Nanomaterials: Introduction, size-dependent properties of nanomaterials, preparation of nanomaterials by sol-gel and co-precipitation method with example. Introduction, properties, and applications. Nanofibers, Nano-photonics and Nano-sensors.

Introduction:

Nanomaterials have one of its dimensions in the range of 1- 100 nm are known to use for centuries.

For example: Chinese used gold nanoparticles as an inorganic dye into their ceramic porcelains more than thousand years ago.

Nanomaterials are promising because at Nano scale, its physical and chemical properties differ significantly from its bulk structured materials.

I. For Example: bulk silver is non-toxic whereas silver nanoparticles can kill viruses upon contact.
II. Properties like electrical conductivity, color and strength change when the Nano scale is reached.

Applications of Nanomaterial's in Real life

1. Nanomaterials used in stain-resistant and wrinkle free textiles, cosmetics, sunscreens, electronics, paints and varnishes etc.
2. Nano coatings and Nano composites are finding uses in consumer products, such as windows, sports equipment, bicycles and automobiles.
3. There are UV- blocking coatings on glass bottles which protect beverages from damage by sunlight, and longer lasting tennis balls using butyl rubber/nano-clay composites.
4. Nanoscale titanium dioxide for instance is finding application in cosmetics, sunblock cleans, and self-cleaning windows, and nanoscale silica is being used as filler in a range of products, including cosmetics and dental fillings.

Size dependent properties of Nanomaterials

Materials in the nanometer scale exhibit physical properties distinctively different from that of the bulk material

1. Surface area
2. Electrical or Conducting properties
3. Optical properties
4. Catalytic properties
5. Thermal properties

1. Surface Area

a. When a bulk material is subdivided into individual nanomaterials, the total volume remains the same, but the collective surface area is enormously increased.

b. Nanomaterial's have a large proportion of atoms existing at the surface.

c. Properties like catalytic activity gas adsorption and chemical reactivity depend on the surface area.

d. Therefore nanomaterial's can show specific surface related properties that are not observed in bulk materials.

Example: Bulk gold is catalytically inactive, but gold nanoparticles are catalytically very active for selective redox reaction.

2. Electrical or Conducting properties

a. Some metals which are good conductor in bulk become semiconductor or insulator as their size is decreased to nano level.

b. The reason is that the electronic bands in bulk material are continuous due to overlapping of orbitals of billions of atoms.

c. Nanomaterial's very few atoms or molecules are present and so the electronic bonds become separate and separation between different electronic states varies with the size of nanomaterial.

3. Optical properties

a. The nanomaterial's of different size can scatter radiation of different wavelengths. Example: Color of few colloidal solutions are due to this scattering effect.

b. Nano particles of metals exhibit unique optical property called as 'Surface Plasmon Resonance' (SPR).

c. When lights hit the surface of metals particle, electron present on the surface (surface plasmon) starts oscillating back and forth in a synchronized way in a small space and the effect is known as surface plasmon resonance.

d. Depending on the frequency of oscillation resonating electrons capture radiation of different wavelength.

4. Catalytic properties

a. The catalytic property of materials depends on particle size.

b. If the size of the particles reduces from bulk to Nano scale, surface to volume increases drastically, that leads to very high catalytic activity of same material. Example: Catalytic properties of gold nanoparticles. Although bulk gold samples are practically inert, nanometer sized gold particles have been proven to be highly active for several reactions, including

c. Low- temperature oxidation of CO

d. Partial oxidation of hydrocarbons.

e. The water-gas shift reaction.
f. Reduction of nitrogen oxides when dispersed over certain oxides and carbides.

5. Thermal properties (Melting point)

a. Melting point is defined as the temperature at which the atoms, ions or molecules in a substance have enough energy to overcome the intermolecular forces that hold them in a fixed position in a solid.
b. As the size of the material decreases to Nano scale, their melting point decreases. Because surface atoms are in contact with only fewer atoms in nanomaterial's and require lesser energy to overcome inter-molecular forces.

Preparation of Nanomaterials Synthesis by Sol-Gel method

Sol-gel method of synthesizing Nanomaterials is very popular amongst chemists and is widely employed to prepare oxide Nanomaterial.
The sol-gel process can be characterized by a series of distinct steps.

a). Preparation of sol

A stable colloidal solution called sol is prepared. (The sol is a liquid suspension of solid particles ranging in size from 1nm to 1 micron). It is prepared by hydrolysis and partial condensation of precursors such as metal alkoxide.

$$\underset{\text{Metal alkoxide}}{\text{M-O-R}} + \text{H2O} \rightarrow \text{M-OH} + \text{ROH (hydrolysis)}$$

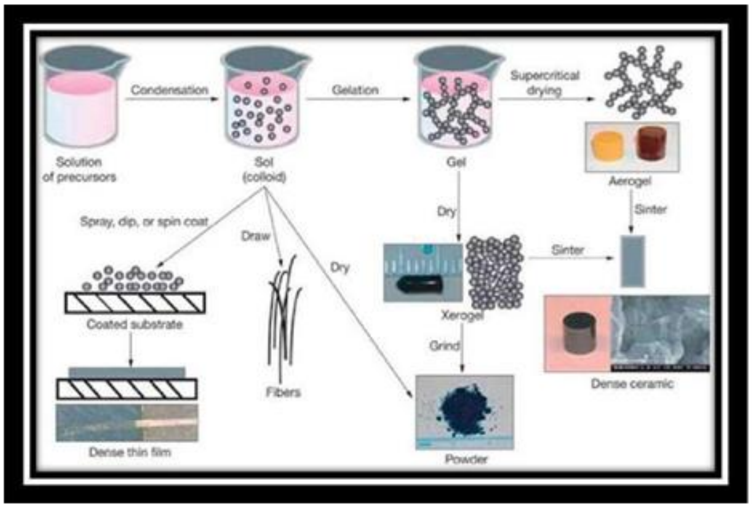
$$\text{M-O-R} + \text{M-OH} \rightarrow \underset{\text{Metal alkoxide}}{\text{MOM}} + \text{ROH (condensation)}$$

b). Conversion of Sol to Gel

Further condensation of sol into a three-dimensional network, produce a gel material (The gel is a diphasic material in which the solids encapsulate the solvent).

c). Aging of the Gel

Polycondensation reaction continues until the gel transforms into a solid mass accompanied by contraction of the gel networks and expulsion of solvent from gel pores. The aging process of gels can exceed 7 days.



The schematic representation for the synthesis of Nanomaterials using the Sol-Gel method.

d). Drying of Gel

Water and other volatile liquids are removed from the gel network. If isolated by thermal evaporation, the resulting monolith is termed a Xerogel. If the solvent (such as water) is extracted under-critical or near super critical conditions, the product is an aerogel.

e). Dehydration

To stabilize the gel against any dehydration the surface-bound M-OH groups are removed by calcining (heating) the monolith at temperature up to 800 ° C. The typical steps that are involved in sol-gel processing are shown in the schematic diagram below.

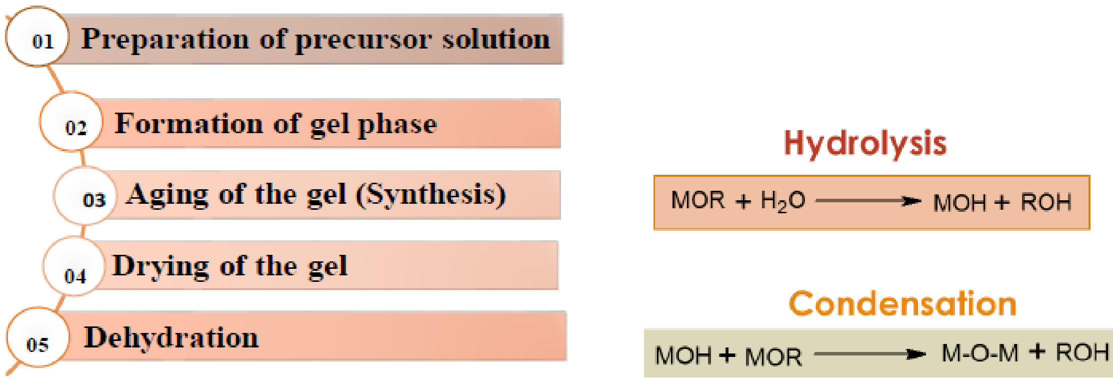
Advantages Sol-gel method

a) Low temperature route (below 200 ° C).
b) Uniform particle size distribution.
c) Can easily shape materials into complex geometries in gel state.
d) Simple, effective method to produce high quality coatings.

Disadvantages:

- Quite expensive
- Since several steps are involved, close monitoring of the process is needed

PROCESS:



Co-precipitation method with example

Introduction

- Simultaneous occurrence of nucleation growth, coarsening's and /or agglomeration.
- Co-precipitation reaction exhibits the following characteristics.
- Insoluble species-high super-saturation
- Nucleation is a key step
- Ostwald ripening and aggregation size, morphology, and properties of the products.
- Chemical reaction

The process is mainly used to prepare metal oxide nano particles.

Steps:

In this technique, an inorganic metal salt (such as chloride, nitrate, acetate or oxy chloride) is dissolved in water.

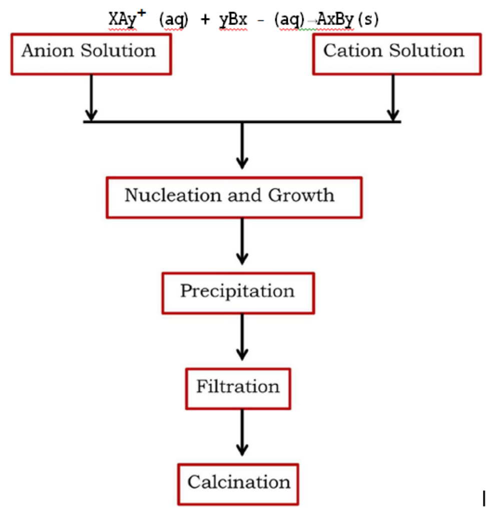
Metal cations in water exist in the form of metal hydrate species such as [Al(H2O)]3+, [Fe(H2O)6]3+.

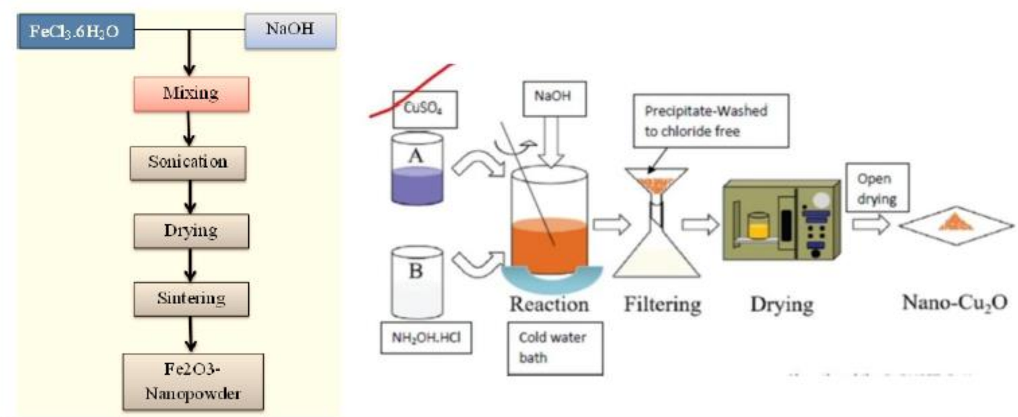
The species are hydrolyzed by adding a base solution, such as NaOH or NH_4OH.

On increasing the concentration of OH- ions, the hydrolyzed species condense with each other to form either metal hydroxide or hydrous metal oxide precipitate.

The precipitate is then washed, filtered and dried.

The dried powder on subsequent calcination to obtain the final crystalline metal oxide nanoparticles.





Advantages:

- The process is relatively economical
- Wide range of single and multi-components of oxide nano powders can be synthesized.

Disadvantages:

- Inability to control the size of the particles
- Chances of aggregation of nanoparticles.

NANOFIBRES:

Nanofibres are defined as fibres with diameters less than 100 nm.

Properties

- Excellent mechanical properties.
- Biodegradability along with nontoxic biodegradability.
- High surface-to-volume ratio, when used as Nano fillers reduce the chain mobility.
- Increase toughness, and abrasion resistance.
- Compared to conventional fibrous structures, Nano fibres are lightweight with small diameters,
- Nano fibres have controllable pore structures

Applications

1. Filtration:

- **Air Filtration:** Nanofibers are used in air filters to remove pollutants, allergens, and microorganisms from the air due to their fine pore structure.
- **Water Filtration:** They are employed in membranes for water purification and desalination processes, efficiently removing contaminants and pathogens.

2. Medical Applications:

- **Drug Delivery:** Nanofibers can be used as carriers for controlled drug release, improving the efficiency and targeting of therapeutic agents.
- **Tissue Engineering:** They provide scaffolds for tissue regeneration, supporting cell growth and mimicking the extracellular matrix.
- **Wound Dressing:** Nanofiber-based dressings promote healing by maintaining a moist environment and providing antimicrobial properties.

3. Energy Storage:

- **Batteries:** Nanofibers enhance the performance of lithium-ion batteries by improving electrode conductivity and capacity.
- **Supercapacitors:** They are used in supercapacitor electrodes to increase energy storage capacity and charge-discharge rates.

4. Sensors:

- **Chemical Sensors:** Nanofibers are used in sensors for detecting gases, chemicals, and biomolecules due to their high sensitivity and fast response times.
- **Biosensors:** They are employed in biosensors for medical diagnostics, detecting biomarkers, and monitoring glucose levels.

5. Textiles:

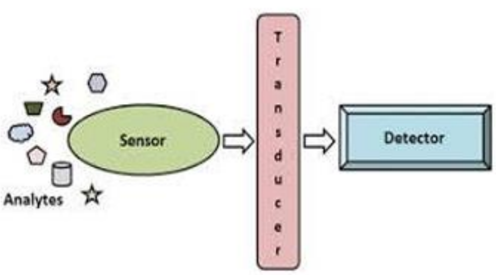
- **Protective Clothing:** Nanofiber coatings can provide enhanced protection against chemical, biological, and environmental hazards.
- **Functional Textiles:** They are used in smart textiles for applications such as moisture management, thermal regulation, and odor control.

6. Electronics:

- **Flexible Electronics:** Nanofibers are utilized in the development of flexible electronic components, such as conductive films and sensors.
- **Optoelectronics:** They are employed in optoelectronic devices, including light emitting diodes (LEDs) and photodetectors.

NANOSENSORS

Nanosensors are chemical or mechanical sensors that can be used to detect the presence of chemical species and nanoparticles, or monitor physical parameters such as temperature, on the nanoscale.




Properties

- **High Sensitivity:** Detect very low concentrations of analytes due to large surface-to volume ratio.
- **Selectivity:** Designed to specifically detect particular substances or conditions.

- **Small Size:** Operate at the nanoscale, allowing integration into small and complex systems.
- **Rapid Response Time:** Quick detection and measurement of target substances.
- **Low Power Consumption:** Efficient energy usage due to their small size and advanced materials.
- **Versatility:** Applicable in various fields such as healthcare, environmental monitoring, and security.
- **High Surface Area:** Enhanced interaction with target molecules due to increased surface area.
- **Biocompatibility:** Can be made from materials compatible with biological systems for medical applications.
- **Multifunctionality:** Capable of detecting multiple analytes simultaneously.
- **Cost-Effectiveness:** Potential for low-cost production due to advancements in nanofabrication techniques.
- **Integration with Electronics:** Easily integrated with electronic systems for data processing and communication.

Applications

- To detect various chemicals in gases for pollution monitoring.
- For medical diagnostic purposes either as blood borne sensors or in lab on- a-chip type devices.
- To monitor physical parameters such as temperature, displacement and flow.
- To monitor plant signaling and metabolism to understand plant biology.
- To study neurotransmitters in brain for understanding neurophysiology.