

Synthesis of nanomaterials

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Why "nano"

Nanomaterials have superior properties than the bulk substances :

- Mechanical strength
- Thermal stability
- Catalytic activity
- Electrical conductivity
- Magnetic properties
- Optical properties
-

A wide range of applications:

Quantum electronics, nonlinear optics, photonics, sensing, information storage and processing, adsorbents, catalysis, solar cells, superplastic ceramics...

New fields:

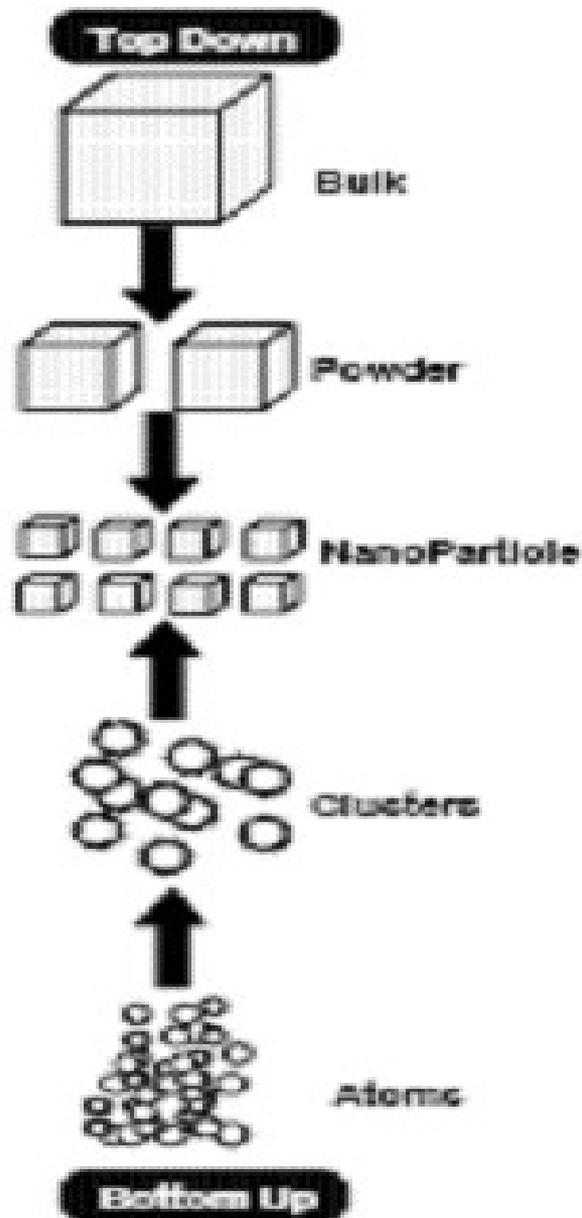
Nanofabrication, nanodevices, nanobiology, and nanocatalysis

Challenges

- Means to achieve monodispersity
- Size and shape control
- Reproducibility
- Scale up
- Building complex nanostructures

The prime requisite for obtaining good quality nanomaterials

- Variation of PH
- Temperature
- Time
- Concentration of Reagent
- Concentration of Catalyzer
- H₂O/Si
- Phase transition Sol \longrightarrow Gel
- Drying



Top Down Methods

Mechanical Grinding

Erosion

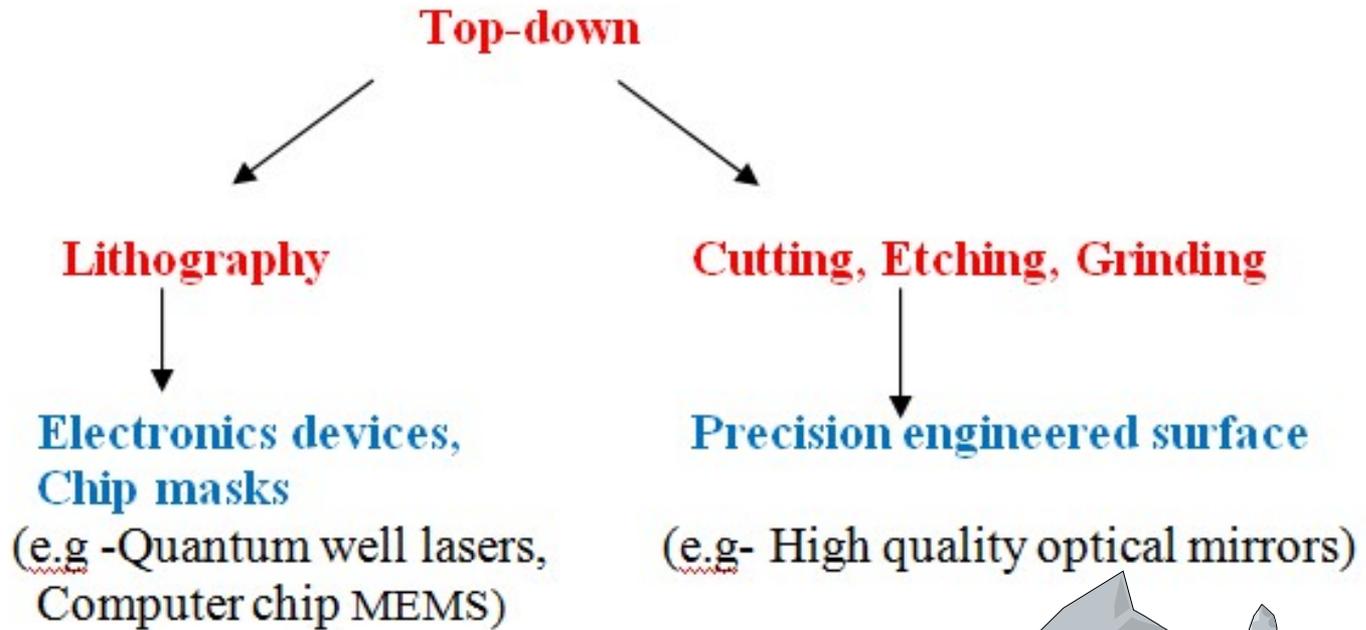
Bottom Up Methods

Aerosol Technique

Chemical precipitation

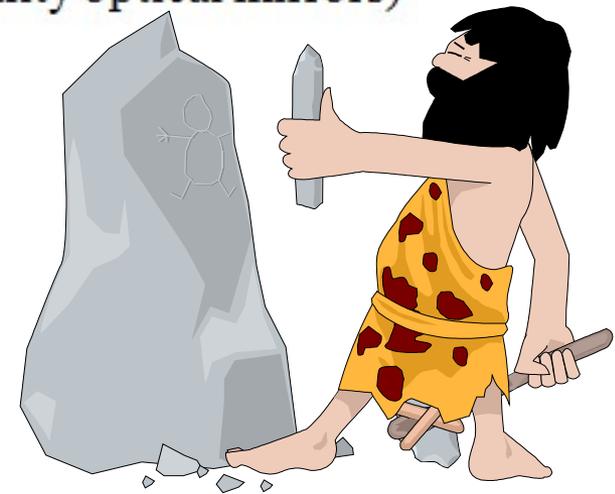
Gas phase agglomeration

Self Assembly

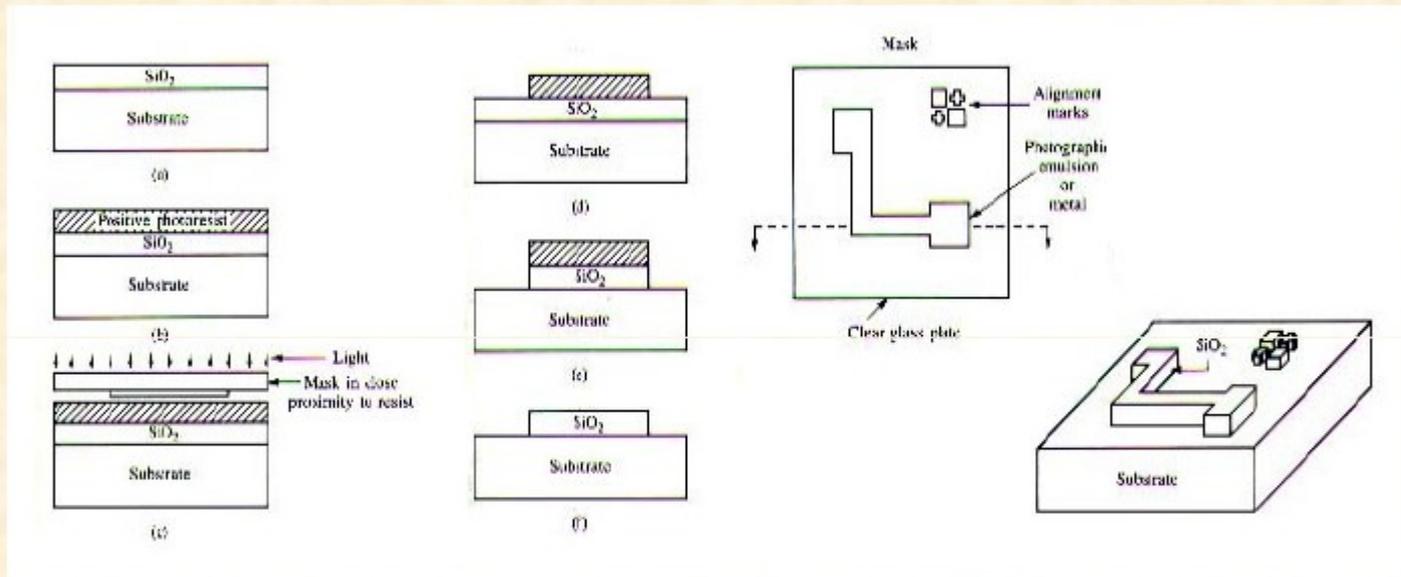


➤ **Top ⇒ Down:**

- Start with the bulk material and “cut away material” to make the what you want



Basic idea behind lithographic processing

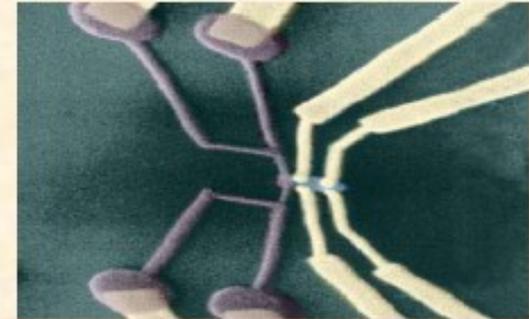
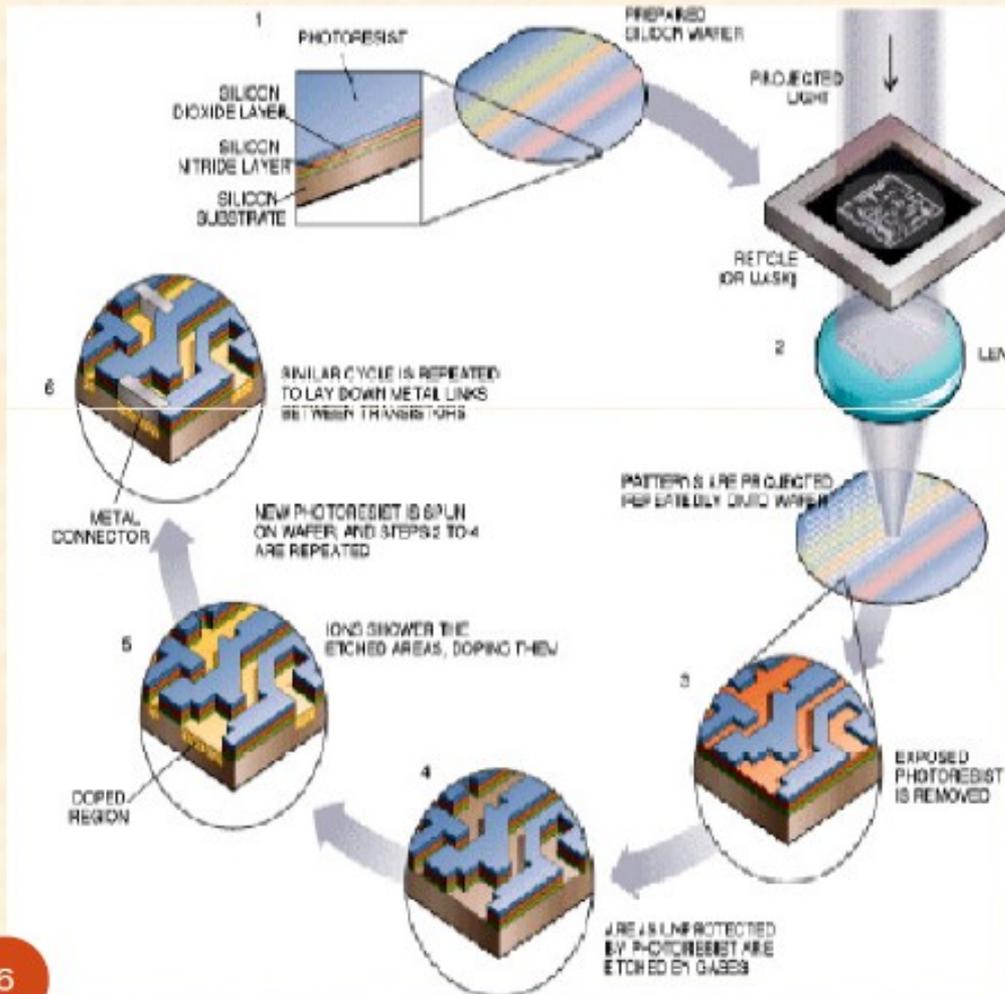


Coat, protect, expose, etch, repeat...

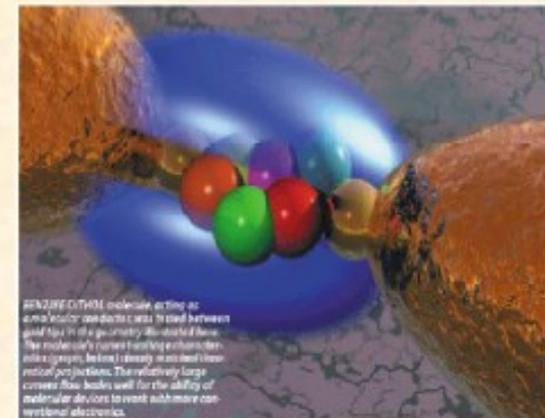
Result:

Multiple patterned layers of different materials.

Top-Down: photolithography



Ferromagnetic / superconducting devices (e-beam lithography)



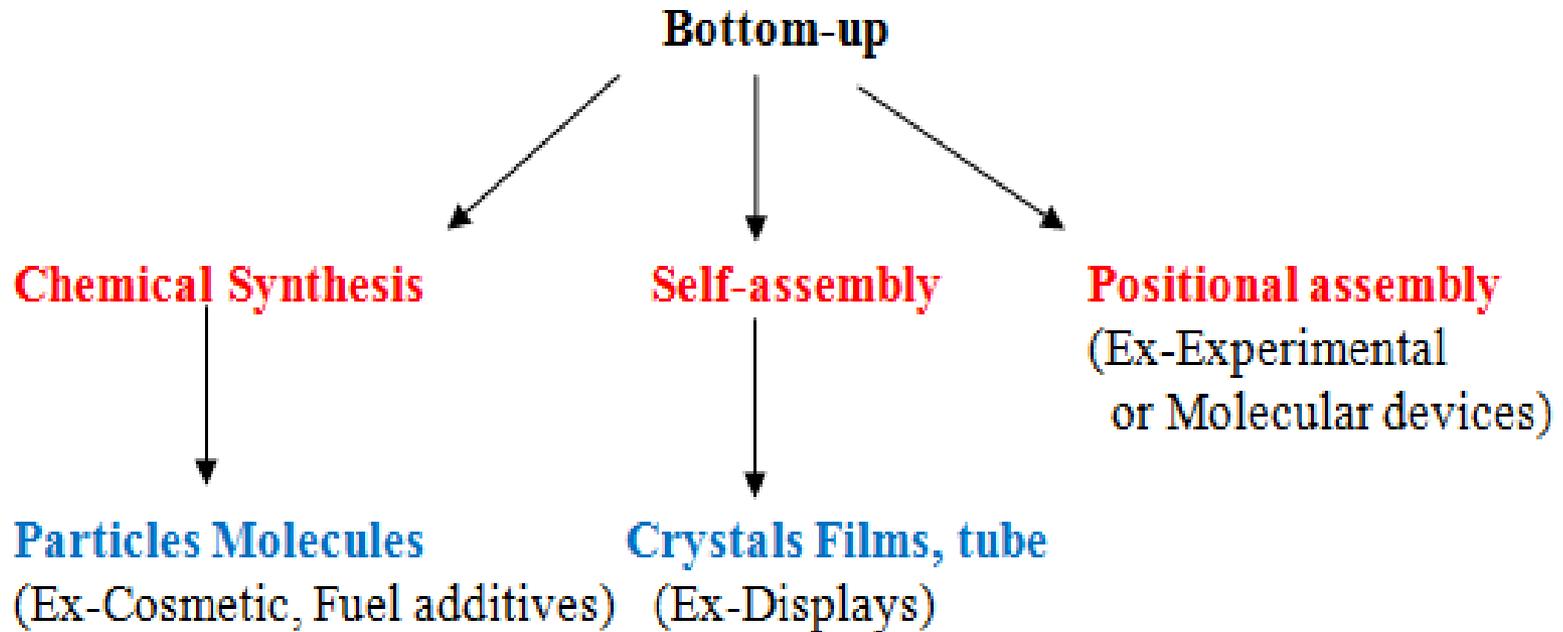
Molecular electronics (e-beam lithography)

Problems in lithography

Though the concept of photolithography is simple, the actual implementation is very **complex and expensive**.

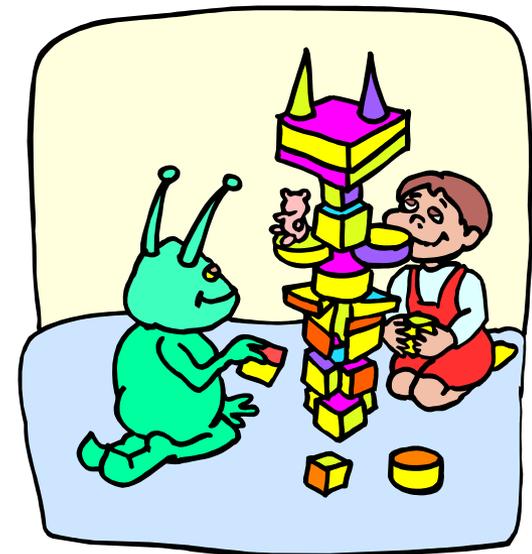
This is because

- (1) nanostructures significantly smaller than 100 nm are difficult to produce due to diffraction effects,
- (2) masks need to be perfectly aligned with the pattern on the wafer,
- (3) the density of defects needs to be carefully controlled, and
- (4) photolithographic tools are very costly, ranging in price from tens to hundreds of millions of dollars.



➤ **Bottom** ⇒ **Up:**

- Building what you want by assembling it from building blocks (such as atoms and molecules).
- Atom-by-atom, molecule-by-molecule, or cluster-by-cluster



Top-down vs. bottom-up

- **Top-down methods**

begin with a pattern generated on a larger scale, then reduced to nanoscale.

- By nature, aren't cheap and quick to manufacture
- Slow and not suitable for large scale production.

- **Bottom-up methods**

start with atoms or molecules and build up to nanostructures

- Fabrication is much less expensive

2. Nanoparticle Synthesis Strategies

2.1 Liquid-phase synthesis

2.2 Gas-phase synthesis

2.3 Vapor-phase synthesis

Synthesis

Physical

Chemical

Biological

Hybrid

Colloids
Sol-Gel
L-B films
Inverse micelles

Using biomembranes
DNA
Enzymes
Micro Organisms

Electrochemical
CVD
Partical arresting in glass or Zeolites
Polymers
Microemulsion

Mechanical

High energy ball milling
Melt mixing
Hydrothermal

Vapour

PVD
Laser ablation
Sputter deposition
Electric arc deposition
Ion implantation

Bottom –Up Approach

2.1 Liquid-Phase Synthesis

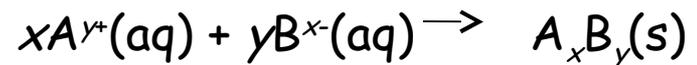
- ✓ Co-precipitation
- ✓ Sol-gel Processing
- ✓ Hydrothermal/Solvothermal Synthesis
 - Microemulsions
 - Microwave Synthesis
 - Sonochemical Synthesis
 - Template Synthesis
 - Biomimetic Synthesis

Coprecipitation

Coprecipitation: Reactions involve the simultaneous occurrence of **nucleation, growth, coarsening and/or agglomeration processes.**

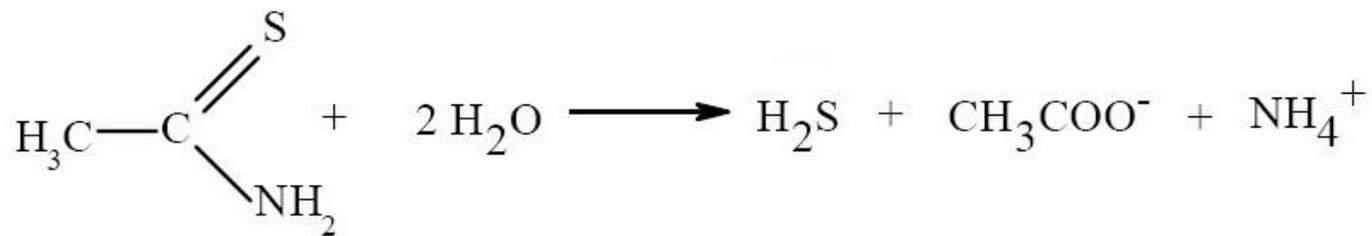
Coprecipitation reactions exhibit the following characteristics:

- (i) The products are generally insoluble species formed under conditions of high supersaturation.
- (ii) Nucleation is a key step, and a large number of small particles will be formed.
- (iii) Secondary processes, such as Ostwald ripening and aggregation, dramatically affect the size, morphology, and properties of the products.
- (iv) The supersaturation conditions necessary to induce precipitation are usually the result of a chemical reaction.

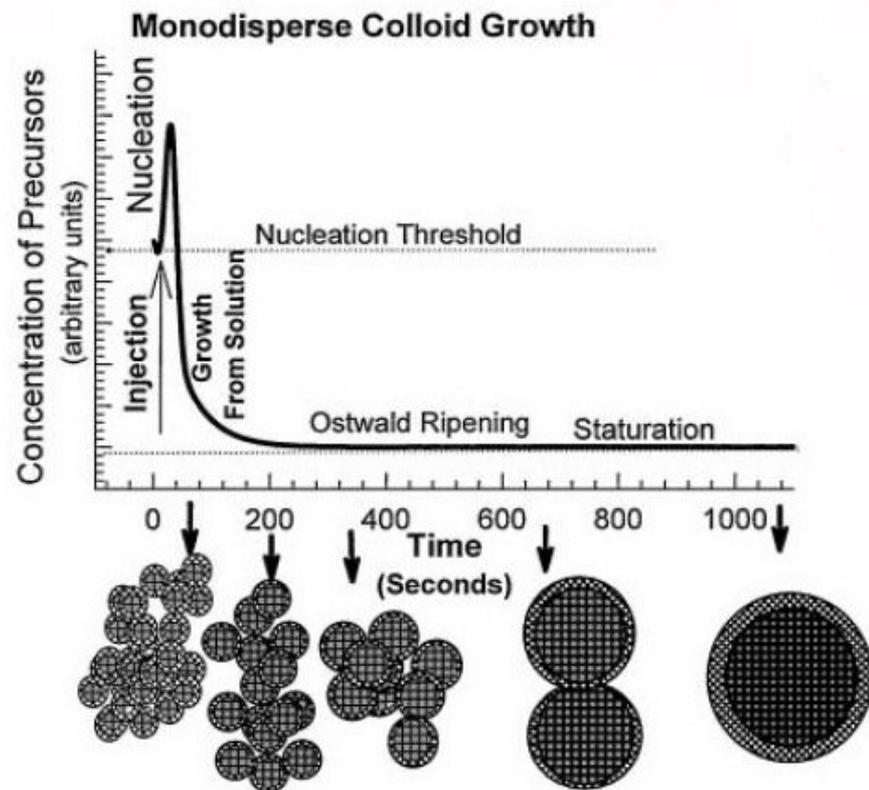


Typical coprecipitation synthetic methods: (i) metals formed from aqueous by reactions of molecular precursors; (ii) micrsolutions, by reduction from nonaqueous solutions, electrochemical reduction, and decomposition of metallorganic precursors; (iii) oxides formed from aqueous and nonaqueous solutions; (iv) metal chalconides formed micro wave/sonication-assisted coprecipitation.

Example: Precipitation of ZnS nanoparticles from a solution containing thioacetamide and zinc acetate



Thioacetamide is used as a sulfide source.



Synthesis of ZnS:Mn²⁺ sols.

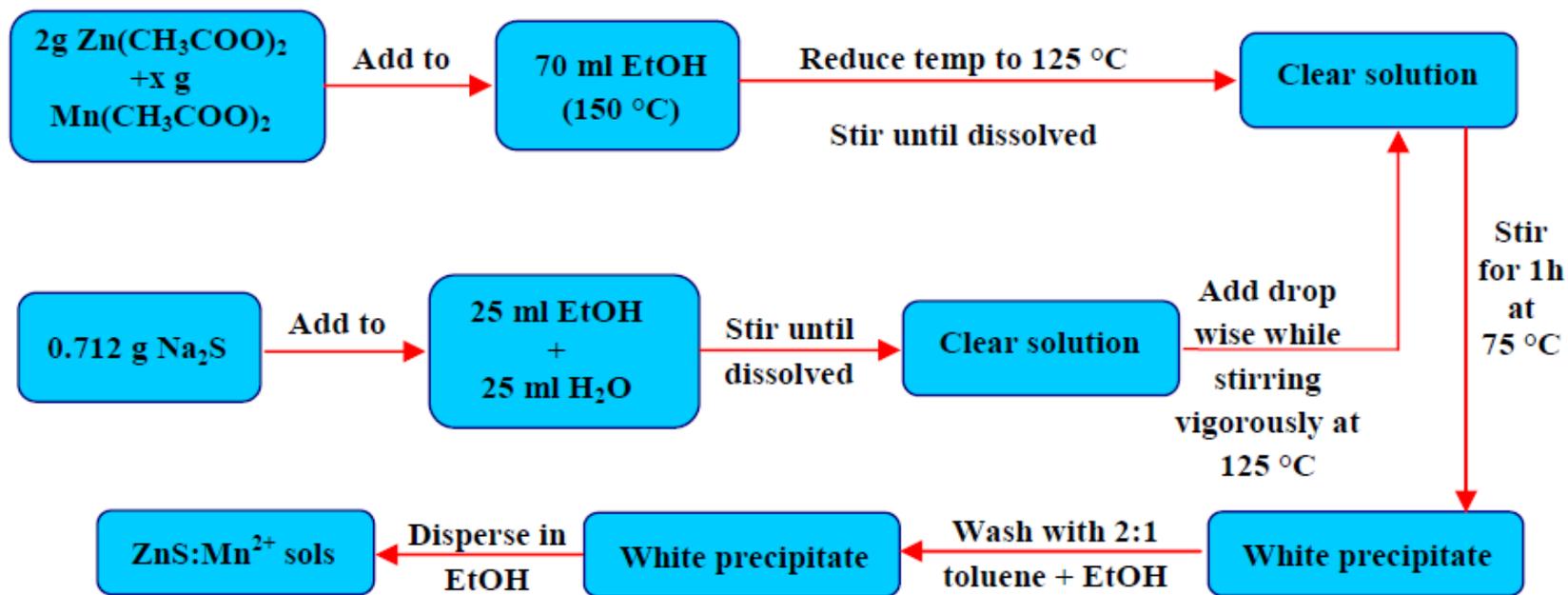


Figure 1: A flow diagram for the preparation of ZnS:Mn²⁺ sols.

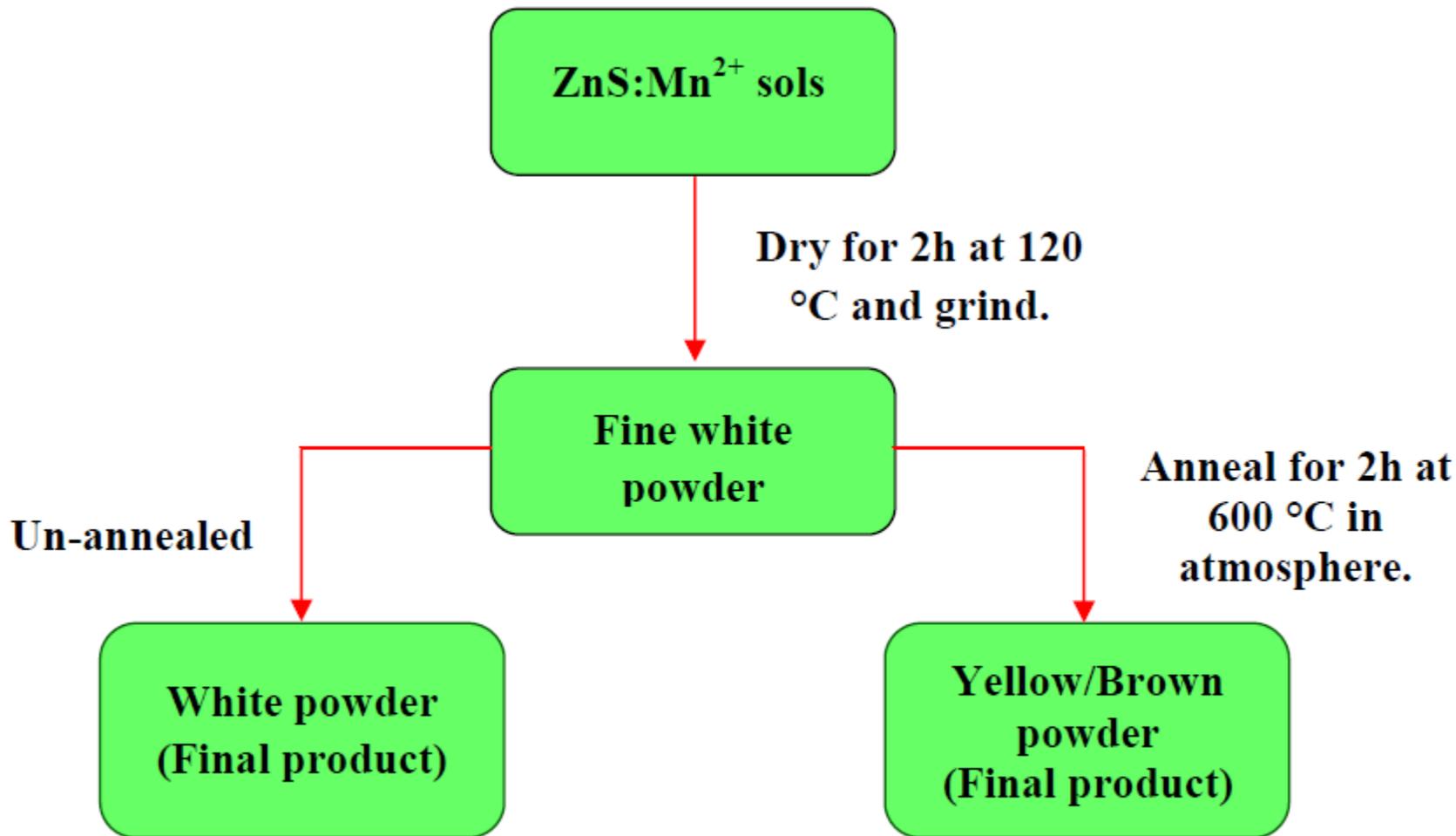
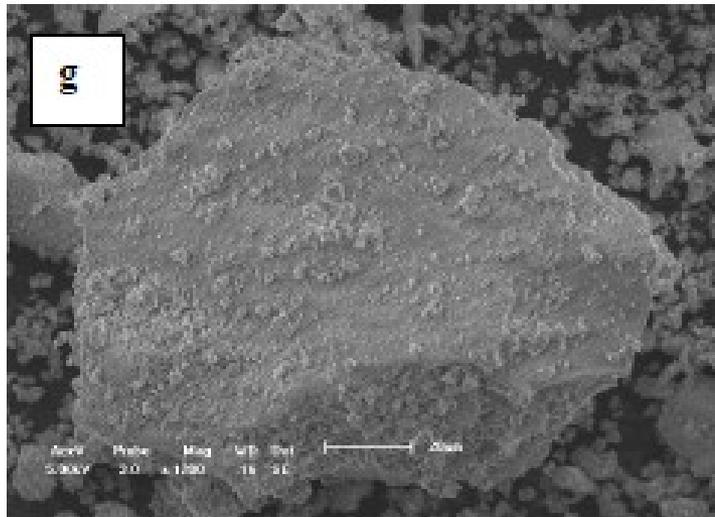
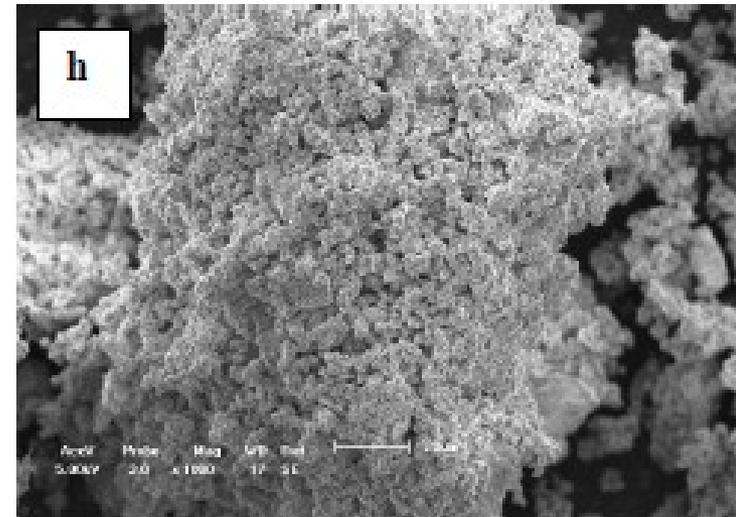


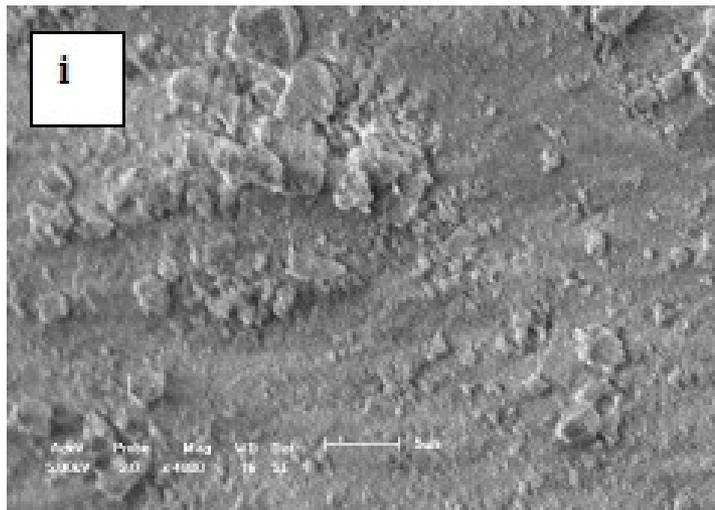
Figure 2: A flow diagram for the preparation of ZnS:Mn²⁺ powders.



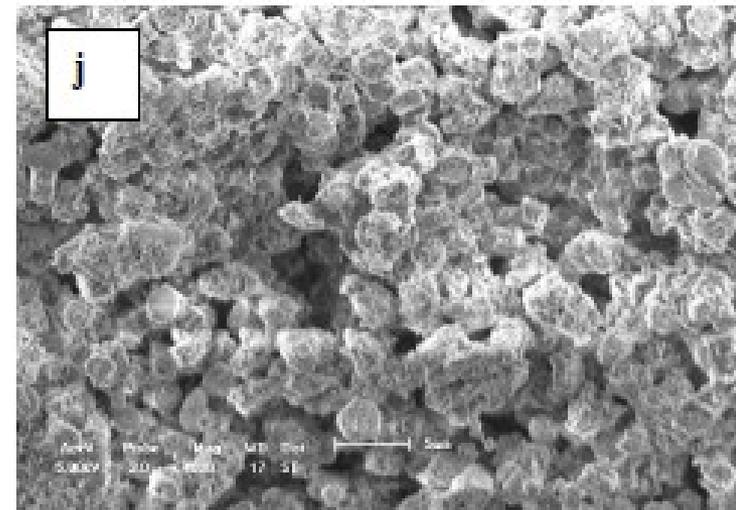
ZnS:Mn²⁺ 20 mol% un- annealed 1200x



ZnS:Mn²⁺ 20 mol% 600°C 1200x



ZnS:Mn²⁺ 20 mol% un- annealed 4000x



ZnS:Mn²⁺ 20 mol% 600°C 4000x

S😊I-Gel Technologies for nanomaterials fabrication



Sol



Gel

2. Material Processing by Sol-Gel Method

Introduction

- ❖ The sol-gel process is very long known since the late 1800s. The versatility of the technique has been rediscovered in the early 1970s when glasses were produced without high temperature melting processes.
- ❖ Sol-gel is a chemical solution process used to make ceramic and glass materials in the form of thin films, fibers, or powders.
- ❖ A **sol is a colloidal** (the dispersed phase is so small that gravitational forces do not exist; only Van der Waals forces and surface charges are present) or **molecular suspension of solid particles of ions in a solvent.**
- ❖ A **gel is a semi-rigid mass** that forms when the solvent from the sol begins to evaporate and the particles or ions left behind begin to join together in a continuous network

Sol-gel Processing

➤ The sol-gel process is a wet-chemical technique that uses either a chemical solution (**sol short for solution**) or colloidal particles (sol for nanoscale particle) to produce an **integrated network (gel)**.



➤ Metal alkoxides and metal chlorides are typical precursors. They undergo **hydrolysis and polycondensation reactions** to form a colloid, a system composed of nanoparticles dispersed in a solvent. The sol evolves then towards the formation of an inorganic continuous network containing a liquid phase (gel).



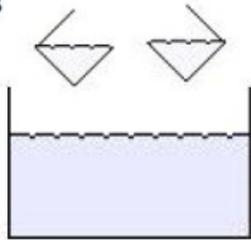
➤ Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating **metal-oxo or metal-hydroxo polymers** in solution.



➤ After a drying process, the liquid phase is removed from the gel. Then, a thermal treatment (**calcination**) may be performed in order to favor further polycondensation and enhance mechanical properties.

Making Gel formation

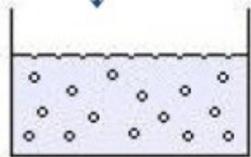
Mix reactives



Hydrolysis and Condensation reactions take place



Sol



Gelification



Gel



Hydrolysis



Condensation



1 – General mechanisms in the metal-organic route

Based on the growth of **metal oxo polymers** in a solvent

- inorganic step polymerization reactions through hydrolysis and condensation of metal alkoxides $M(OR)_Z$, where $M = Si, Ti, Zr, Al, Sn, Ce...$, OR is an alkoxy group and Z is the valence or the oxidation state of the metal
- first step : hydroxylation upon the **hydrolysis** of alkoxy groups :



- second step : polycondensation process leading to the formation of branched oligomers and polymers with a metal oxo based skeleton and reactive residual hydroxo and alkoxy groups ; 2 competitive mechanisms :

- **oxolation** : formation of oxygen bridges :



where $X = \text{H}$, generally when **hydrolysis ratio** $h = \text{H}_2\text{O}/\text{M} \gg 2$
or $X = \text{R}$, when $h = \text{H}_2\text{O}/\text{M} < 2$

- **olation** : formation of hydroxo bridges when the coordination of the metallic center is not fully satisfied ($N - Z > 0$) :



The kinetics of olation are usually faster than those of oxolation

➤ formation of a metal oxo macromolecular network :

- a **sol** where the polymerized structures do not reach macroscopic sizes

■ a **gel** when the recombination of the metal oxo polymers can produce bushy structures which invade the whole volume inside which the solvent, reaction by-products and free polymers are trapped

- a **precipitate** when the reactions produce dense rather than bushy structures

Depending on the control of the structures of these oxo polymers through

- the hydrolysis ratio h
- the use of catalysts, complexing ligands or nucleophilic reagents
- the steric hindrance of the alkoxy groups
- the nature of solvents
- the temperature

2.2 Preparation of SiO₂-ZnS:Mn²⁺ nano particles

SiO₂ sols were prepared by using the method described by Ntwaeaborwa et al. [9], by mixing 10 g of tetraethylorthosilicate (TEOS) with 14 ml of deionized water, 8 ml of ethanol and 5 ml of 0.15 M HNO₃ (catalyst). The mixture was stirred at room temperature for 1 hour until a transparent solution formed. The ZnS:Mn²⁺ sol dispersed in ethanol was added to the SiO₂ sol drop by drop with vigorous stirring at room temperature. The mixture was stirred for 24 hours until a gel formed. The gels were dried in air at room temperature for 3 days. The resulting white solids were then ground and sieved to get a fine white powder, which was also annealed at 600°C for two hours. The concentration of Mn²⁺ in ZnS:Mn²⁺ and SiO₂-ZnS:Mn²⁺ was varied from 2 – 20 mol%. The synthesis process is illustrated in Figure 3.

Synthesis of ZnS:Mn²⁺ sols.

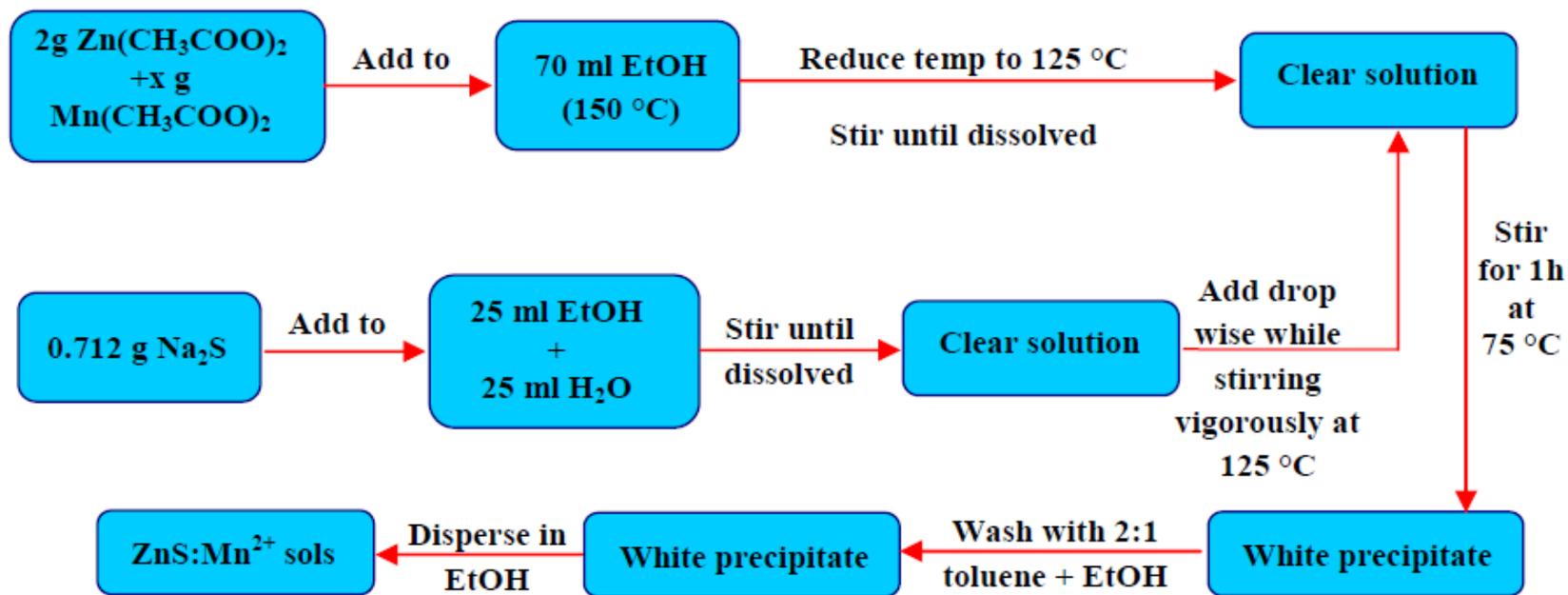


Figure 1: A flow diagram for the preparation of ZnS:Mn²⁺ sols.

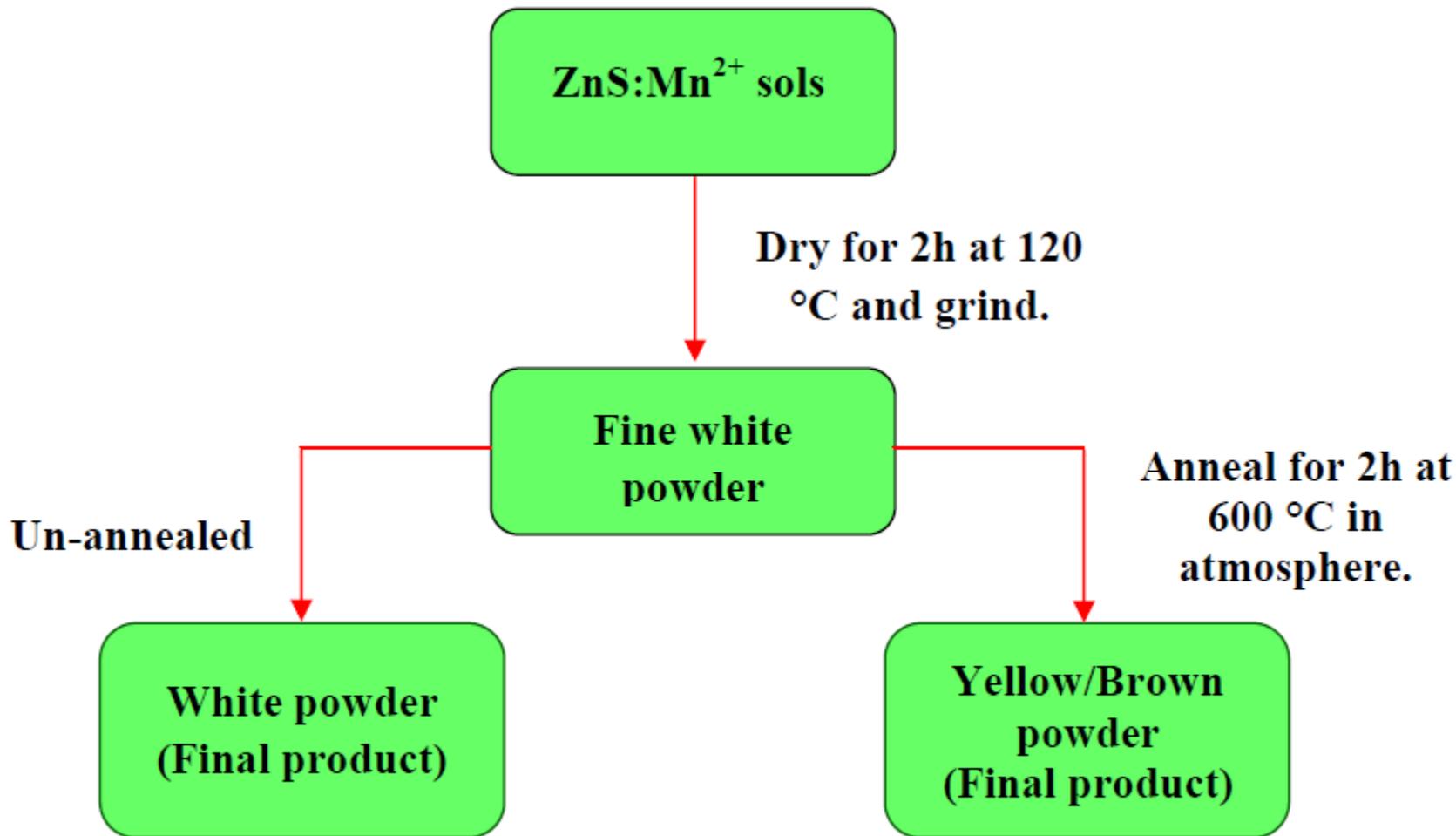
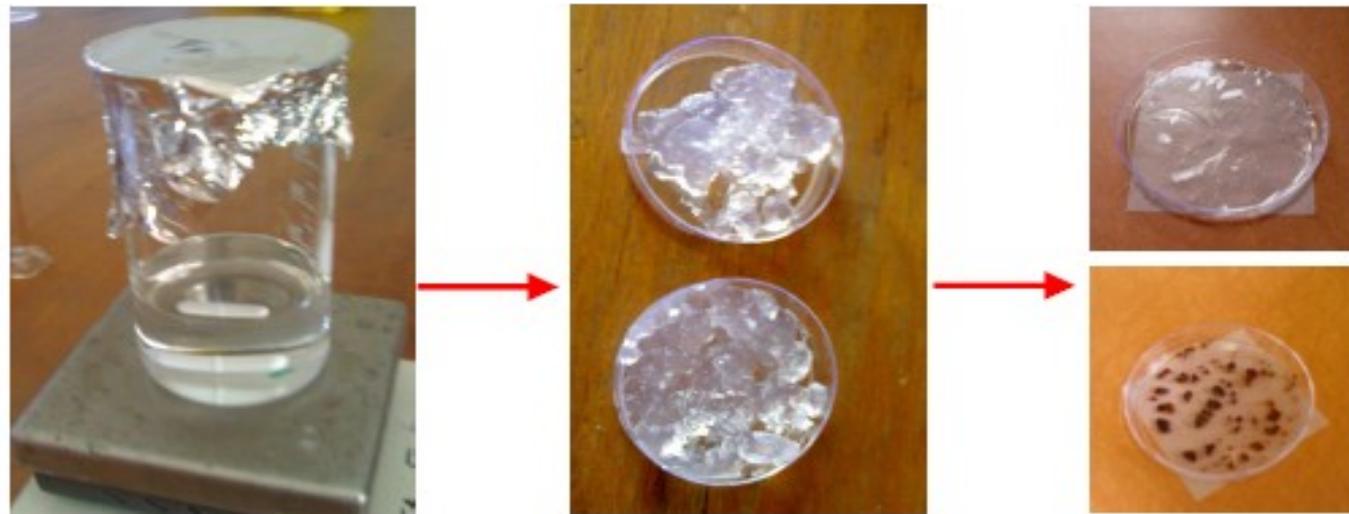


Figure 2: A flow diagram for the preparation of ZnS:Mn²⁺ powders.



Sol

Gel

**Dried
gels**

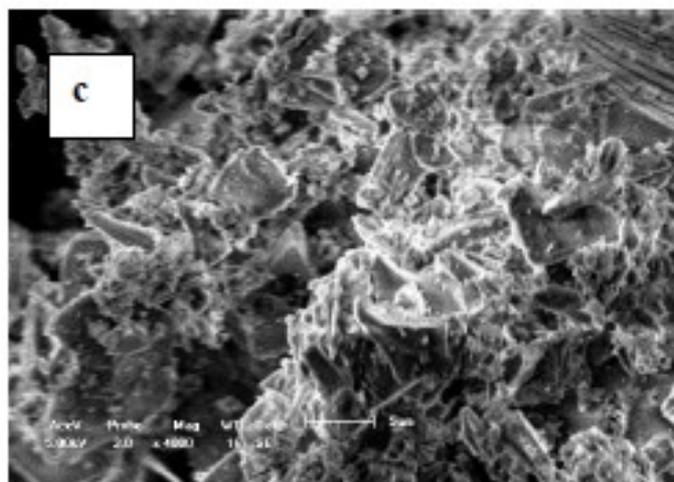


Sifting

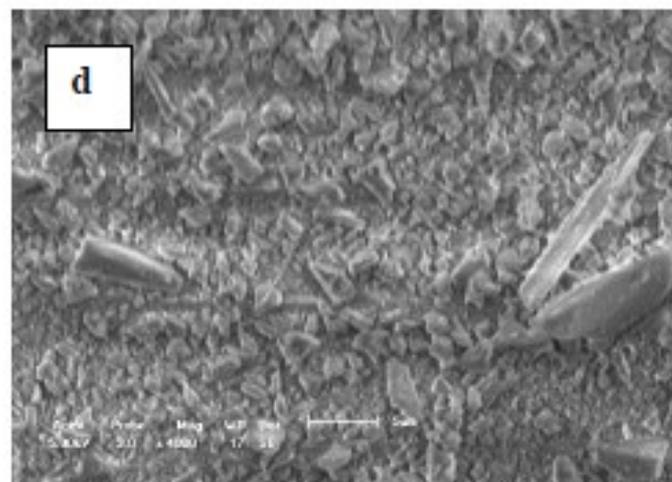


Grinding

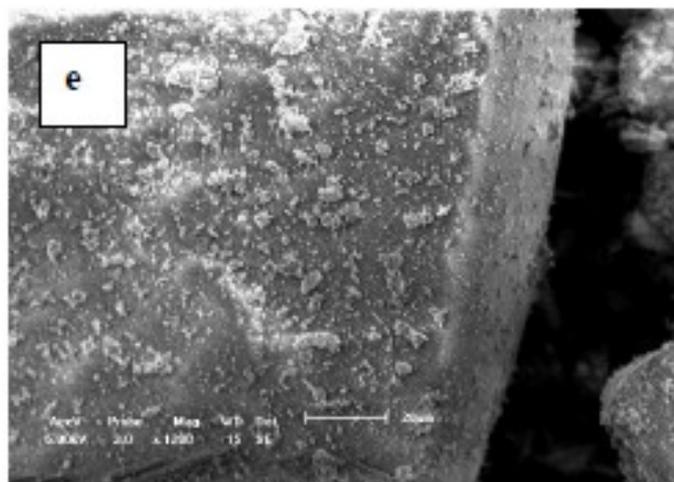
Figure 3: The synthesis process of $\text{SiO}_2\text{-ZnS:Mn}^{2+}$.



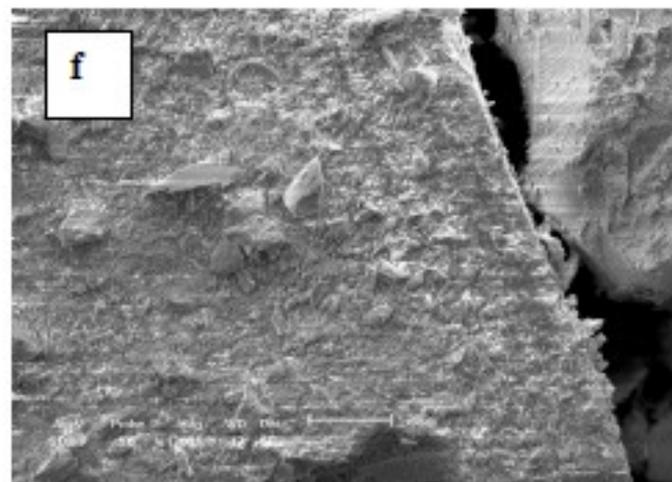
$\text{SiO}_2:\text{Mn}^{2+}$ un-annealed 4000x



$\text{SiO}_2:\text{Mn}^{2+}$ 600°C 4000x



$\text{SiO}_2:\text{ZnS}$ un-annealed 1200x



$\text{SiO}_2:\text{ZnS}$ 600°C 1200x

Reaction Characteristics

- In simple terms, whole process control is on control of relative rate between (a) hydrolysis ; (b) poly-condensation
- $M-OH + M-OR \rightarrow M-O-M + ROH$; Yet M-OH & M-OH condensation rate, and whether M-OR & M-OR can condense; whether linear condensation or branched form \rightarrow affect microstructure
- Effect of catalyst: acid or base
- Effect of temperature: e.g. $Al(OR)_3$ low temperature hydrolysis \rightarrow amorphous form, further aging \rightarrow hydroxide; at high temperature ($> 80^\circ C$) \rightarrow crystalline boehmite $AlO(OH)$, sintering behavior different
- $Zr(OR)_4$ hydrolysis, easy to get oxo bond, instead of hydroxy bond

More Characteristics

- Alcohol as solvent, same as alcohol in alkoxide, one can also use different alcohols (or co-solvent), may affect reaction; sometime the steric effect
- Another reason for gelation: solvent evaporation, increase of concentration; mostly due to reaction; → end result 3D network structure, system viscosity increase → continue aging, stronger structure, begin to shrink, expel solvent.

More and more applications, become an independent category;

Use metal alkoxide, to go through hydrolysis reaction, then condensation polymerization, to obtain desired colloids

During process, system viscosity increase with time, it can also be used for coating into films, or even directly forming into desired objects → variety;

Most common example: TEOS (tetraethyl orthosilicate) hydrolysis to make silica; $(OC_2H_5)_4Si + H_2O \rightarrow (OC_2H_5)_3SiOH + C_2H_5OH \rightarrow \dots$ Gradual hydrolysis and then condensation reactions.....

Decomposition and Sintering

- Up to 150°C, continuous dehydration, some ligand may desorb and leave, micropores will limit its movement
- Over 250°C, molecule begin to decompose, continue to loss weight. Decomposition affected by gel structure, extent of cross-linking; atmosphere also important, incomplete decomposition may have residual char;
- Skeleton collapse, particle sintering and densification, mostly by viscous sintering (faster than conventional diffusion mechanism), i.e. can be achieved at lower temperature (one advantage of sol-gel process); if fast heating, may contain residual pores.

Advantages of Sol-Gel Technique:

- ❖ Can produce thin bond-coating to provide excellent adhesion between the metallic substrate and the top coat.
- ❖ Can produce thick coating to provide corrosion protection performance.
- ❖ Can easily shape materials into complex geometries in a gel state.
- ❖ Can produce high purity products because the organo-metallic precursor of the desired ceramic oxides can be mixed, dissolved in a specified solvent and hydrolyzed into a sol, and subsequently a gel, the composition can be highly controllable.
- ❖ Can have low temperature sintering capability, usually 200-600°C.

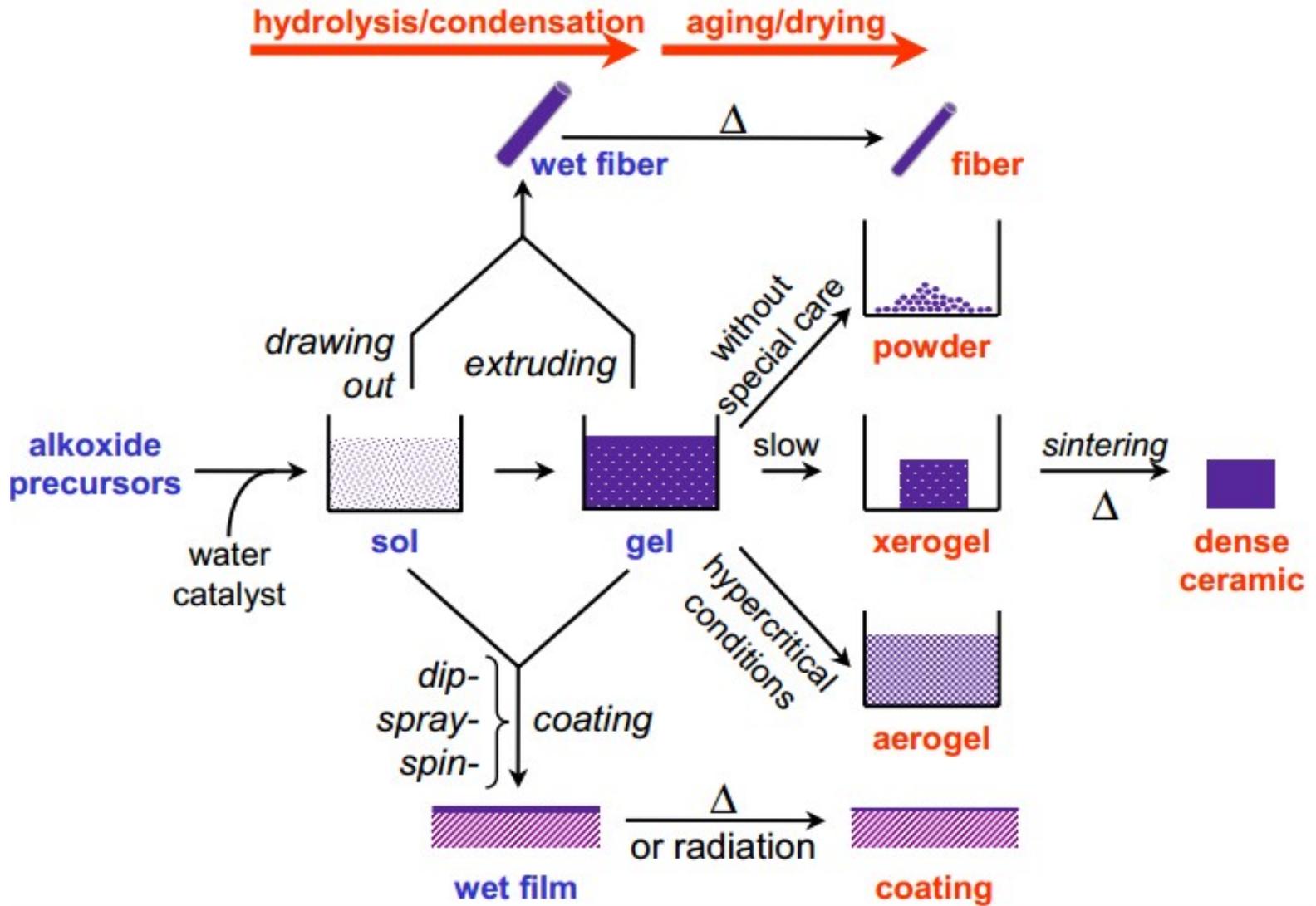
Advantages of Sol-Gel Processes

In general:

- ❖ Able to get uniform & small sized powder
- ❖ Can get at low temperature high density glass, without high temperature re-crystallization
- ❖ Can get new compositions of glass
- ❖ New microstructure and composition
- ❖ Easy to do coating for films
- ❖ Can get objects or films with special porosity
- ❖ Can get metal (inorganic) – organic composites
- ❖ Can coat onto large area or complex shape objects
- ❖ Can get fibers
- ❖ High uniformity, multicomponent systems

- ✦ The sol-gel approach is interesting in that it is a cheap and low-temperature technique that allows for the fine control on the product's chemical composition.
- ✦ as even small quantities of dopants, such as organic dyes and rare earth metals, can be introduced in the sol and end up in the final product finely dispersed.
- ✦ An overview of the sol-gel process is presented in a simple graphic work below.

summary of sol-gel process, techniques and products



Pore filling by Sol-Gel technique and oxide nanowire formation.

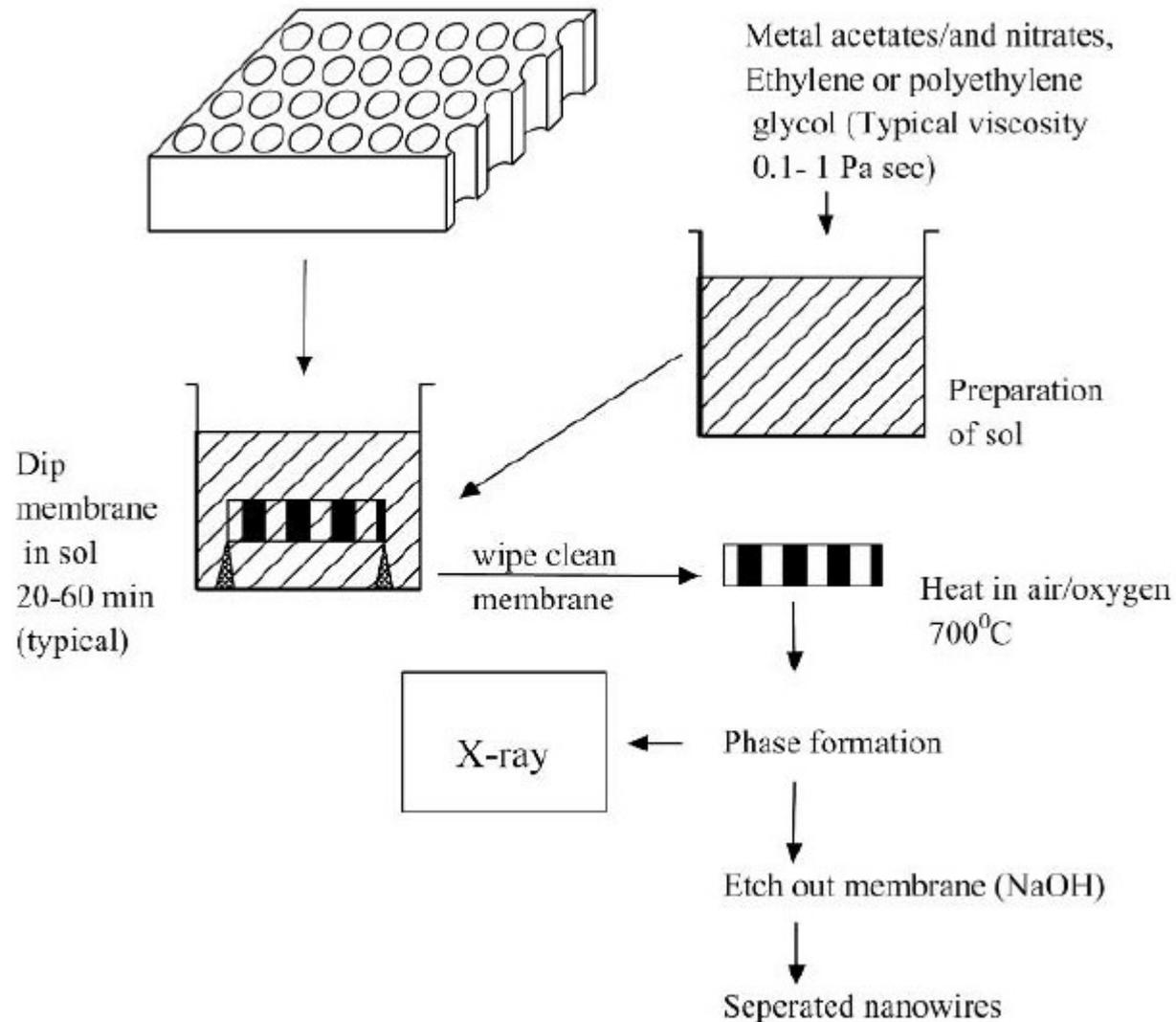


Fig. 21.10. The sol-gel route to the formation of oxide nanowires in templates.

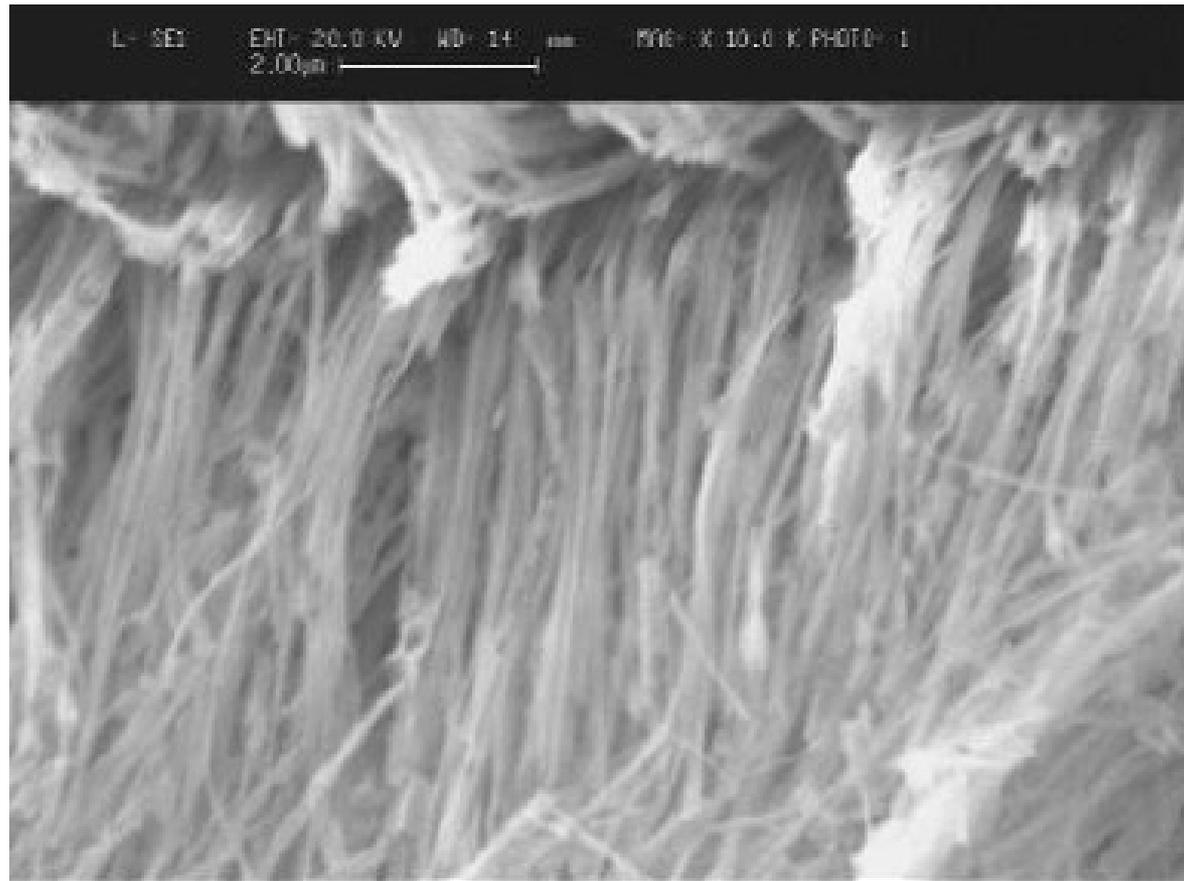
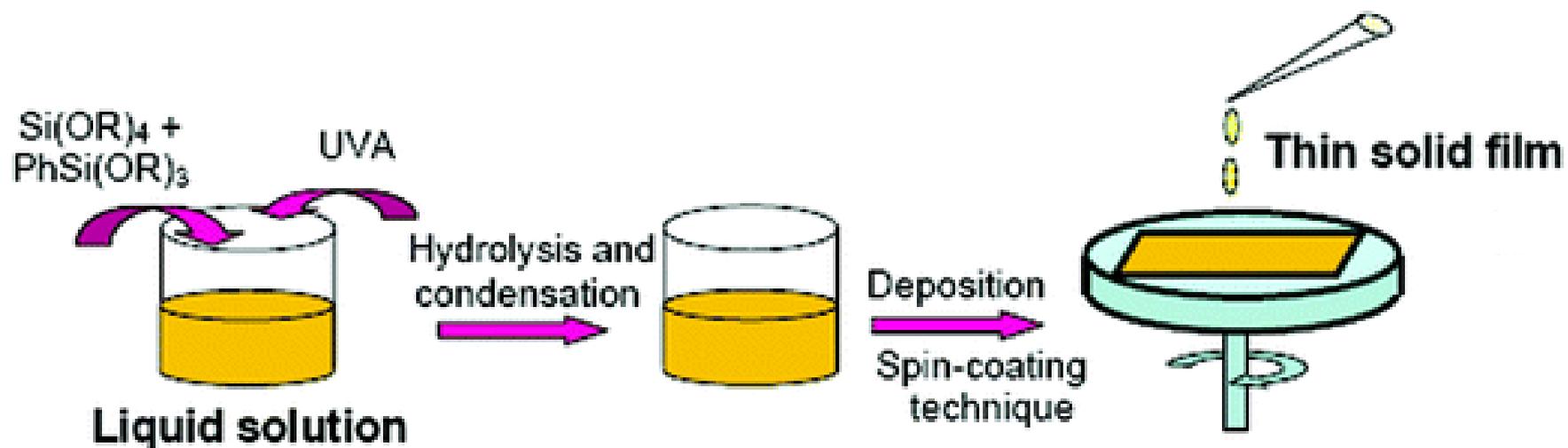
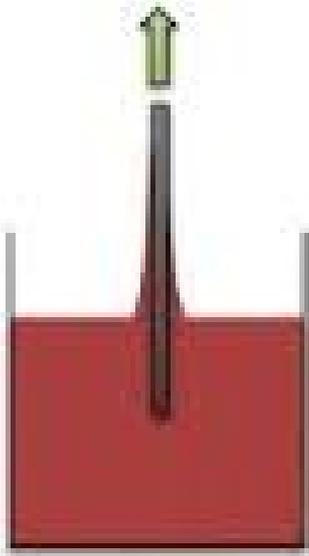


Fig. 21.11. SEM of nanowires of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (LCMO) grown by the sol-gel method in alumina templates.





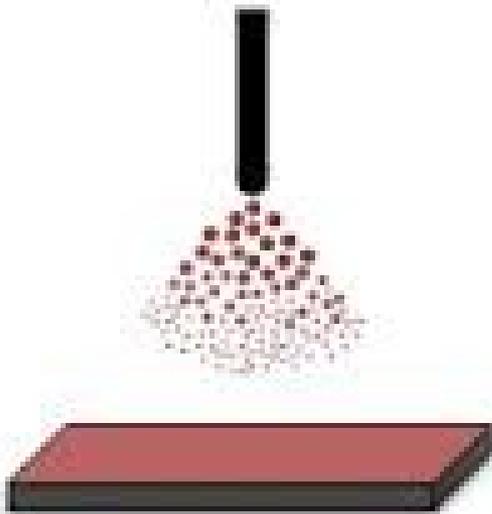
(a)

Dip coating



(b)

Spin coating



(c)

Spray pyrolysis

Sol-Gel process overview

