SYNTHESIS OF NANO - STRUCTURED MATERIALS

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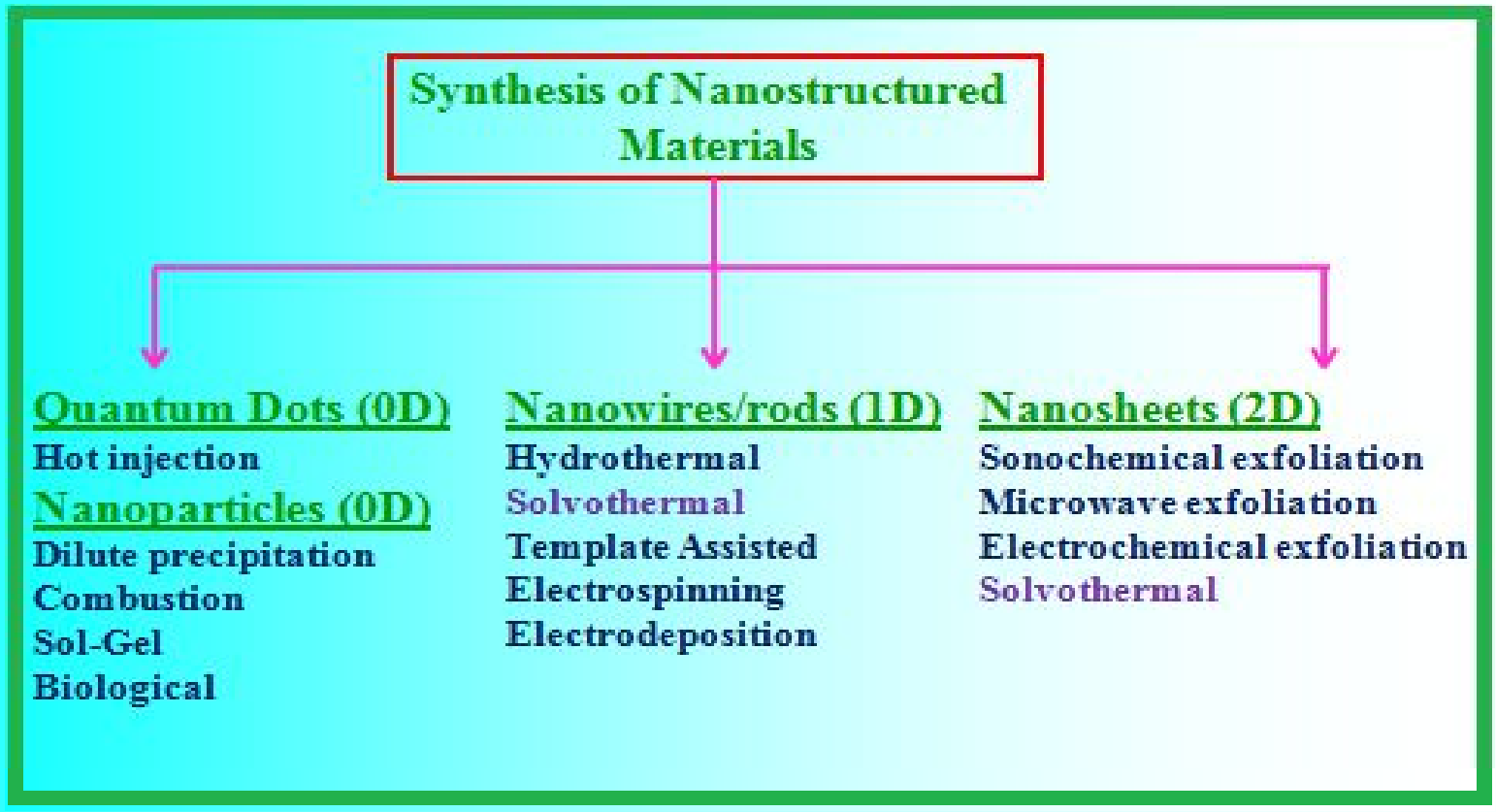
Many methods are available to synthesis different types of nano-structured materials in the form of

Particles,
Wires,
Rods,
Tubes,
Thin films/sheets etc.

- The most important and simple methods are given below;



- Depending on the interest of the nanostructure (0-D / 1-D / 2-D), we can choose the method of synthesis.

O-D Nanoparticles Synthesis

1. Dilute precipitation method

The metal chlorides are dissolved in deionized water in stoichiometric proportions.

These metal ions are co-precipitated as **hydoxides** by using a suitable precipitating agent (NaOH or aq.NH_3) at the required pH.

They separated out and then converted into their **oxides** by simple heating .

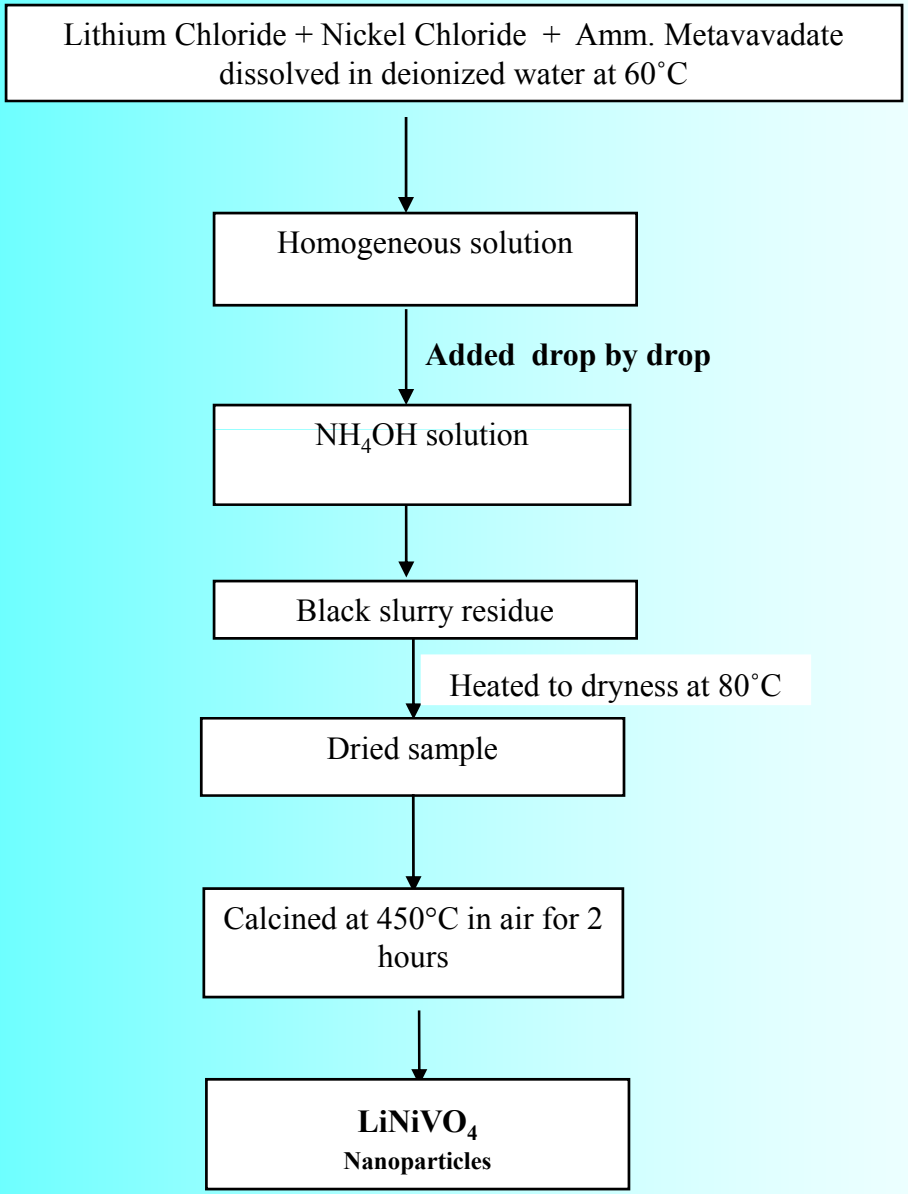
The formation of nanoparticles depend on

the Solution concentration,

Rate of precipitation and

Calcination temperature.

Typical example for Dilute Co-Precipitation method



2. Low temperature combustion method

- In this method, combustion of Metal nitrates/acetates with an organic fuel, will produce nanoparticles.
- Urea/ hexamine/glycine/gelatine etc. – Combustion fuel.
- The maximum heat will produce during the combustion reaction is by controlling **the ratio of** oxidizing valency of metal salts (O) / Reducing valency of fuel (F) as **one.**

Compound	Formula	Oxidizing Valency
Individual Elements	C	+4
	H	+1
	O	-2
	N	0
	M^{2+}	+2
	M^{3+}	+3
	M^{4+}	+4

$LiNO_3$ = **- 5**

$Ca(NO_3)_2$ = **- 10**

$Mn(CH_3COO)_2$ = **+16**

OXIDIZING VALENCY

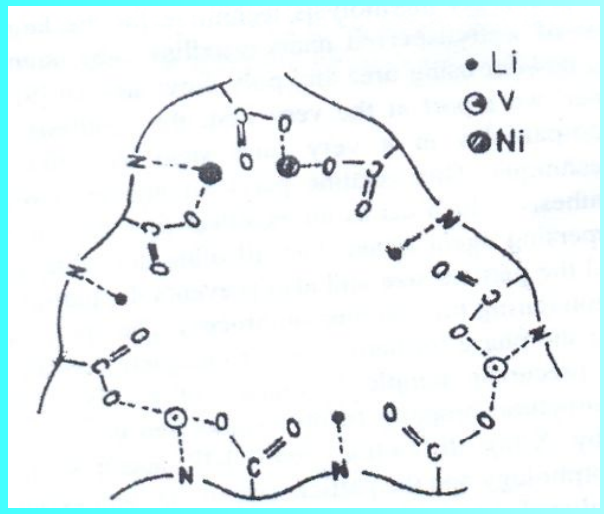
Nickel nitrate $Ni(NO_3)_2 .6H_2O$

Element		Valency
1 Ni	=	2
12 O	=	-24
12 H	=	12
2 N	=	0

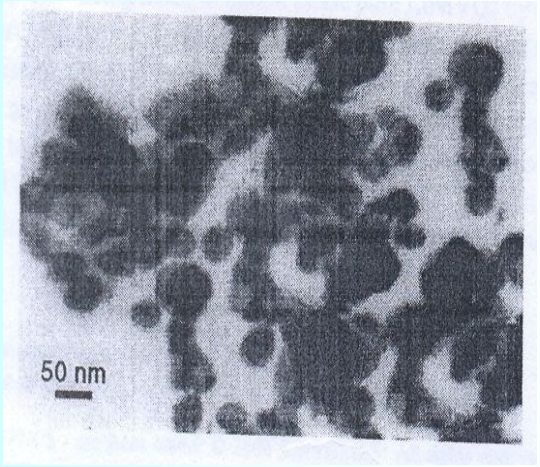
		-10

Role of Gelatine:

- Gelatine contains a large number of glycine (H_2N-CH_2-COOH) .
- Due to its long chain linkage of amino acids - act as an excellent fuel as well as capping agent.
- Hence, **metal ions** are **trapped homogeneously** in the gelatine matrix to control effectively the particles size and also keep the nanoparticles free from agglomeration during the combustion process.



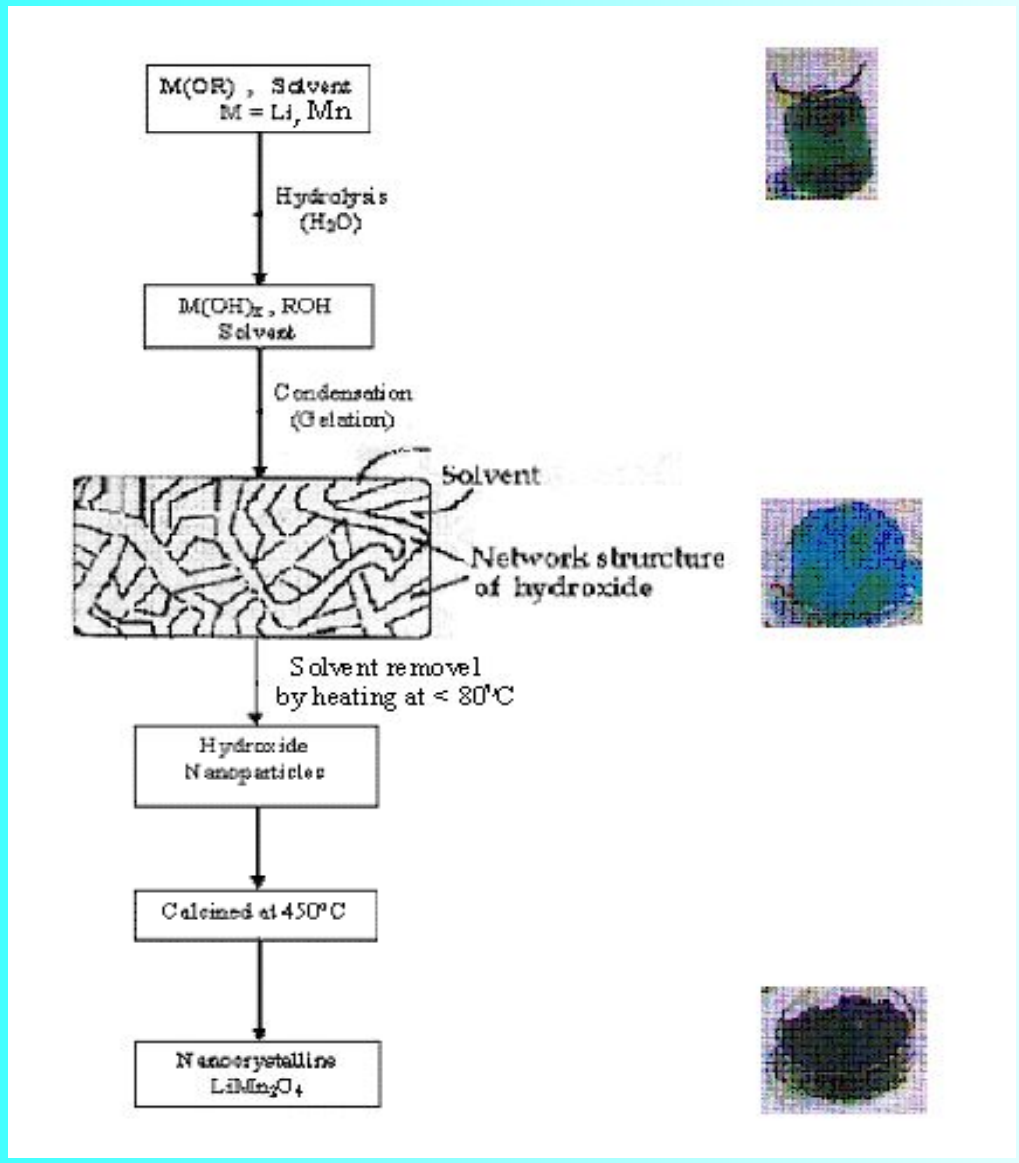
Structure of gelatine trapped with metal ions

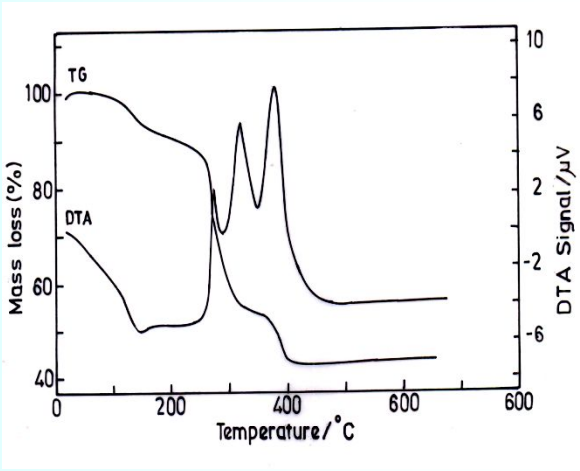


TEM photograph of $LiNiVO_4$

3. SOL-GEL METHOD

- An appropriate amount of metal alkoxides are dissolved in deionized water to form **sol.**
- It is then converted into a **hydroxide network** (**gel**) by simple hydrolysis followed by condensation processes.
- Subsequent drying and calcination of the **gel** will produce nanoparticles.
- Components for which alkoxides are not available, are introduced as acetate salts.
- *Hydrolysis is carried out under controlled temperature, pH in presence of alcohol and water.*





TG/DTA results of $LiMn_2O_4$ precursor

Flow chart for the preparation of $LiMn_2O_4$ nanopowder by sol-gel method

Important features of the sol-gel method are;

- Better homogeneity.
- High purity.
- Lower processing temperature.
- Uniform phase distribution even in the **multi-component systems.**

4. Bio-Synthesis

By using selected microorganisms such as bacteria, fungi, yeast, enzymes or even plant extract, we can prepare Nanoparticles.

Advantages of bio-synthesis:

Green synthesis and eco-friendly.

Single step process.

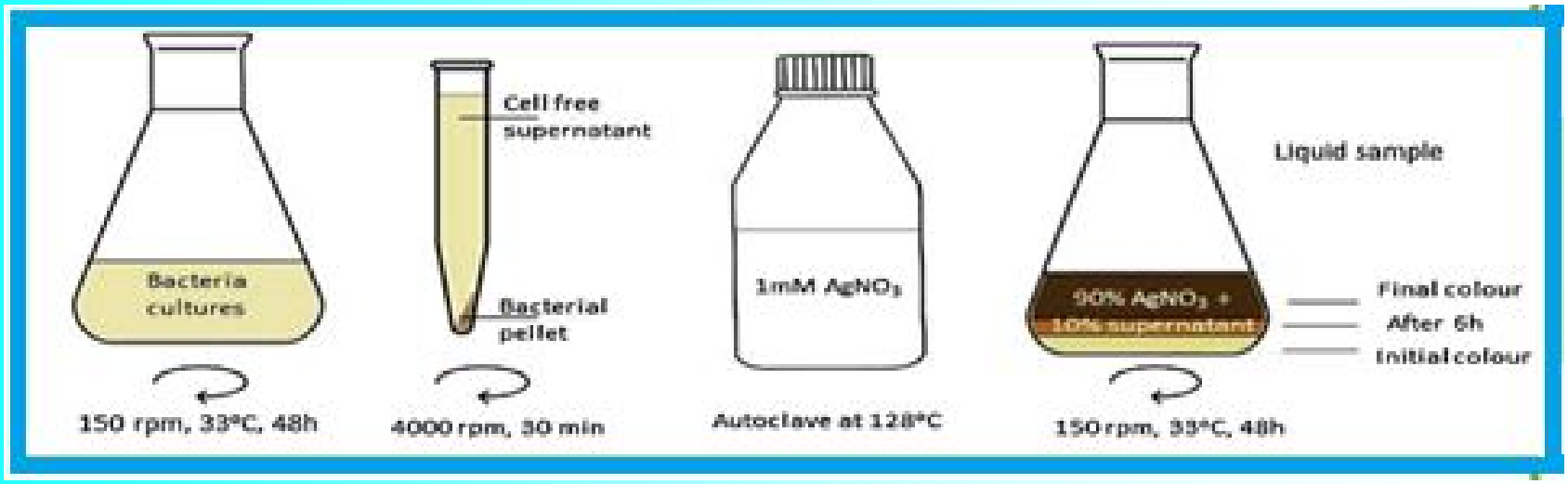
Low cost.

Can be used for large scale synthesis.

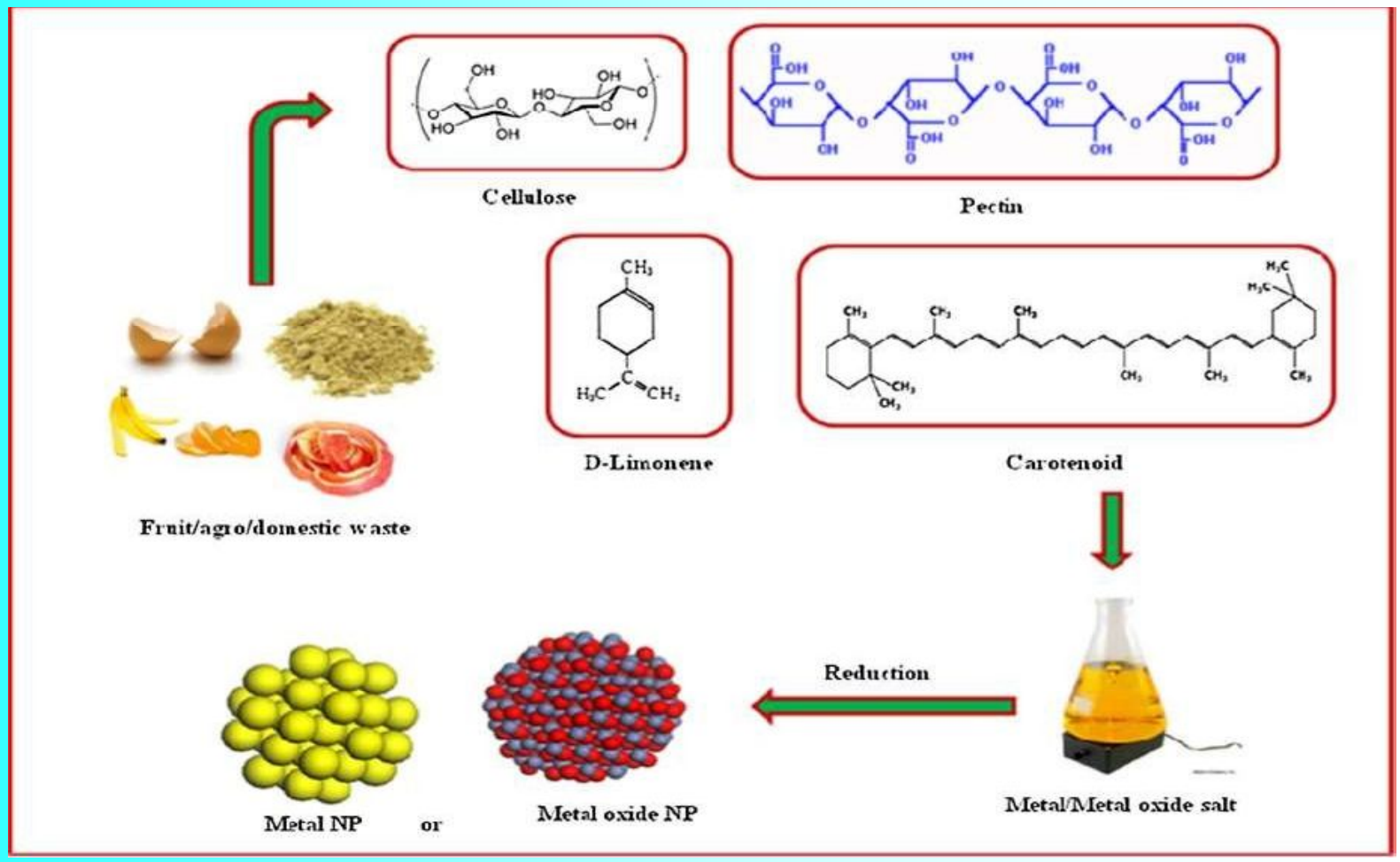
No need to use high pressure, temperature and toxic chemicals.

Not required any special culture preparation and isolation technique.

Synthesis of Ag Nanoparticles from Microorganisms:



Synthesis of Metal & Metal Oxides Nanoparticles from Agro-waste extracts:



Synthesis of Metal Nanoparticles from plant extracts:

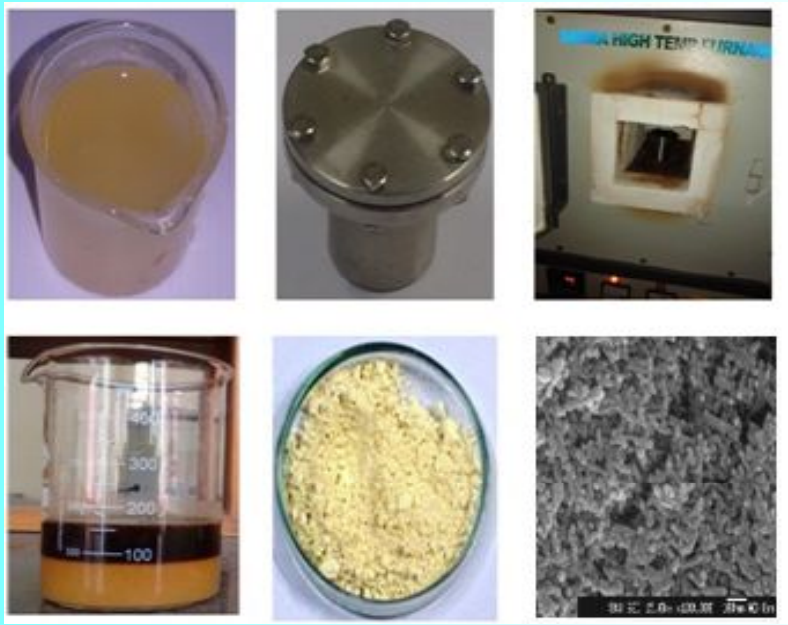
Key Factors
pH
Concentrations
Reaction Time
Reaction Temperature

1-D Nanostructured Materials Synthesis

1. Hydrothermal method

- The starting chemicals were dissolved in deionized water under high pressure and or elevated temperature to induce chemical reaction.

- During this process, the tiny particles were directly assembled together to form **nanowires** at lower temperature of <150°C.



Main advantages of hydrothermal processes are:

- *The* obtained powders do not need calcination/ball milling processes.

- ***The disadvantages of this process is the requirement of high pressure reactor with temperature controller.***

3. Solvothermal Synthesis

- Ethylene glycol - **Served both as solvent and reducing agent.**
- Due to its strong reducing power and relatively high boiling point.

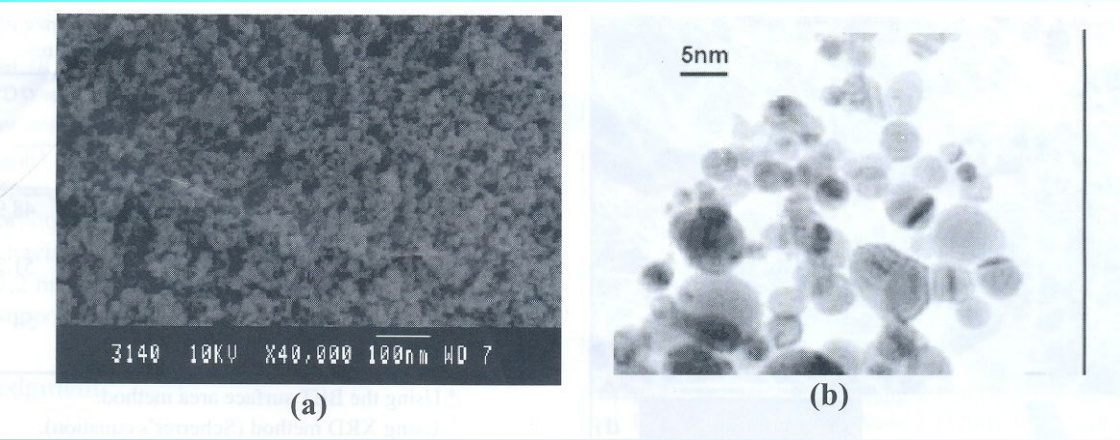
- PVP is used as a capping agent as well as the stabilizer.
- To promote **the anisotropic growth of the nanocrystalline metal seed into nanowires.**

- By make use of EG and PVP, metal oxide nanoparticles/ nano-wires can be prepared.

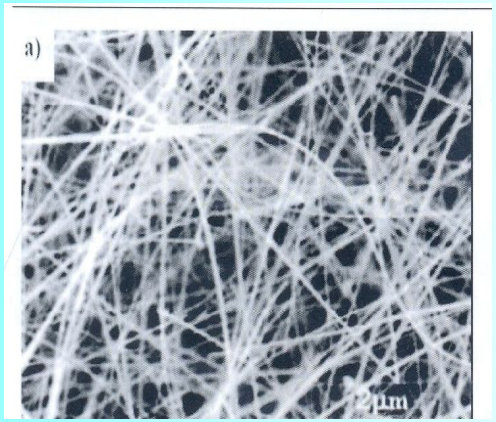
Synthesis of MgO Nanoparticles/Nanowires

MgO nanoparticles synthesis:

- Magnesium acetate **(0.1mol)** and PVP **(0.02mol)** are dissolved in ethylene glycol and refluxed at ~ 195°C for 2 hours to get a white flocculate.
- This white precipitate is collected by centrifugation followed by washing with de-ionized water and ethanol.
- The collected precipitate is dried in a vacuum oven at 80°C for 2 hrs and then subjected into TG/DTA analysis to know the complete crystallization temperature.
- The flocculate is then calcined at 500°C in air for 2hrs to get MgO nanoparticles.
- **If the molar ratio of Mg acetate : PVP is 0.1mol : 0.002mol, we can get MgO nanowires.**



(a) SEM image of MgO nanoparticles (b) TEM image of MgO nanoparticles.



SEM image of MgO nanowires obtained from the PMT process at 500° C

2-D Nanostructured Materials Synthesis

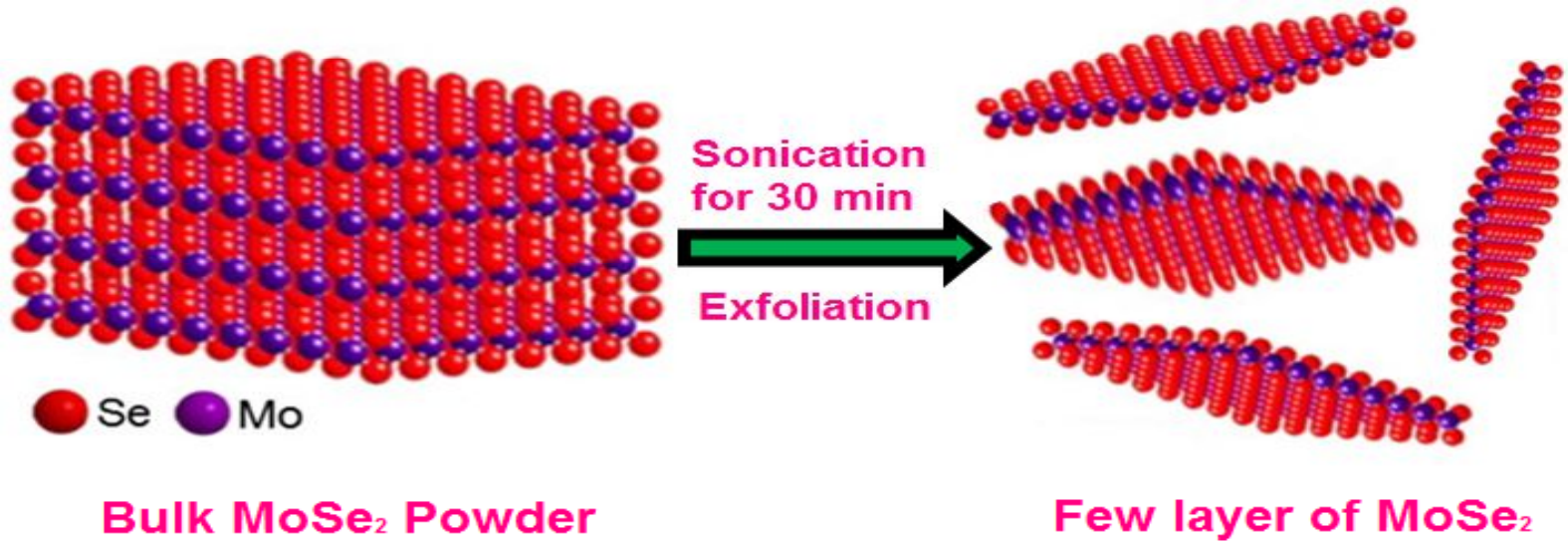
1. Sonochemical exfoliation method

- A simple **sonochemical exfoliation method** was used to exfoliate the bulk $MoSe_2$ powder into $MoSe_2$ Nanosheets.
- 1 g of $MoSe_2$ NPs are taken in 100 mL of IPA . To this, 2.5 vol% of H_2O_2 is added as an expoliating agent.
- This reaction mixture was subjected to sonication for 30 min. in an ice-cooled condition to get $MoSe_2$ NS.

$MoSe_2$ NPs

Probe Sonication for 30 min.

$MoSe_2$ NS


Sonication
for 30 min
Exfoliation
Se
Mo
Bulk $MoSe_2$ Powder
Few layer of $MoSe_2$

2. Microwave exfoliation method

- Graphene was synthesized from **natural graphite** by **microwave assisted thermal exfoliation method**.
- Natural graphite (1 g) and H_2O_2 (1 ml) were taken in a 50 ml beaker.
- To this, 0.5 g of APS was added.
- This reaction mixture was then directly placed in a domestic microwave **irradiation for 2-3min** to get Graphene nanosheets.

Natural Graphite

H_2O_2

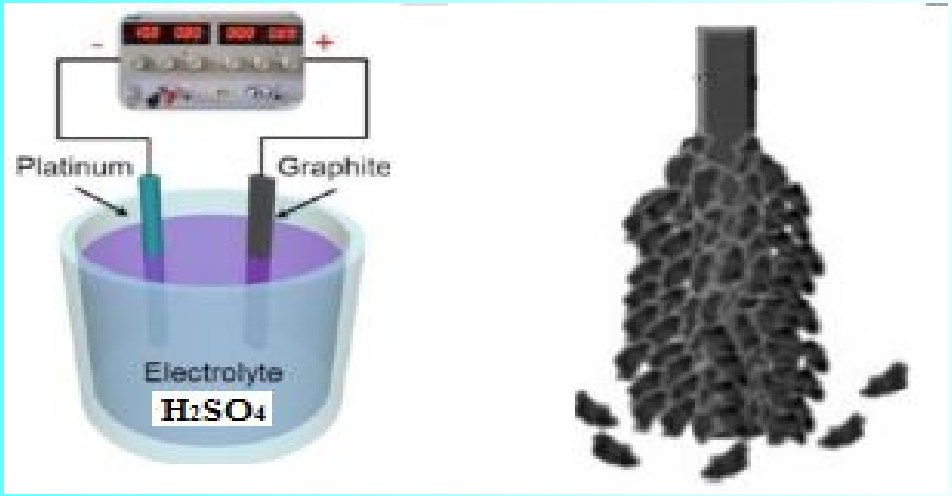
APS

Microwave Treatment

Exfoliated Graphene

3. Electrochemical exfoliation method

- The graphite plate and Pt plate were immersed in 1M H_2SO_4 solution.
- To this, the potential of 10 V was applied for 30 min through a DC power supplier to get EG at the cathode.
- This was collected and then vacuum drying at 70 °C for 12 h.

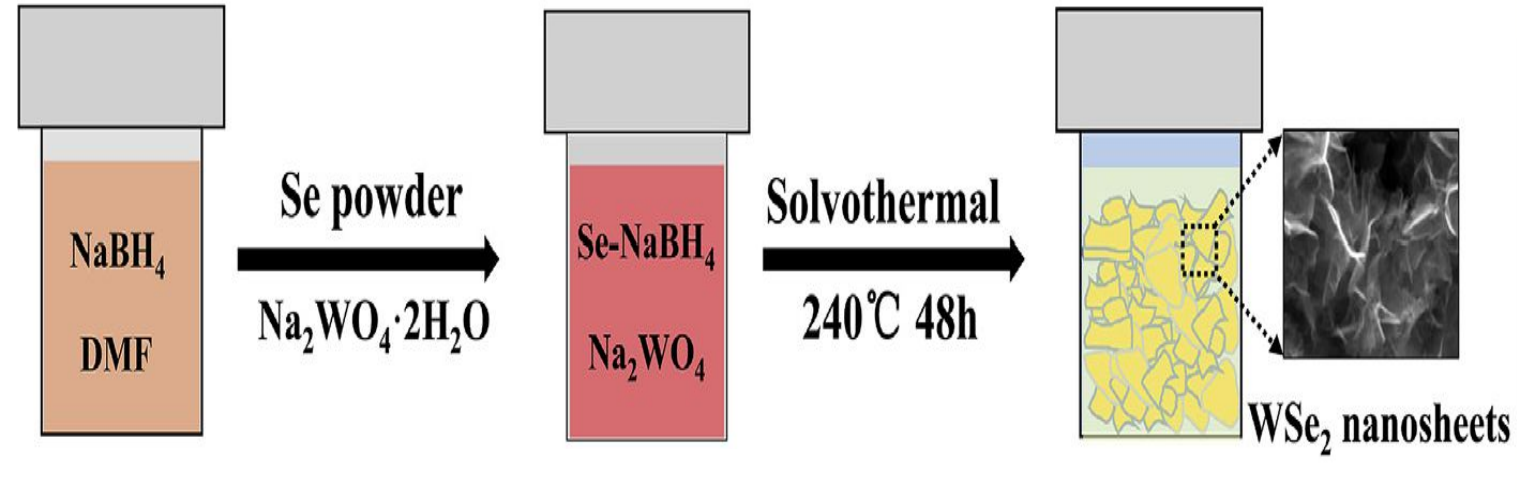


4. Solvothermal method

The graphene-like WSe_2 nanosheets were prepared by dissolving

0.64 g of Se powder, 1.32 g of Na_2WO_4 and
0.20 g of $NaBH_4$ in 60 ml DMF.

This precursor solution was transferred into the autoclave, sealed, and then heated at 240 ℃ for 48 h to get WSe_2 nanosheets.



CHARACTERIZATION TECHNIQUES FOR NANOSTRUCTURED MATERIALS

Studies	Information
TG/DTA	Phase formation and/or complete crystallization temperature
XRD	Phase analysis and Crystallinity
FTIR	Structural conformation
UV-Visible	Structural conformation
FE-SEM	Surface morphology and Average particle size
HR-TEM	Particle size and microstructure
DRS	Band gap determination
BET	Specific surface area
AC-Impedance	Ionic conductivity


THANK
YOU