Used in high energy density batteries
4. Used in CNT-based cross bar memory called Nano-RAM
5. Used in aerospace vehicle construction
6. Used for customized fabrication of artificial joints & body parts for implants
7. Used as drug delivery vehicles

5.6 PREPARATION OF NANOMATERIALS

A) PREPARATION OF CARBON NANOTUBE (CNT):

1. Laser ablation
2. Chemical vapour deposition – CVD

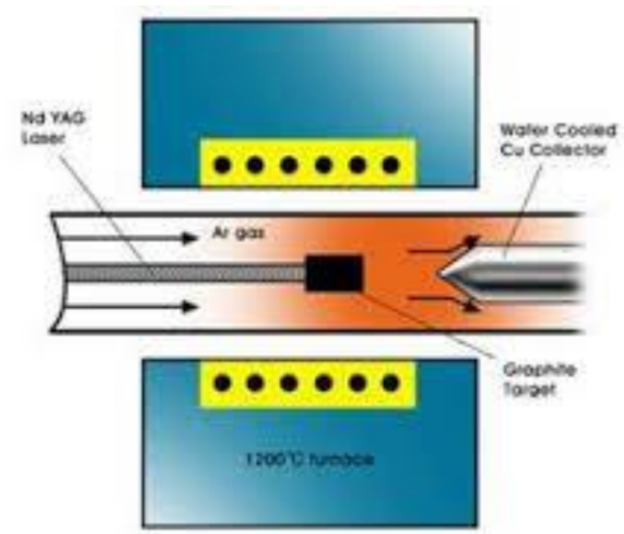
1. Laser ablation for CNT preparation:

Principle:

A graphite target is vapourised and ablated by a beam of laser. The evaporated carbon atoms are swept by an inert gas to a cooler zone. The carbon atoms condense as nanotubes in presence of nucleation sites.

Reactor:

The reactor consists of a quartz tube filled with an inert gas like He (or) Ar. One end of a quartz tube is fitted with a laser torch and the other end has a water-cooled copper collector. A graphite target containing a small amount of Ni (or) Co is placed in-between these two ends. The entire quartz tube reactor is placed in an electric furnace.



Procedure:

- Quartz tube is heated up to 1200˚C using the external furnace.
- Graphite target at high temperature is exposed to intense pulsed laser beam.
- Supersonic jet of carbon particles, called plume is ejected.
- Plume is swept by the inert gas towards the colder copper collector.
- The plume expands & forms the tube on the copper surface.
- Co (or) Ni acts as nucleation sites for the formation of CNT.

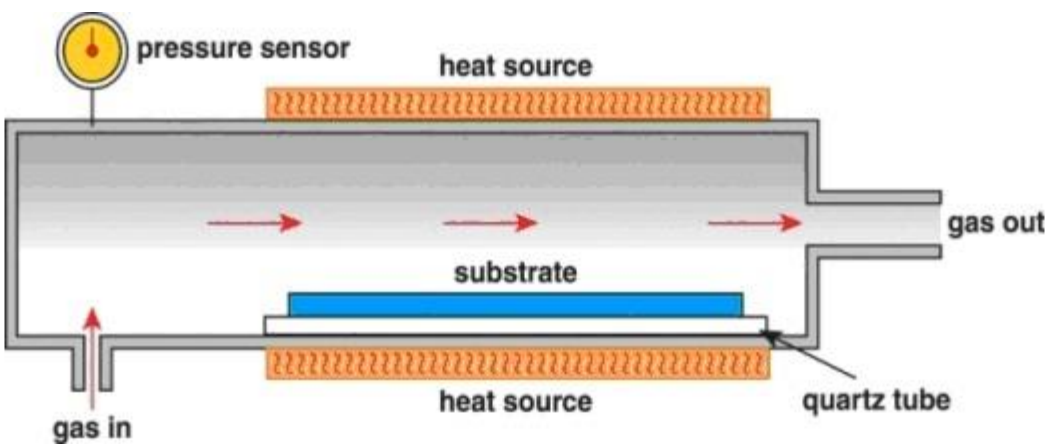
Advantages:

- ❖ Single-walled CNT of 10-20 nm dia and 100 nm lengths can be prepared by this method.
- ❖ CNT is obtained in high yield.
- ❖ Diameter of CNT can be critically controlled.

2. Chemical Vapour Deposition (CVD) for CNT preparation:

Principle:

Hydrocarbon gas is decomposed at a high temperature in presence of a metal nanoparticle catalyst. Vapours of carbon atoms travel to a cooler surface containing metal catalysts & condense to form CNT. The size of the metal nanoparticles determines the diameter of CNT.



Procedure:

- ✓ A hydrocarbon gases such as methane (or) acetylene is sent along with a carrier gas into a quartz reactor tube.
- ✓ The tube is heated with an external heater.
- ✓ On decomposition, hydrocarbon produces carbon atoms which are allowed to condense on a cooler surface.
- ✓ Ni (or) Co metal nanoparticles mixed with MgO act as catalyst and also determine the size of CNT.

Advantages:

- ❖ Suitable for the continuous production of CNT on industrial scale.
- ❖ High purity of product.

B. PREPARATION OF NANOPARTICLES:

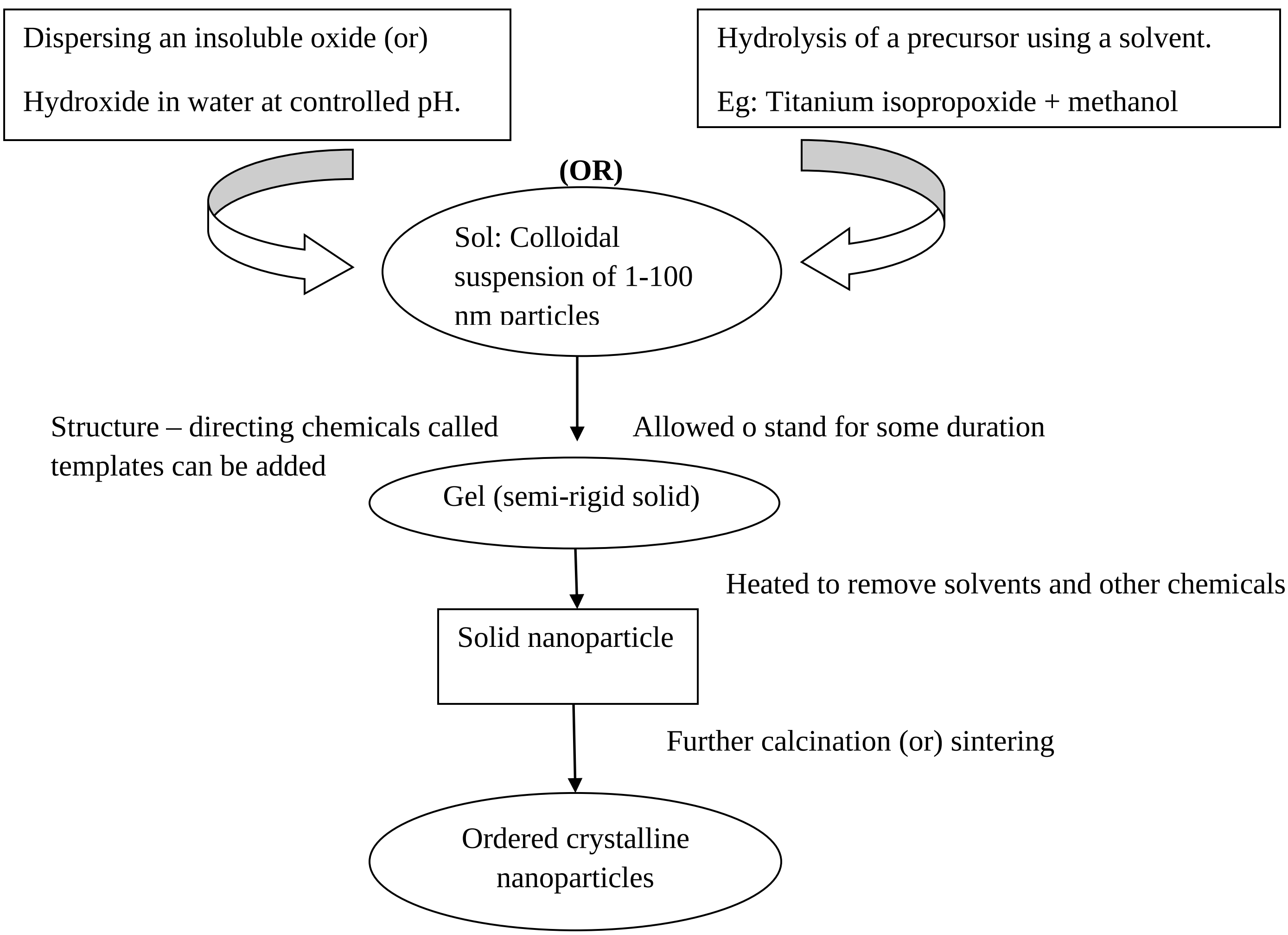
1. Preparation of nanoparticles by sol-gel method:

Principle:

[Sol- is a colloidal (or) a molecular suspension of solid particles in a solvent. Gravity does not act on it and size is 1-100 nm. Gel- is a semi-rigid mass that is formed when the sol begins to evaporate. The particles then join together to form a continuous network.]

- The sol of the nanoparticle is prepared by dispensing the solid (or) hydrolysis of precursor compound in a suitable solvent.
- Sol is aged to form a gel.
- Gel is subjected to heat treatment to form crystalline nanoparticles.

Procedure:



Advantages:

- ❖ Porous as well as dense solids can be prepared.
- ❖ Both amorphous (g/ms) and crystalline (silica, alumina, zeolites) materials can be prepared.
- ❖

2. Preparation of nanoparticles by solvothermal method:

Principle:

Metal salt solution in an aqueous (or) non-aqueous solvent + Reducing agent

↓ Heated in a closed vessel a temperature above the Boiling point of solvent at atmosphere pressure

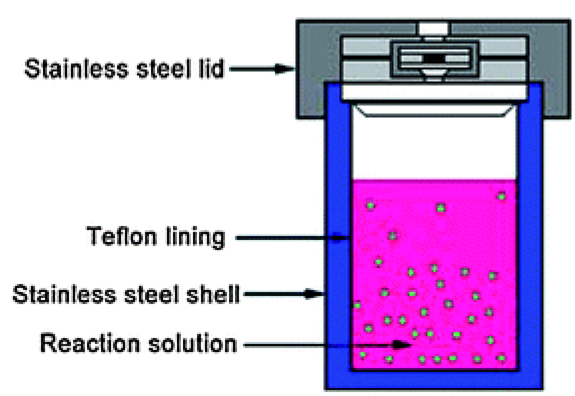
Nanocrystals

Procedure:

- ➢ Reaction vessel is an autoclave made of steel and lined inside with Teflon.
- ➢ Metal salt + an organic template + a reducing agent are dissolved in a suitable solvent. The solvent can be water (hydrothermal) (or) methanol, toluene, cyclohexane, etc.
- ➢ The function of the template is to provide nucleating sites of desired size & shape around which nanoparticle can grow.
- ➢ The sol is stirred, aged and converted into a gel.
- ➢ The gel is placed in an autoclave. Autoclave is tightly closed & heated in an oven at a controlled rate up to a temperature above the boiling point of the solvent.
- ➢ Temperature & pressure created by the super-heated solvent vapours and the action of the reducing agent convert the starting material to the nanocrystals.
- ➢ After sometime, the product crystals are collected on a filter, washed and dried.

Advantages:

- ❖ Single crystals can be grown.
- ❖ Autoclave can be fitted with baffle stirrers to control the growth of crystals.
- ❖ High yield
- ❖ Nanoparticle can be prepared at relatively low temperature.



C. PREPARATION OF NANOWIRES:

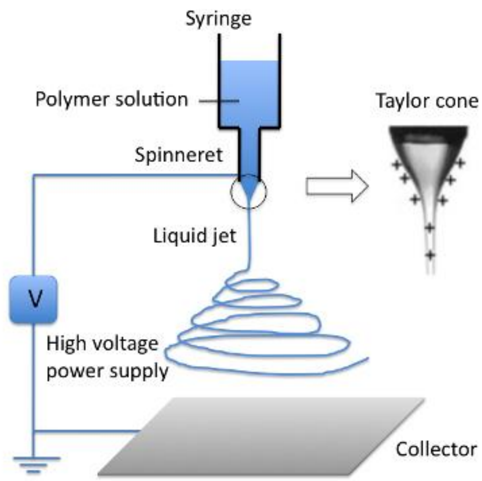
1. Preparation of nanowires by Electrospinning method:

Electrospinning is suitable for the preparation of nanowires and nanofibers of polymers, ceramics & composite materials.

Principle

When a high voltage is applied to a polymer fluid taken in a syringe, charges are induced within the fluid. When the charges within the fluid reache a critical amount, the fluid can overcome the surface tension forces and hence is ejected as a jet from the tip of the needle, forming a Taylor cone. This jet is allowed to travel to a region of lower potential where a grounded collector in the form of a drum or sheet is placed. The jet solidifies into nanofibers or nanowires of desired dimensions.

Procedure



A pipette with a syringe is filled with the chosen polymer fluid. Two electrodes are fitted- one to the syringe and another to the collector. When a high DC voltage in kV range is applied to the fluid, a jet of nanofibers is ejected.

Factors that influence electrospinning are:

1. Nature & viscosity of polymer fluids
2. Applied voltage
3. Temperature
4. Needle diameter
5. Flow rate
6. Needle to collector distance

Advantages

1. Uniform nanofibers and nanowires can be prepared.
2. High product purity.
3. Highly aligned fibers can be prepared.

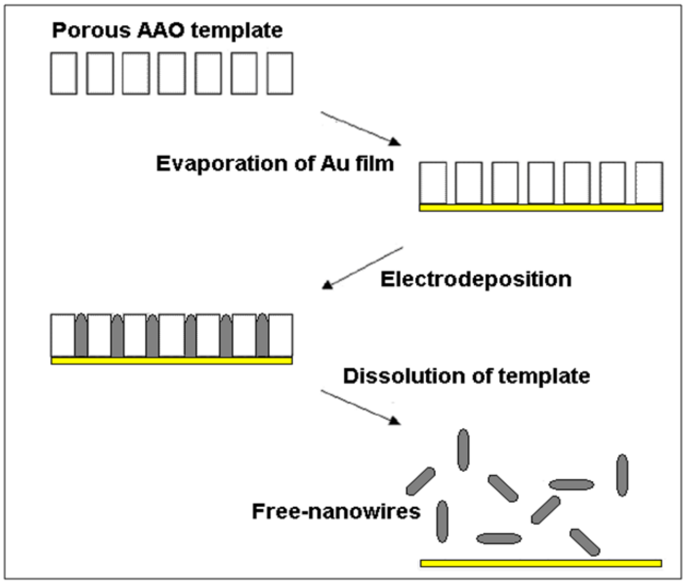
2. Preparation of nanowires by elecrodeposition method:

Principle

A porous metal oxide acts as a cathode as well as a template. On electrolysis, metal from metal salt solution get deposited into the porous of the cathode. When the cathodic template is dissolved, the deposited nanowires can be separated.

Procedure

A porous template of alumina with desired pore dimension is made as the cathode. A thin film of silver or gold is deposited onto it by evaporation. On electrolysis, the metal from the electrolytic solution gets deposited in the pores of the alumina template. On dissolution of alumina, individual nanowires are released.



Advantages

1. Easy to operate and low cost
2. Densely packed continuous nanowires are obtained.
3. The aspect ratio of metal nanowires can be easily controlled.

Nanomaterial Applications

In Medicine

1) The use of **polymeric micelle nanoparticles** to deliver drugs to tumors.
2) The use of **polymer coated iron oxide nanoparticles** to break up clusters of bacteria, possibly allowing more effective treatment of chronic bacterial infections.
3) The surface change of **protein filled nanoparticles** has been shown to affect the ability of the nanoparticle to stimulate immune responses. Researchers are thinking that these nanoparticles may be used in inhalable vaccines.
4) Researchers at Rice University have demonstrated that **cerium oxide nanoparticles act as an antioxidant** to remove oxygen free radicals that are present in a patient's bloodstream following a traumatic injury. The nanoparticles absorb the oxygen free radicals and then release the oxygen in a less dangerous state, freeing up the nanoparticle to absorb more free radicals.
5) Researchers are developing ways to use carbon nanoparticles called nano-diamonds in medical applications. For example, **nano-diamonds with protein molecules** attached can be used to increase bone growth around dental or joint implants.
6) Researchers are testing the use of **chemotherapy drugs attached to nano-diamonds** to treat brain tumors. Other researchers are testing the use of chemotherapy drugs attached to **nano-diamonds to treat leukemia.**

In Environment

1) Researchers are using photocatalytic **copper tungsten oxide nanoparticles** to break down oil into biodegradable compounds. The nanoparticles are in a grid that provides high surface area for the reaction, is activated by sunlight and can work in water, making them useful for cleaning up oil spills.
2) Researchers are using **gold nanoparticles embedded in a porous manganese oxide** as a room temperature catalyst to breakdown volatile organic pollutants in air.
3) **Iron nanoparticles** are being used to clean up carbon tetrachloride pollution in ground water.
4) Iron oxide **nanoparticles are being used to clean arsenic** from water wells.

In Energy and Electronics

1) Researchers have used nanoparticles called nanotetrapods studded with nanoparticles of carbon to develop **low cost electrodes for fuel cells.** This electrode may be able to replace the expensive platinum needed for fuel cell catalysts.
2) Researchers at Georgia Tech, the University of Tokyo and Microsoft Research have developed a method to print prototype circuit boards using standard inkjet printers.
3) **Silver nanoparticle ink** was used to form the conductive lines needed in circuit boards.
4) Combining gold nanoparticles with organic molecules creates a transistor known as a NOMFET (**Nanoparticle Organic Memory Field-Effect Transistor.** This transistor is unusual in that it can function in a way similar to synapses in the nervous system.
5) A **catalyst using platinum-cobalt nanoparticles** is being developed for fuel cells that produces twelve times more catalytic activity than pure platinum. In order to achieve this performance, researchers anneal nanoparticles to form them into a crystalline lattice, reducing the spacing between platinum atoms on the surface and increasing their reactivity.
6) Researchers have demonstrated that sunlight, concentrated on nanoparticles, can produce steam with high energy efficiency. The "**solar steam device** " is intended to be used in areas of developing countries without electricity for applications such as purifying water or disinfecting dental instruments.
7) A lead-free solder reliable enough for space missions and other high stress environments using **copper** nanoparticles.
8) **Silicon nanoparticles coating** anodes of lithium-ion batteries can increase battery power and reduce recharge time.
9) **Semiconductor nanoparticles** are being applied in a low temperature printing process that enables the manufacture of low-cost solar cells.
10. **A layer of closely spaced palladium nanoparticles is being used** in a hydrogen sensor. When **hydrogen is absorbed, the palladium nanoparticles swell**, causing shorts between nanoparticles. These shorts lower the resistance of the palladium layer.

In Agriculture

Contribution of nanoscience research in agriculture will be in the following areas:

- Food safety and biosecurity
- Material science
- Food processing and product development

NANO-PARTICLES CONTROLLING THE PLANT DISEASES

Some of the nano particles that have entered into the arena of controlling plant diseases are nanoforms of carbon, silver, silica and aluminosilicates.

NANOPARTICLES FOR THE CONTROL OF DISEASE AND PEST INCIDENCES IN PLANTS

Nanoparticles of defined concentrations could be successfully used for the control of various plant diseases caused by several phytopathogens.

Nano silver: Nano silver is the most studied and utilized nano particle for bio-system. It has long been known to have strong inhibitory and bactericidal effects as well as a broad spectrum of antimicrobial activities. Silver nanoparticles, which have high surface area and high fraction of surface atoms, have high antimicrobial effect as compared to the bulk silver.

Nano alumina-silicate: Leading chemical companies are now formulating efficient pesticides at nano scale. One of such effort is use of alumina-silicate nano tubes with active ingredients. The advantage is that alumina-silicate nanotubes sprayed on plant surfaces are easily picked up in insect hairs. Insects actively groom and consume pesticide-filled nanotubes. They are biologically more active and relatively more environmentally-safe pesticides. Silica nanoparticles have shown that mesoporous silica nano particles can deliver DNA and chemicals into plants thus, creating a powerful new tool for targeted delivery into plant cells.

Titanium dioxide (TiO_2) nanoparticles: Since TiO_2 is harmless, it is approved for use in food products upto 1% of product final weight. TiO_2 photocatalyst technique has great potential in various agricultural applications, including plant protection since it does not form toxic and dangerous compounds and possesses great pathogen disinfection efficiency.

In Catalysis

Important Applications of Nano-catalysis

1. **Application:** Biomass gasification to produce high syn gas and biomass pyrolysis for production of bio-oil

   Catalyst: Nano NiO catalyst supported on γ- Al_2O_3 microspheres of 3 mm size.

2. **Application:** Production of biodiesel from waste cooking oil

   Catalyst: Aluminium dodeca-tungsto-phosphate ($Al_{0.9}H_{0.3}PW_{12}O_{40}$) nanotubes as solid catalysts with surface area of 278 m^2/g

3. **Application:** Green diesel production using Fischer-Tropsch Synthesis (FTS)

   Catalyst: • Nano Fe and Co powders (10-50 nm) are used as FTS catalysts.

4. **Application:** Improved economic catalytic combustion of *JP-10* aviation fuel using hydrocarbon fuel soluble nano catalyst

Catalyst: Hexanethiol monolayer protected Palladium clusters < 1.5 nm

5. **Application:** Hydrogen production by steam reforming of ethanol over nanostructured indium oxide catalysts

   Catalyst: Mesoporous In_2O_3 prepared using Mobil Composition of (MCM-41) silica catalyst as templates with particle size of 2-3 nm and surface area of 107 m^2/g to 173 m^2/g

6. **Application:** Adsorptive desulfurization and bio desulfurization of fossil oils

   Catalyst: Nano γ- Al_2O_3 (10 nm in width and 100-200 nm in length) with specific surface area of 339 m^2/g

7. **Application:** Hydrodesulfurization of diesel

   Catalyst: Synthesis of new NiMo/Al hexagonal, mesoporous structured nanocomposite catalyst by supercritical deposition method

8. **Application:** Core-shell nanocatalysts for fuel cell applications

   Catalyst: Smooth and compact Pt shell for better oxygen reduction reactions in fuel cell applications

9. **Application:** In situ hydrogen production by reaction of ammonia and nanocatalysts

   Catalyst: The dissociation catalyst is a mixture of nanometer size particles of Co-NiO-Cu-Zr catalyst deposited on high surface area of TiO_2 and 2% Pt deposited on alumina particles