ECE 5320

Lecture #6 and 7

Homework notes:

- The homework will be posted on the web as a pdf/word file: Homework1-2016spring
- Your work has to be typed, and I assume that you have sufficient proficiency using MS work eq. editor. I will not accept the hand written returns. Only first page where you have to sing, will be filled with your hand writing and your ID#. This page has to be imported from the pdf file of the homework posting.
- In the homework, problems that are marked with * mean that this question belong to a group of question you will could have on your final and/or midterm exam.
- Points associated with each problem are given in the brackets. Bonus problems do not have to be answered, yet, they can bring you extra points. Remember, I assume that you all have books, notes itself are not sufficient to do homework. Bonus problems require extra reading beyond the class material (graduates)

Title Calibri Bold 32pt.

- Text Calibri 24 pt.
- Eq. 24pt use equation editor in ppt. Make sure you check your derivations on units, and on consistent notation
- Graph sketches is up to your artistic talent.
- Figures from the notes incorporate as is in the ppt.
- Your are due with this work in the last week of the semester. NO COLLABORATION IS ALLOWED. YOUR WILL NOT GET CREDIT IF YOUR SHARE YOUR PPT WITH YOUR FRIENDS.
- Name files as lecture notes-your last name
- Do not make files of the notes that are already ppt, only the ones done by my hand writing.

Nanoparticle Synthesis

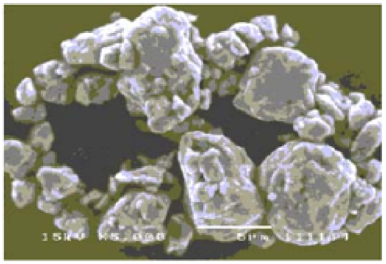
Top-Down

via Attrition / Milling

Involves mechanical thermal cycles
Yields
- broad size distribution (10-1000 nm)
- varied particle shape or geometry
- impurities

Application:
- Nanocomposites and
- Nano-grained bulk materials

Milling



Nanostructured Magnetic Alloys
12 nm Fe-Co crystals
(Nanyang Techn. Univ.)

Bottom-Up

Via
- Pyrolysis
- Inert gas condensation
- Solvothermal Reaction
- Sol-gel Fabrication
- Structured Media

Homogeneous nucleation

- Liquid, vapor or solid
- supersaturation
  - temperature reduction
  - metal quantum dots in glass matrix by annealing
  - *in situ* chemical reactions (converting highly soluble chemicals into less soluble chemicals)

Homogeneous nucleation

- Driving force

$$\Delta G_v$$

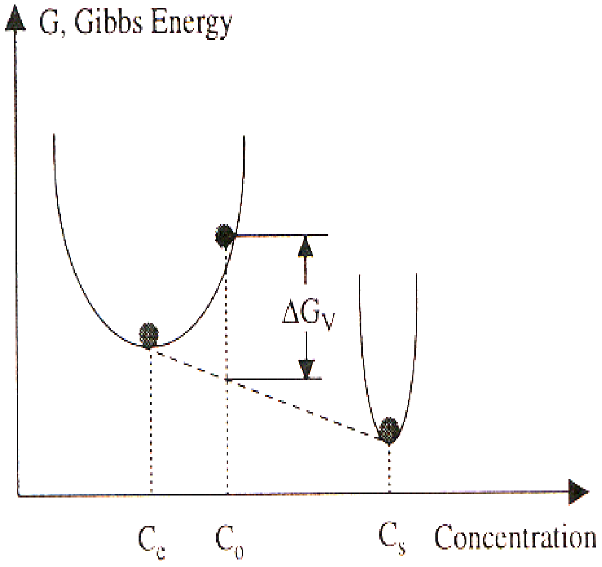


Fig. 3.1. Schematic showing the reduction of the overall Gibbs free energy of a supersaturated solution by forming a solid phase and maintaining an equilibrium concentration in the solution.

Homogeneous nucleation

- Energy barrier

Surface energy

$$\Delta G^* = \frac{16\pi\gamma}{(3\Delta G_v)^2} \qquad r^* = -2\frac{\gamma}{\Delta G_v}$$

Gibss free energy change

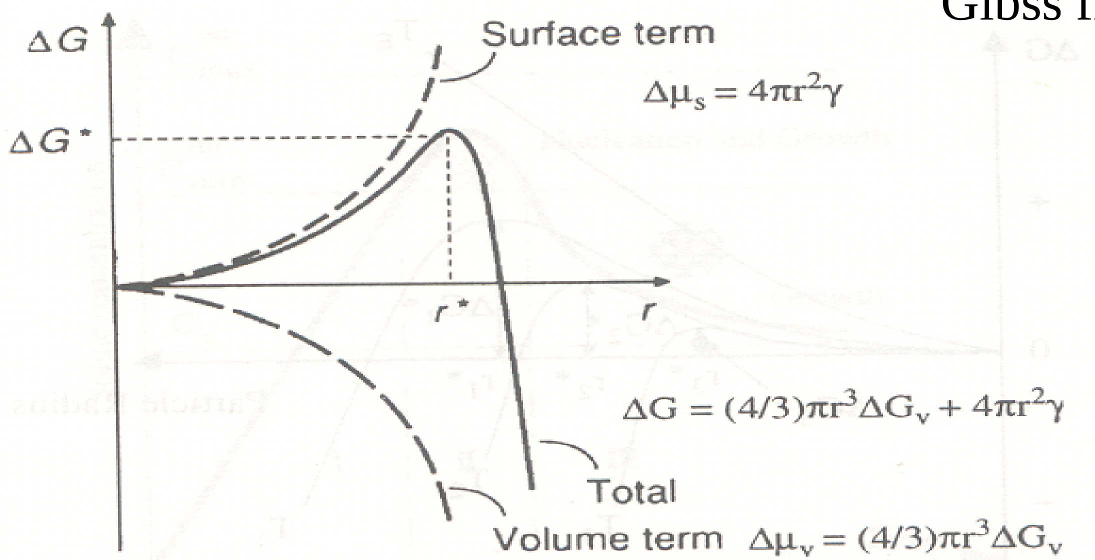


Fig. 3.2. Schematic illustrating the change of volume free energy, $\Delta\mu_v$, surface free energy, $\Delta\mu_s$, and total free energy, ΔG, as functions of nucleus' radius.

Homogeneous Condensation

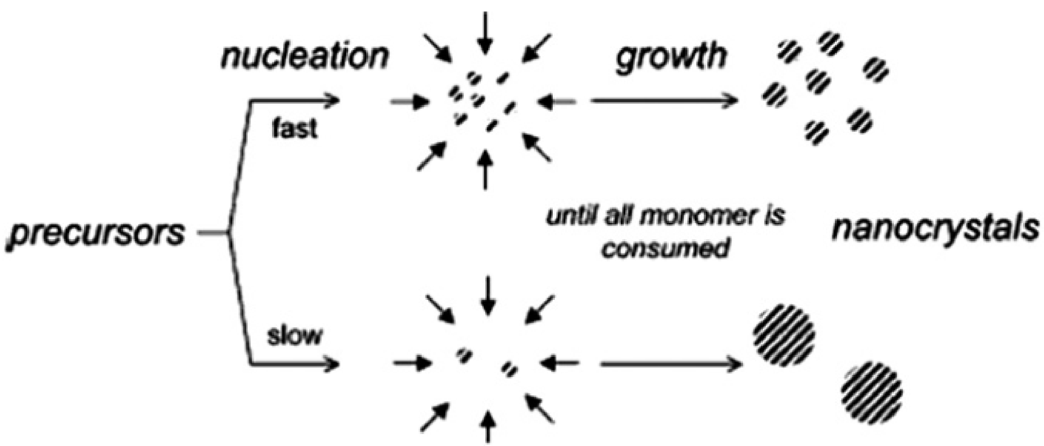
Cluster free energy:

negative volume term *positive surface term*

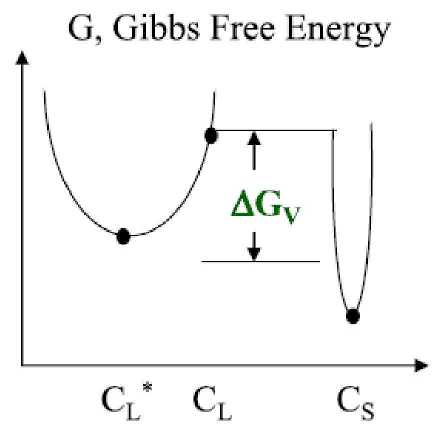
$$\Delta G^* = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

Driving Force: ΔG_V

Bulk free energy difference between old and new phase



E.E. Finney, R.G. Finke / J. Coll. Inter. Sci. **317** (2008) 351–374



Concentration:

C_L^* … Solution in Equilibrium

C_L … Supersaturated Solution

C_S … Solid phase

Nuclei

- formation favor:
  - high initial concentration or supersaturation
  - low viscosity
  - low critical energy barrier
- uniform nanoparticle size:
  - same time formation
  - abruptly high supersaturation -> quickly brought below the minimum nucleation concentration

Nuclei growth

- Steps
  - growth species generation
  - diffusion from bulk to the growth surface
  - adsorption
  - surface growth
- size distribution
  - A diffusion-limited growth VS. a growth-limited processes

Diffusion-limited growth

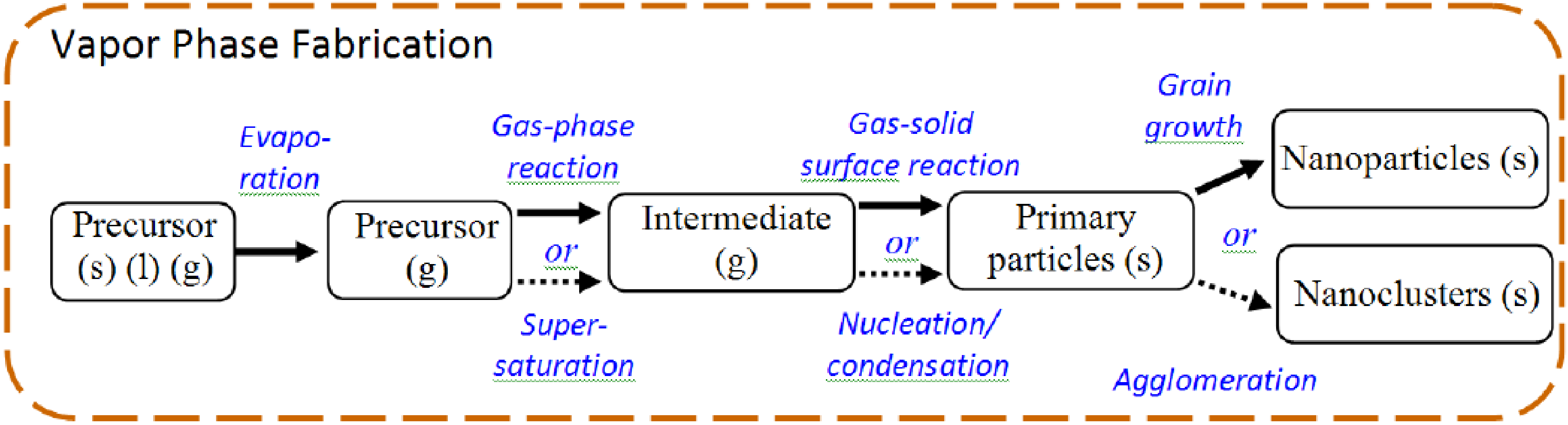
- monosized nanoparticles
- how?
  - Low/controlled supply growth species concentration
  - increase the solution viscosity
  - introduction a diffusion barrier

Bottom – Up Synthesis

Phase Classification:

I. Gas (Vapor) Phase Fabrication: Pyrolysis, Inert Gas Condensation, ….

II. Liquid Phase Fabrication: Solvothermal Reaction, Sol-gel, Micellar Structured Media



Bottom – Up Synthesis

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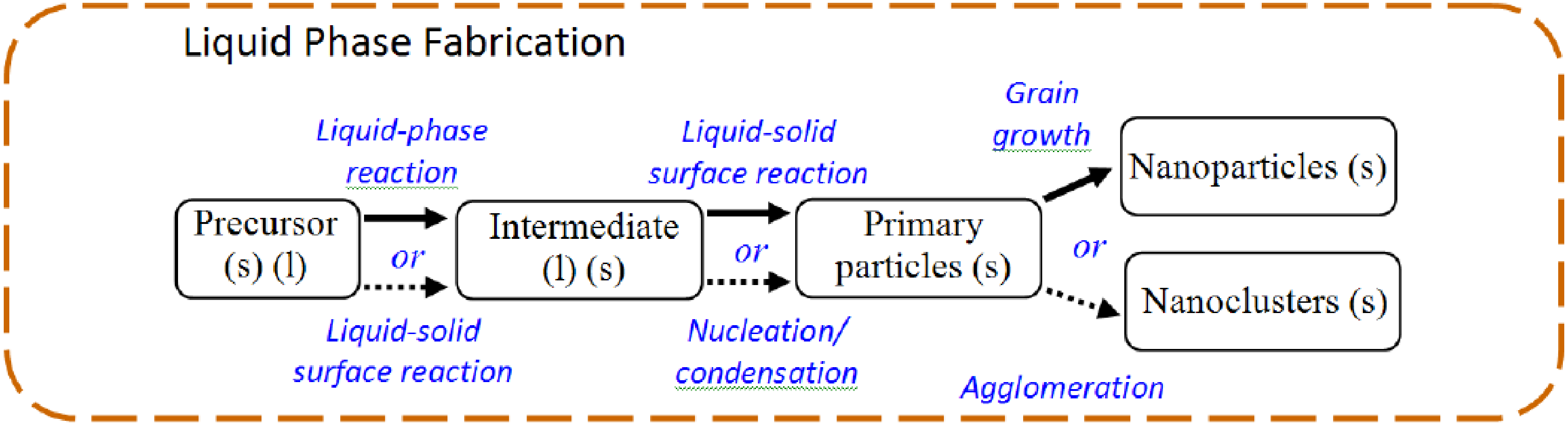


Vapor Phase Growth

Growth rate of vapor condensation:

Flux from gas kinetic theory

$$R = \xi A_{NP} \frac{\Delta p}{\sqrt{2\pi m k_B T}};$$

$$\Delta p = p_V - p_e$$

Spherical NP: $A_{NP} = 4\pi d_{NP}$

ξ... condensation coefficient (between 0 and 1)

A_{NP}... surface area of condensate (nanoparticle NP)

m .... mass of gas molecule

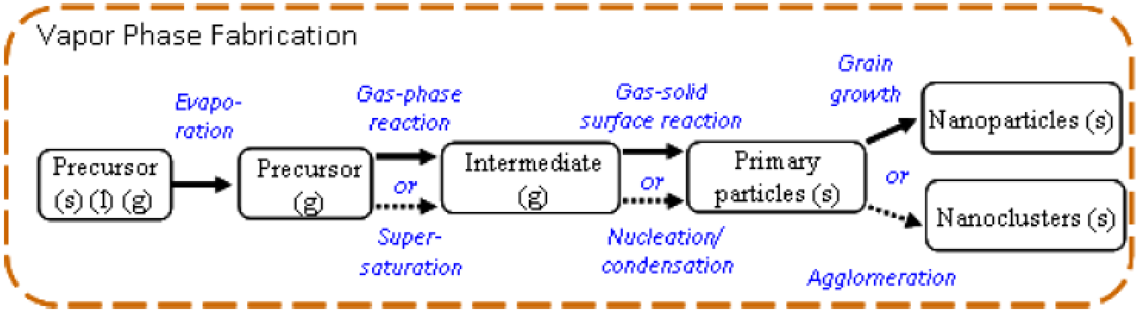
k_B .... Boltzmann constant, and T … absolute temperature

Driving force: pressure difference Δp

p_V ….instantaneous vapor pressure

P_e …. local equilibrium pressure at the growing cluster

Mechanism and Effectiveness



(i) precursor vaporization (typically involves a catalyst)

(ii) nucleation, and

(iii) growth stage

Effectiveness demands:

- simple process
- low cost
- continuous operation
- high yield

} Aerosol Spray Methods (e.g., Spray Pyrolysis)

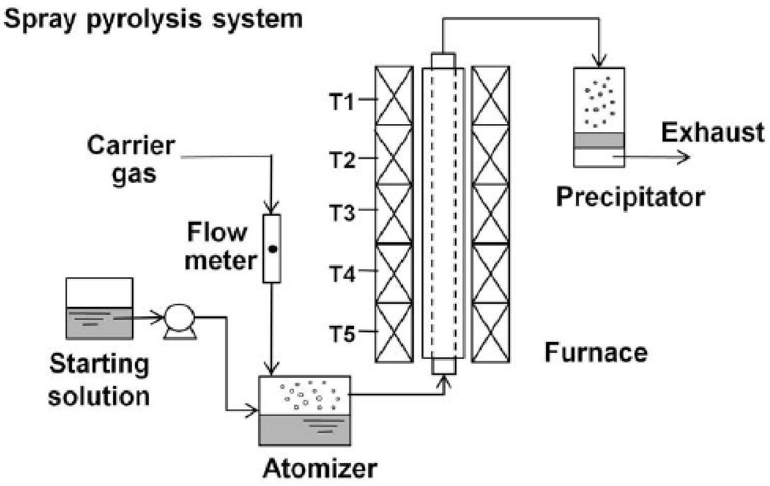
Vapor Phase Synthesis Methods

Discussed are:

- Pyrolysis

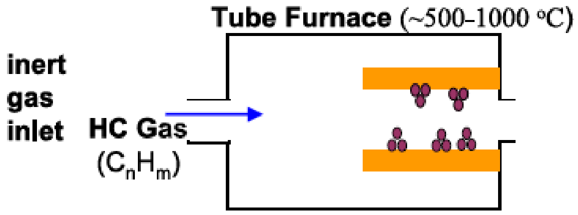
  (Spray Pyrolysis)

  Spray pyrolysis is the aerosol process that atomizes a solution and heats the droplets to produce solid particles

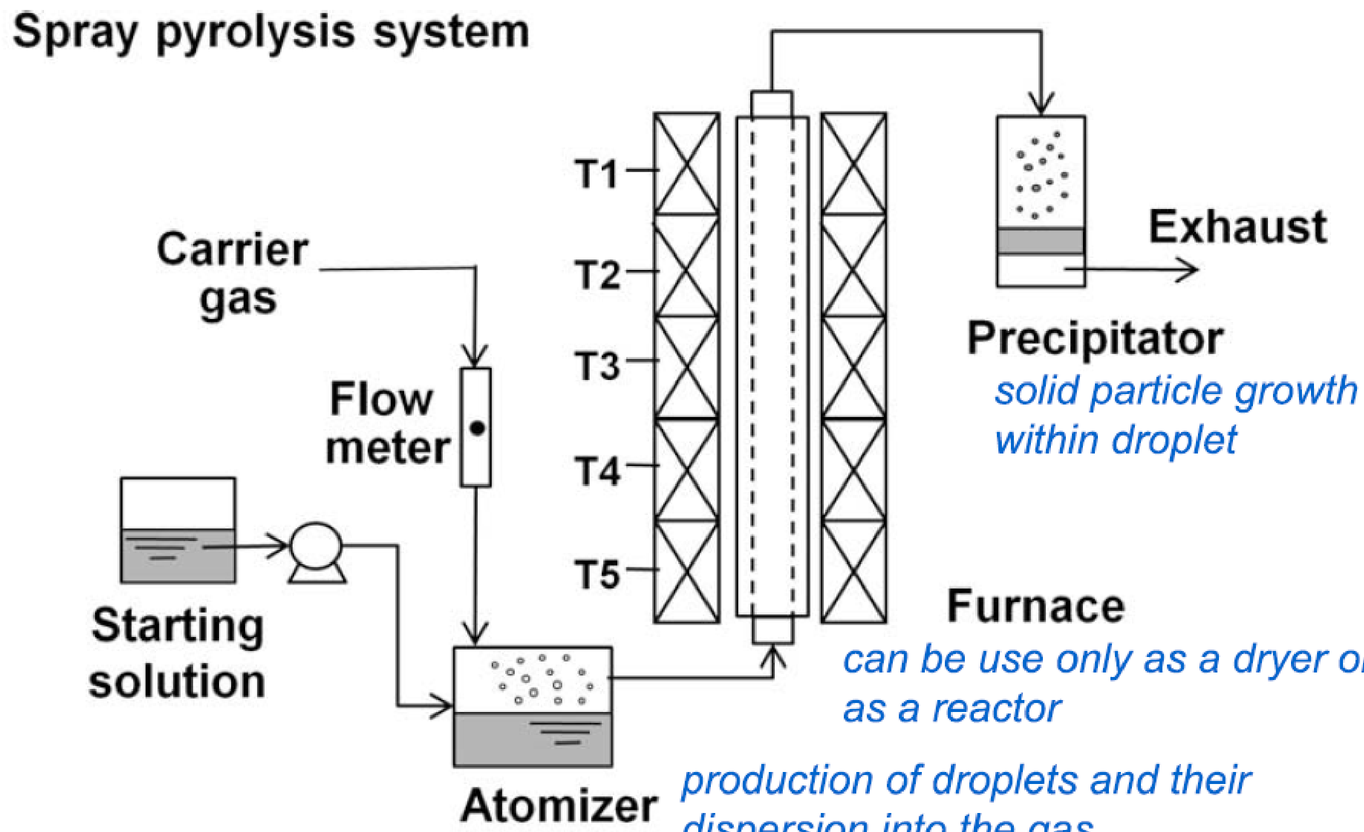


- Inert Gas Condensation

  (Chemical Vapor Deposition)



Spray Pyrolysis



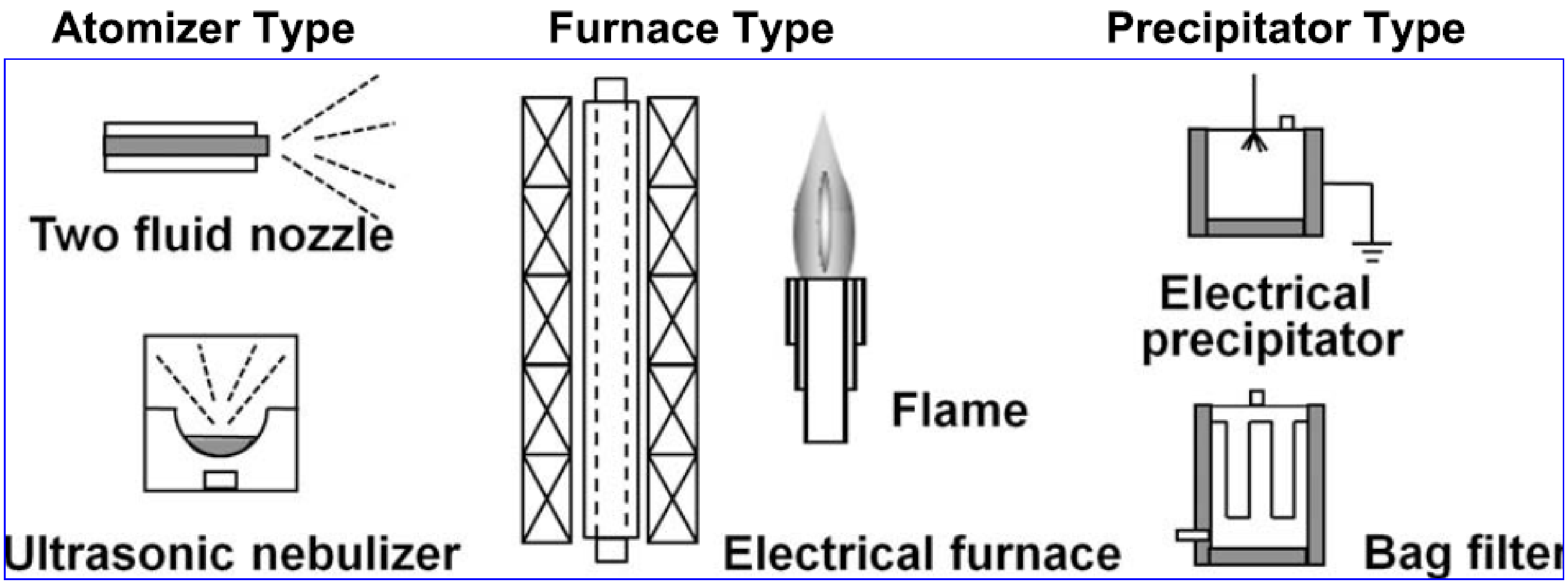
solid particle growth within droplet

can be use only as a dryer or also as a reactor

production of droplets and their dispersion into the gas

F. Iskandar, Adv. Powder Techn. **20** (2009) 283

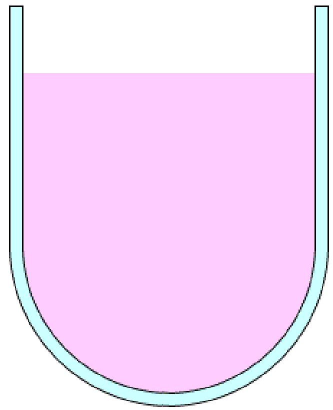
Spray Pyrolysis

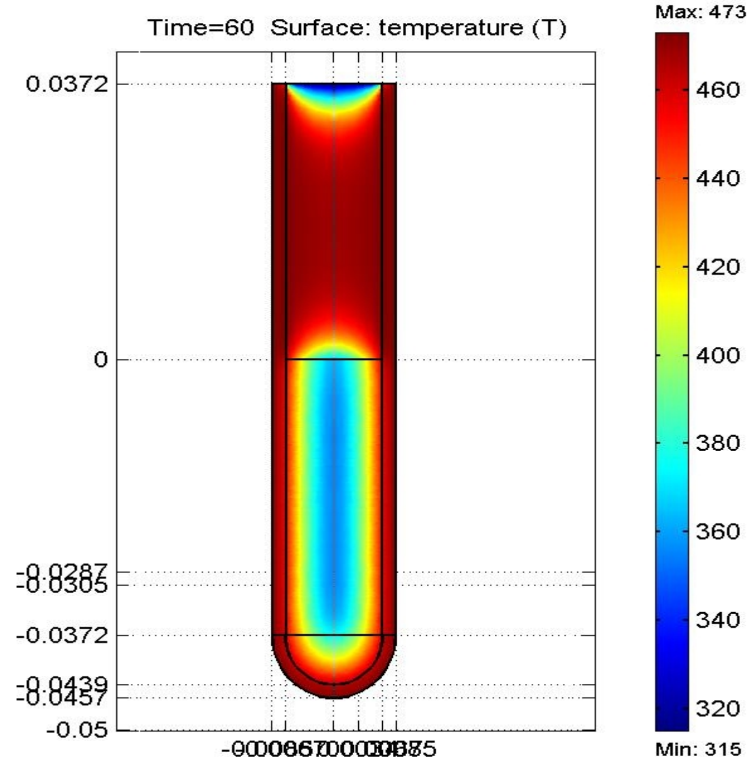


F. Iskandar, Adv. Powder Techn. **20** (2009) 283

Conventional Heating by Conduction

- conductive heat
- heating by convection currents
- slow and energy inefficient process

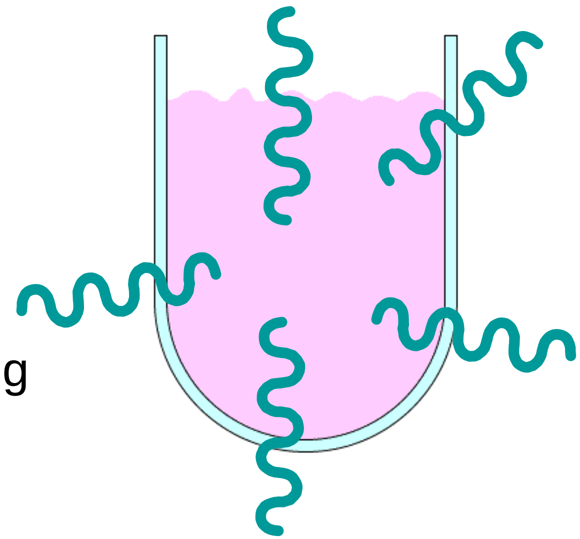


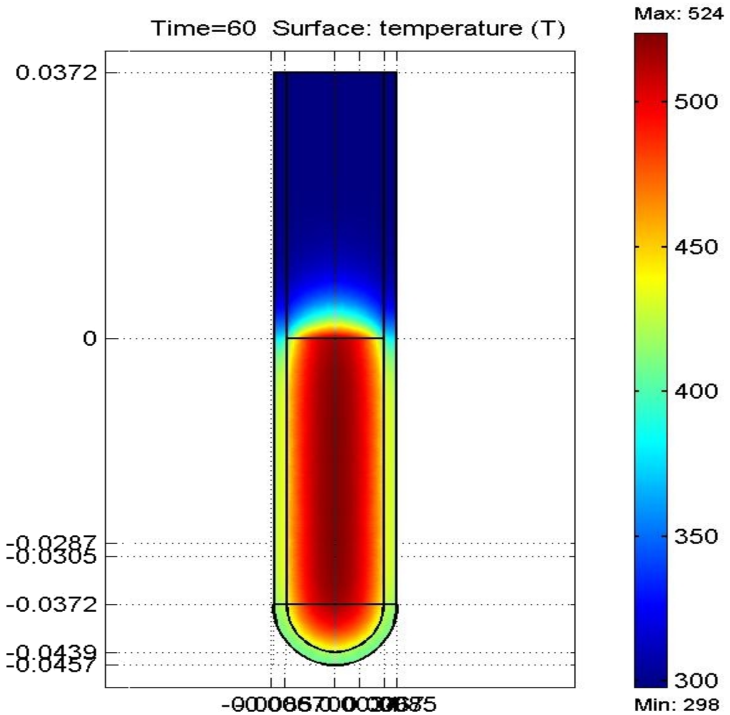


The temperature on the outside surface is in excess of the boiling point of liquid

Heating by Microwave Irradiation

- Solvent/reagent absorbs MW energy
- Vessel wall transparent to MW
- Direct in-core heating
- Instant on-off



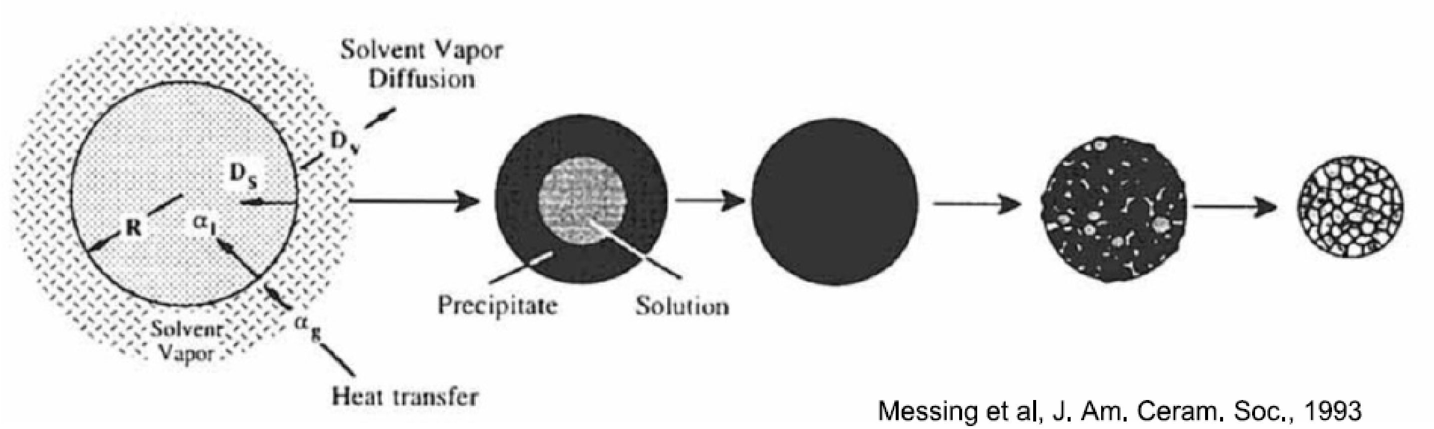


inverted temperature gradients !

Spray Pyrolysis

Droplet Evolution

Evaporation Precipitation Drying Decomposition Sintering



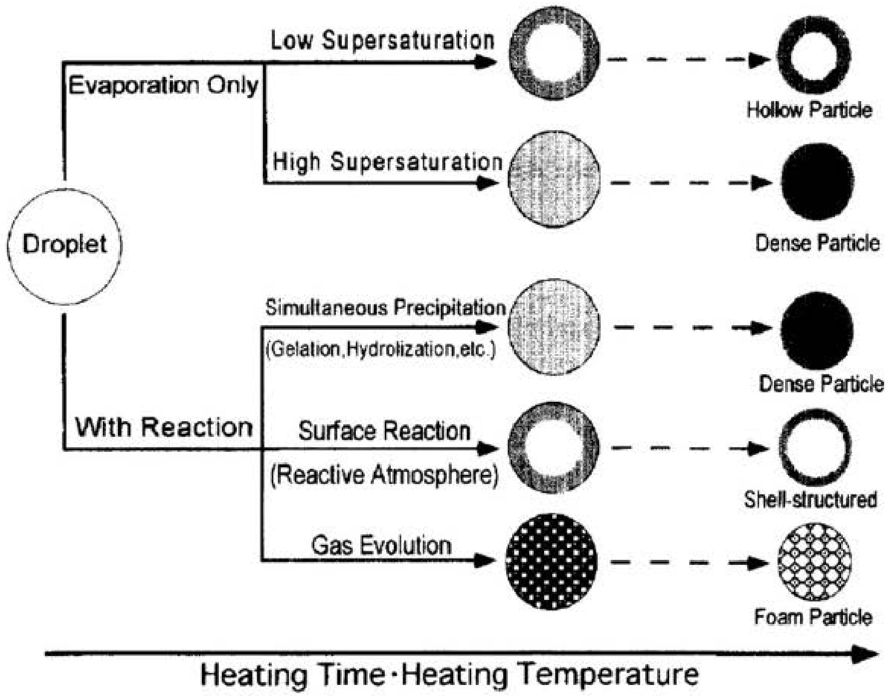
Messing et al, J. Am. Ceram. Soc., 1993

If the solute concentration at the center of the drop is less than the equilibrium saturation of the solute at the droplet temperature, then precipitation occurs only in that part of the drop where the concentration is higher than the equilibrium saturation, i.e., surface precipitation.

Spray Pyrolysis

Precipitation Control

Messing et al, J. Am. Ceram. Soc., 1993



Che et al, J. Aer. Sci., 1998

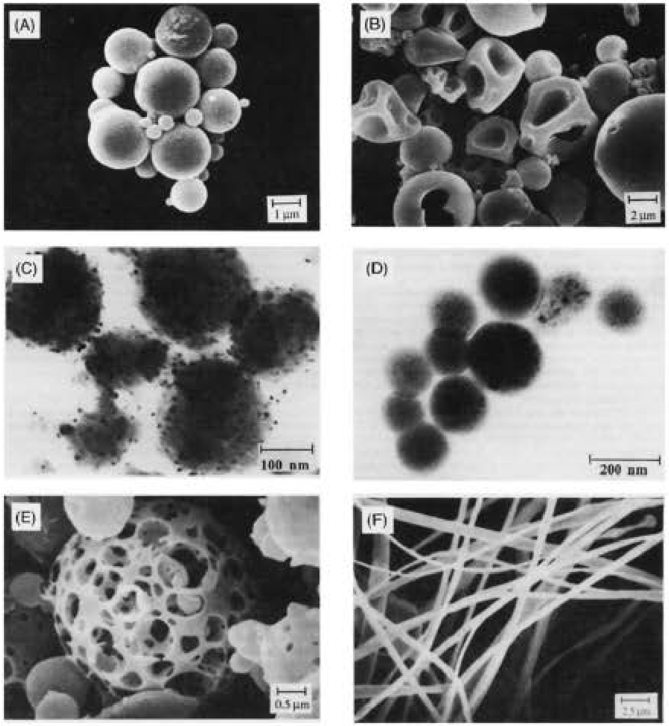
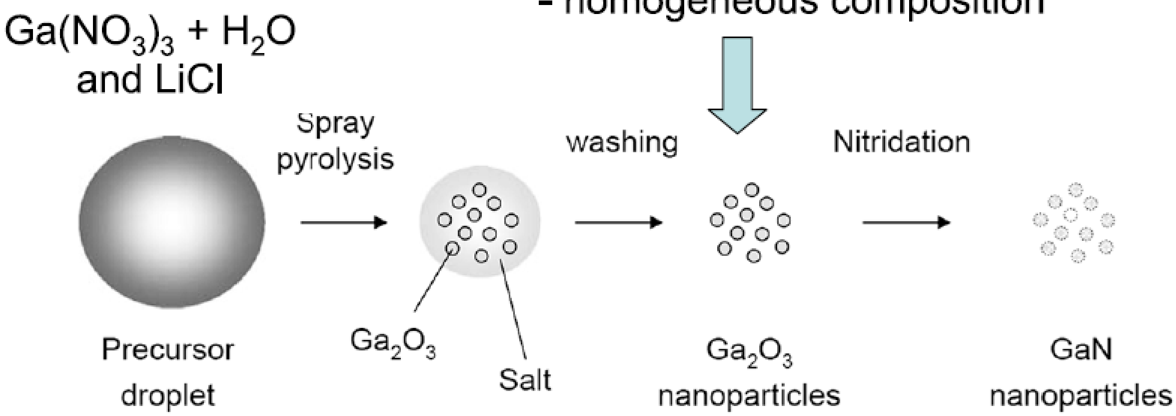
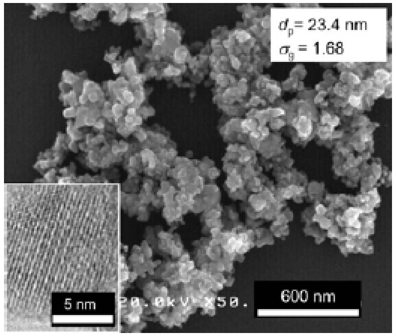


Fig. 3. Various morphologies of particles produced by SP processes: (A) solid ZrO_2 particles derived from 0.1*M* ZHC solution, (B) irregular ZrO_2 particles derived from 1*M* ZAC solution, (C) Al_2O_3/platinum nanocomposite particles derived from 0.5*M* $Al_2(SO_4)_3$–H_2PtCl_6 solution, (D) Al_2O_3/platinum nanocomposite particles derived from 0.5*M* $Al(OBu^s)_3$–H_2PtCl_6 solution, (E) catalyst particles derived from 0.1*M* NH_4VO_3–H_3PO_4–citric acid solution, and (F) Y_2O_3-stabilized ZrO_2 discontinuous fiber derived from ZAC–6 wt%–PVOH–surfactant solution.

Spray Pyrolysis: $Ga(NO_3)_3$ and GaN

Goal: Fabricate GaO_3 with
- narrow size distribution, and
- homogeneous composition



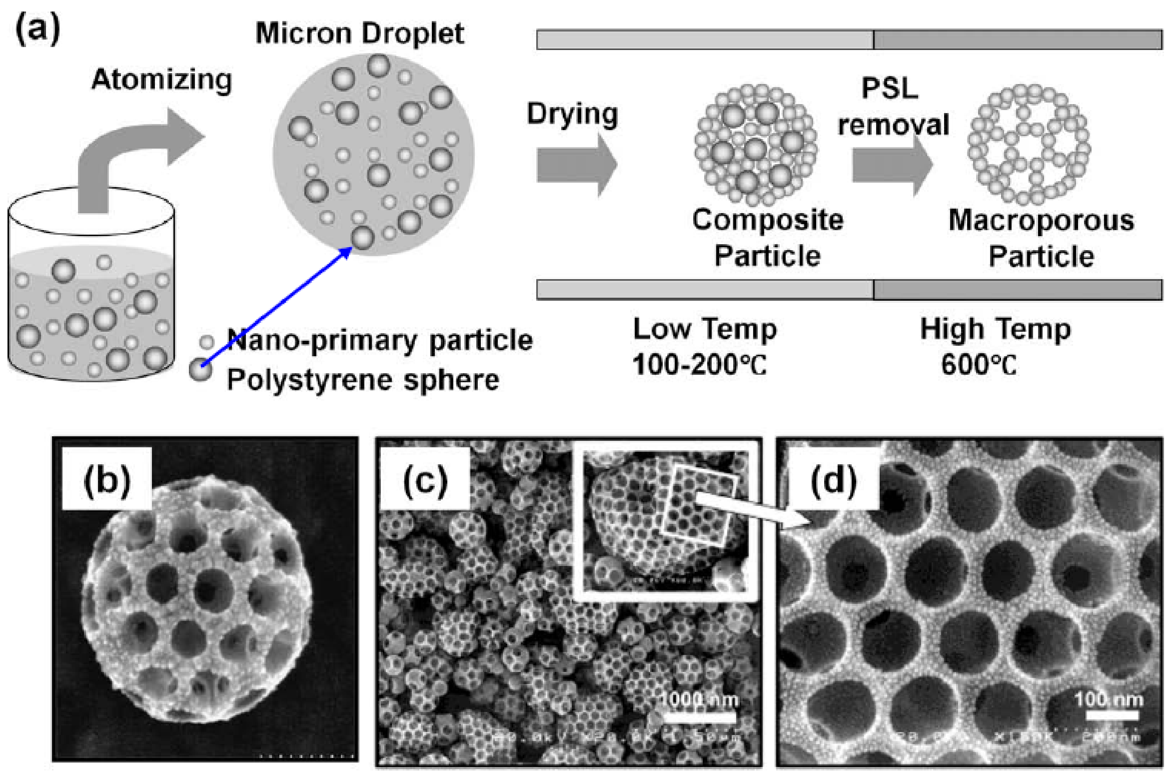


GaN nanoparticles of
23.4 ± 1.7 nm diameter

T. Ogi et al., Adv. Powder Technology 20 (2009) 29

Spray Pyrolysis: Porous Silica NP

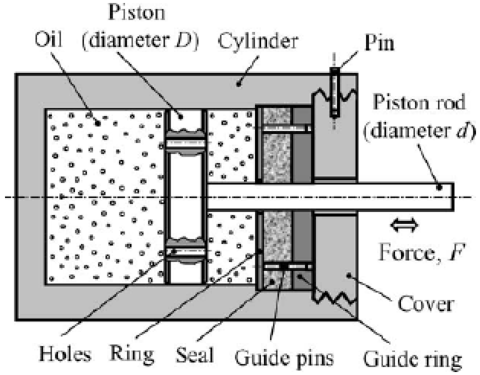
Pyrolysis: Generate droplet mixtures of “Primary Particles” with Polymer Particles



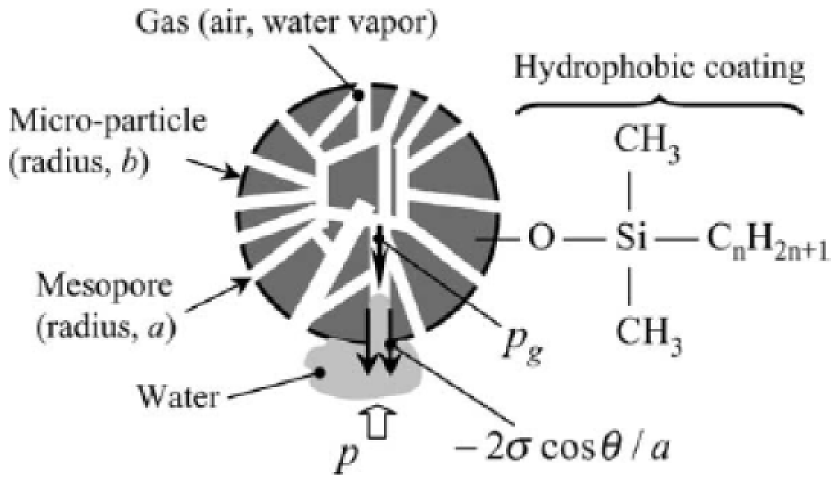
F. Iskandar / Advanced Powder Technology 20 (2009) 283

Porous Silica NP Application: Colloidal Damper

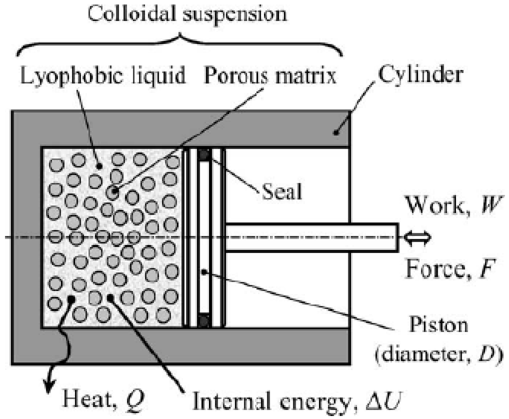
Hydraulic Damper (oil is working fluid, energy is dissipated via orifice flow)



Hydrophobized porous silica particle (outside and inside) suspended in water as the working fluid



Colloidal Damper

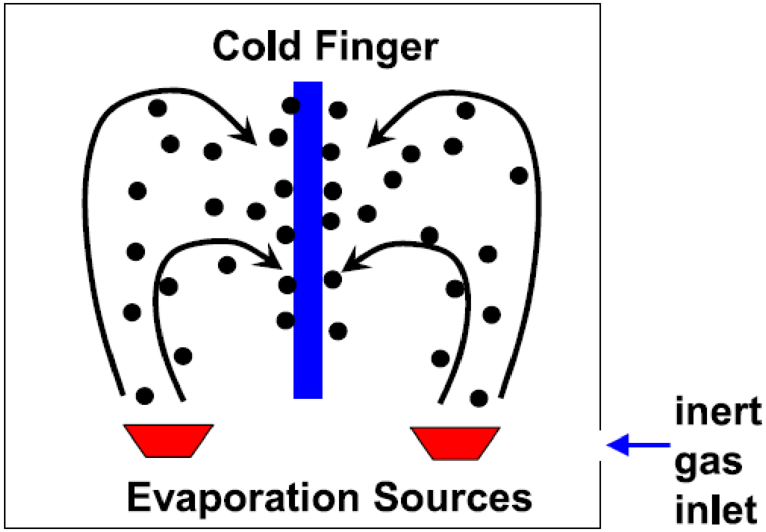


Advantage: Little heat generation in colloidal damper.

C.V. Suciu et al., J. Coll. Interf. Sci., 259 (2003) 62.

Inert Gas Condensation (IGC)

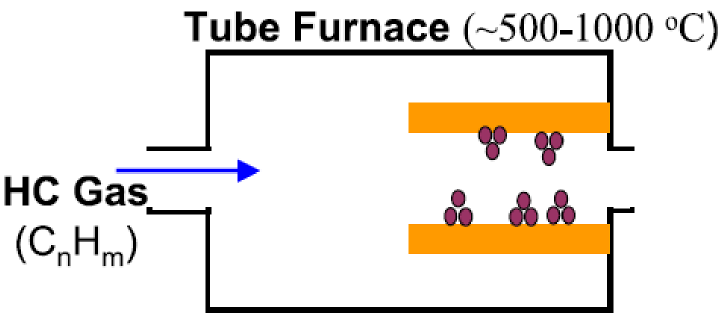
Entails the evaporation of a course substance in an inert gas atmosphere.



Methods:

- Physical Vapor Deposition (PVD)
  (no catalytic interaction)

- Chemical Vapor Deposition (CVD)
  (with catalytic interaction)



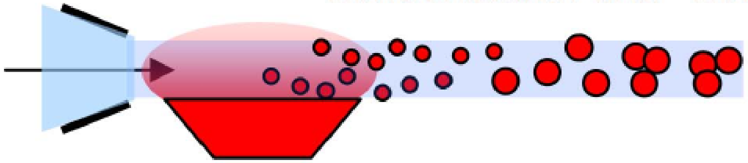
F. Iskandar, Adv. Powder Techn. **20** (2009) 283

Coalescence and Agglomeration

One of the big challenges in condensation growth is that the particles coalesce and agglomerate.

A solution proposed: **Use of a gas jet stream.** A jet stream of carrier gas positioned above the evaporation sites is used to carry away the metal vapor.
Utilize that carrier gas vapor mixture cools downstream

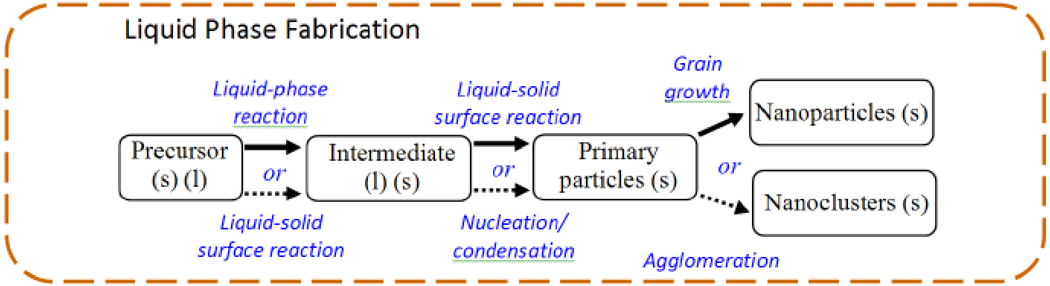
→**Continuous Particle growth**
(nucleation, condensation and coagulation)



2.1 Liquid-Phase Synthesis

- Coprecipitation
- Sol-gel Processing
- Microemulsions
- Hydrothermal/Solvothermal Synthesis
- Microwave Synthesis
- Sonochemical Synthesis
- Template Synthesis
- Biomimetic Synthesis

Mechanism and Effectiveness



(i) precursor solution (typically involves a catalyst)

(ii) nucleation, and

(iii) growth stage

Effectiveness demands:

- simple process
- low cost
- continuous operation
- high yield

} Sol-Gel and Solvothermal Synthesis

Coprecipitation

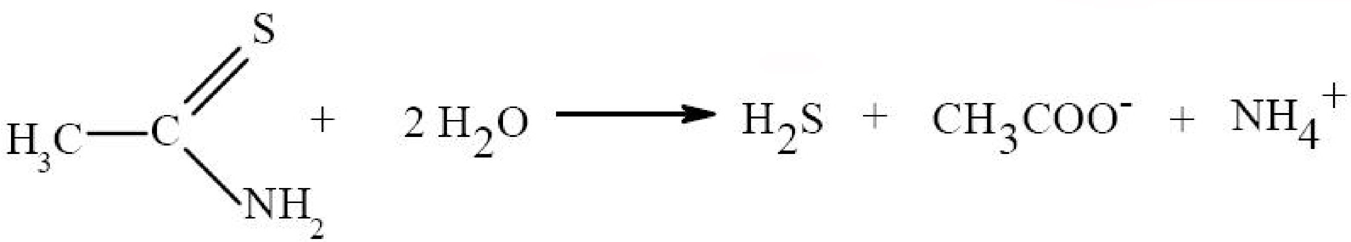
Coprecipitation reactions involve the simultaneous occurrence of nucleation, growth, coarsening, and/or agglomeration processes.

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.

$$xA^{y+}(aq) + yB^{x-}(aq) \leftrightarrow A_xB_y(s)$$

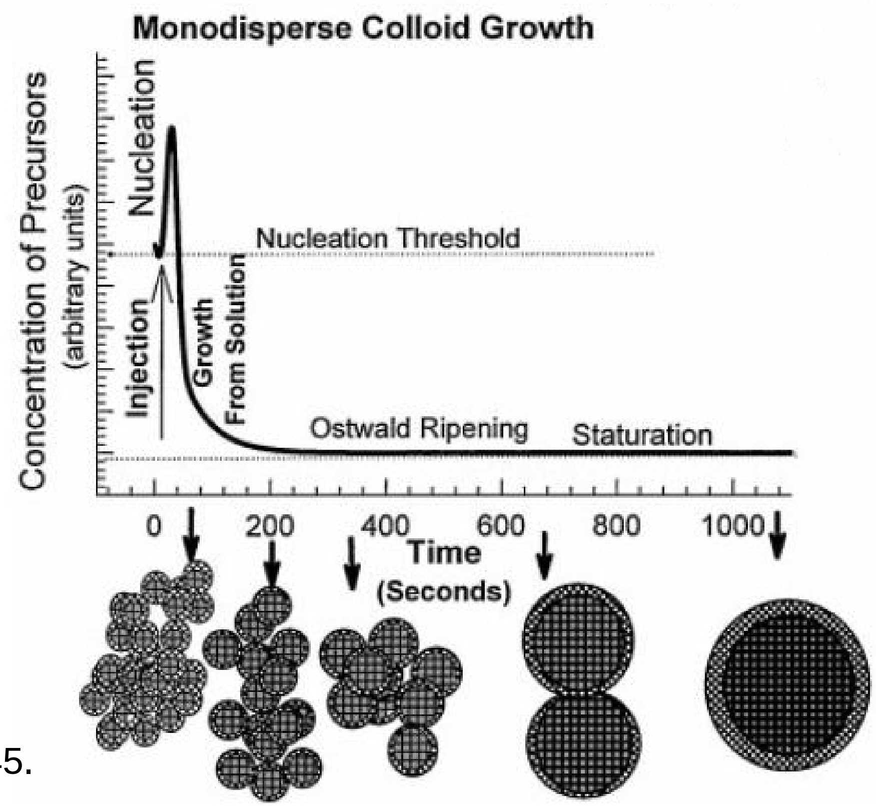
Typical coprecipitation synthetic methods: (i) metals formed from aqueous solutions, by reduction from nonaqueous solutions, electrochemical reduction, and decomposition of metallorganic precursors; (ii) oxides formed from aqueous and nonaqueous solutions; (iii) metal chalconides formed by reactions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

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



Thioacetamide is used as a sulfide source.

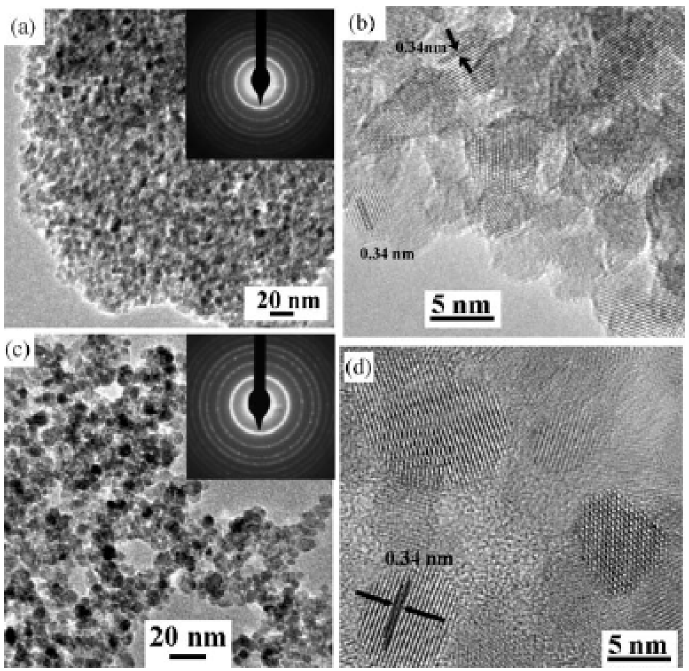
$Zn^{2+} + S^{2-} \rightarrow$ **ZnS**



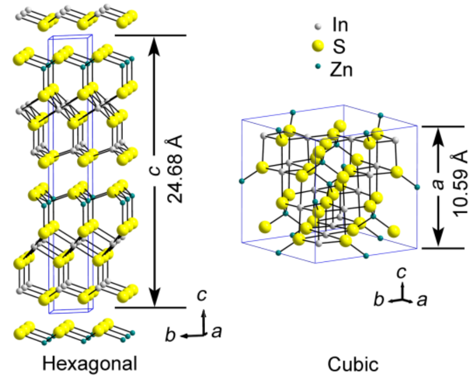
Murray C.B. et al., *Annu. Rev. Mater. Sci.* **2000**, *30*, 545.

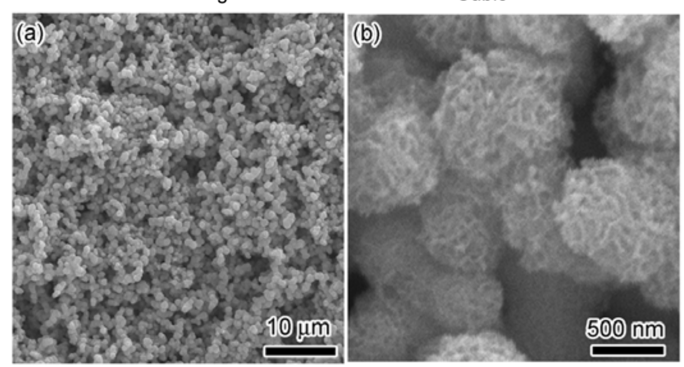
Hydrothermal/Solvothermal Synthesis

In a sealed vessel (bomb, autoclave, etc.), solvents can be brought to temperatures well above their boiling points by the increase in autogenous pressures resulting from heating. Performing a chemical reaction under such conditions is referred to as solvothermal processing or, in the case of water as solvent, hydrothermal processing.



TiO_2





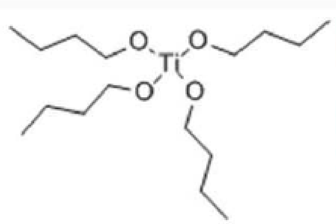
$ZnIn_2S_4$

Yu, J. C. et al. *J. Solid State Chem.* **2005**, *178*, 321; *Cryst. Growth Des.* **2007**, *7*, 1444

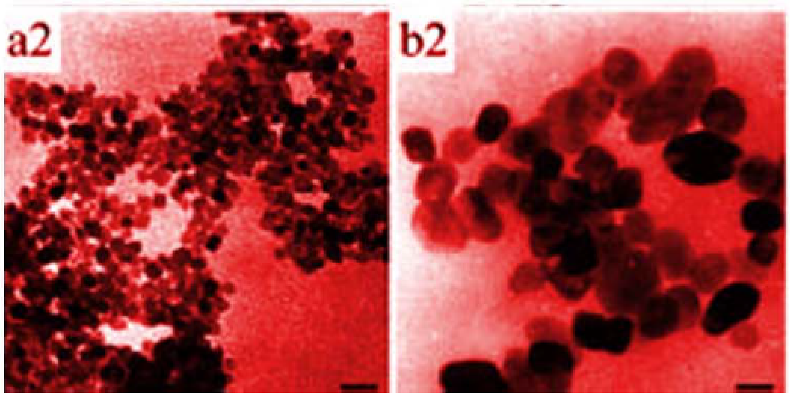
Solvothermal Synthesis

- Precursors are dissolved in hot solvents (e.g., n-butyl alcohol)
  - Solvent other than water can provide milder and friendlier reaction conditions If the solvent is water then the process is referred to as hydrothermal method.

Precursor: Titanium n-butoxide

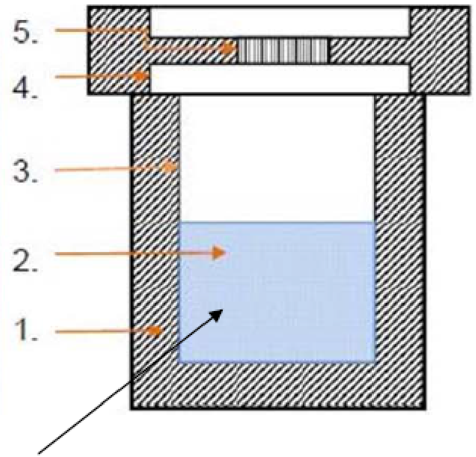


Example: TiO_2 Nanocrystallites



X.F. Yang et al., Euro. J. Inorganic Chem., 2229 (2006).

Autoclave



Precursor solution with butyl alcohol

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).

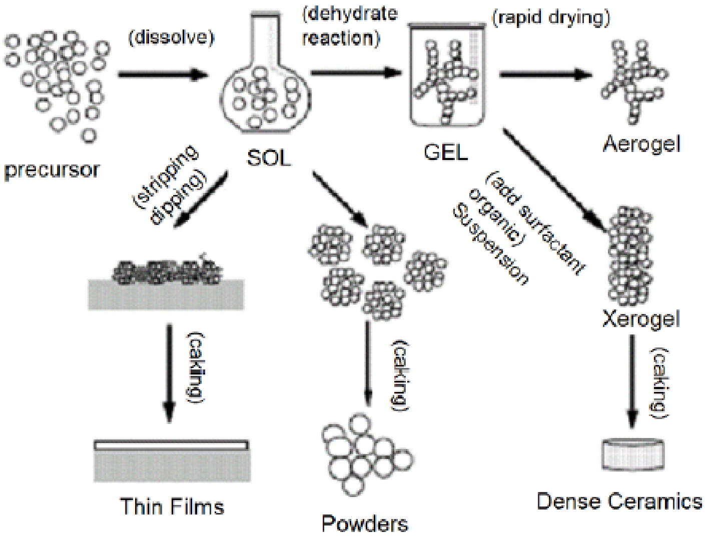
Metal alkoxides and metal chlorides are typical precursors. They undergo hydrolysis and polycondensation reactions to form a colloid, a system composed of nanoparticles dispersed in a solvent. The sol evolves then towards the formation of an inorganic continuous network containing a liquid phase (gel).

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.

Sol-Gel Steps:

- Formation of stable sol solution
- Gelation via a polycondensation or polyesterification reaction
- Gel aging into a solid mass. → causes contraction of the gel network, also
  (i) phase transformations and
  (ii) Ostwald ripening.
- Drying of the gel to remove liquid phases. Can lead to fundamental changes in the structure of the gel.
- Dehydration at temperatures as high as 8000 °C, used to remove M-OH groups for stabilizing the gel, i.e., to protect it from rehydration.
- Densification and decomposition of the gels at high temperatures (T > 8000 oC), i.e., to collapse the pores in the gel network and to drive out remaining organic contaminants



Sol-Gel Processing

- Creation of Sol (solid particles in solution)
- Followed by the following two generic sol-gel processes (assuming as a precursor a metal alkoxide MOR):

hydrolysis: –MOR + H2O → –MOH + ROH

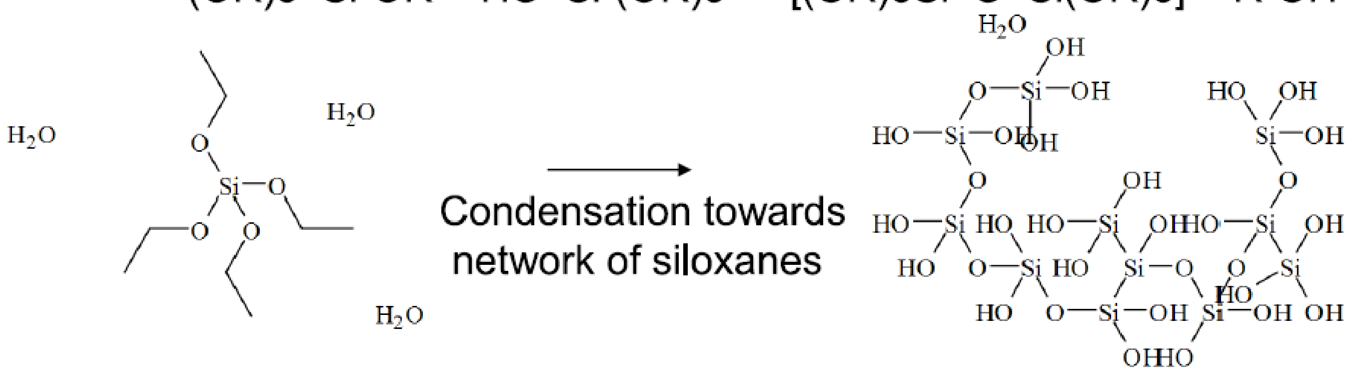
Ex.: $Si(OR)_4 + 4\ H_2O \rightarrow Si(OH)_4 + 4\ R\text{-}OH$

condensation: –MOH + ROM– → –MOM– + ROH

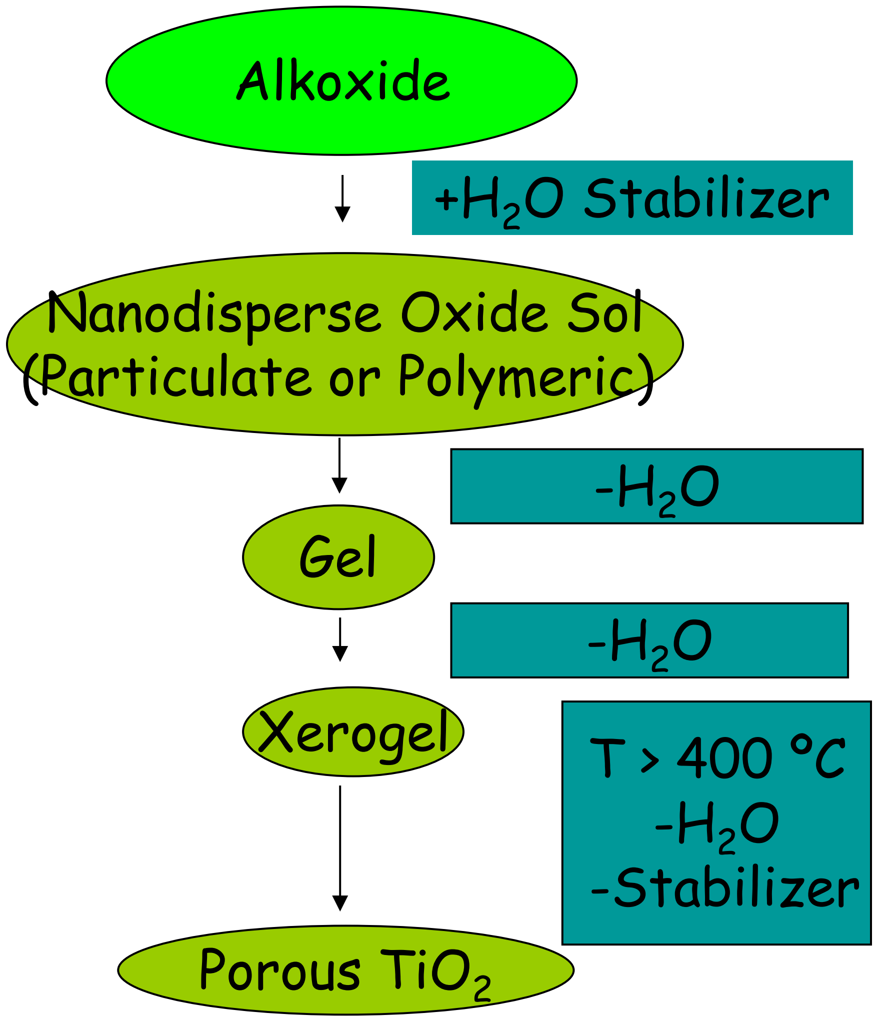
$(OR)_3\text{–}Si\text{-}OH + HO\text{–}Si\text{-}(OR)_3 \rightarrow [(OR)_3Si\text{–}O\text{–}Si(OR)_3] + H\text{-}O\text{-}H$

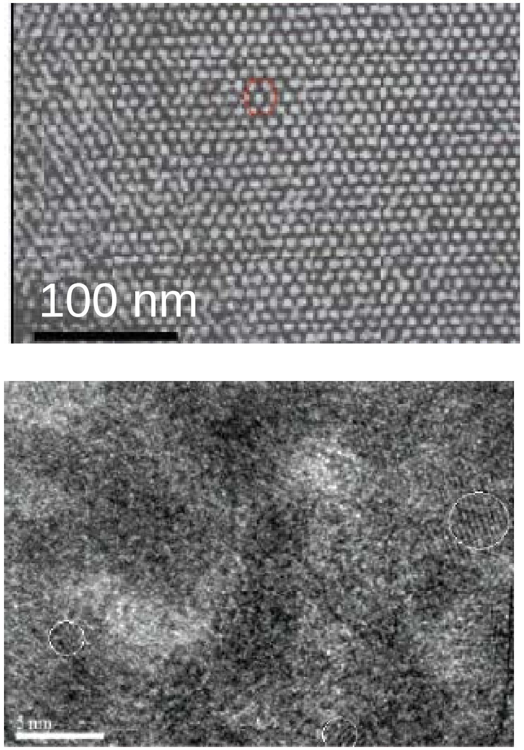
or –MOH + HOM– → –MOM– + H2O

(OR)3–Si-OR + HO–Si-(OR)3 → [(OR)3Si–O–Si(OR)3] + R-OH



Example: TiO_2 nanoparticle-mediated mesoporous film by sol-gel processing

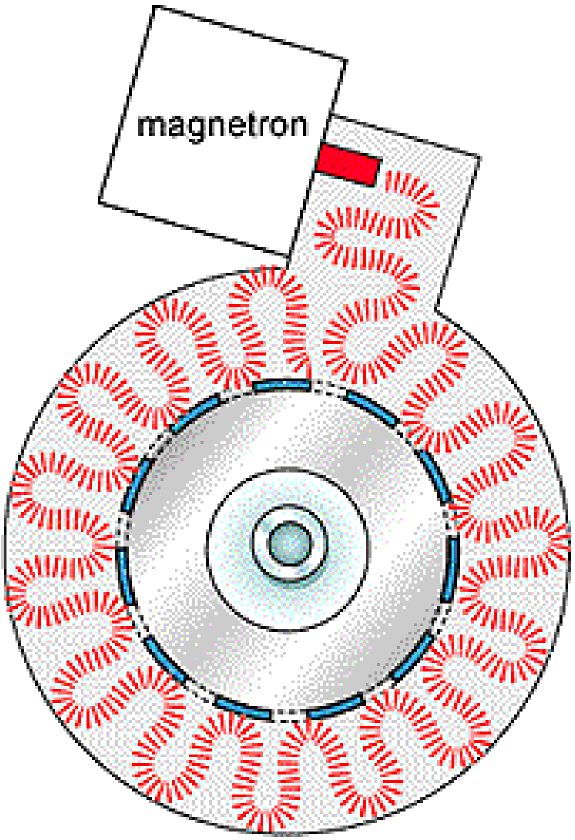




TiO_2 nanoparticle-mediated mesoporous film (Yu, J. C. et al. *Chem. Mater.* **2004**, 16, 1523.)

Microwave-Assisted Synthesis

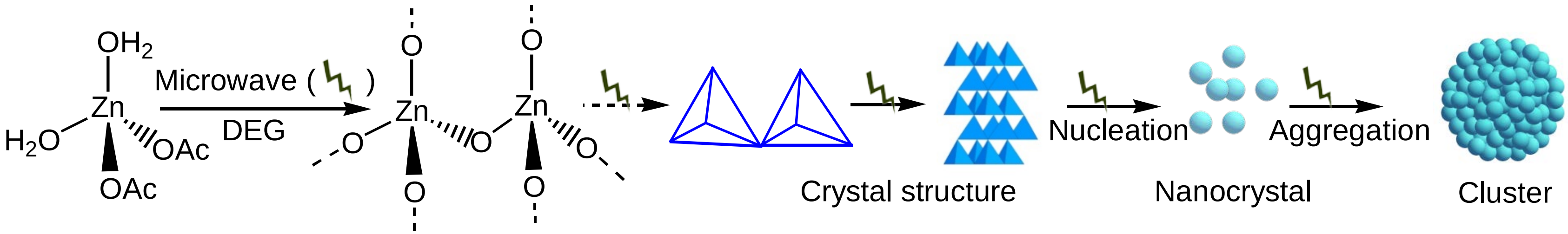
Microwaves are a form of electromagnetic energy with frequencies in the range of 300 MHz to 300 GHz. The commonly used frequency is 2.45G Hz.

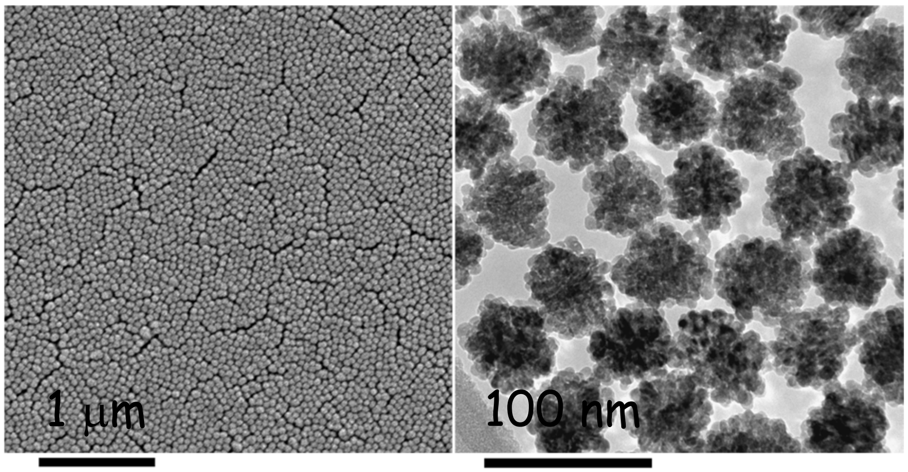


Interactions between materials and microwaves are based on two specific mechanisms: dipole interactions and ionic conduction. Both mechanisms require effective coupling between components of the target material and the rapidly oscillating electrical field of the microwaves.

Dipole interactions occur with polar molecules. The polar ends of a molecule tend to re-orientate themselves and oscillate in step with the oscillating electrical field of the microwaves. Heat is generated by molecular collision and friction. Generally, the more polar a molecule, the more effectively it will couple with the microwave field.

Example: Microwave-assisted synthesis of ZnO nanoparticles





Schematic representation and transmission electron microscope (TEM) images of ZnO-cluster nanoparticles prepared by microwave irradiation

Yu, J. C. et at., *Adv. Mater.* 2008, in press.

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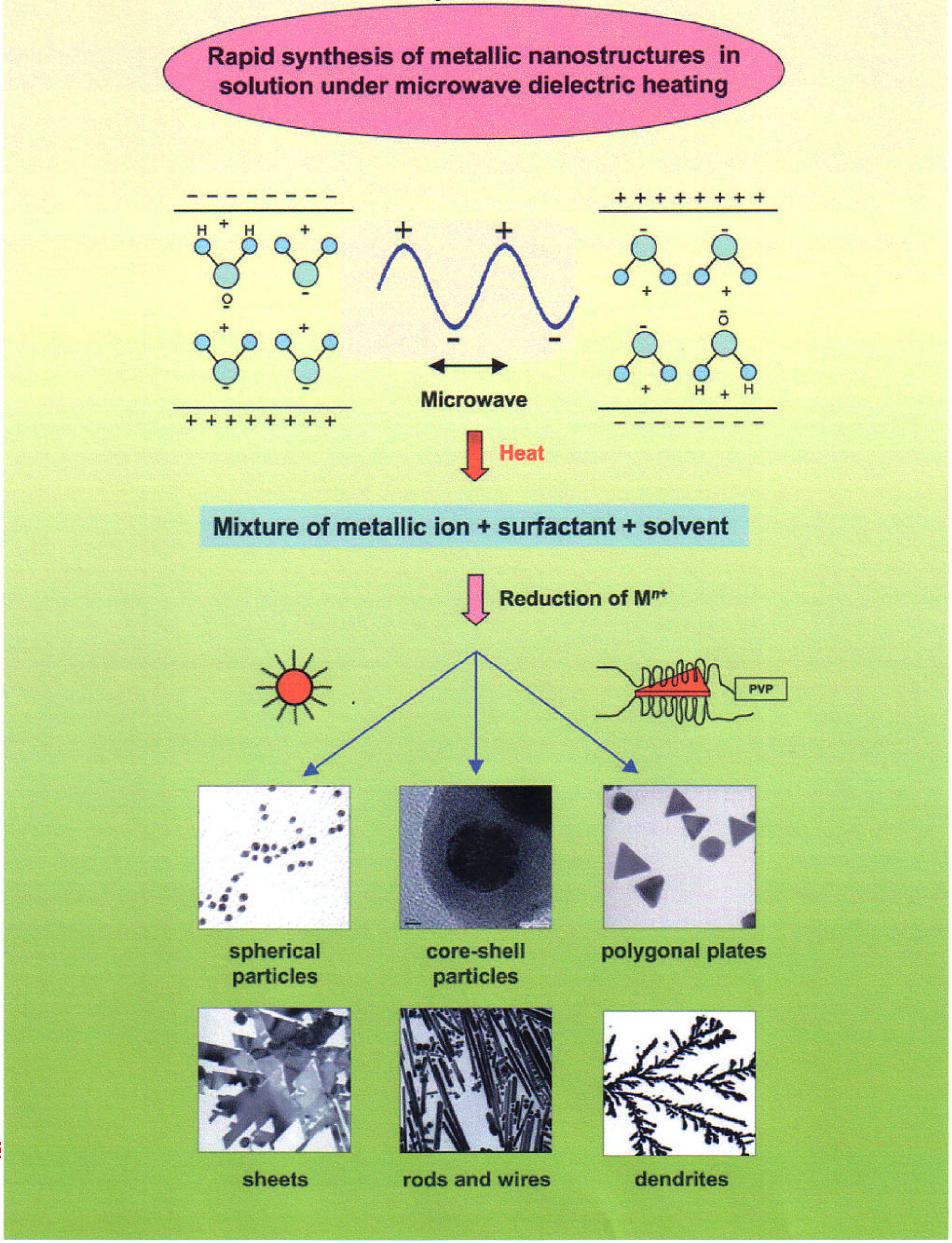
Tsuji M. et al.



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DOI: 10.1002/chem.200400417 Chem. Eur. J. 2005, 11, 440–452

Microwave (MW) rapid heating has received considerable attention as a new promising method for the one-pot synthesis of metallic nanostructures in solutions.

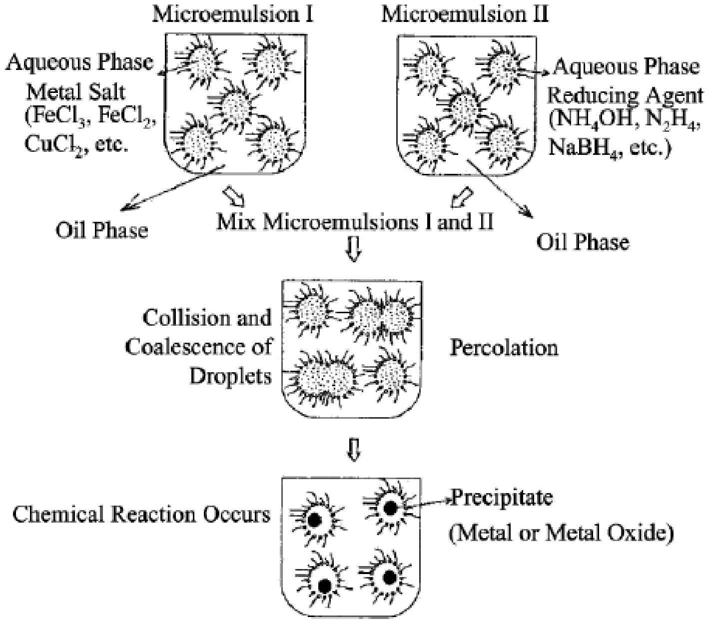
In this concept, advantageous application of this method has been demonstrated by using some typical examples for the preparation of Ag, Au, Pt, and AuPd nanostructures. Not only spherical nanoparticles, but also single crystalline polygonal plates, sheets, rods, wires, tubes, and dendrites were prepared within a few minutes under MW heating. Morphologies and sizes of nanostructures could be controlled by changing various experimental parameters, such as the concentration of metallic salt and surfactant polymer, the chain length of the surfactant polymer, the solvent, and the reaction temperature. In general, nanostructures with smaller sizes, narrower size distributions, and a higher degree of crystallization were obtained under MW heating than those in conventional oil-bath heating.

Stanko R. Brankovic

Synthesis in Structured Medium

Influence Growth Kinetics by Imposing Constraints in Form of Matrices:

- Zeolites
- Layered Solids
- Molecular Sieves
- Micelles/Microemulsions
- Gels
- Polymers
- Glasses

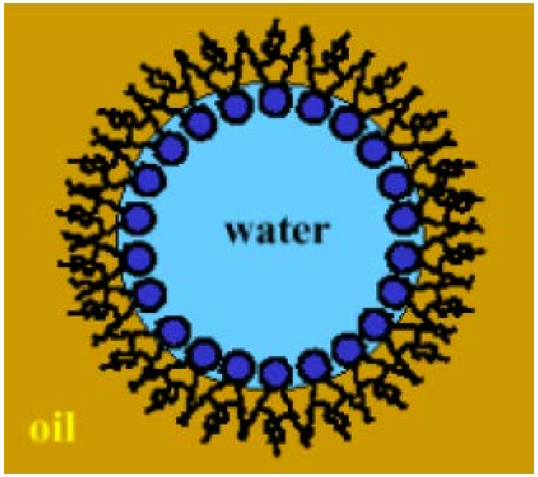


Ex.: Mixing of two Microemulsion carrying metal salt and reducing agent

I. Capek, Adv. Coll. Interf. Sci. 110 (2004) 49

→Intermicellar interchange process via coalescence (rate limiting)
(much slower than diffusion: 10 μs and 1 ms

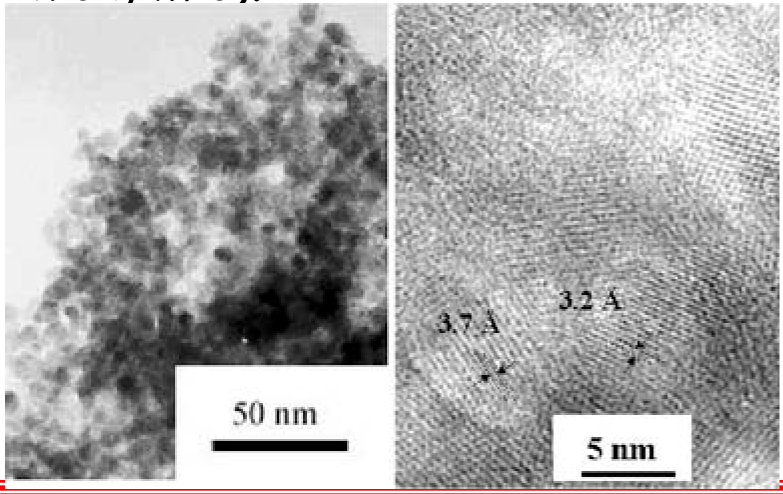
Microemulsion



Microemulsions are clear, stable, isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a cosurfactant.

The aqueous phase may contain salt(s) and/or other ingredients, and the "oil" may actually be a complex mixture of different hydrocarbons and olefins.

The two basic types of microemulsions are direct (oil dispersed in water, o/w) and reversed (water dispersed in oil, w/o).



Nanosized CdS-sensitized TiO_2 crystalline photocatalyst prepared by microemulsion. (Yu, J. C. et al. *Chem. Commun.* **2003**, 1552.)

Sonochemical Synthesis

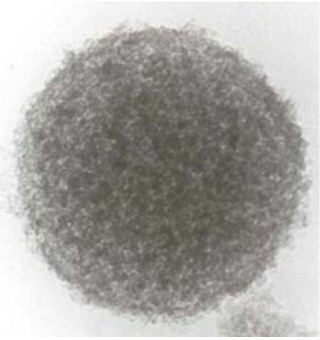
Ultrasound irradiation causes acoustic cavitation -- the formation, growth and implosive collapse of the bubbles in a liquid

The implosive collapse of the bubbles generates a localized hot spots of extremely high temperature (~5000K) and pressure (~20MPa).

The sonochemical method is advantageous as it is nonhazardous, rapid in reaction rate, and produces very small metal particles.

Examples: sonochemical synthesis of mesoporous TiO_2 particles

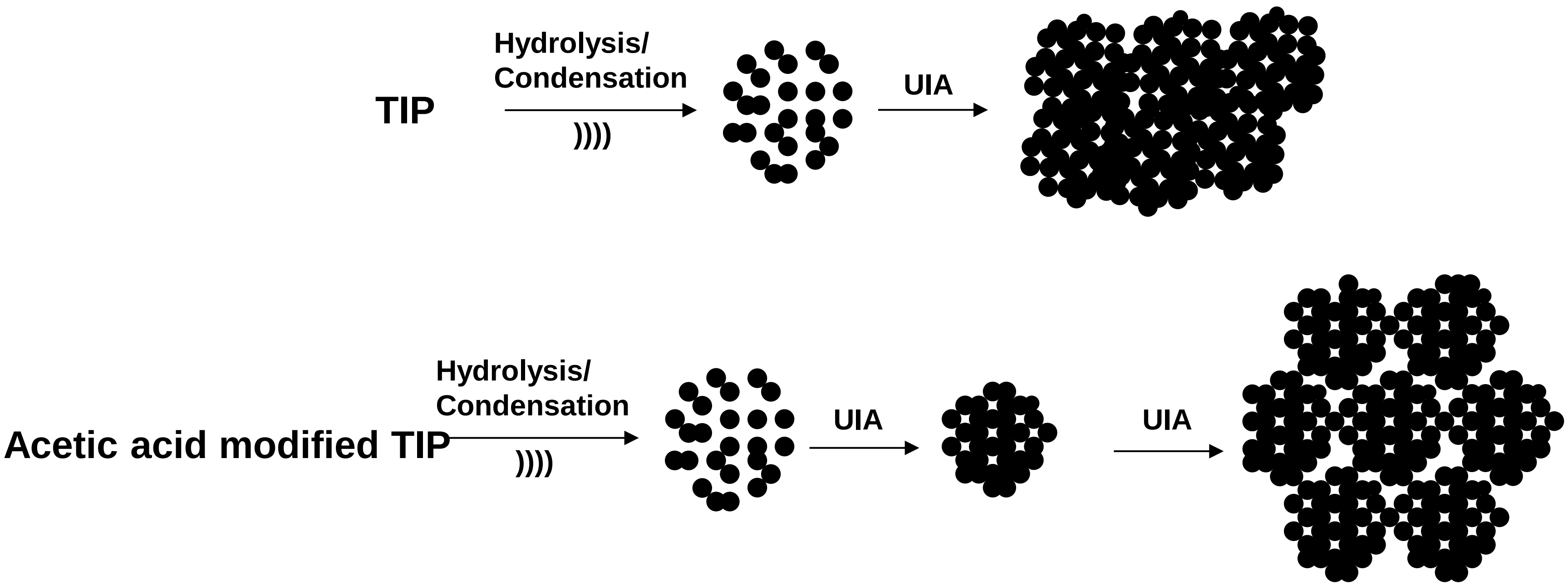
20 kHz sonochemical processor



Mesoporous TiO_2

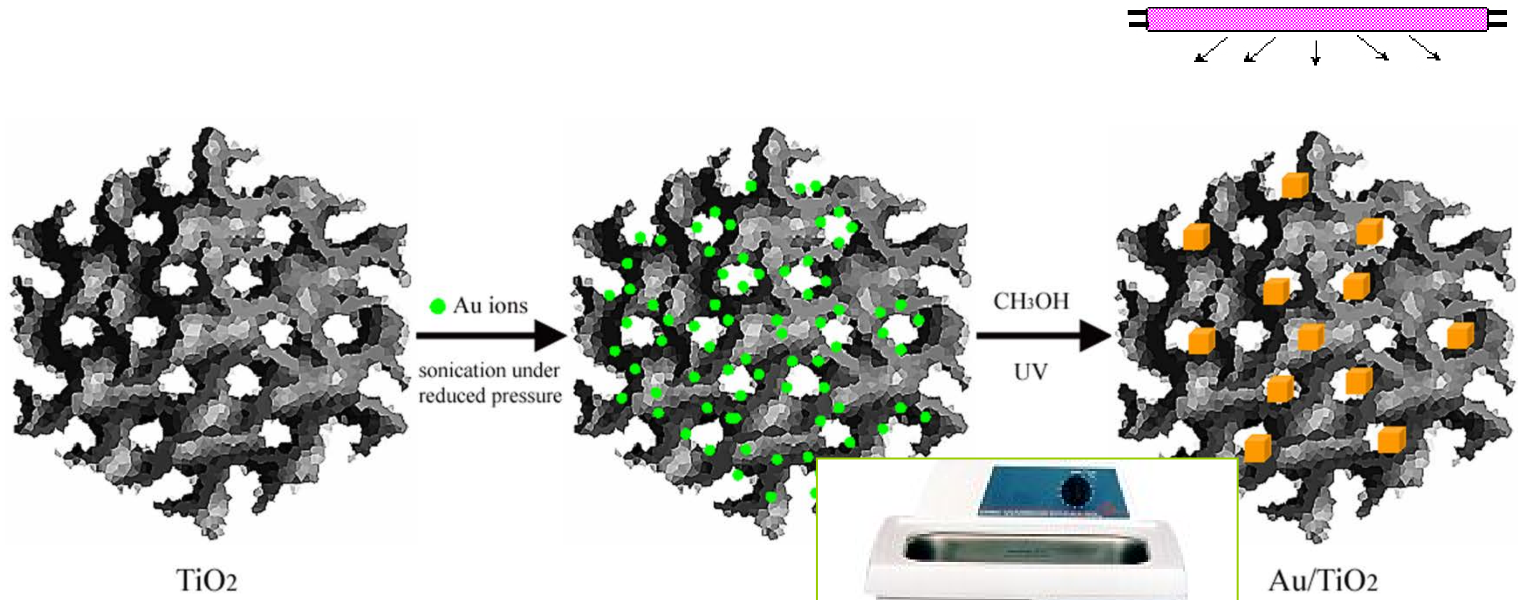
Formation of mesoporous TiO_2 by sonication

TIP: Titanium isopropoxide ● Titanium Oxide Sol Particle **UIA**: Ultrasound Induced Agglomeration



Yu J. C. et al., *Chem. Commun.* **2003**, 2078.

Sono- and Photo-Chemical Deposition of Noble Metal Nanoparticles



40 kHz ultrasound
Cleaning Vessel

Yu J.C. et al., *Adv. Funct. Mater.* **2004**, *14*, 1178.