ZERO-DIMENSIONAL NANOSTRUCTURES: NANOPARTICLES

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MATERIAIS NANOESTRUTURADOS E NANOTECNOLOGIAS

M. Clara Gonçalves

Summary

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- **Introduction**
- **Nanoparticles through Homogeneous Nucleation**
  - Fundamentals of Homogeneous Nucleation
  - Synthesis of Oxide Nanoparticles
  - Sol-gel processing
- **Nanoparticles through Heterogeneous Nucleation**
  - Fundamentals of Heterogeneous Nucleation
  - Synthesis of Metallic Nanoparticles
- **Kinetically Confined Synthesis of Nanoparticles**
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- **Further Reading**

Types of Nanotechnologies

Artificial nanostructures (difficult to synthesize).

- **Top-Down** (*scaling down*, larger to smaller size)

Here, the mechanisms and structures are miniaturized to a nanometric scale. This approach is widely following in the miniaturization of electronic products, and electronic components manufacturing processes.

- **Bottom-Up** (*scaling up*, smaller to larger size)

Approach less complex, but difficult to control defects (‘self-assembly’ or auto-organization of monodisperse spheres, nanocrystallization).

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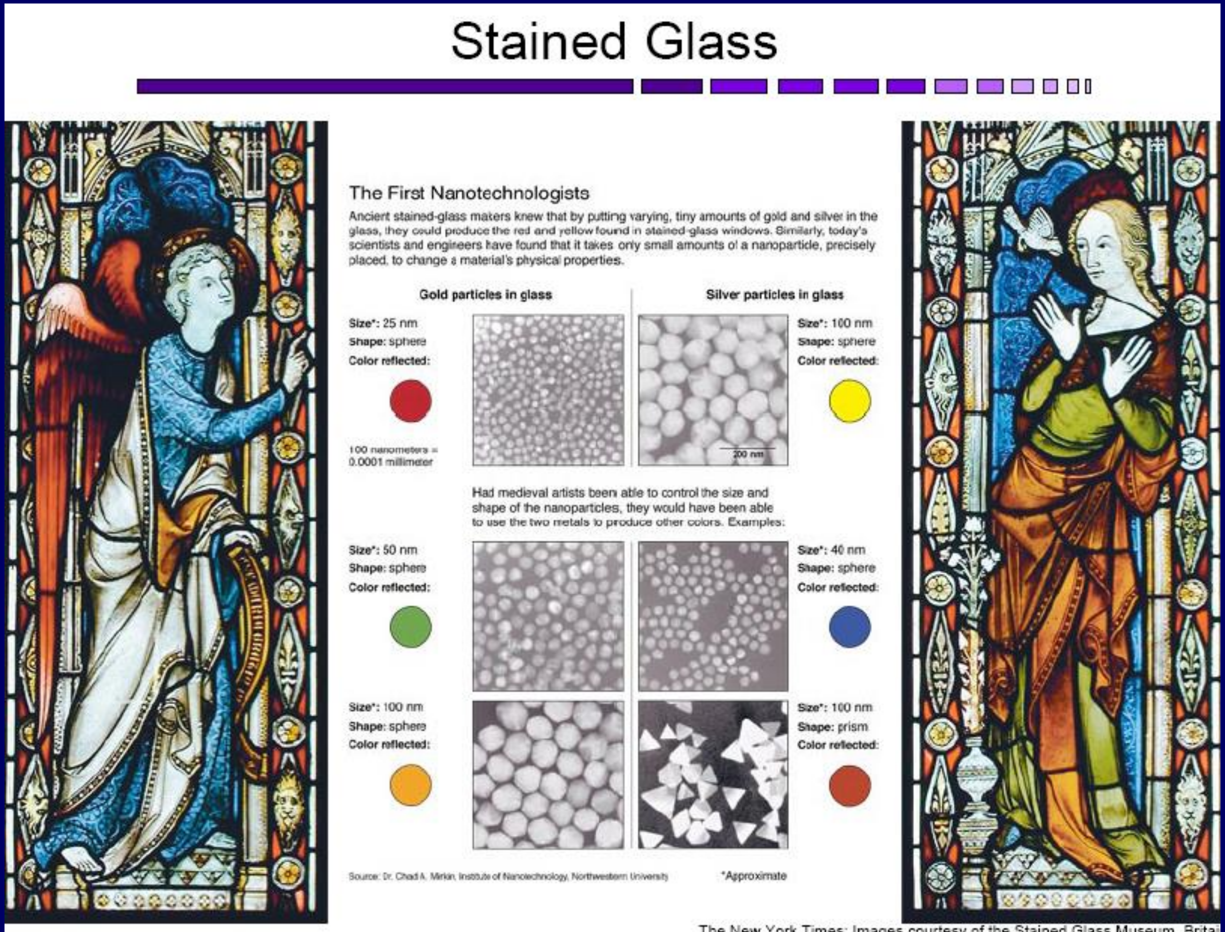
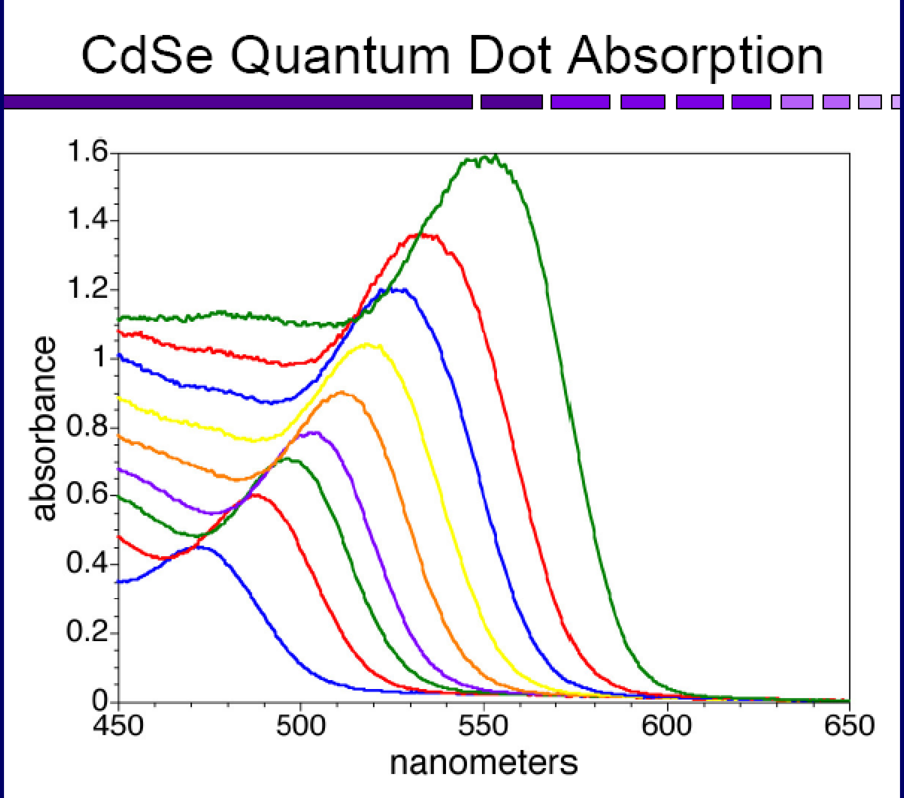
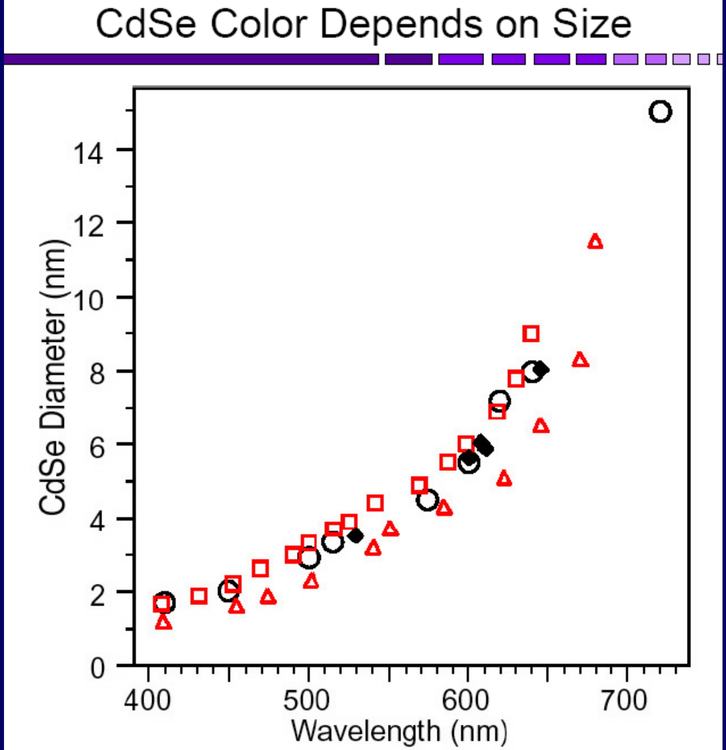


The New York Times; Images courtesy of the Stained Glass Museum, Britai

Kenneth Chang, "Tiny Is Beautiful: Translating 'Nano' Into Practical", The New York Times, February 22, 2005

Introduction





Geoff Strouse, UC-Santa Barbara http://www.evidenttech.com/events/siena_seminar/resources/Siena - Evident NC Seminar Aug 03.pdf

Nanoparticles through Homogeneous Nucleation

• HOMOGENEOUS NUCLEATION

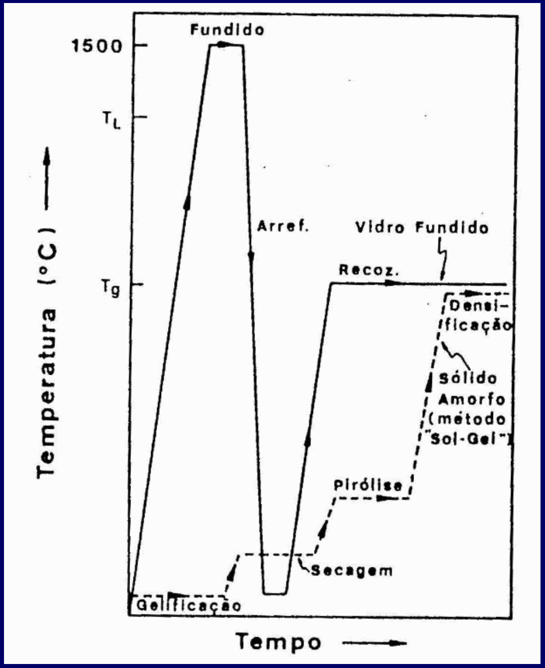
Characteristics of Nanoparticles

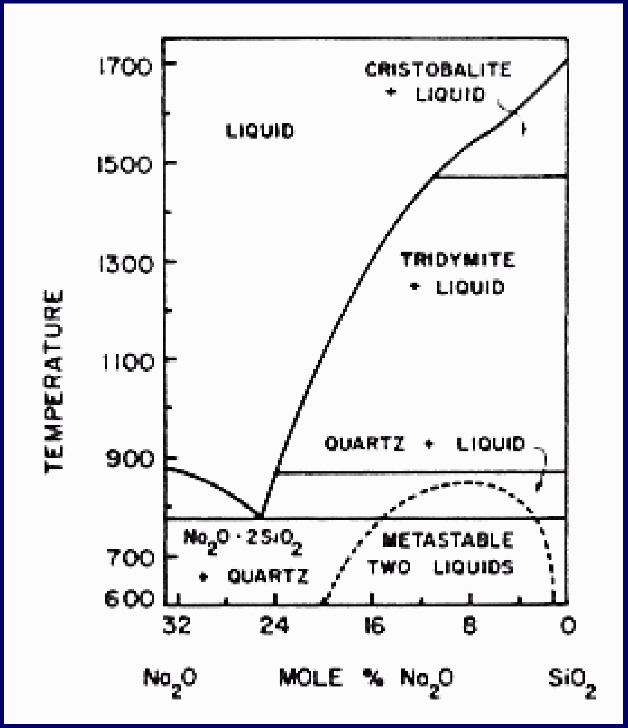
For the **fabrication of nanoparticles**, **small size** is not the only requirement. **Nanoparticles** should have the following characteristics:

- **Identical size** of all the particles (monosized or with uniform size distribution).
- **Identical shape** or morphology.
- **Identical chemical composition** and **crystal structure** among **different particles** and within **individual particles**, such as core and surface composition.
- Individual dispersed or monodispersed, i,.e., **no agglomeration**.

Nanoparticles through Homogeneous Nucleation

• HOMOGENEOUS NUCLEATION





Nanoparticles through Homogeneous Nucleation

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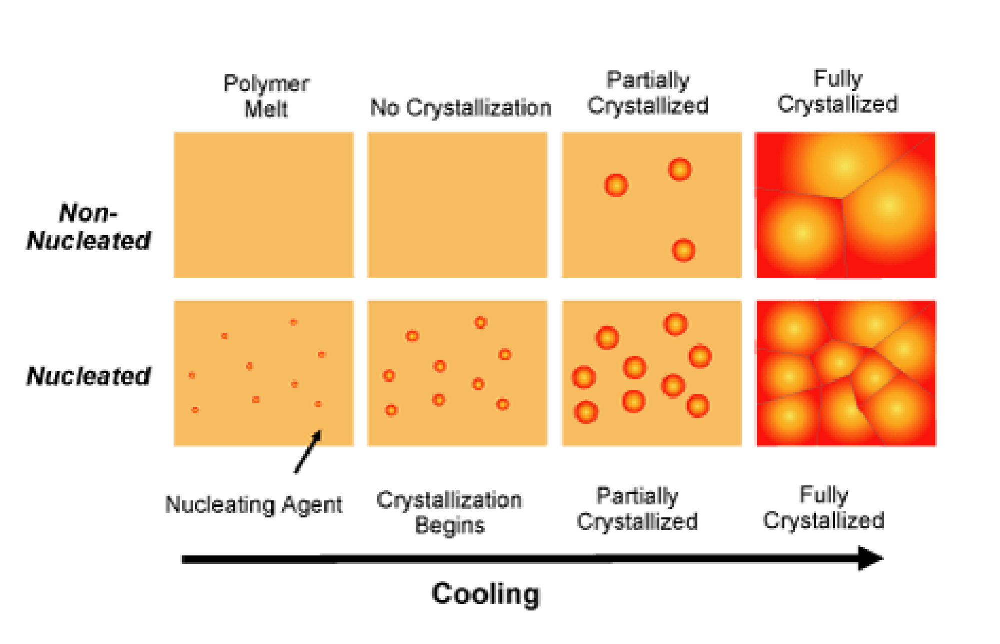
- **HOMOGENEOUS NUCLEATION**

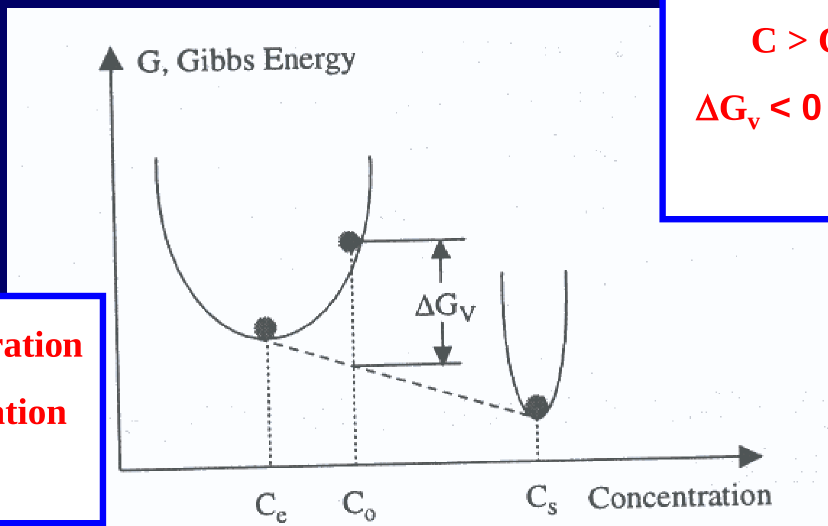


Fundamentals of Homogeneous Nucleation

- **THE REDUCTION OF GIBBS FREE ENERGY IS THE DRIVING FORCE FOR BOTH NUCLEATION AND GROWTH**

$$\Delta G_v = -\frac{kT}{\Omega}\ln\left(C/C_0\right) = -\frac{kT}{\Omega}\ln\left(1+\sigma\right)$$

- C: **concentration of the solute**
- C_0: **equilibrium concentration or solubility**
- Ω: **atomic volume**
- σ: **supersaturation, defined by** $(C - C_0)/C_0$



$C > C_0 \Leftrightarrow$ supersaturation

$\Delta G_v < 0 \Rightarrow$ spontaneous nucleation

$C < C_0 \Leftrightarrow$ non saturation

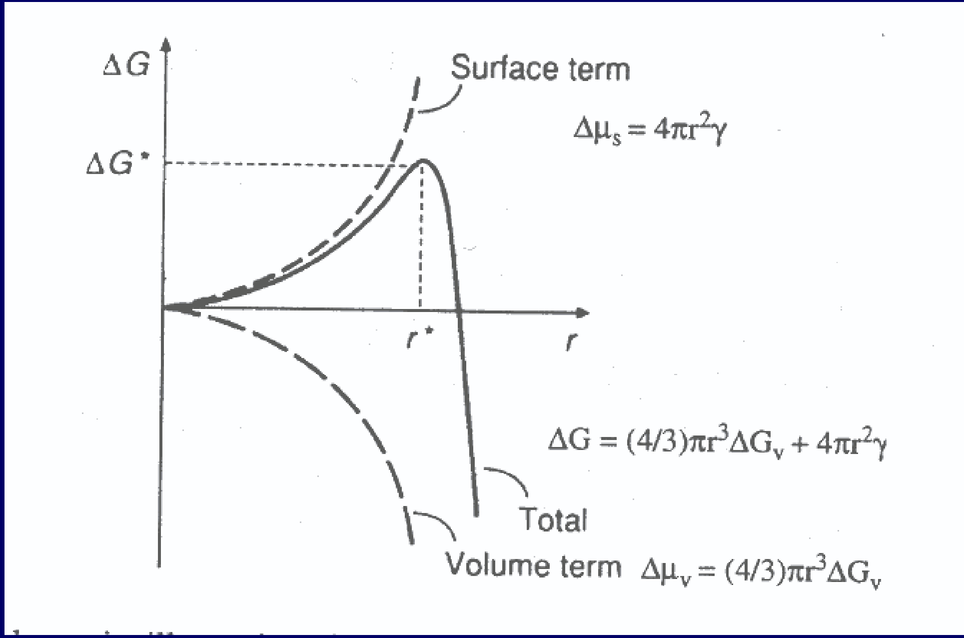
$\Delta G_v = 0 \Rightarrow$ no nucleation

Fundamentals of Homogeneous Nucleation

● **THE REDUCTION OF GIBBS FREE ENERGY IS THE DRIVING FORCE FOR BOTH NUCLEATION AND GROWTH**

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

Gibbs free energy — **volume energy** — **surface energy**

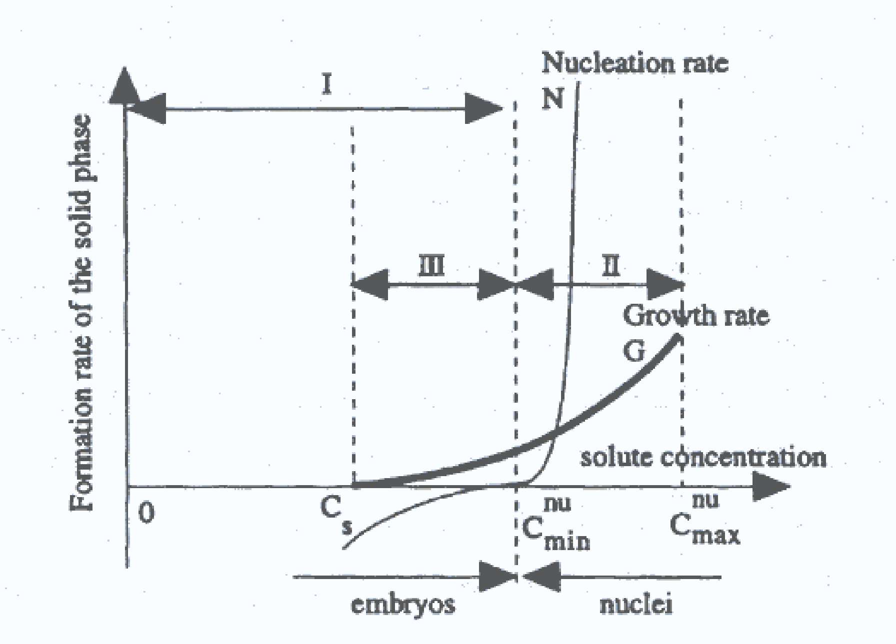


Fundamentals of Homogeneous Nucleation

● **THE REDUCTION OF GIBBS FREE ENERGY IS THE DRIVING FORCE FOR BOTH NUCLEATION AND GROWTH**

radius critical size ← $$r^* = -2\frac{\gamma}{\Delta G_v}$$

critical Gibbs energy ← $$\Delta G^* = \frac{16\pi\gamma}{(3\Delta G_v)^2}$$



Fundamentals of Homogeneous Nucleation

In the synthesis of **nanoparticles** or **quantum dots** by **homogeneous nucleation** from supersaturated solution or vapor, the **radius critical size** represents the **limit** on **how small nanoparticles** can be synthesized.

radius critical size ← $$r^* = -2\frac{\gamma}{\Delta G_v}$$

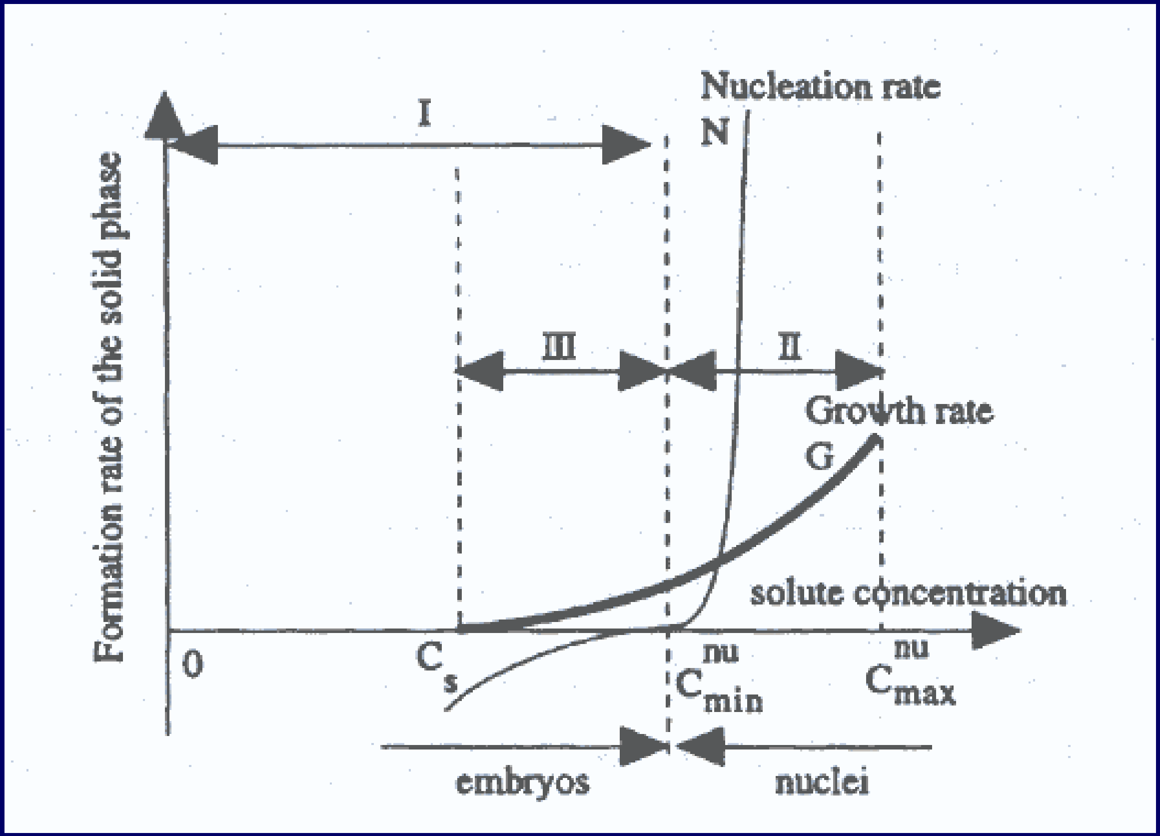
critical Gibbs energy ← $$\Delta G^* = \frac{16\pi\gamma}{(3\Delta G_v)^2}$$

↓ r*, ↓ΔG* ⟷ **↑ ΔGv , ↓ γ**

↑ ΔGv ⟷ **↑σ (supersaturation)**

Fundamentals of Homogeneous Nucleation

- **CRYSTAL GROWTH CONTROLLED BY DIFFUSION**



Fundamentals of Homogeneous Nucleation

● **CRYSTAL GROWTH CONTROLLED BY DIFFUSION**

initial size of the nucleous

initial radius difference for two particles

$$\delta r = \frac{r_0 \delta r_0}{r}$$

radius difference for two particles

$$\delta r = \frac{r_0 \delta r_0}{\sqrt{k_D t + r_0^2}}$$

$$k_D = 2D(C - C_s)V_m$$

diffusion coefficient of the growth species

concentration on the surface of solid particles

bulk concentration

δr ↓ , ↑ r and/or ↑ t

The **diffusion-controlled growth** promotes the formation of **uniformly sized particles.**

Fundamentals of Homogeneous Nucleation

- **CRYSTAL GROWTH CONTROLLED BY SURFACE PROCESS**

MONOLAYER GROWTH

The growth proceeds **layer by layer**. The growth species are incorporated into one layer and proceeds to another layer **only** after the growth of the **previous layer is complete**.

This growth mechanism does **not** favor the **synthesis of monosized particles**.

POLY-NUCLEAR GROWTH

Surface process is so fast that **second layer growth** proceeds **before** the **first layer grow is complete**.

This growth mechanism favor the **synthesis of monosized particles**.

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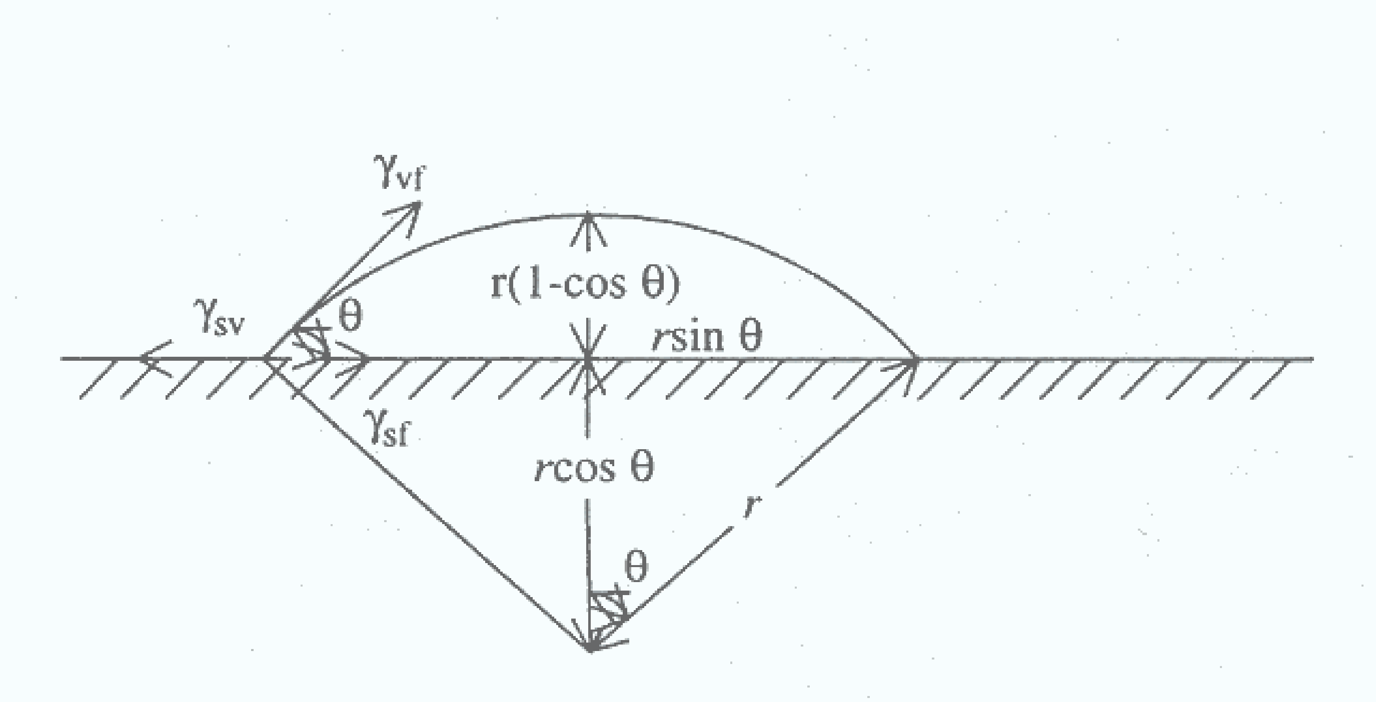
Nanoparticles through Heterogeneous Nucleation

γ_{vf}- interface free energy of vapor-nucleous

γ_{fs} - interface free energy of nucleous-substrate

γ_{sv}- interface free energy of substrate-vapor



Nanoparticles through Heterogeneous Nucleation

radius critical size
for homogeneous nucleation

$$r^* = \underbrace{\frac{2\pi\gamma_{vf}}{\Delta G_v}}\left\{\frac{\sin^2\theta.\cos\theta + 2\cos\theta - 2}{2 - 3\cos\theta + \cos^3\theta}\right\}$$

wetting factor

$$\Delta G^* = \left\{\frac{16\pi\gamma_{vf}}{3(\Delta G_v)^2}\right\}\left\{\frac{2 - 3\cos\theta + \cos^3\theta}{4}\right\}$$

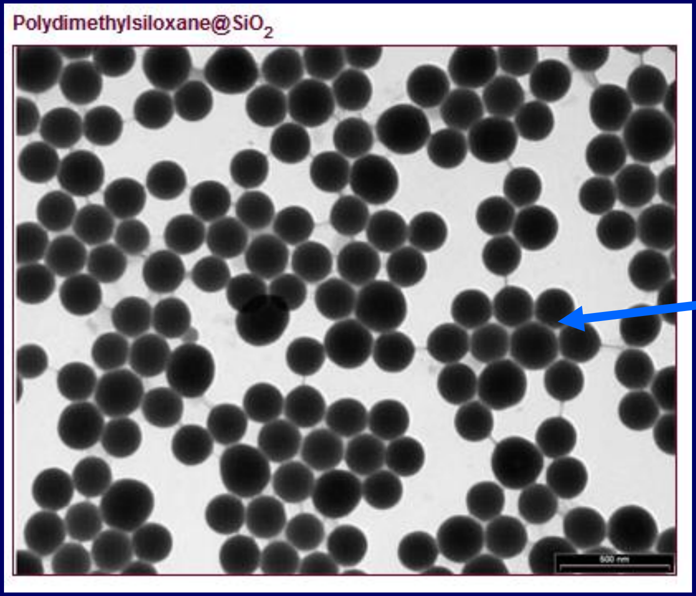
critical energy barier
for homogeneous nucleation

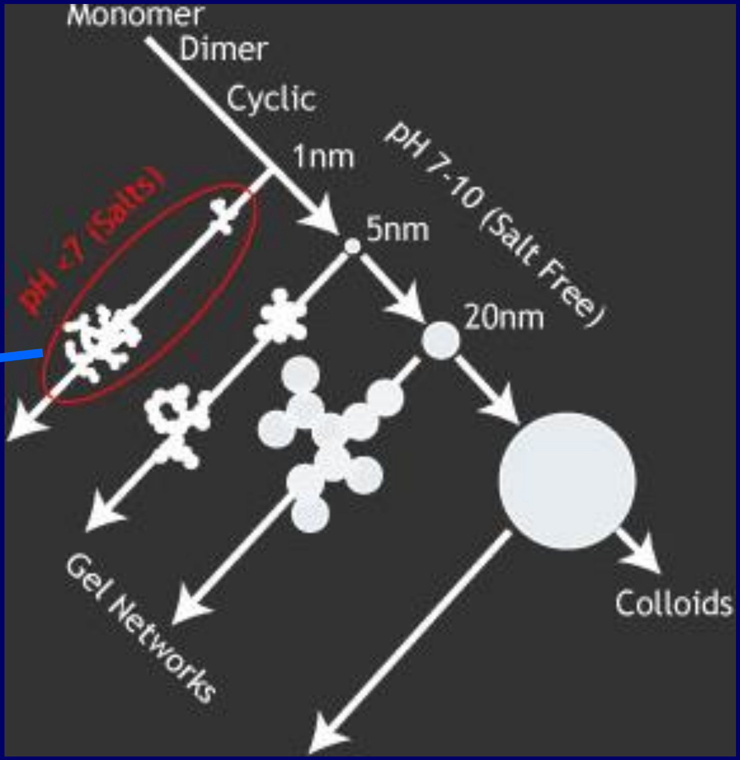
For the synthesis of **nanoparticles** or **quantum dots** on substrates, $\theta > 0$:

$$\gamma_{sv} < \gamma_{fs} + \gamma_{vf}$$

Synthesis of Oxide Nanoparticles

•SOL-GEL PROCESSING





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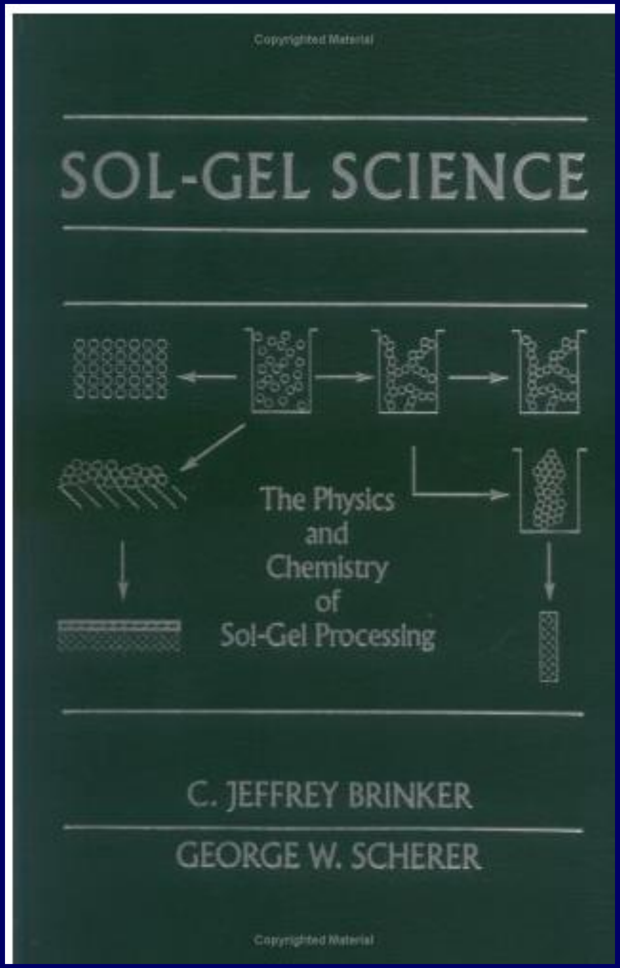
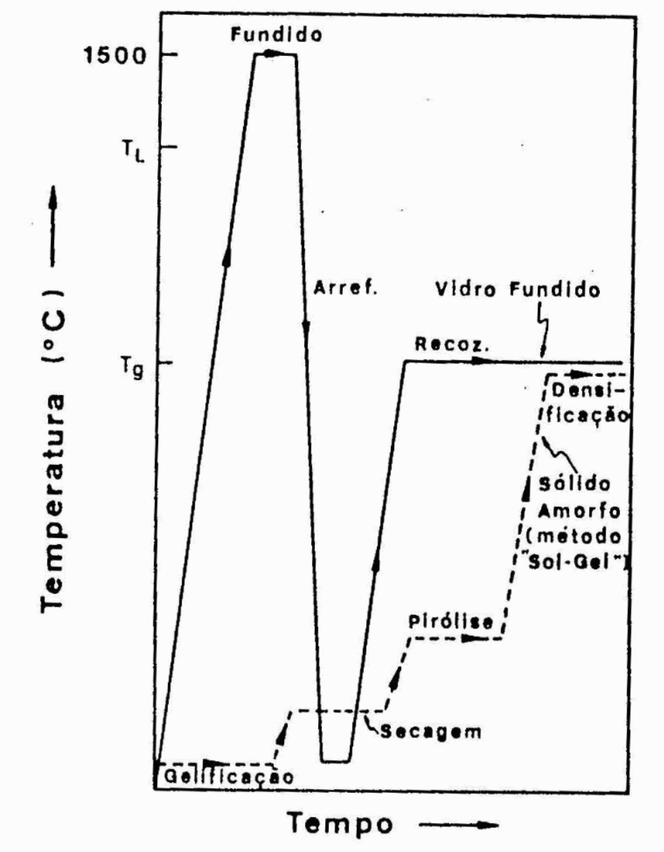
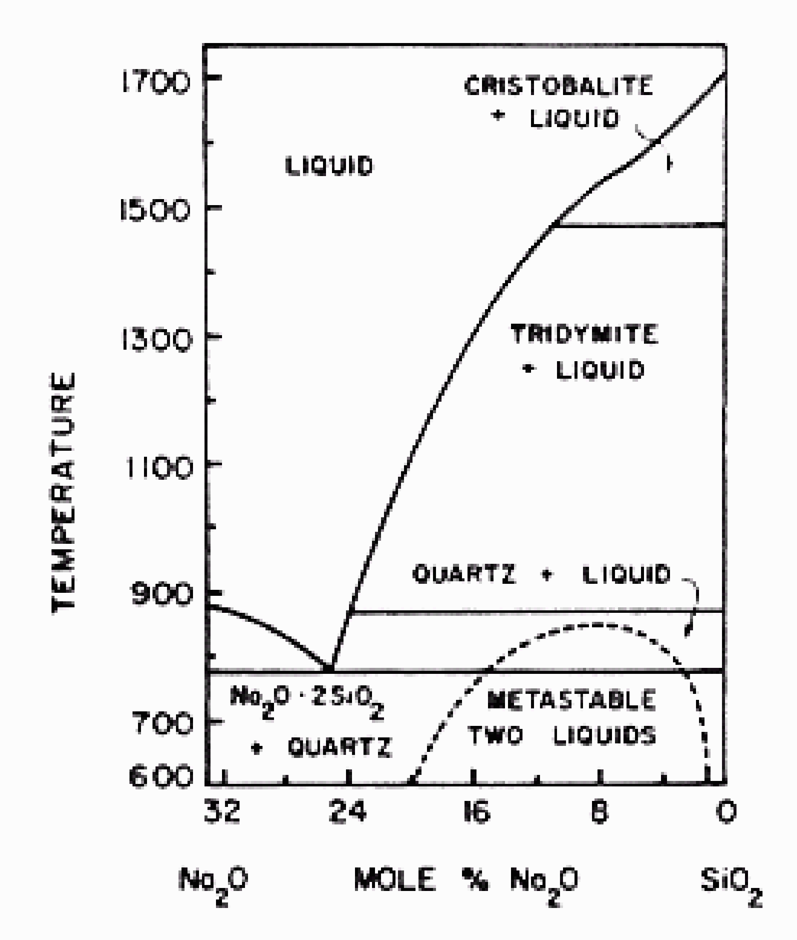


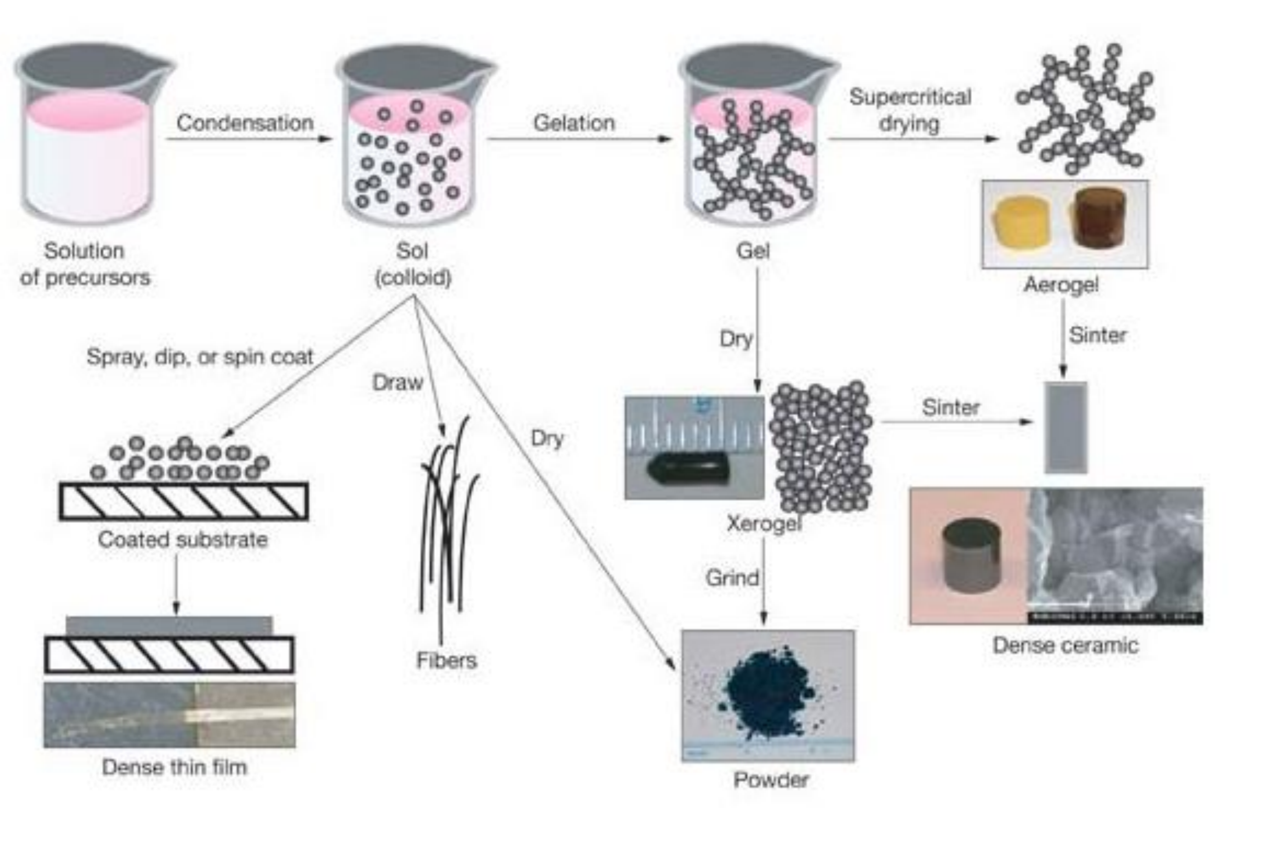
•SOL-GEL PROCESSING





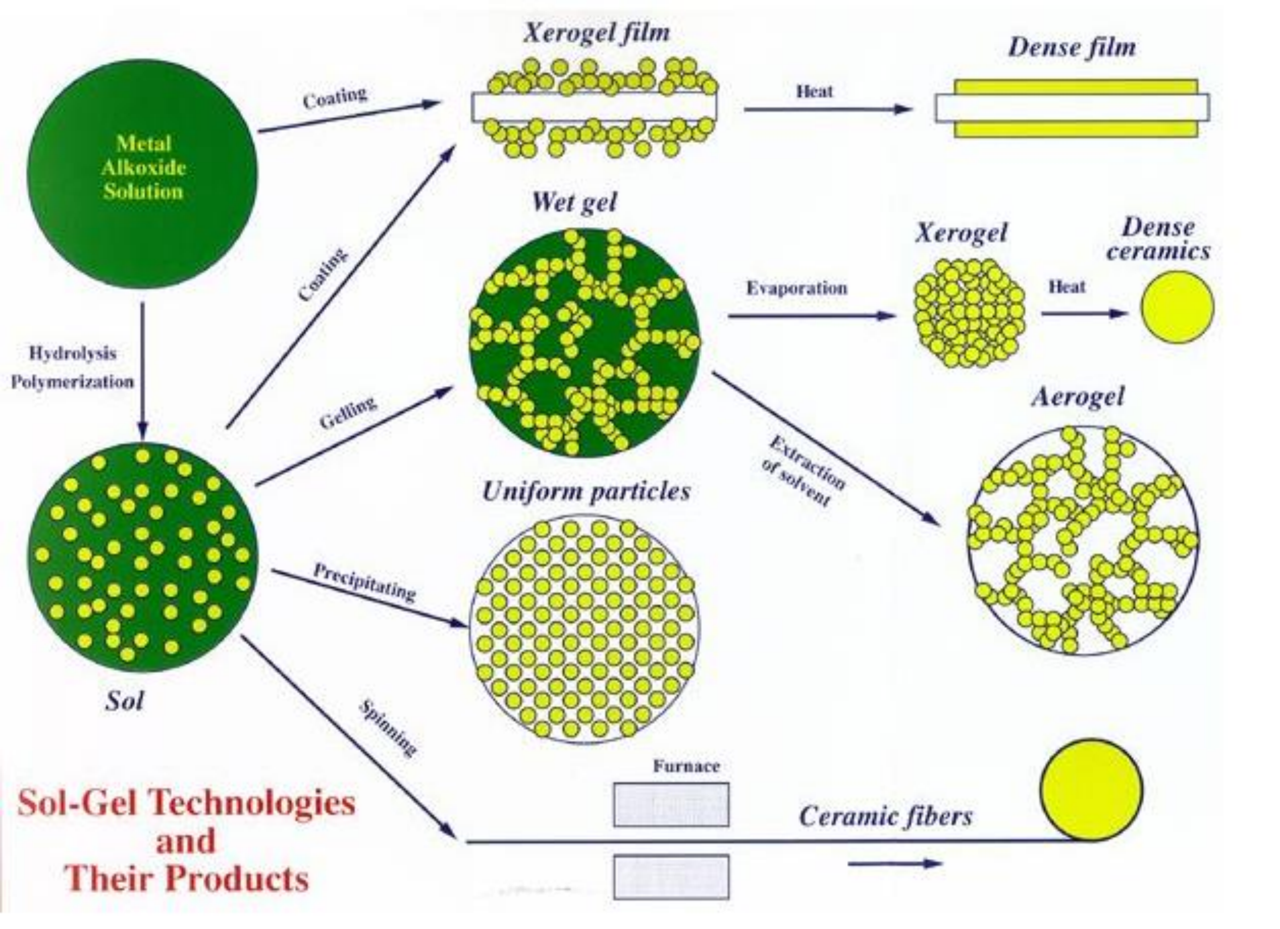
Sol-Gel Processing

•SOL-GEL PROCESSING

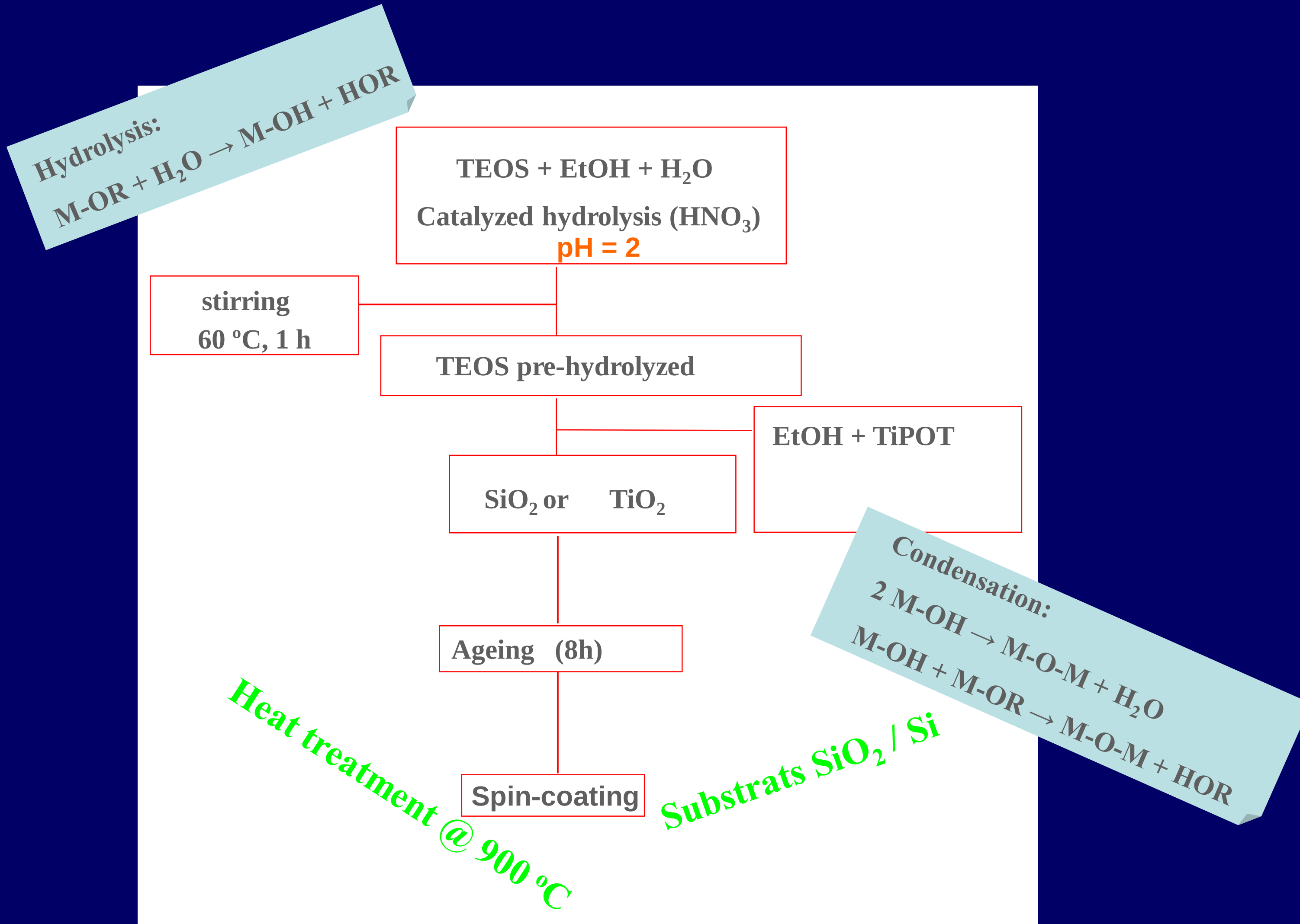


Sol-Gel Processing

- **SOL-GEL PROCESSING**



Sol-Gel Processing



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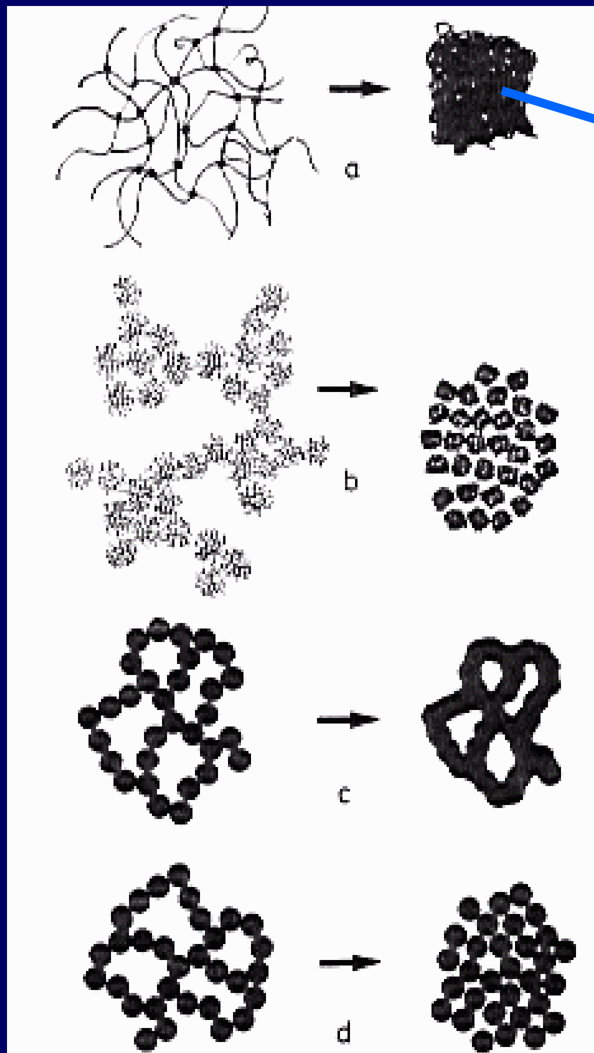
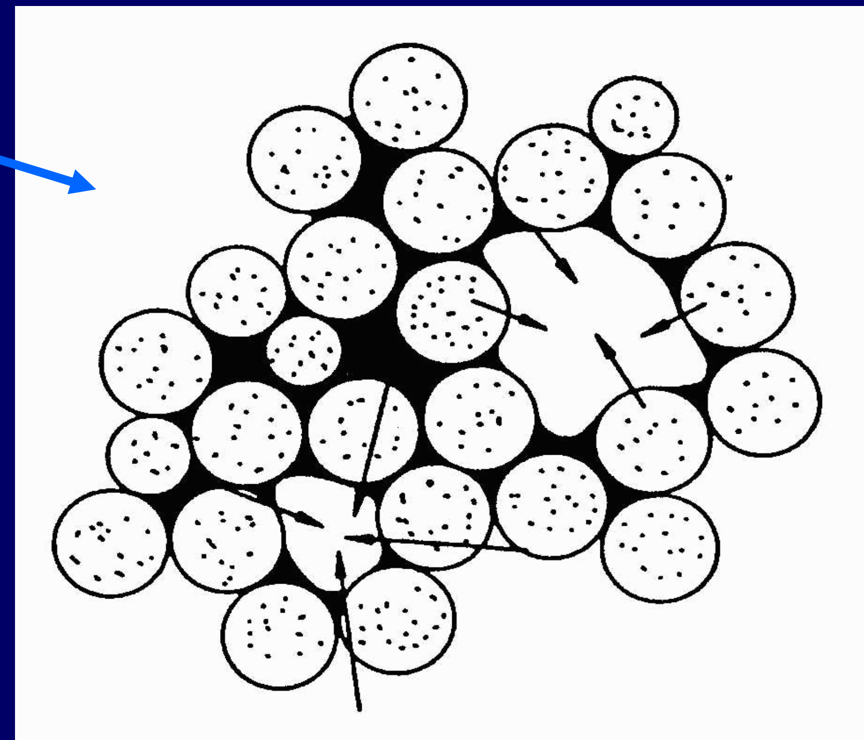
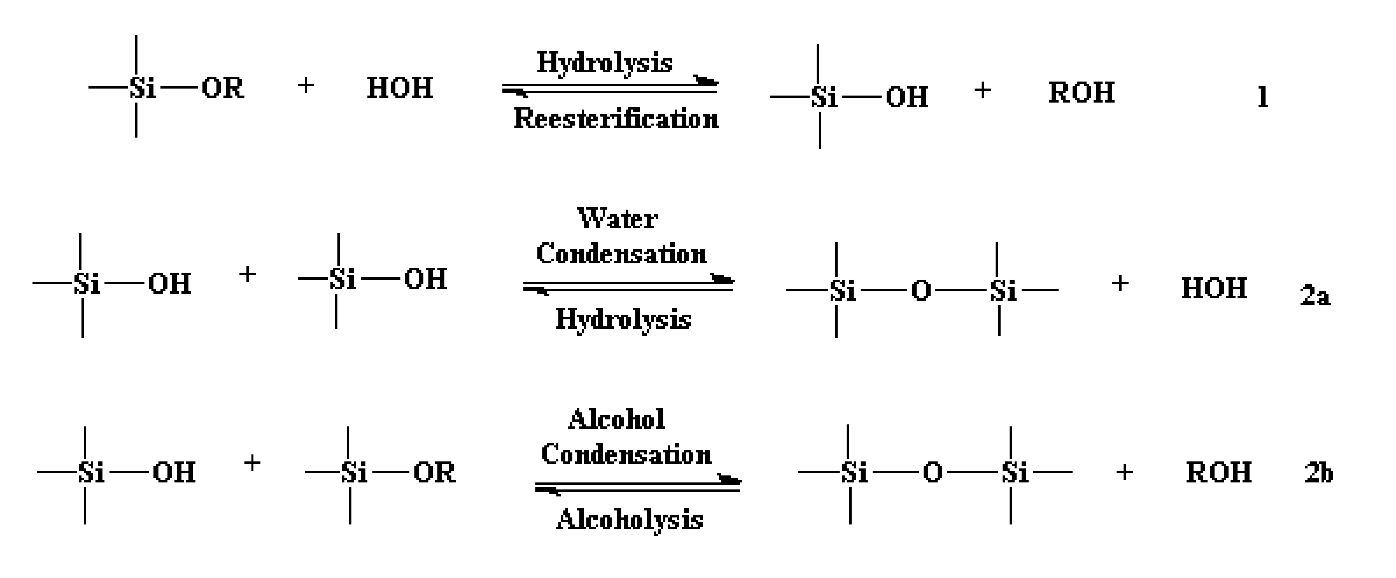
Sol-Gel Processing





Sol-Gel Processing

•ACID CATALYSIS



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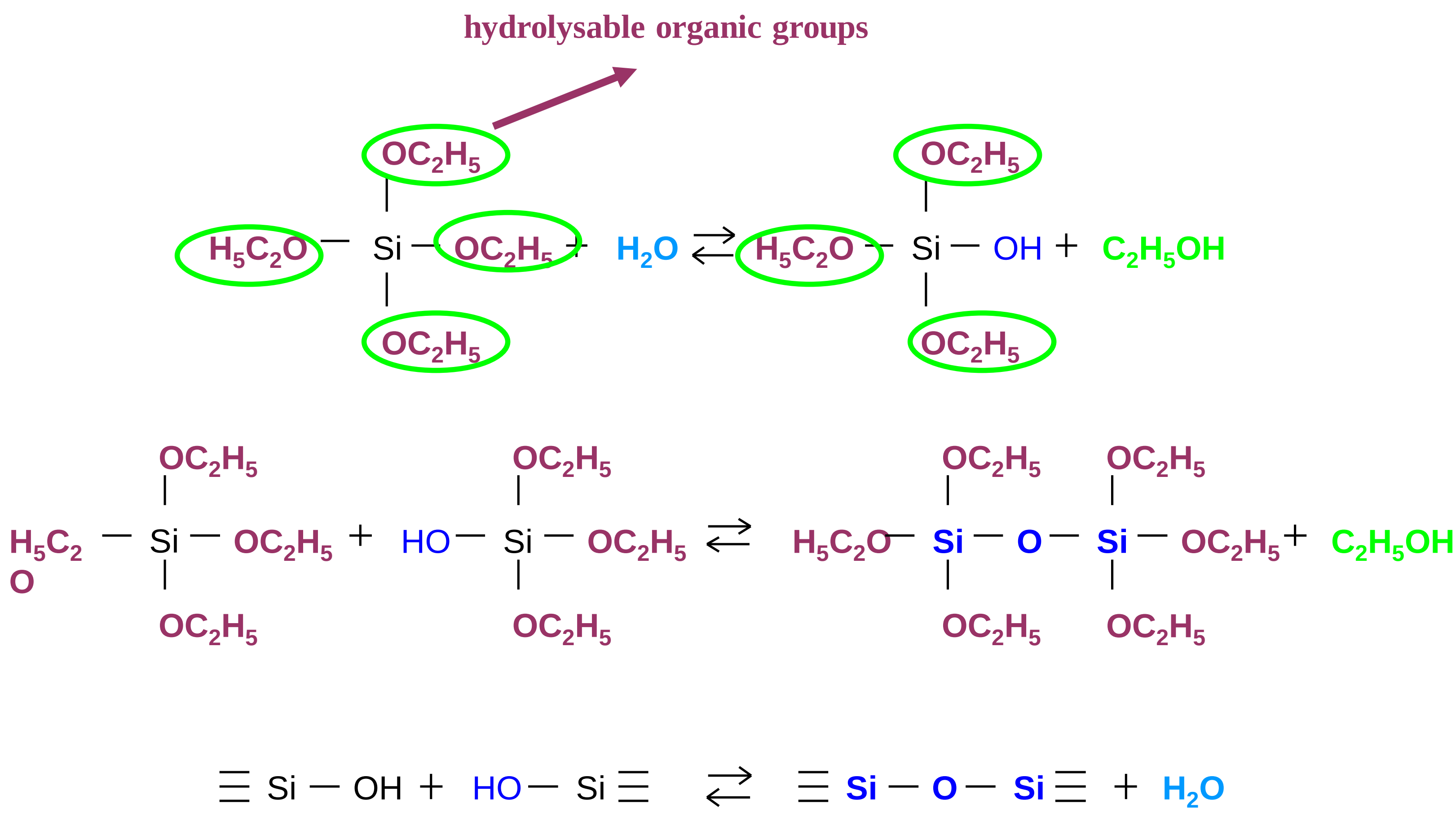
•HYDROLYSIS AND CONDENSATION OF SILICIO ALKOXIDE (TEOS)



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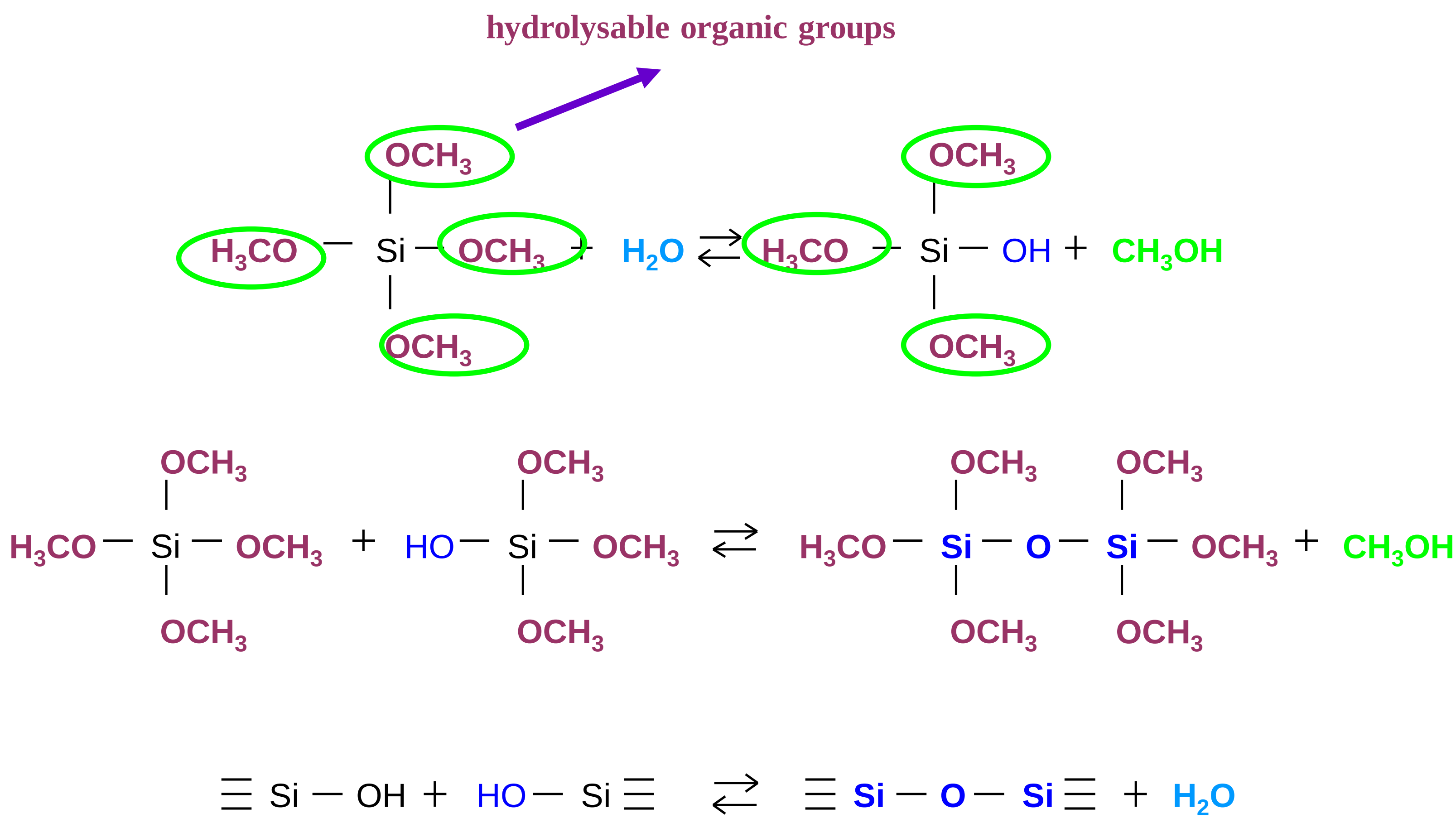
•HYDROLYSIS AND CONDENSATION OF SILICIO ALKOXIDE



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$$-\overset{|}{\underset{|}{Si}}-OR + H_2O \rightleftharpoons -\overset{|}{\underset{|}{Si}}-OH + CH_3OH$$

reações de condensação

$$-\overset{|}{\underset{|}{Si}}-OR + HO-\overset{|}{\underset{|}{Si}}-OR \rightleftharpoons -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-OR + CH_3OH$$

$$\equiv Si-OH + HO-Si\equiv \rightleftharpoons \equiv Si-O-Si\equiv + H_2O$$

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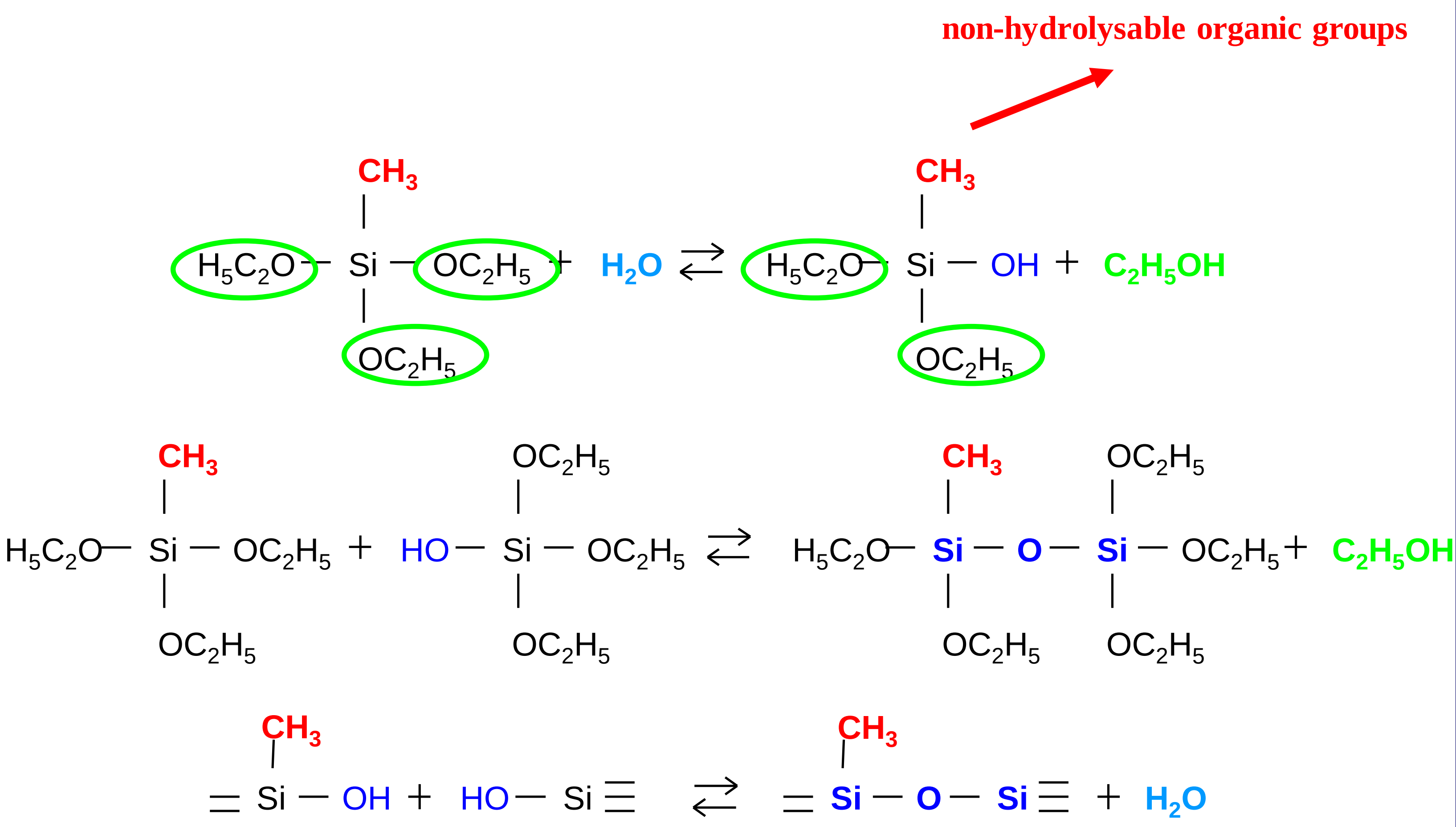
•HYDROLYSIS AND CONDENSATION OF HYBRID SILICIO ALKOXIDE (MTEOS)



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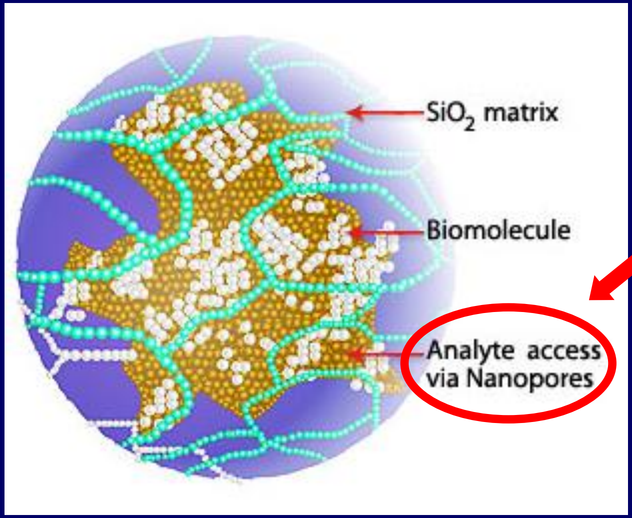

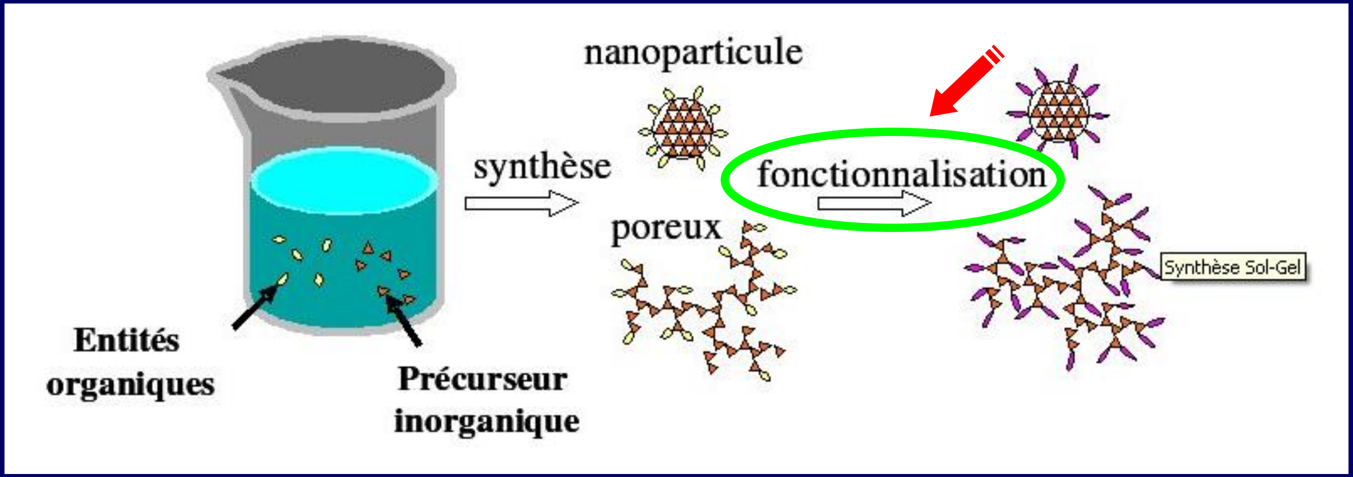

Kinetically Confined Synthesis of Nanoparticles

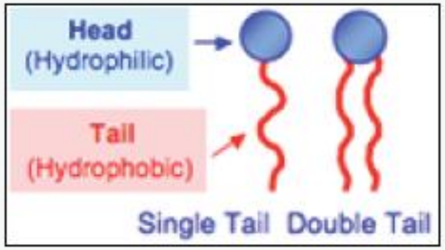

Figure 1. Amphiphilic molecule (Surfactant)

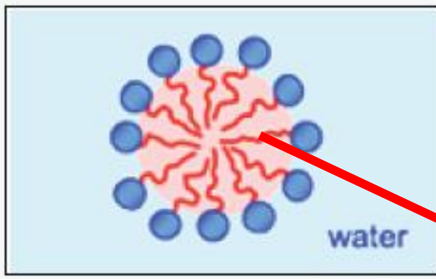

Figure 2. Micelle

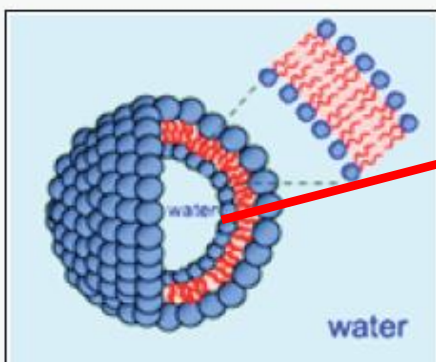

Figure 3. Vesicle

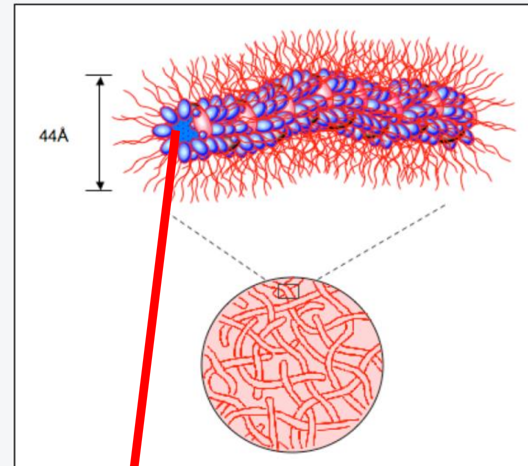

Figure 7. Reverse wormlike micelles and their entangled network

The synthesis of nanoparticles can be achieved by confining the reaction in a restricted space.

Further Reading

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• Sol-Gel Science, C. J. Brinker, G.W. Scherer, Academic Press 1990 (ISBN 0-12-134970-5).

• Nanotechnology. An Introduction to Nanostructuring techniques. M. Köhler, W. Fritzche, Wiley-VCH Verlag, 2004 (ISBN 3-527-30750-8).

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