ECE 5320
Lecture #7

Thermodynamics of Nucleation

$$p = const., T = const$$

$$\Delta G = G_2 - G_1$$

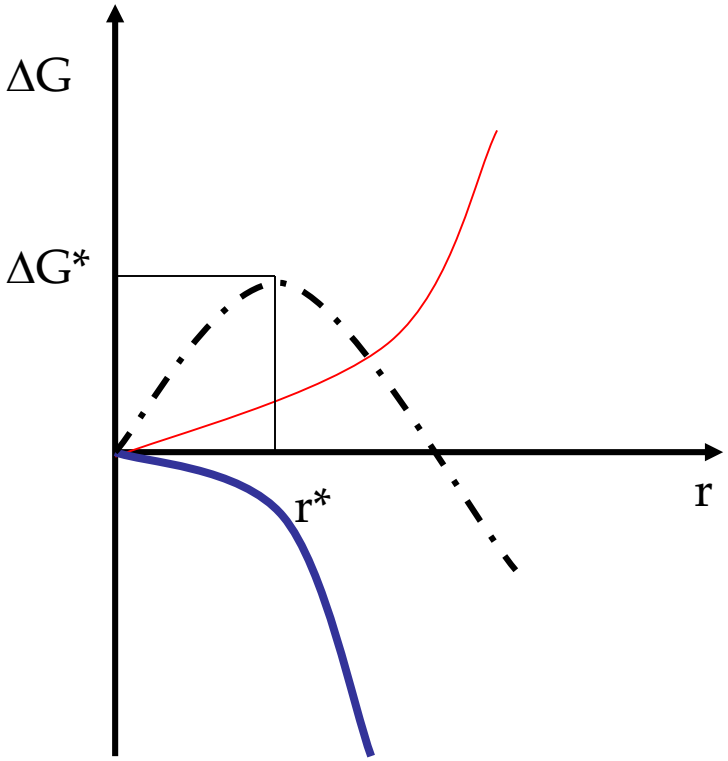
$$\Delta G = -n_l(\mu_g - \mu_l) + 4\pi r^2\gamma;\ \ \mu_g - \mu_l = \Delta\mu$$

$$\Delta G = -\frac{V}{v_{m,l}}\Delta\mu + 4\pi r^2\gamma;\quad V = \frac{4}{3}\pi r^3 (sphere)$$

$$\Delta G(r) = -\frac{4}{3}\pi r^3\frac{\Delta\mu}{v_{m,l}} + 4\pi r^2\gamma;$$

$$\frac{\partial\Delta G}{\partial r} = 0$$

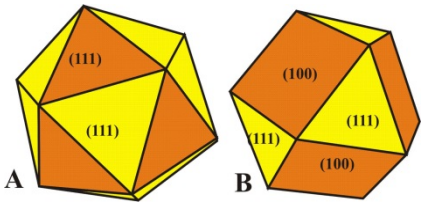
$$\Rightarrow r^* = \frac{2\gamma v_{m,l}}{\Delta\mu}$$



$$\Delta G(r^*) = \Delta G^* = \frac{16\pi}{3}\cdot\frac{\gamma^3 v_{m,l}^2}{\Delta\mu}$$

Thermodynamics of Nucleation

$$\mu_g - \mu_l = \Delta\mu = 2\gamma_l v_{m,l}\frac{1}{r};$$ **GT equation**



$$\Delta G(r^*) = \Delta G^* = \frac{16\pi}{3}\cdot\frac{\gamma^3 v_{m,l}^2}{\Delta\mu}$$

$$\Rightarrow \Delta G^* = \frac{1}{3}4\pi r^{*2}\gamma = \frac{1}{3}\gamma A^*$$

For solids:

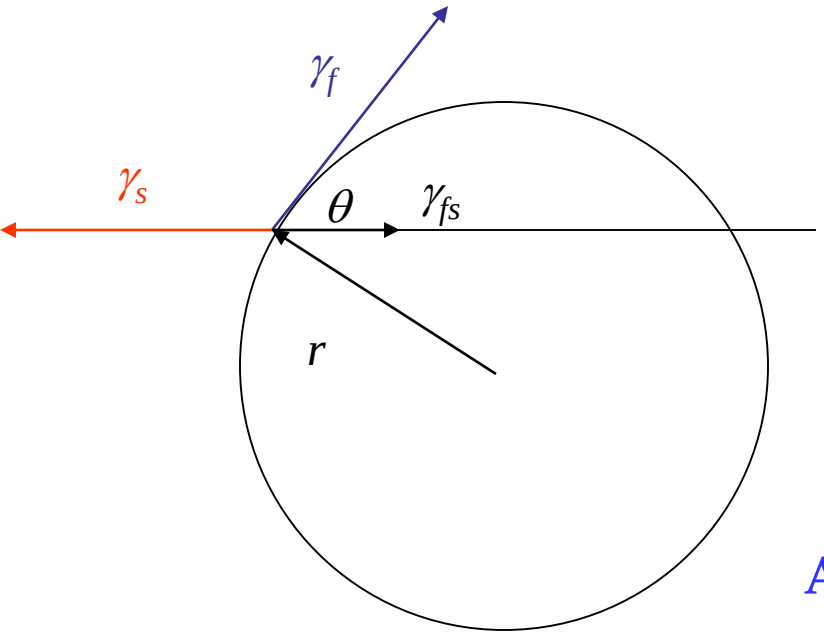
$$\Rightarrow \Delta G^* = \frac{1}{3}\sum \gamma_n A_n$$

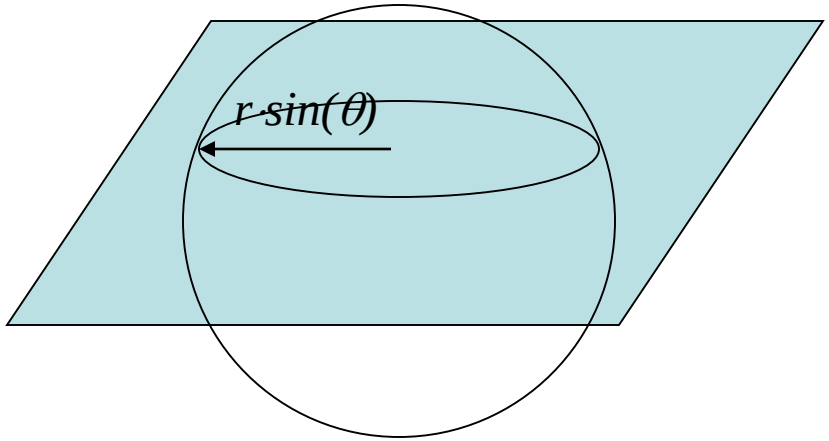
The energy required to form a new stable nucleus of new phase in equilibrium with equilibrium shape and size is equal to one third of the surface energy, *Gibbs, 1878*

Thermodynamics of Nucleation (Heterogeneous)

Young's relation-wetting arguments

$$\gamma_s = \gamma_f \cos(\theta) + \gamma_{fs}$$





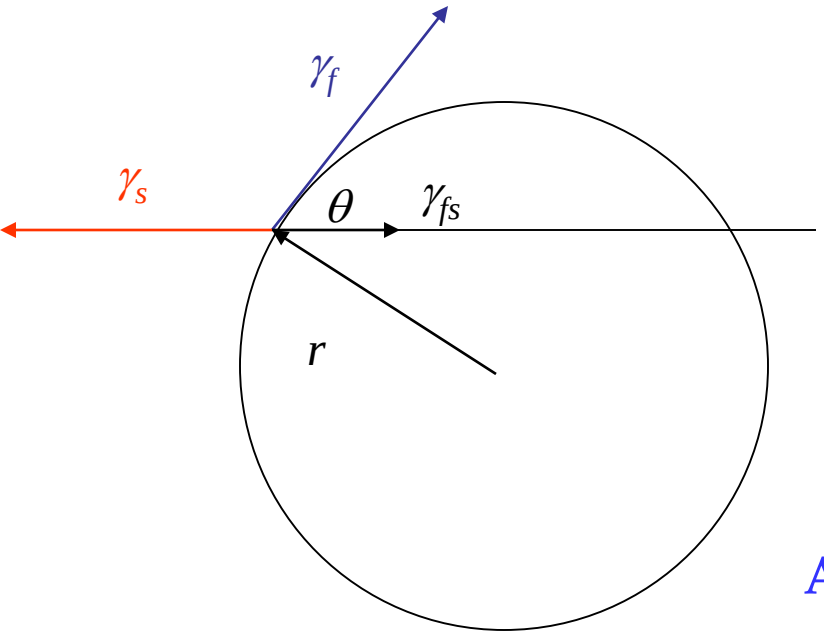
Area of the contact: $A_{sf} = \pi r^2 \sin^2(\theta)$

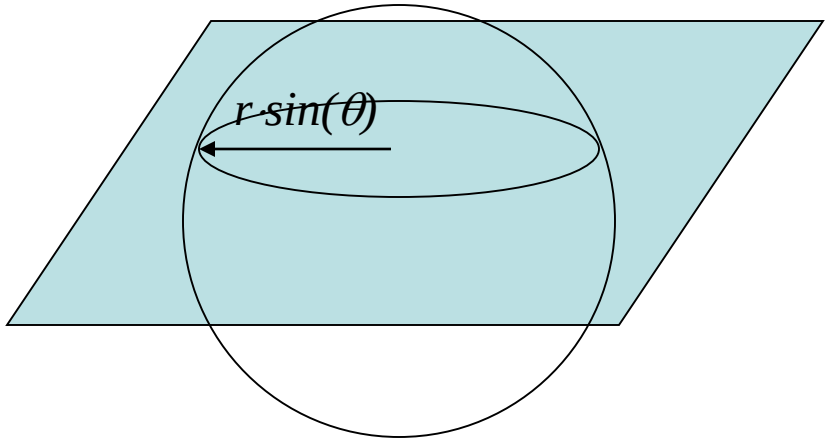
Area of the film: $A_f = 2\pi r^2 (1 - \cos(\theta))$

Thermodynamics of Nucleation (Heterogeneous)

Young's relation-wetting arguments

$$\gamma_s = \gamma_f \cos(\theta) + \gamma_{fs}$$





Area of the contact: $A_{sf} = \pi r^2 \sin^2(\theta)$

Area of the film: $A_f = 2\pi r^2 (1 - \cos(\theta))$

Thermodynamics of Nucleation (Heterogeneous)

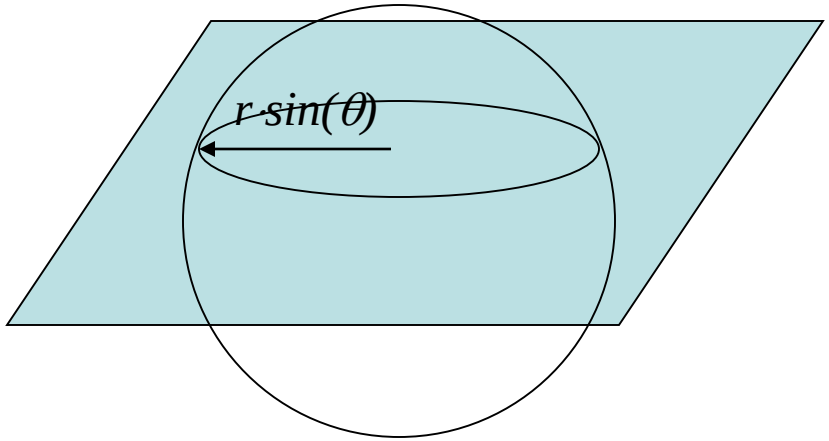
Total surface free energy of the nucleus

$$\Phi = 2\pi r^2(1-\cos(\theta))\gamma_f + \pi r^2 \sin^2(\theta)(\gamma_s - \gamma_{sf})$$

Total volume of the nucleus

$$V_{nuc} = \frac{4}{3} r^3 \pi \frac{(1-\cos(\theta))^2 \cdot (2+\cos(\theta)}{4}$$

$$\phi(\theta) = \frac{(1-\cos(\theta))^2 \cdot (2+\cos(\theta)}{4}$$



Free energy change of nucleation:

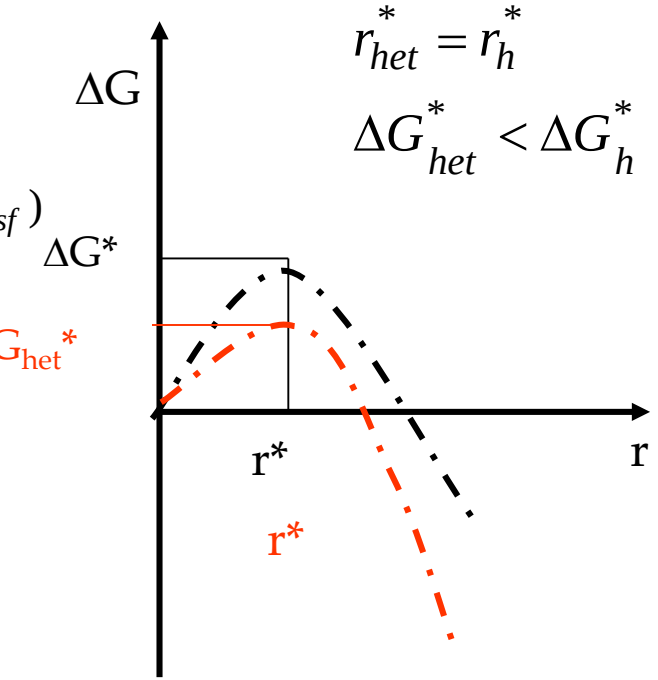
$$\Delta G = -\frac{V_{nuc}}{v_{m,f}} \Delta\mu + 2\pi r^2(1-\cos(\theta))\gamma_f + \pi r^2 \sin^2(\theta)(\gamma_s - \gamma_{sf})$$

Thermodynamics of Nucleation (Heterogeneous)

Free energy change of nucleation:

$$\Delta G = -\frac{\frac{4}{3}\pi r^3 \cdot \phi(\theta)}{v_{m,f}}\Delta\mu + 2\pi r^2(1-\cos(\theta))\gamma_f + \pi r^2 \sin^2(\theta)(\gamma_s - \gamma_{sf})$$

$$\gamma_s - \gamma_{sf} = -\gamma_f \cos(\theta)$$



$$r_{het}^* = r_h^*$$

$$\Delta G_{het}^* < \Delta G_h^*$$

Minimizing for r:

$$\frac{\partial \Delta G_{het}}{\partial r} = 0$$

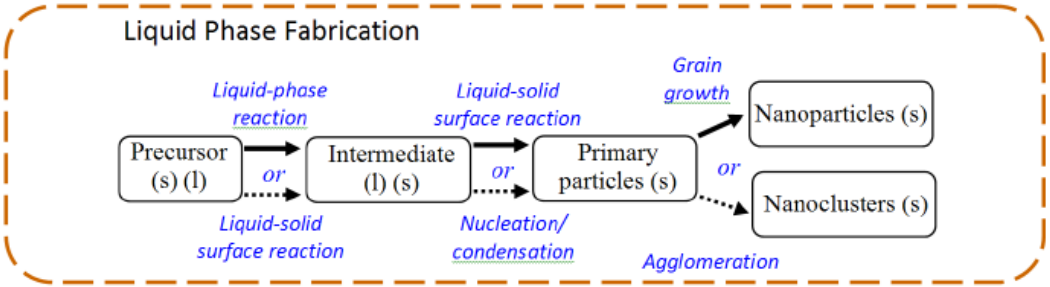
$$\Rightarrow r_{het}^* = r_h^* = \frac{2\gamma_f}{\Delta\mu}$$

$$r_{het}^* \rightarrow \Delta G_{het} \Rightarrow \Delta G_{het}^* = \frac{16}{3}\frac{\gamma_f^3}{\Delta\mu^2} \cdot v_{m,f}^2 \cdot \phi(\theta) = \Delta G_h^* \phi(\theta)$$

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 Synthsis

Coprecipitation

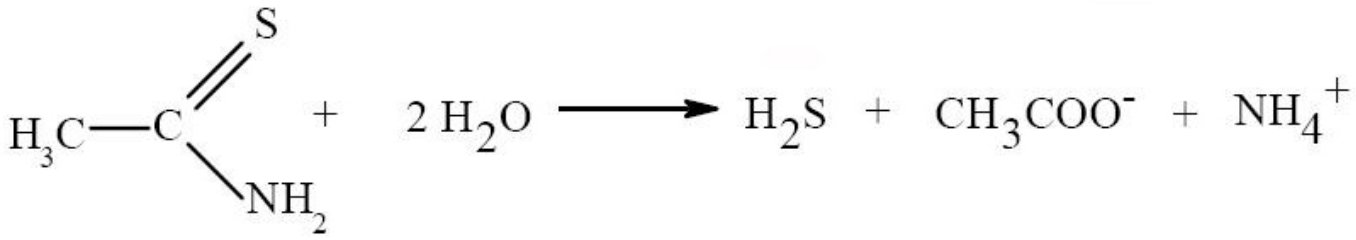
Coprecipitation reactions involve the simultaneous occurrence of nucleation, growth, coarsening, and/or agglomeration processes.

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.

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

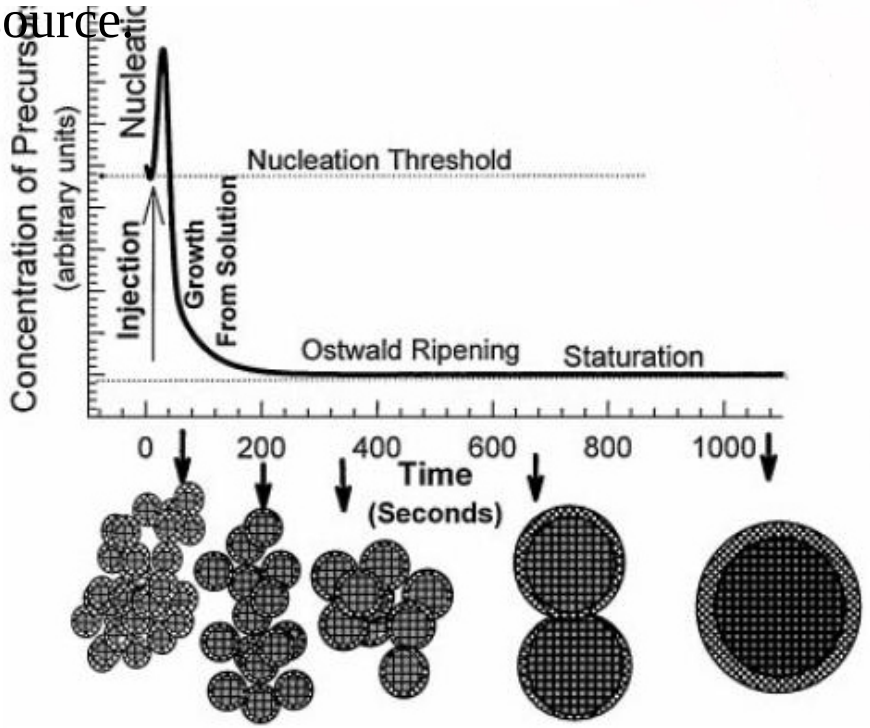
Typical coprecipitation synthetic methods: (i) metals formed from aqueous solutions, by reduction from nonaqueous solutions, electrochemical reduction, and decomposition of metallorganic precursors; (ii) oxides formed from aqueous and nonaqueous solutions; (iii) metal chalconides formed by reactions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

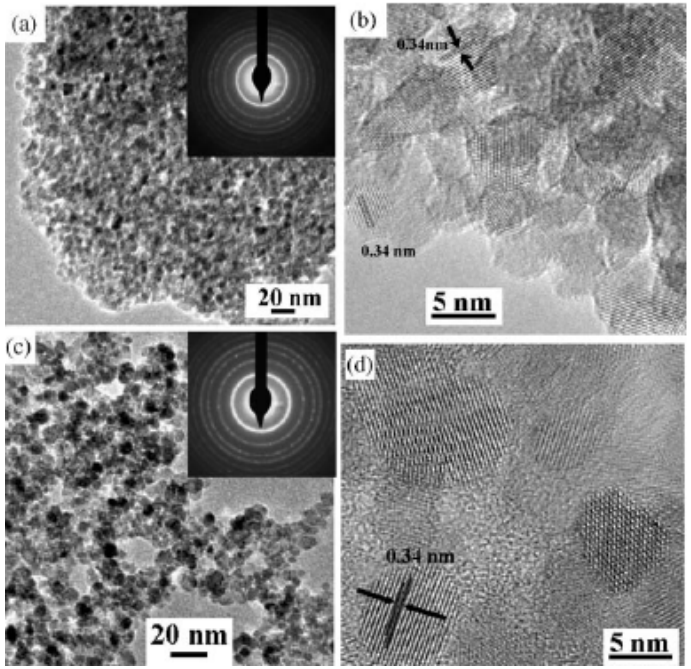
$Zn^{2+} + S^{2-} \rightarrow \mathbf{ZnS}$



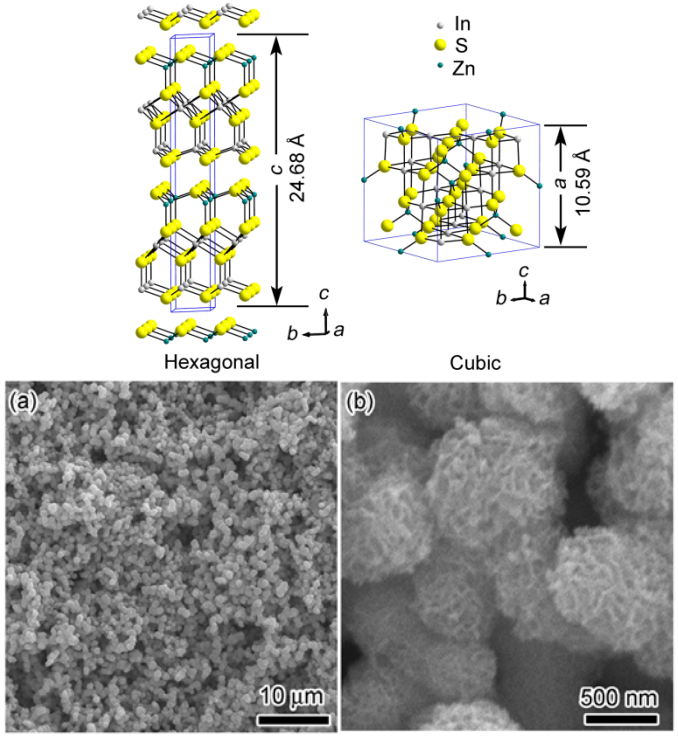
Murray C.B. et al., *Annu. Rev. Mater. Sci.* **2000**, *30*, 545.

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



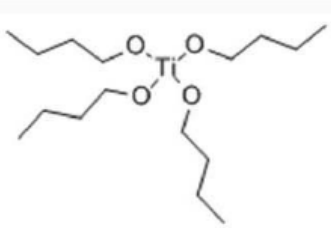
$ZnIn_2S_4$

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

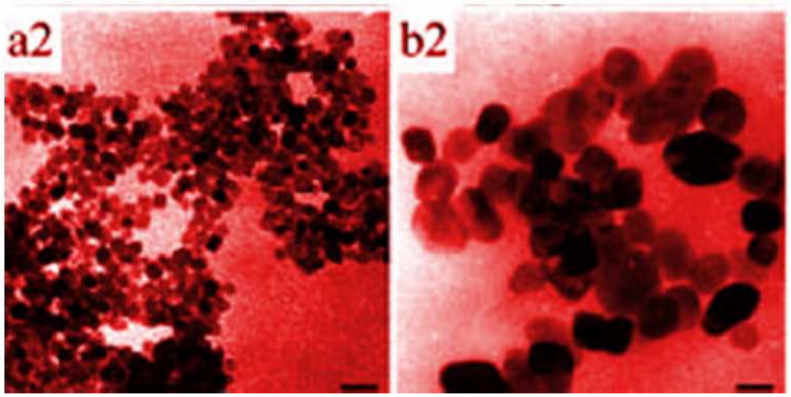
Solvothermal Synthesis

- 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

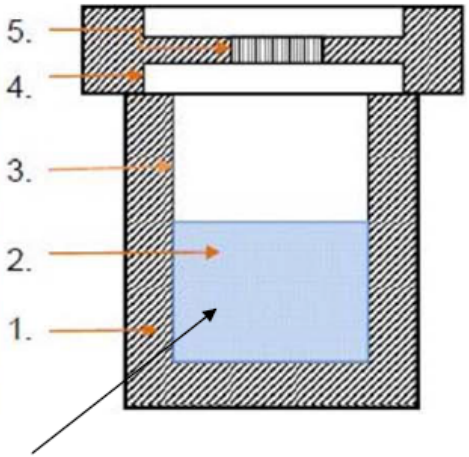


Example: TiO_2 Nanocrystallites



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).

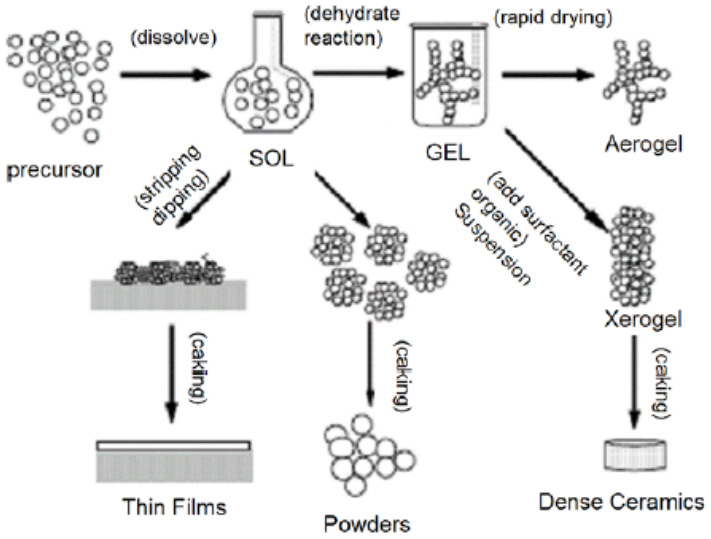
Metal alkoxides and metal chlorides are typical precursors. They undergo hydrolysis and polycondensation reactions to form a colloid, a system composed of nanoparticles dispersed in a solvent. The sol evolves then towards the formation of an inorganic continuous network containing a liquid phase (gel).

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

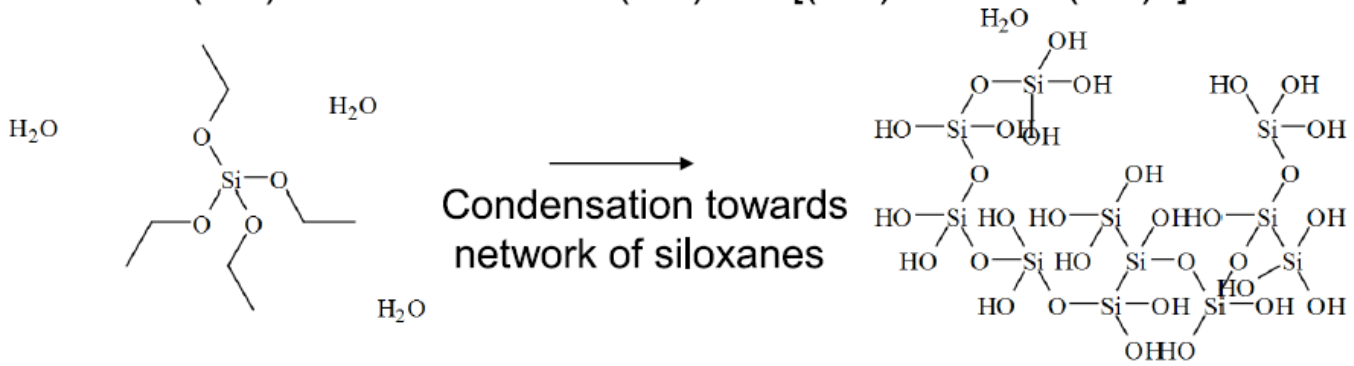
Ex.: $Si(OR)_4 + 4\ H_2O \rightarrow Si(OH)_4 + 4\ R\text{-}OH$

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

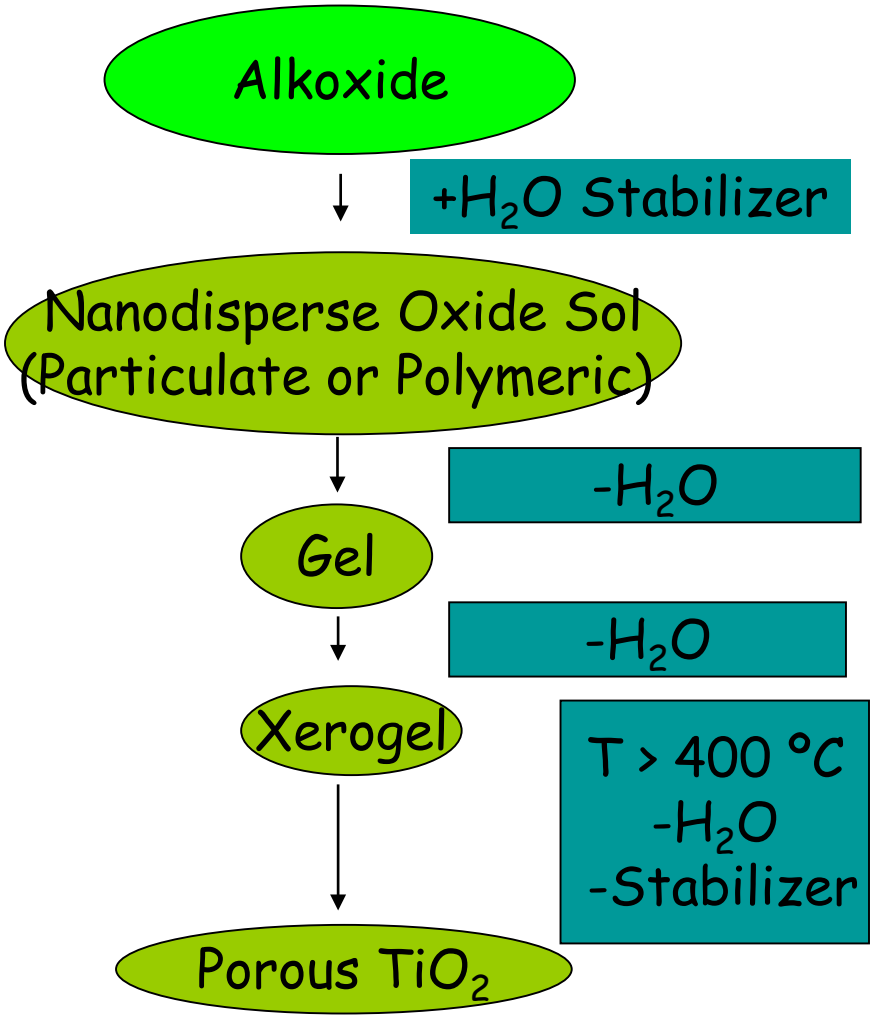
$(OR)_3\text{–}Si\text{-}OH + HO\text{–}Si\text{-}(OR)_3 \rightarrow [(OR)_3Si\text{–}O\text{–}Si(OR)_3] + H\text{-}O\text{-}H$

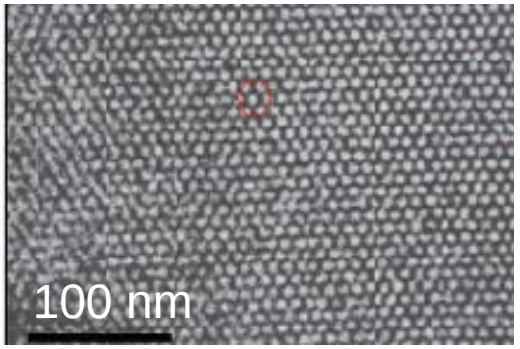
or –MOH + HOM– → –MOM– + H2O

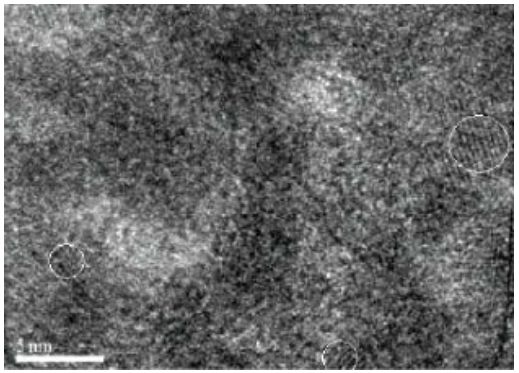
(OR)3–Si-OR + HO–Si-(OR)3 → [(OR)3Si–O–Si(OR)3] + R-OH



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







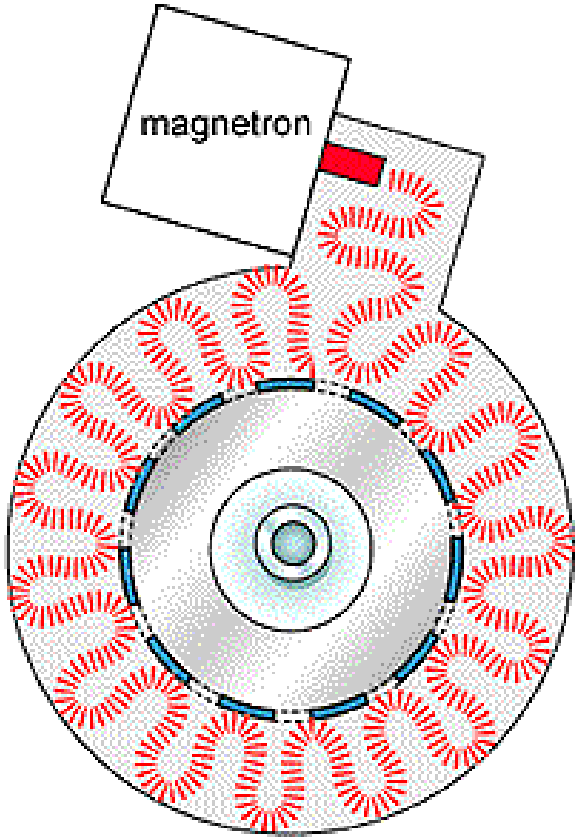
TiO_2 nanoparticle-mediated mesoporous film (Yu, J. C. et al. *Chem. Mater.* **2004**, 16, 1523.)

Microwave-Assisted Synthesis

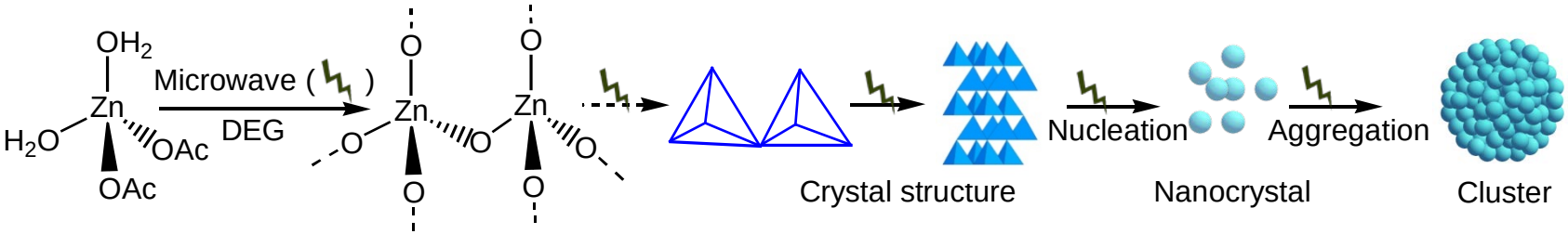
Microwaves are a form of electromagnetic energy with frequencies in the range of 300 MHz to 300 GHz. The commonly used frequency is 2.45G Hz.

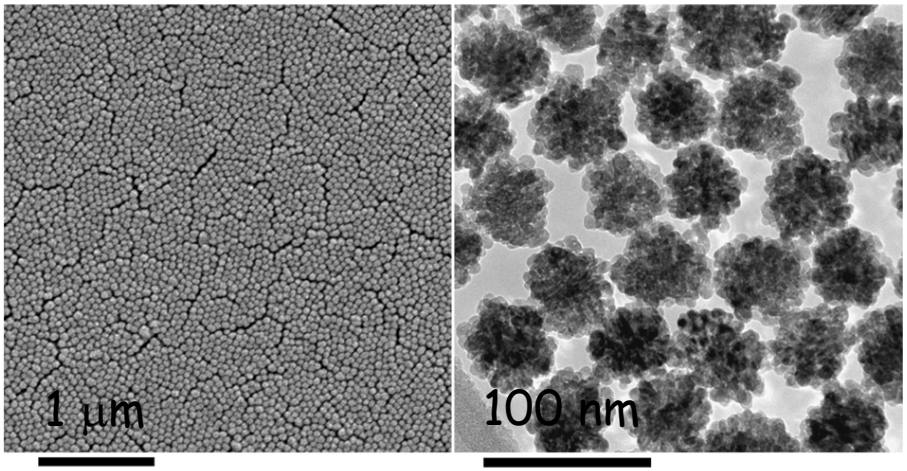
Interactions between materials and microwaves are based on two specific mechanisms: dipole interactions and ionic conduction. Both mechanisms require effective coupling between components of the target material and the rapidly oscillating electrical field of the microwaves.

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

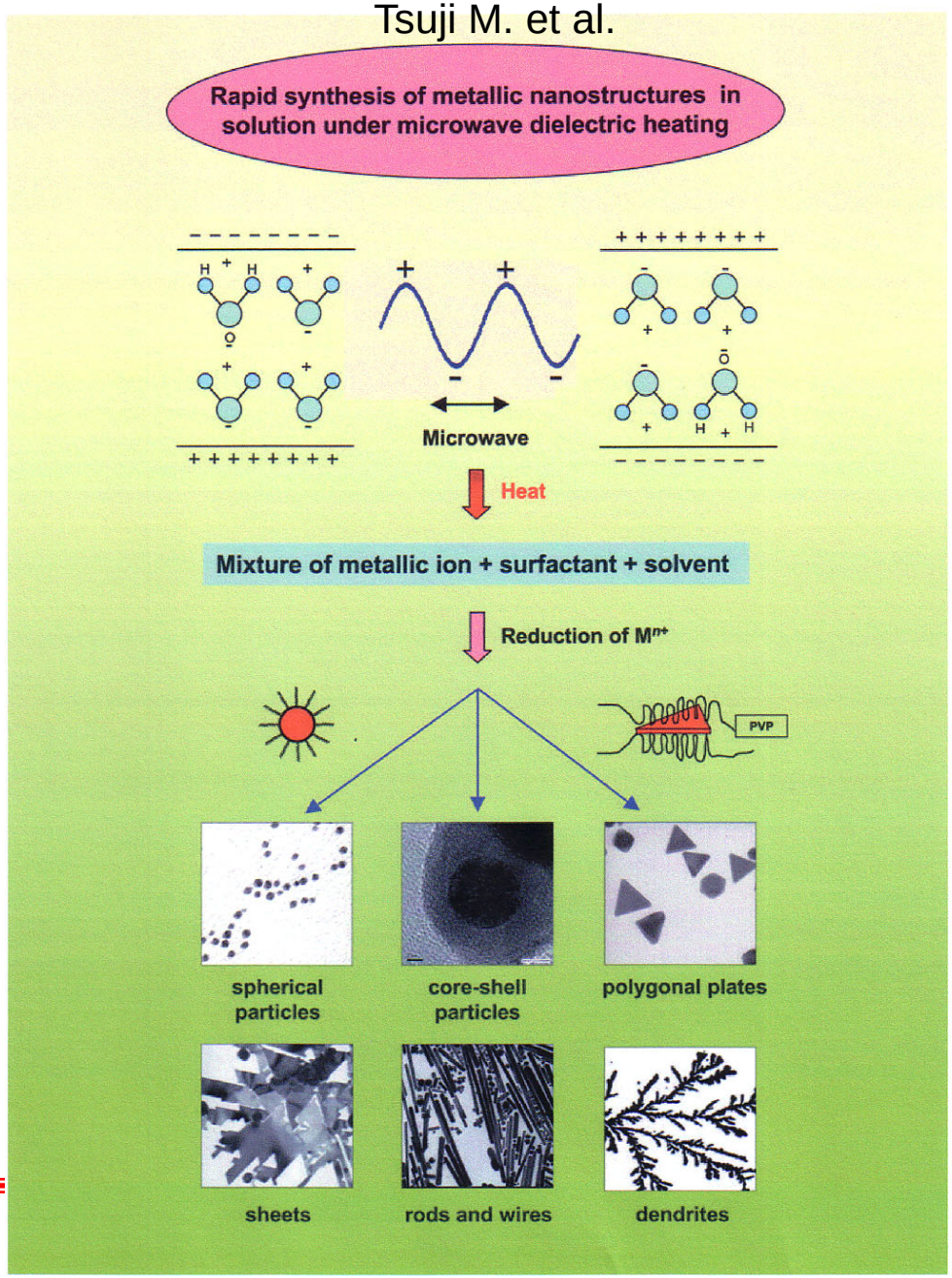




Schematic representation and transmission electron microscope (TEM) images of ZnO-cluster nanoparticles prepared by microwave irradiation

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

Tsuji M. et al.



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.

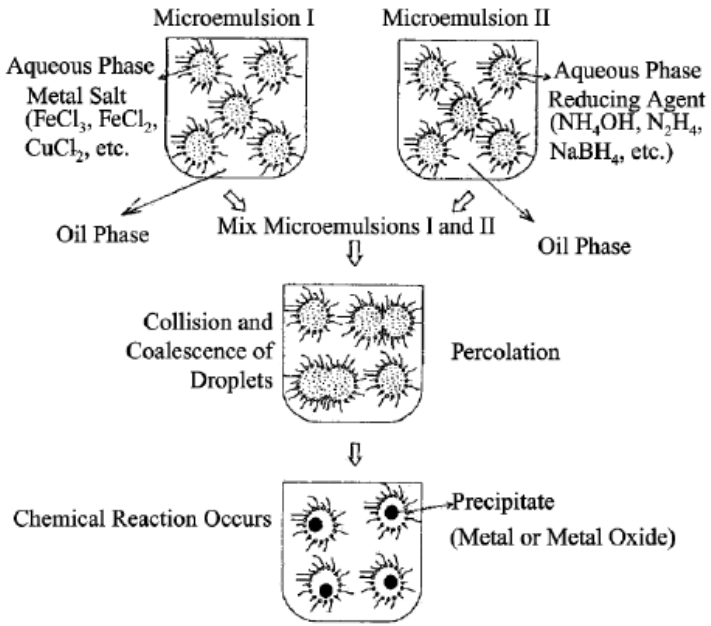
Stanko R. Brankovic

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim
DOI: 10.1002/chem.200400417 *Chem. Eur. J.* **2005**, *11*, 440–452

Synthesis in Structured Medium

Influence Growth Kinetics by Imposing Constraints in Form of Matrices:

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



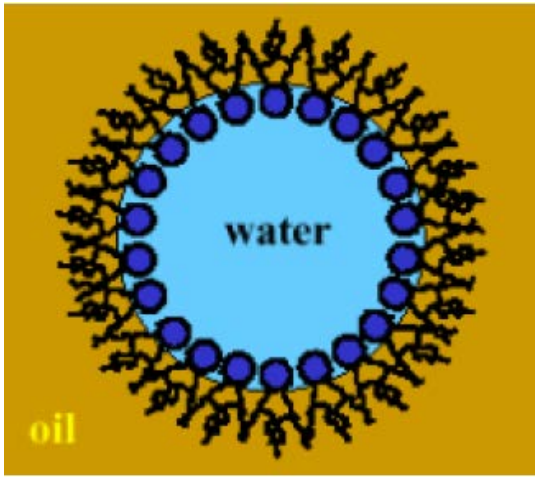
I. Capek, Adv. Coll. Interf. Sci. 110 (2004) 49

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

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

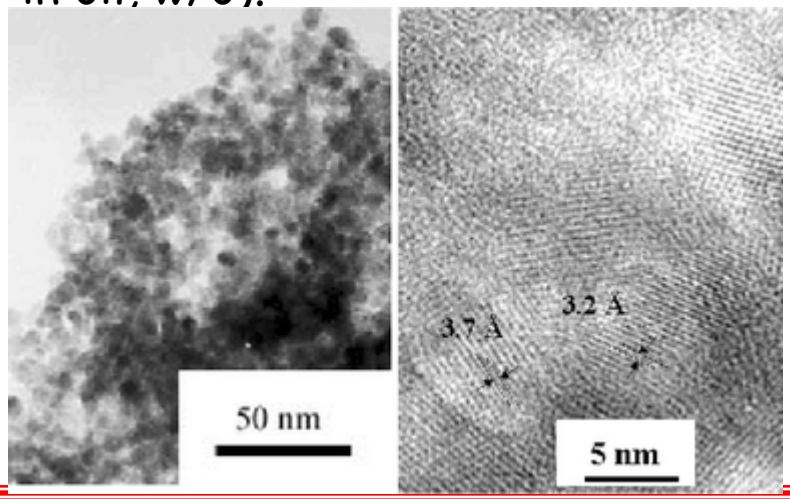
Microemulsion

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

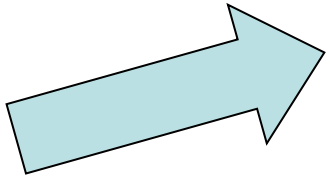
Ultrasound irradiation causes acoustic cavitation -- the formation, growth and implosive collapse of the bubbles in a liquid

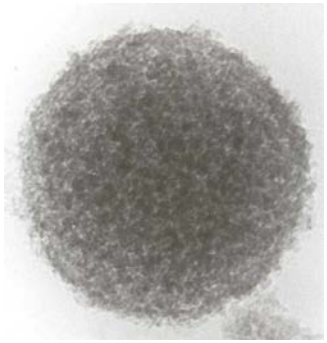
The implosive collapse of the bubbles generates a localized hot spots of extremely high temperature (~5000K) and pressure (~20MPa).

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

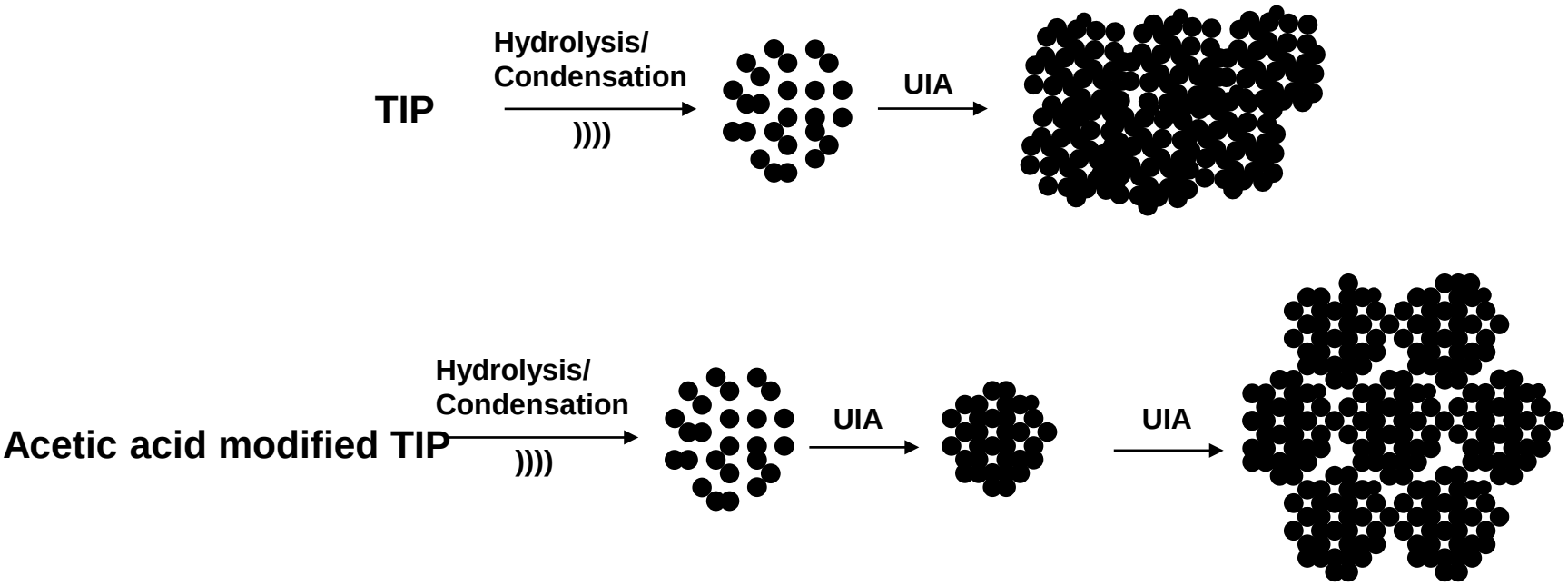




Mesoporous TiO_2

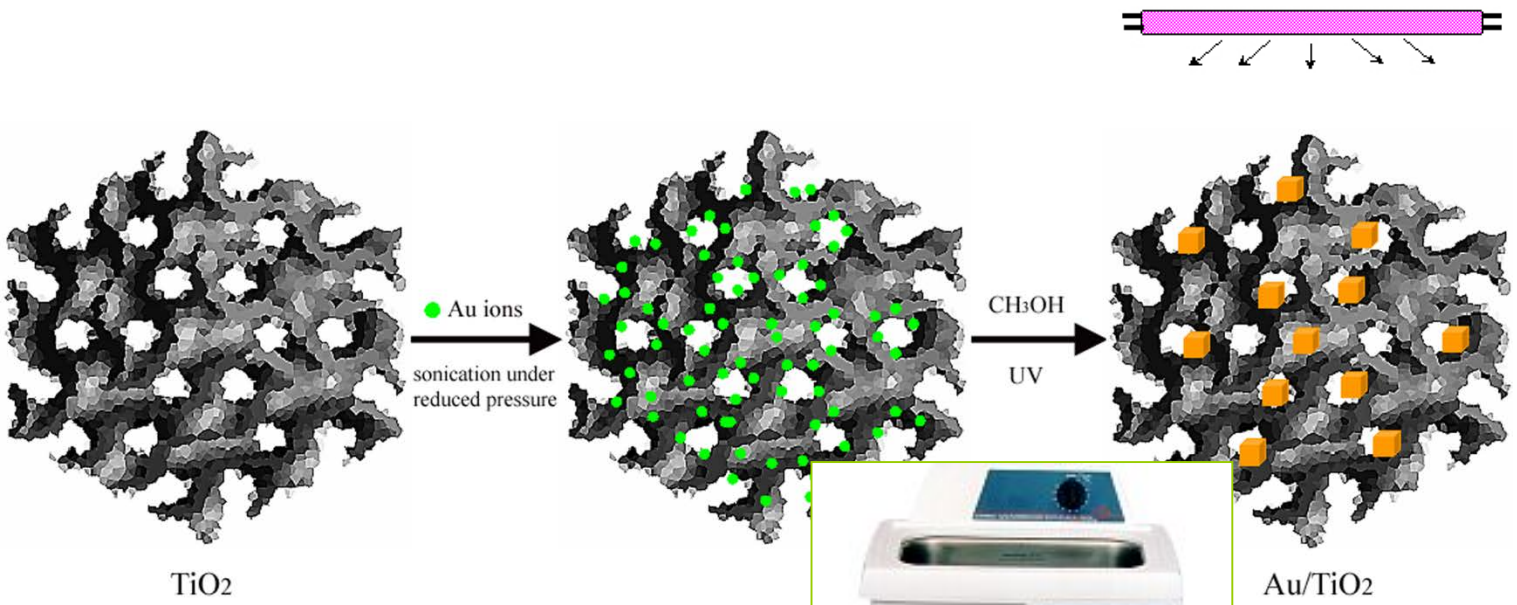
Formation of mesoporous TiO_2 by sonication

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.