

# History

"The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom."

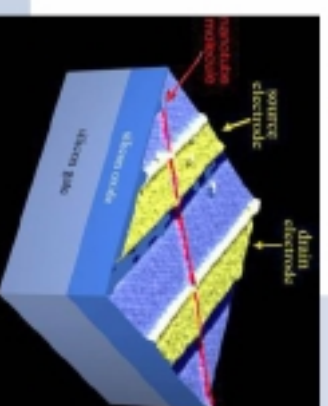
I am afraid to consider the final question as to whether, ultimately in the great future we can arrange the atoms the way we want; the very atoms, all the way down! ... "



**Richard Feynman (1959)**

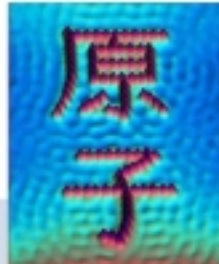
- "...Why can't we make them very small, make them of little wires... the wires could be 10 or 100 atoms in diameter, and the circuits could be a few [hundred nanometers] across."

– Richard Feynman  
on computers.



## Introduction: Definition

- Nanoscience refers to the world as it works on the atomic or molecular scale, from one to several hundred nanometers.
- Nanometer =  $10^{-9}$  meters: roughly the size of 10 hydrogen atoms lined up or the width of DNA.



- Old philosophy of creating things was to start with something big, and make it smaller. Nanoscience starts with something atomic and builds things with it.
- *“Nanotechnology has given us the tools... to play with the ultimate toy box of nature – atoms and molecules. Everything is made from it... The possibilities to create new things appear limitless.”*

- Nobel Laureate Horst Stormer

## Nano – Tree

*essential is invisible to the eye” A. de Saint-Exupery, “La Petit Prince”*

Atoms and molecules are generally less than a nm and we study them in chemistry.

Quantum chemistry does not apply,  
But the fundamental laws hold, and  
And the system are not large enough  
For classical laws of physics.



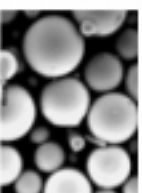
# Realize Size



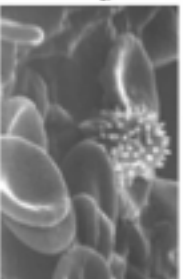
Dust mite  
200  $\mu\text{m}$



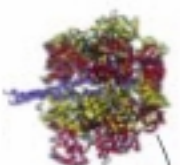
Ant  
~5 mm



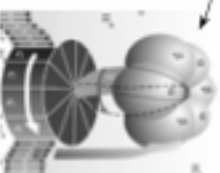
Fly ash  
~10-20  $\mu\text{m}$



Red blood cells  
with white cell  
~2-5  $\mu\text{m}$



~10 nm  
diameter

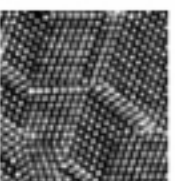


ATP synthase

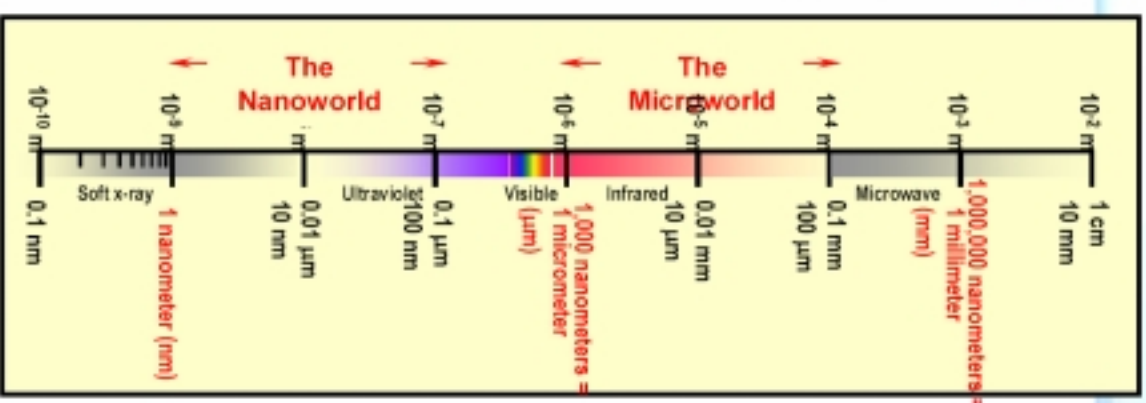


DNA

~2-1/2 nm diameter

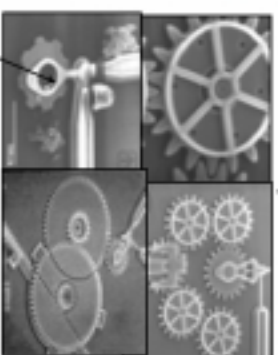


Atoms of silicon  
spacing ~tenths of nm

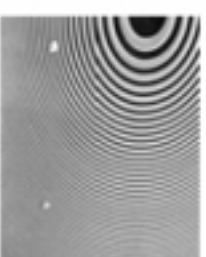


Head of a pin  
1-2 mm

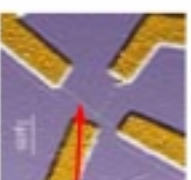
MicroElectroMechanical devices  
10 - 100  $\mu\text{m}$  wide



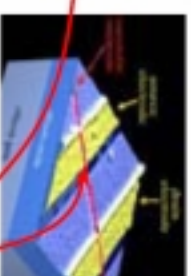
Red blood cells



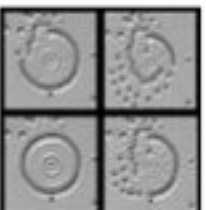
Zone plate x-ray "lens"  
Outermost ring spacing  
~35 nm



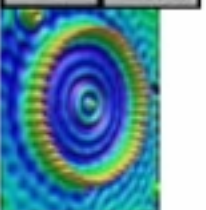
Nanotube electrode



Nanotube transistor



Quantum corral of 48 iron atoms on copper  
surface  
positioned one at a time with an STM tip  
Corral diameter 14 nm



Carbon nanotube  
~2 nm diameter

## Things Natural

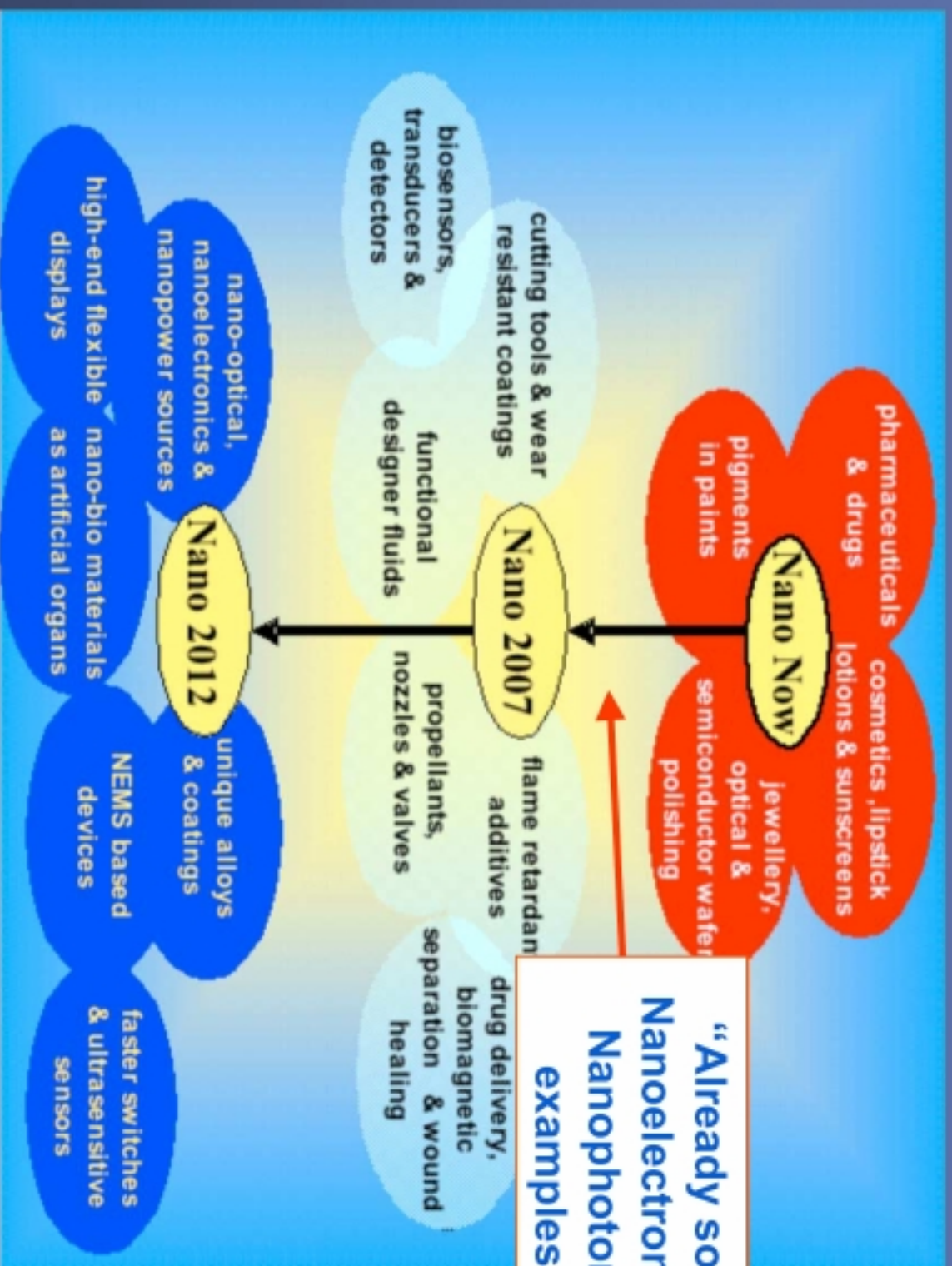
## Things Manmade

## Nanoparticles

## Research Lab.



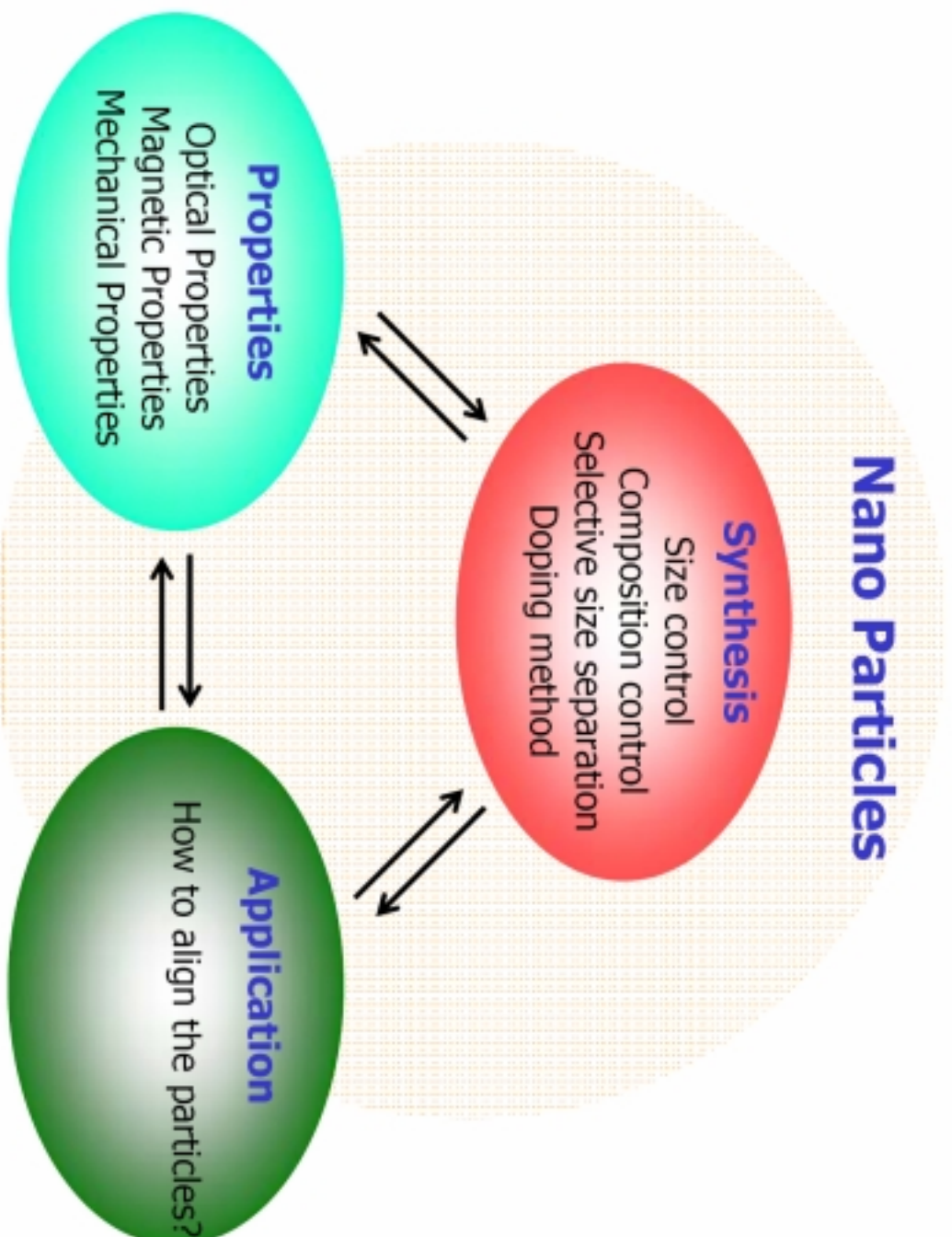
# Nanotechnology Timeline



(Small Wonders, Endless Frontiers, Review NNI, NRC, 2002)



# Research in Nanoparticles



# Overview of Nanoparticle

- **Basic Concept**

- Introduction of nanoparticles 125-70,000 atoms, < 100 nm
- Size Dependent Properties
- Colloidal Stability

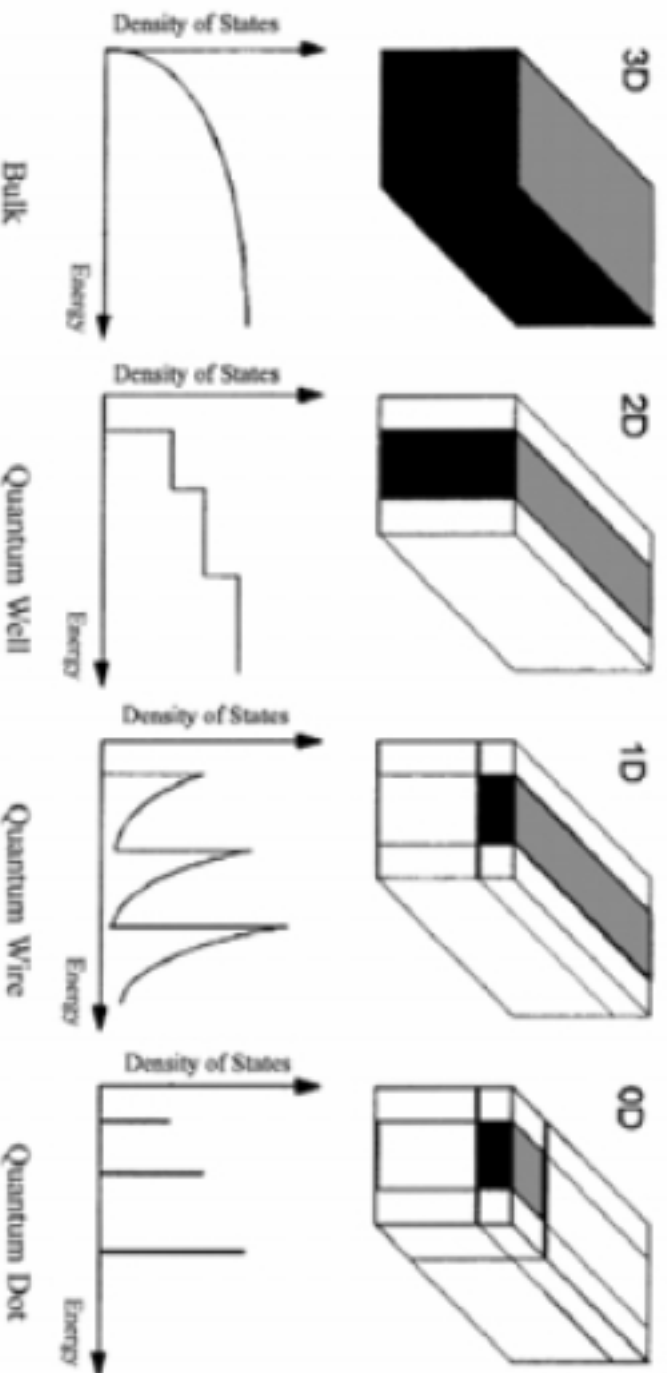
- **Wet Chemistry**

- Metal Nanoparticles
- Semiconductor
- Ceramics
- Polymer nanoparticles

- **Other Methods**

- Mechanochemical Process
- VLC mechanism
- Combustion method

# Important Parameter



**FIGURE 2.5** Formation of a zero-dimensional (0D) quantum dot by the formal reduction of dimensions, correlating with the continuing discretization of the energy states.

## 1. Metal : Electron mean path



**Figure 1** Comparisons of

quantum wells, wires, rods and dots. **a**, Geometries of the

different structures. **b**, Plots of

$\Delta E_g$  (the increase in the bandgap over the bulk value) against  $d$  (the thickness or diameter) for

rectangular quantum wells, cylindrical quantum wires and

spherical quantum dots obtained from particle-in-a-box

approximations. The grey area between the dot and wire curves is the intermediate zone

corresponding to quantum rods.

The vertical dotted line and

points qualitatively represent the expected variation in the

bandgap for InAs quantum rods of varying length/diameter ratio,

as studied by Kan *et al.*<sup>1</sup>. **c**, A plot

of  $\Delta E_g$  against length/diameter ratio for the InAs quantum rods

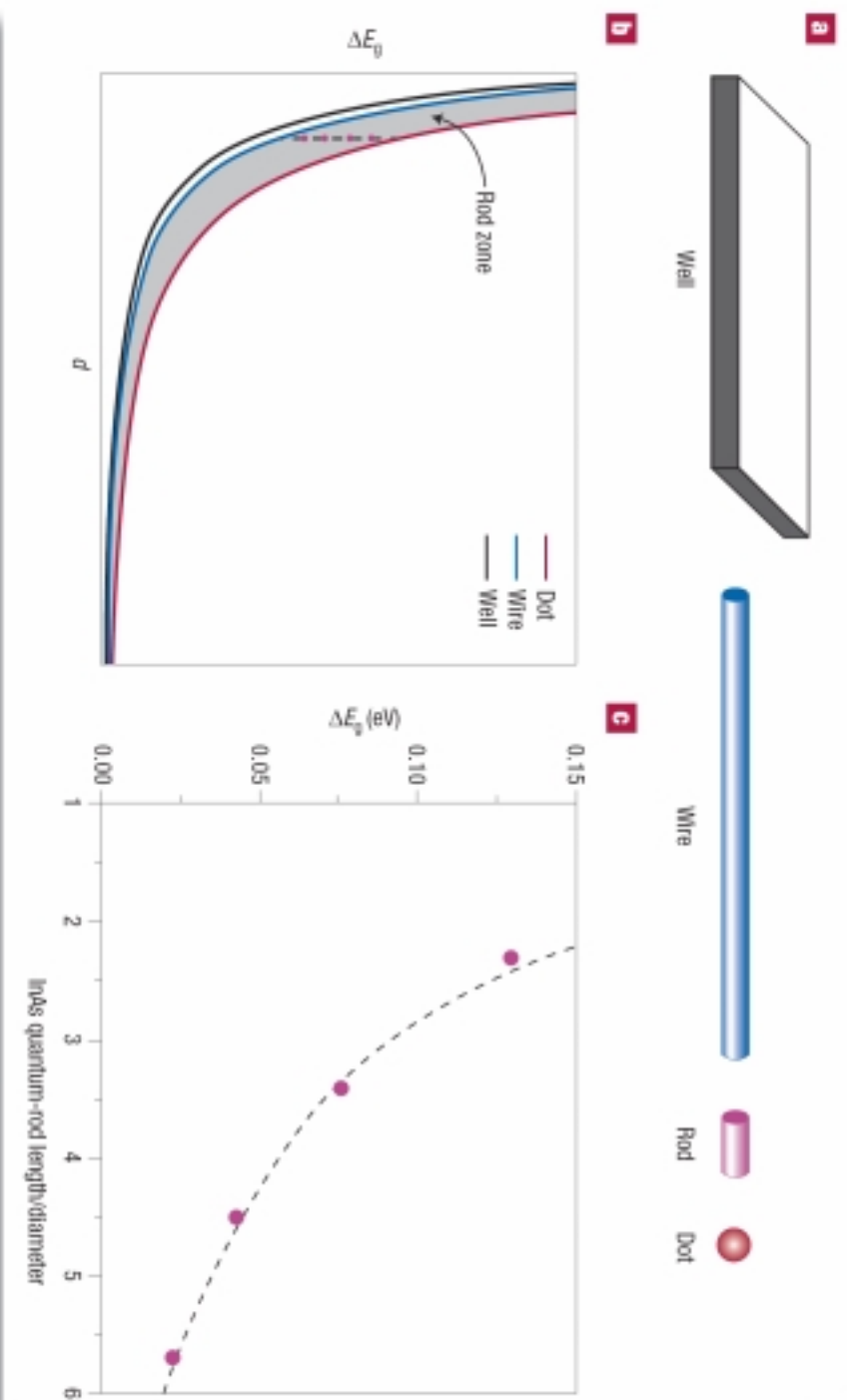
synthesized by Kan *et al.*, showing the dependence of the

bandgap on the shape of the quantum rods. The dotted line

represents the variation

expected from a particle-in-a-

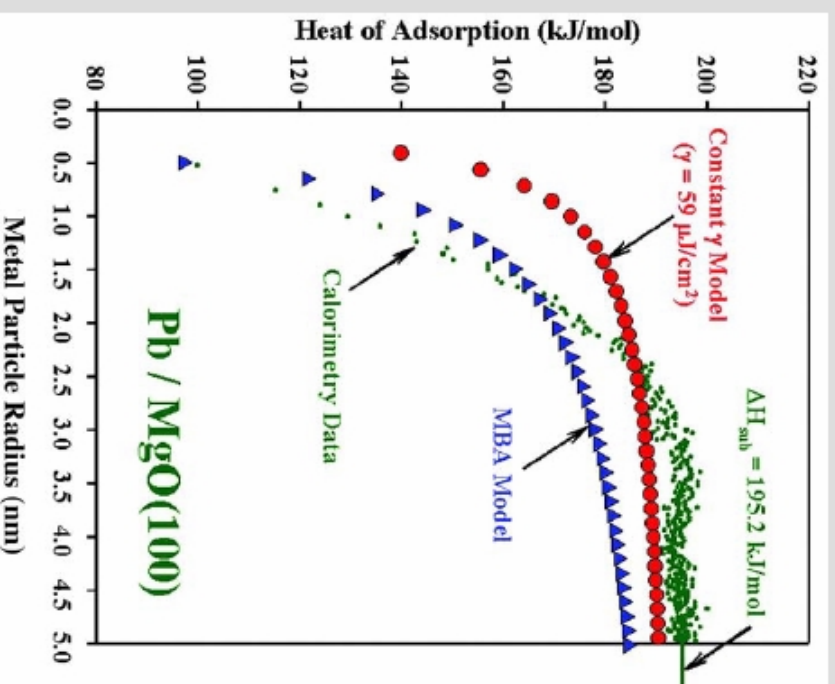
box approximation<sup>1</sup>.



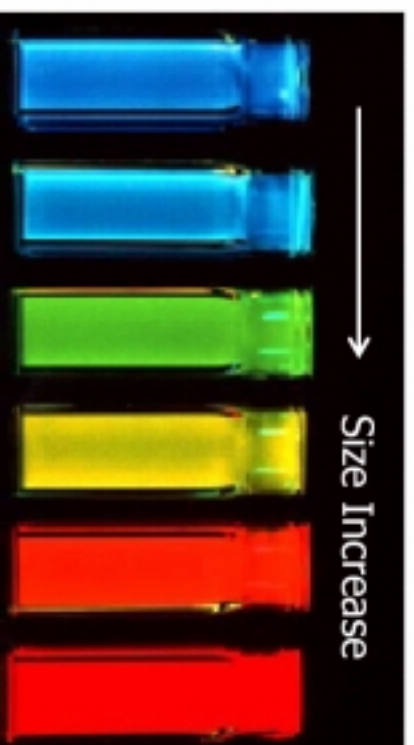
Calorimetric measurements show that the energy dependence of supported Pb particles vary much more quickly than predicted by the Gibbs-Thompson relationship.

“This shows that the surface energy increases substantially as the radius decreases below 3 nm.”

C.T Campbell et. al. Science 298 (2002) 811-814



# Important Parameter-Semiconductor



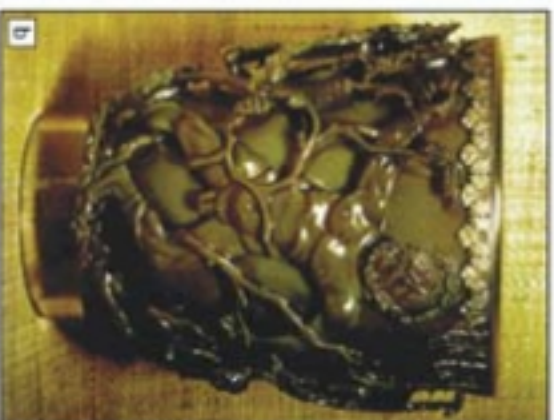
Ex) CdSe

## 2. Semiconductor : Exciton radius



# Size Dependent Optical Properties

- Lycurgus cup (AD 4세기)



Transmitted light

Reflected light

→ 20nm 이하의 gold nano particle를 첨가

- Not all that's Gold does glitter

## Gold Building Blocks

Atoms:  
colorless, 1 Å

Gold clusters:  
orange, nonmetallic,  
<1 nm

Gold nanoparticles:  
3–30 nm, red, metallic,  
“transparent”

Gold particles:  
30–500 nm

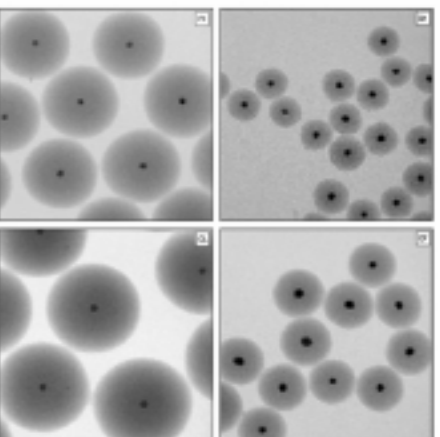
metallic, turbid,  
crimson to blue



Bulk gold film



## Size Dependent Optical Properties



- Au@SiO<sub>2</sub> particles
  - Core : 15nm Au
  - Shell : SiO<sub>2</sub>

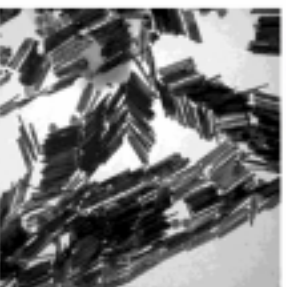
### • Coating Thickness

→ Control of Dipole coupling btw particles

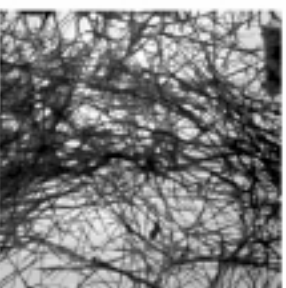
→ Change of Assembly color

## Size Dependent Optical Properties

### • Nano Rod



### • Nano Wire



### • The Seed Mediated Method



## Size Dependent Optical Properties

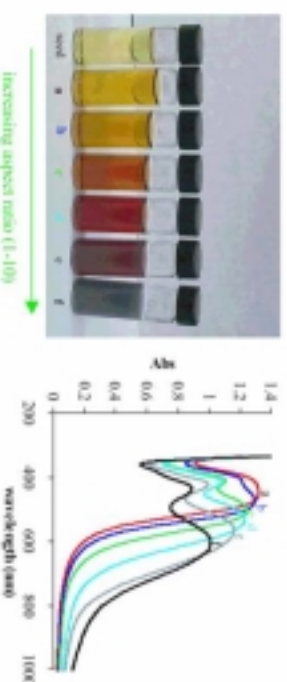
### • Au@SiO<sub>2</sub> particles



Decreasing gold particle spacing →

The transmitted colors of a series of gold particle films with decreasing particle spacing. The gold core particles are 15nm in diameter; the shell thickness are from left to right, 17.5nm, 12.5nm, 4.6nm, 2.9nm, 1.5nm and 0nm. Films are each 1cm × 3cm. The spectra shift smoothly between the two curves shown in right figure as the spacing is varied.

## Size Dependent Optical Properties



Aqueous solution of silver nanoparticles show a beautiful variation in visible color depending on the aspect ratio of the suspended nanoparticles: far left in the photograph, silver nanoparticles 4nm in diameter that are used as seeds in subsequent reactions; a-f) silver nanorods of aspect ratio 1~10.

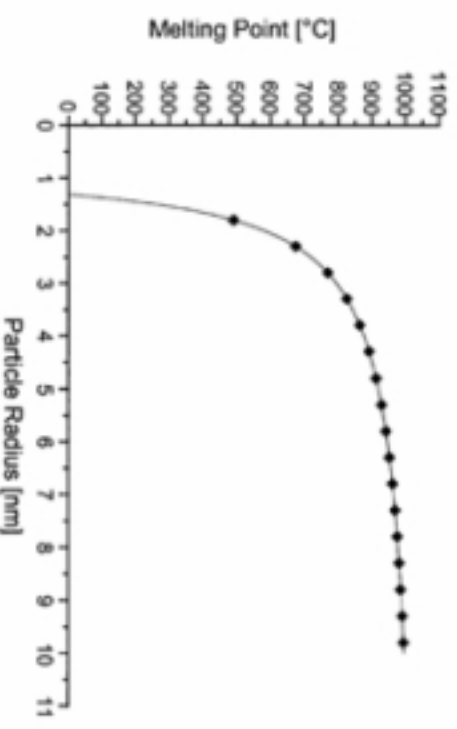
# Size Dependent Melting Point

**TABLE 2.1** The relation between the total number of atoms in full shell clusters and the percentage of surface atoms

Full-shell Clusters	Total Number of Atoms	Surface Atoms (%)
1 Shell	13	92
2 Shells	55	76
3 Shells	147	63
4 Shells	309	52
5 Shells	561	45
7 Shells	1415	35

**\*Gold atomic size : 1.79Å (50nm : 6%)**

## •Melting Point of Gold (T<sub>m</sub>=1064°C)

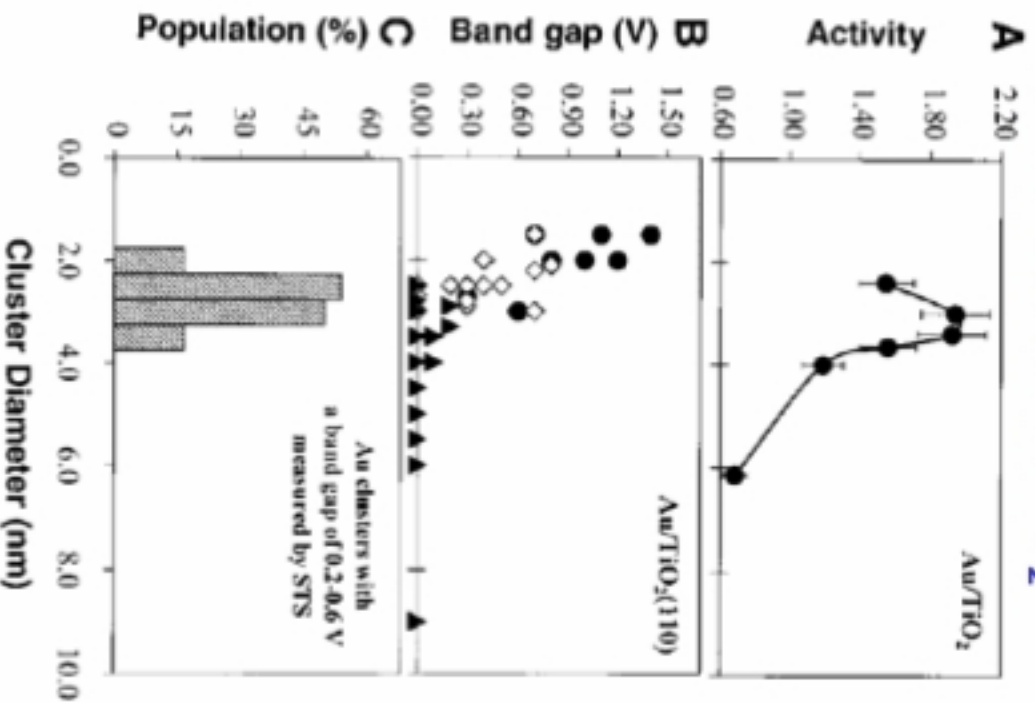


**FIGURE 2.6** Relation between the size of gold particles and their melting point.

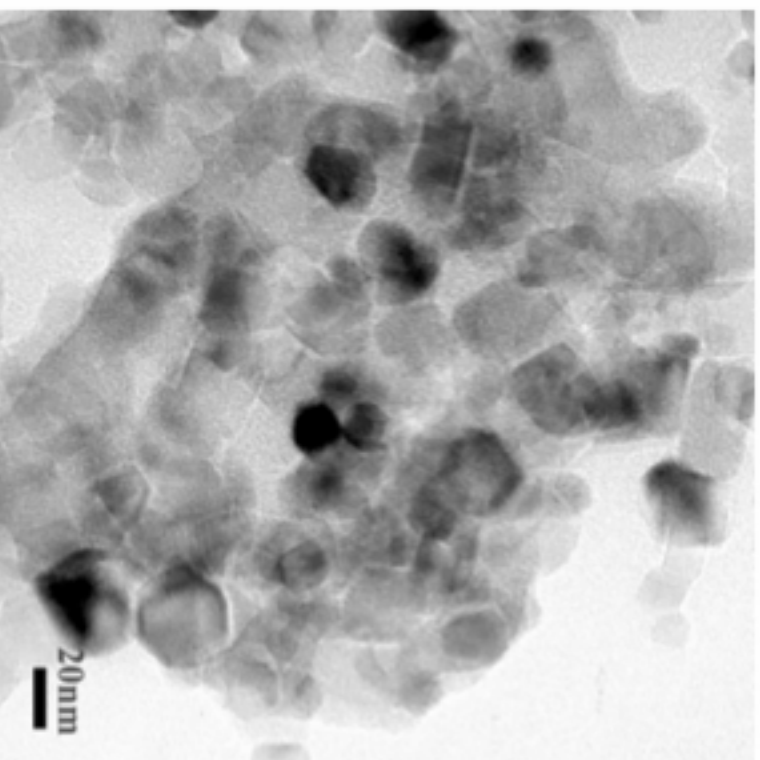


# Size Dependent Chemical Reaction

## • Catalytic Activity of Au Cluster on $\text{TiO}_2$



## • Photocatalyst $\text{TiO}_2$ (Degussa P-25)



# Colloids ?

## • Definition

A suspension of finely divided particles in a continuous medium in which the particles are approximately 5 to 5,000 angstroms in size, do not settle out of the substance rapidly, and are not readily filtered

	Dispersed phase	Media	Example
Aerosol	Liquid	Gas	Fog, aerosol sprays
Colloids	Micelles	Liquid	Soap
Gels	Polymers	Liquid	Jellies, Glue
Emulsion	Liquid	Liquid	Milk, Butter

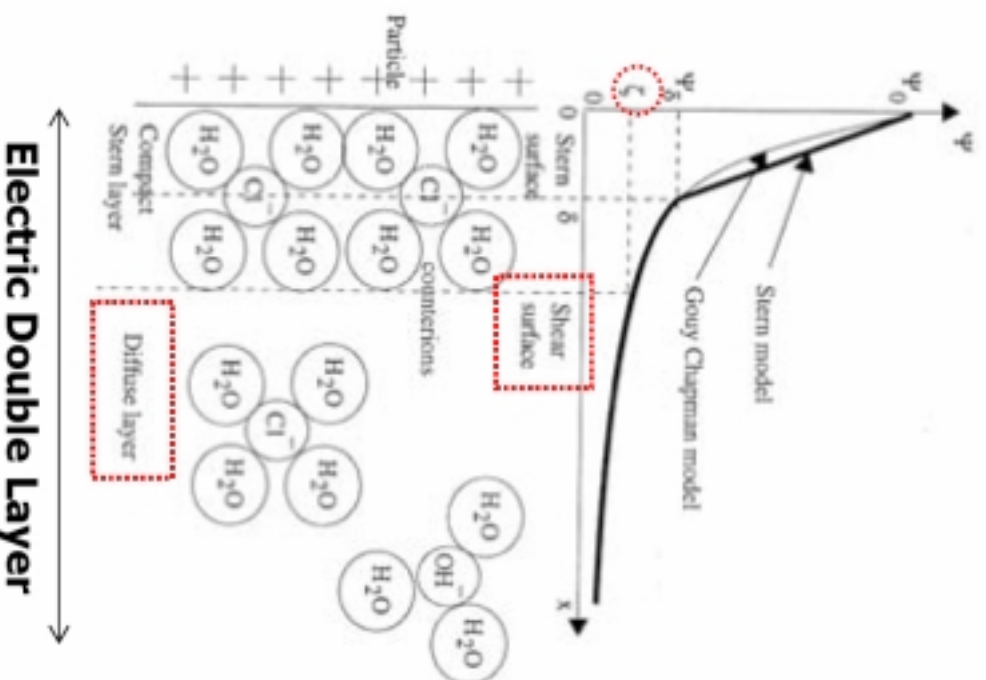
## • Thermodynamics → Agglomeration (Stable)

→ **Need other forces for colloidal stability**

**Electrostatic force & Steric repulsive force**

# Force for Colloidal Stability

- **Electrostatic force**



- **Electric double layer**

; Stern Layer + Diffuse Layer :

- Stern layer : immobile adsorbed layer
- Diffuse layer : mobile by thermal vibration

- **Zeta potential**

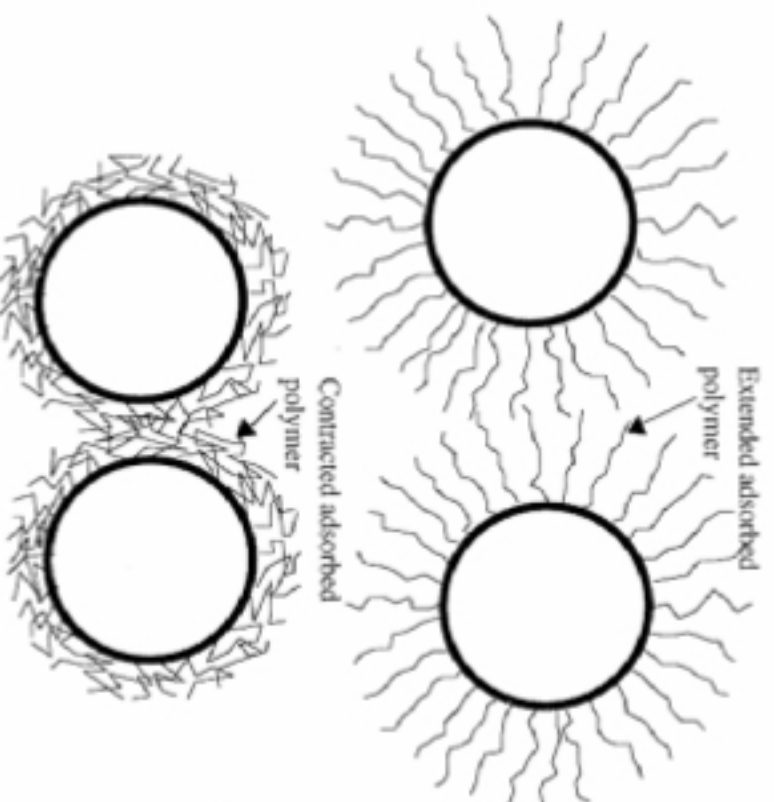
; the potential at the slippage plane.



# Force for Colloidal Stability

- **Steric repulsive force**

a - Repulsion between particles



Enthalpy : Osmosis pressure ( $\Delta H > 0$ )

Entropy : Deg. of Freedom ( $\Delta S < 0$ )

$$\Delta G > 0$$



**Prohibit coagulation btw. particles**

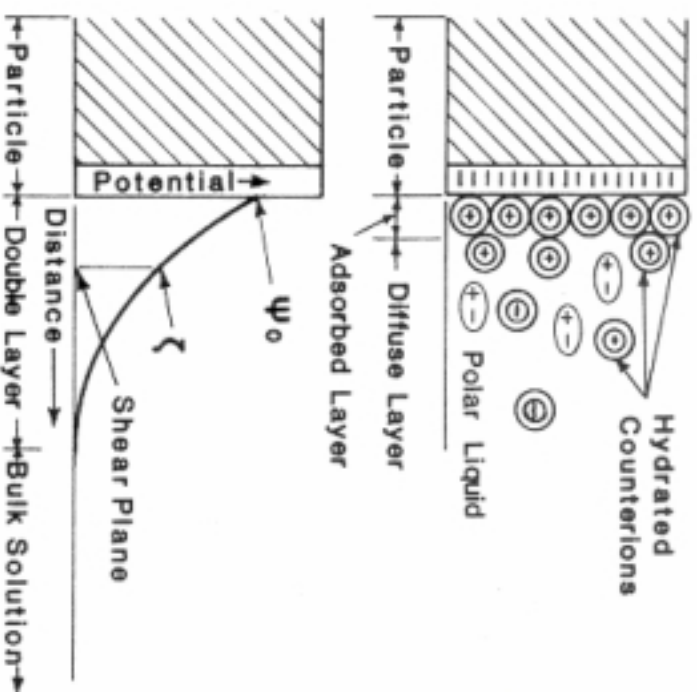
# Surface Potential

## 1. Electrostatic interaction

favors a locally ordered ionic arrangement

## 2. Entropic factor

randomized the uniform distribution (∵ thermal E)



## Poisson Equation!!

$$\frac{d^2\psi}{dx^2} = -\frac{\rho}{\epsilon_r \epsilon_0}$$

$$\rho = \sum n_i z_i e = \sum n_{i0} z_i e \exp\left(-\frac{z_i e \psi}{kT}\right)$$

Solution

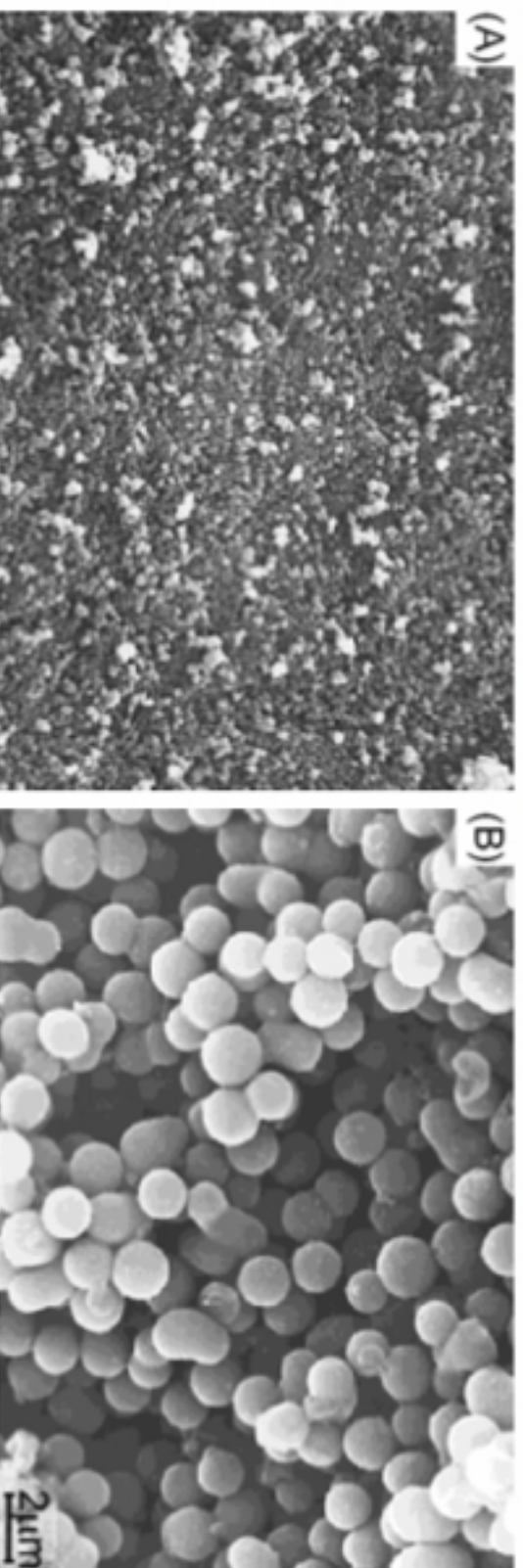
$$\psi = \psi_0 \exp(-\kappa x)$$

Double Layer Thickness

$$\kappa^{-1} = \left( \frac{\epsilon_r \epsilon_0 N_A k_B T}{F^2 \sum N_i Z_i^2} \right)^{1/2}$$

# Control the Particle Size

- TiO<sub>2</sub>
- Different Solvent (Mixed solvent = n-PrOH + H<sub>2</sub>O)



RH ratio	Dielectric Constant of solvent at 20 °C	Zeta Potential at 20 °C	Particle Morphology
0	80	18.3	Fine (aggregated)
1	48	11.4	Aggregated
2	36	6.7	Spherical, aggregated
3	32	4.5	Spherical, discrete

# Control the Particle Size

- **Energy barrier** for colloidal stability

$$V_b = -\frac{Ad}{12h} + 2\pi d\epsilon_r\epsilon_0\psi^2$$



Only dependent on Dielectric constant of solvent  
Zeta potential of precipitate



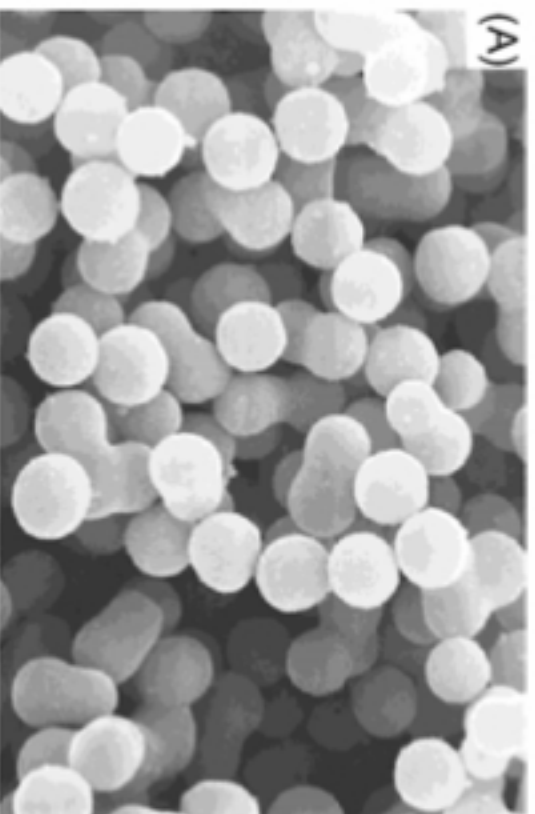
Lower Barrier → Larger size  
Higher Barrier → Smaller size

Hamaker constant (A)  $\approx 10^{-20}$  J (water and aliphatic alcohol)

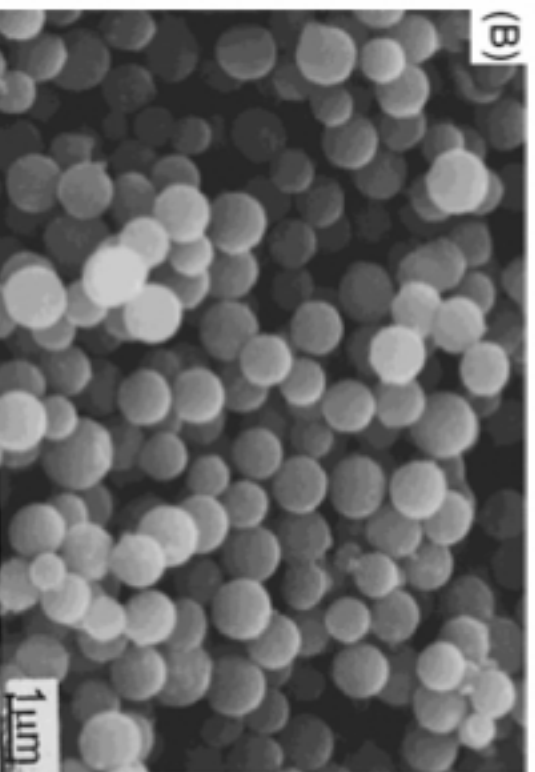


# Dispersant Effect (Steric Force)

- Without HPC



- With HPC

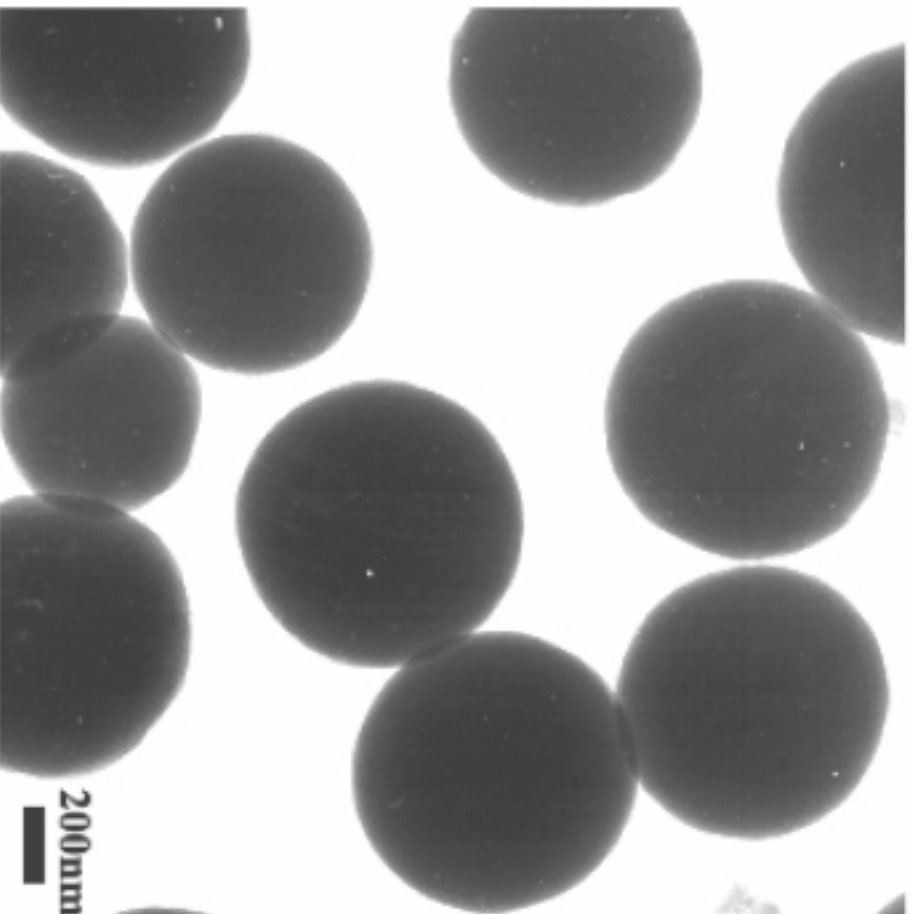


- HPC: hydroxypropyl cellulose (m.w. = 100,000)

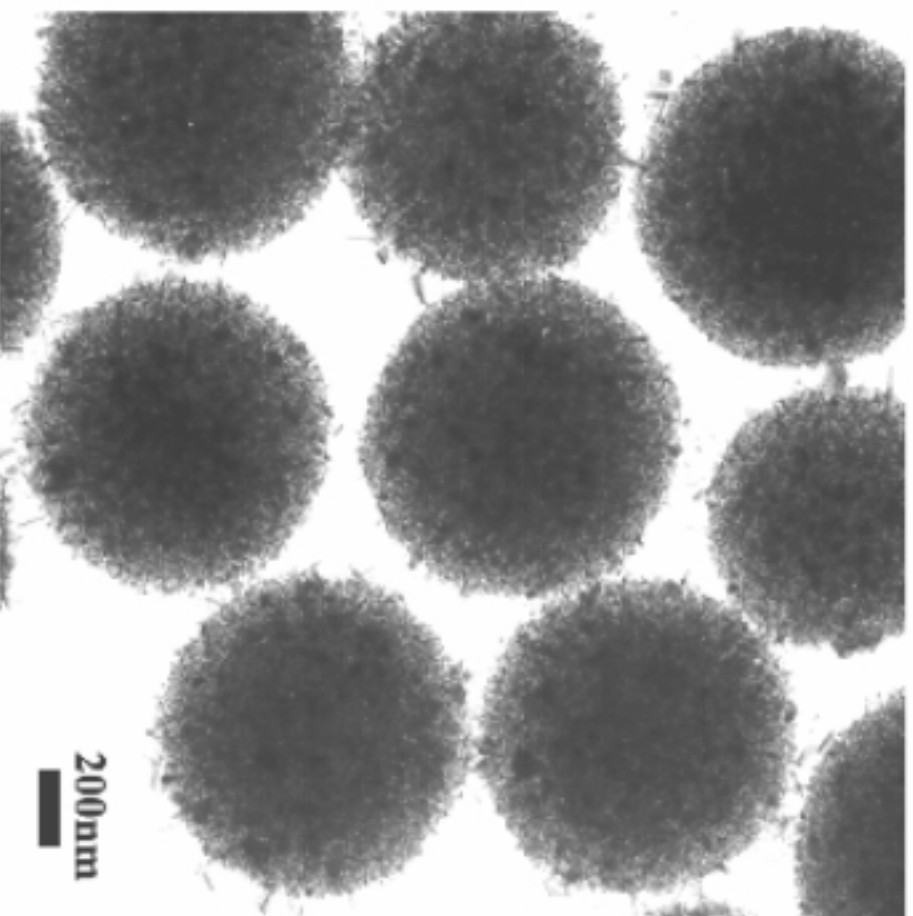
- Reduce agglomeration
- Smaller particles size
- Spherical shape (No irregular shape)
- Well dispersed

# TEM Micrograph of $\text{TiO}_2$

- Amorphous Particles



- Crystallized Particles



# How to Synthesize Nanoparticles



# How to Control nanoparticles

## Nanoparticles

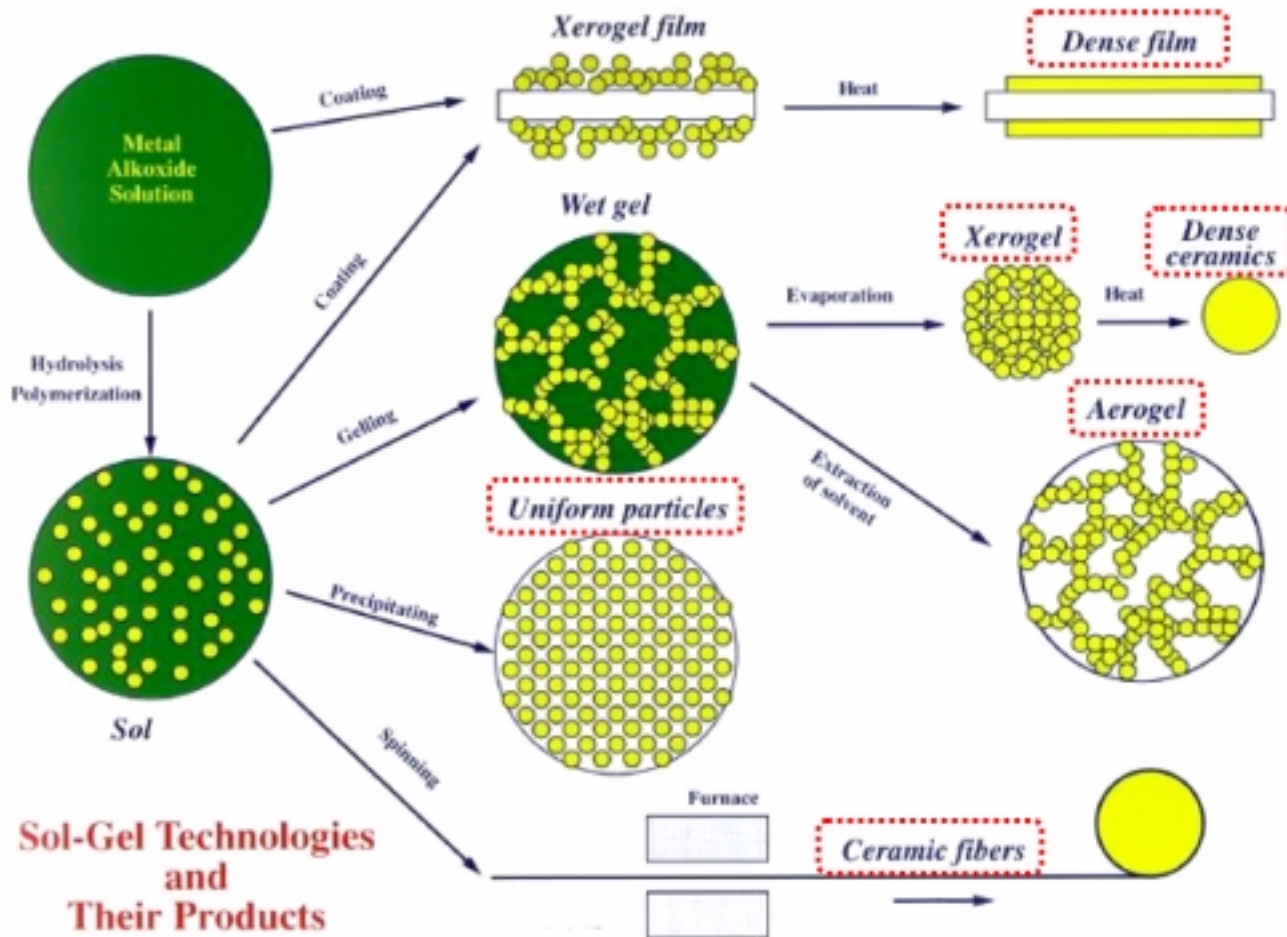
- Particle size
- Morphology
- Degree of Crystallization
- Crystallinity
- Chemical Composition

## Bottom-up Process

Major efforts in nanoparticle synthesis can be grouped into two broad areas: gas phase synthesis and sol-gel processing. Additional nanoparticle synthesis techniques include sonochemical processing, cavitation processing, microemulsion processing, and high-energy ball milling.



# Sol-gel Process



Sol-gel processing is a wet chemical synthesis approach that can be used to generate nanoparticles by gelation, precipitation, and hydrothermal treatment



# Advantage & Disadvantage

## Advantage

- Large Area Scale
- Precise Composition Control
- Low-Temperature Synthesis
- High Homogeneity
- Easy Achieved

## Disadvantage

- Sensitivity for Atmosphere Condition
- Expensive of Raw Materials
- Use of Toxic Solvent System

# Application

**Optical Coating**



**Optical Coating**



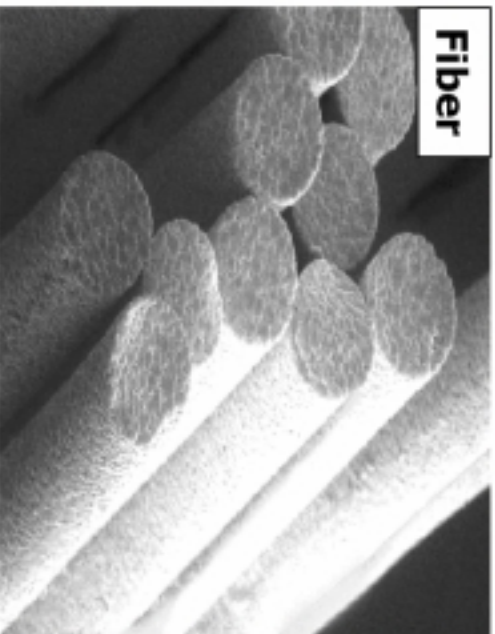
**Dense Ceramics**



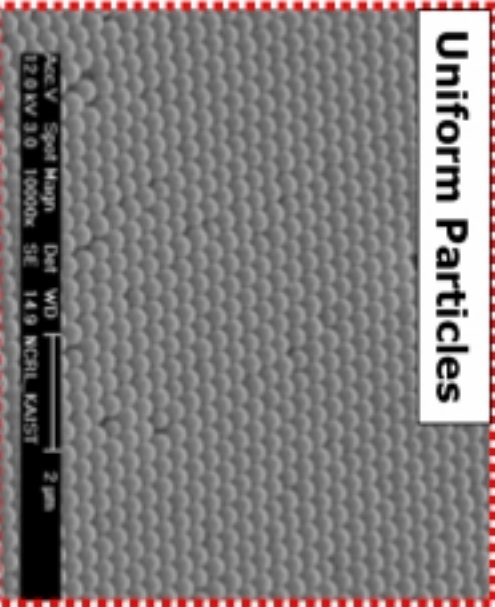
**Thin Films**



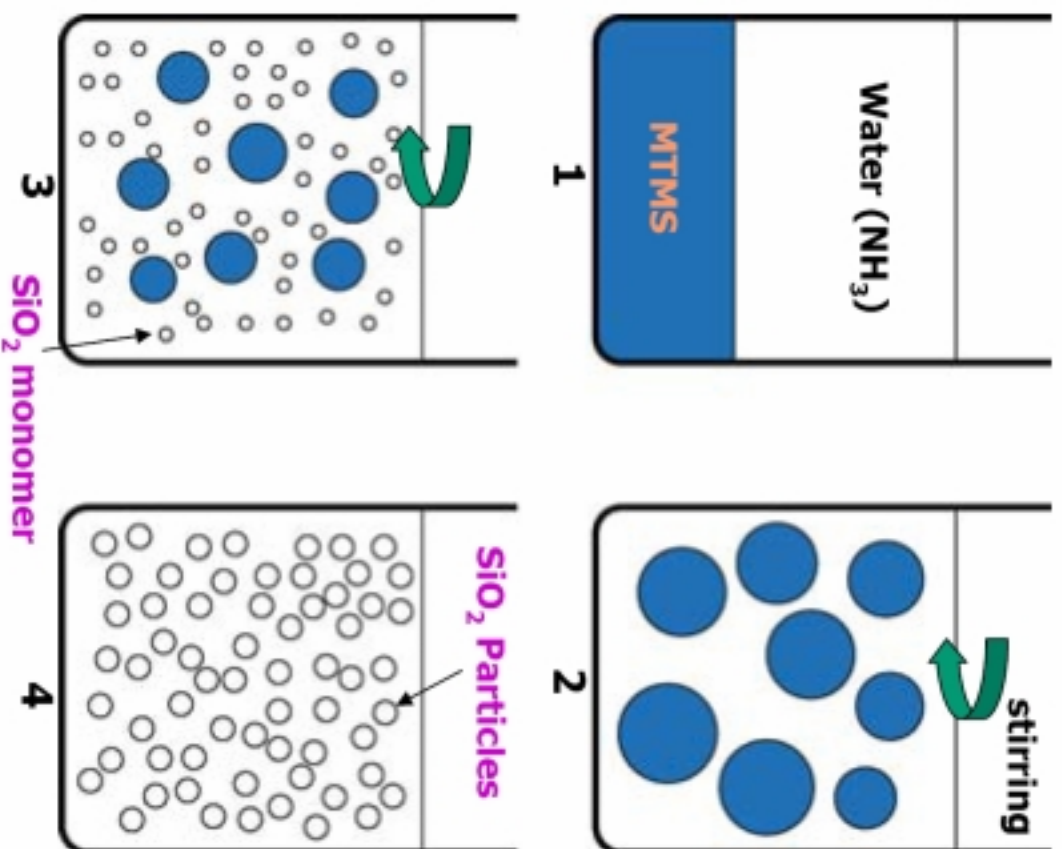
**Fiber**



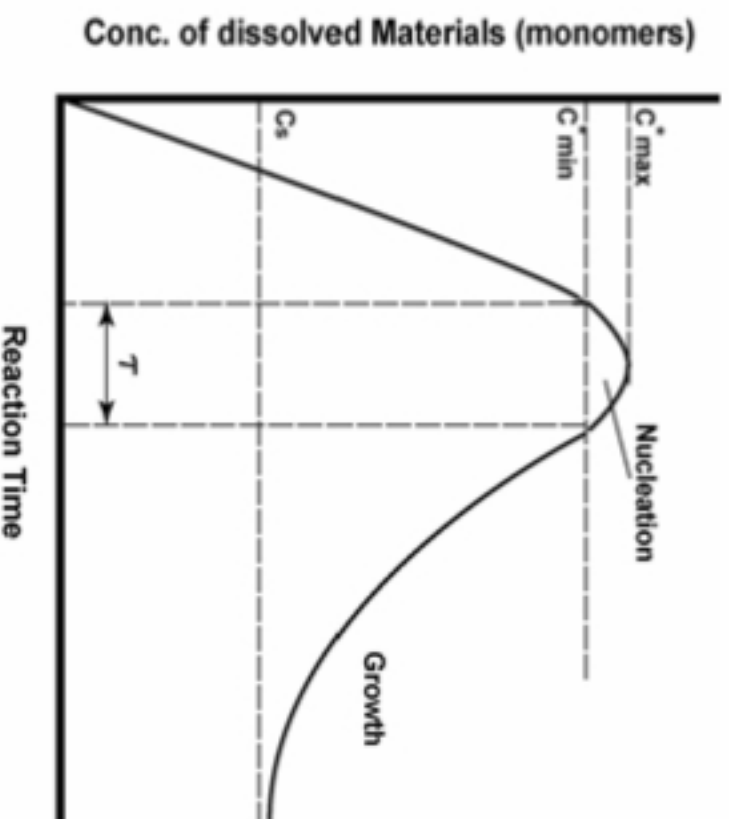
**Uniform Particles**



# Formation of Monodisperse $\text{SiO}_2$ Particles

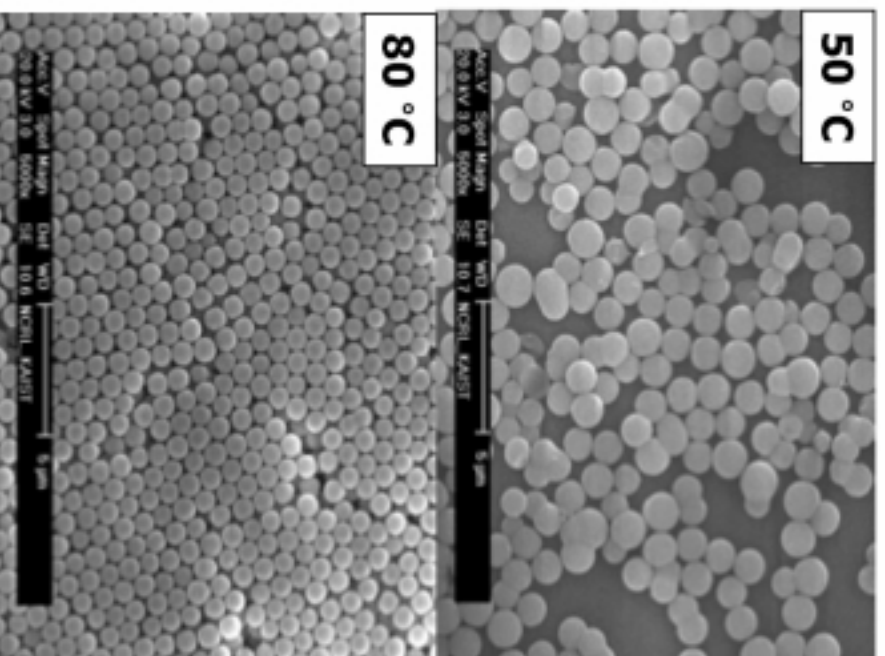


## Lamer diagram



► To make monodispersed Particles, the time  $\tau$  should be decreased.

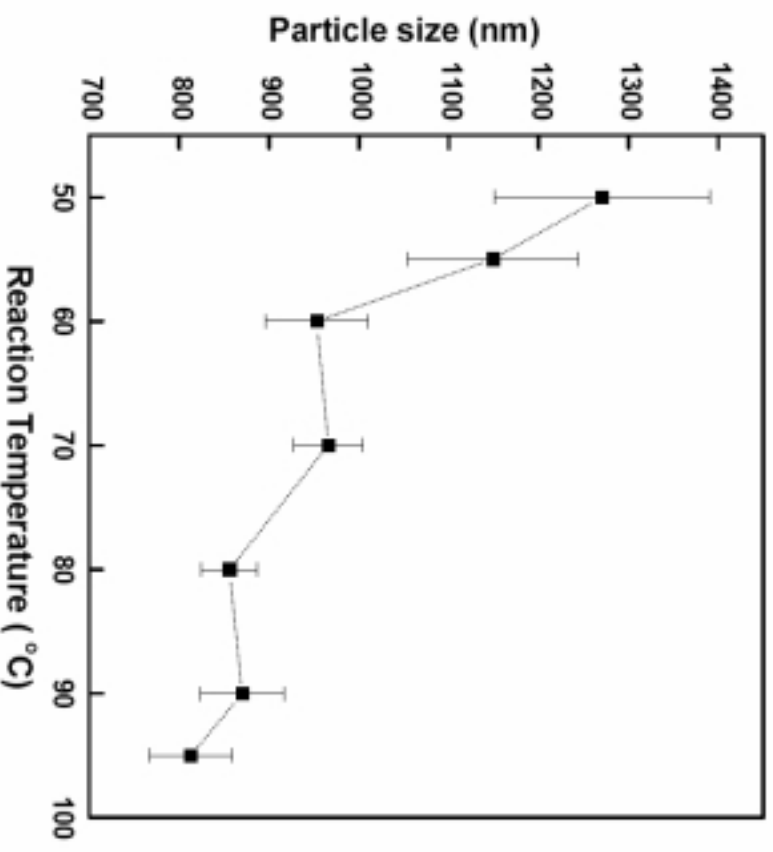
# Monodispersed $\text{SiO}_2$ From MTMS



- $[\text{MTMS}] = 0.6\text{M}$ ,  $[\text{NH}_3] = 1\text{M}$

MTMS; Methytrimethoxysilane

- Particle size vs. Rx Temp.

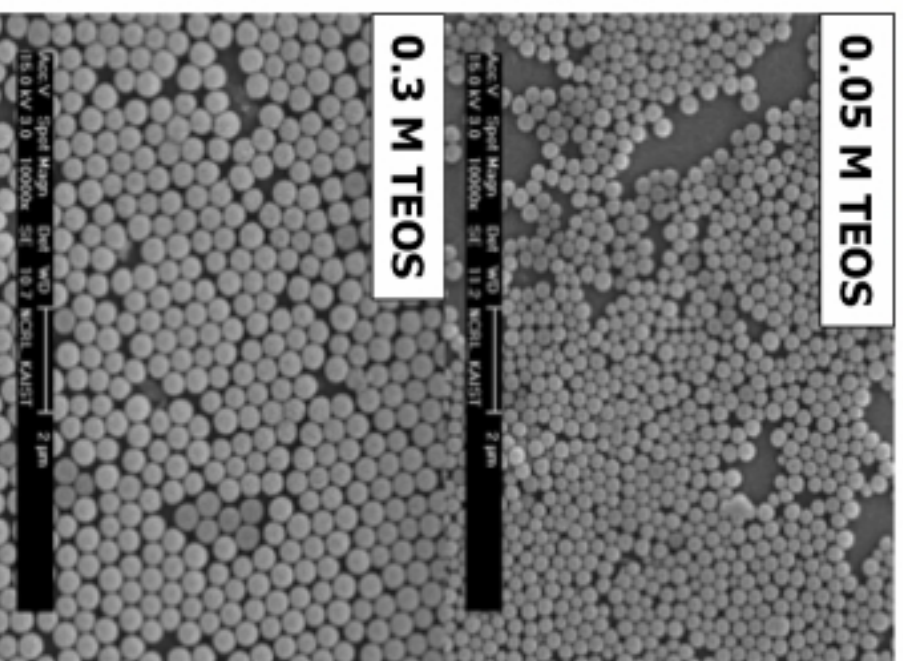


- Temp.  $\uparrow$   $\rightarrow$  Reaction rate  $\uparrow$
- $\rightarrow$  Nucleation time  $\downarrow$
- $\rightarrow$  Size Distribution  $\downarrow$

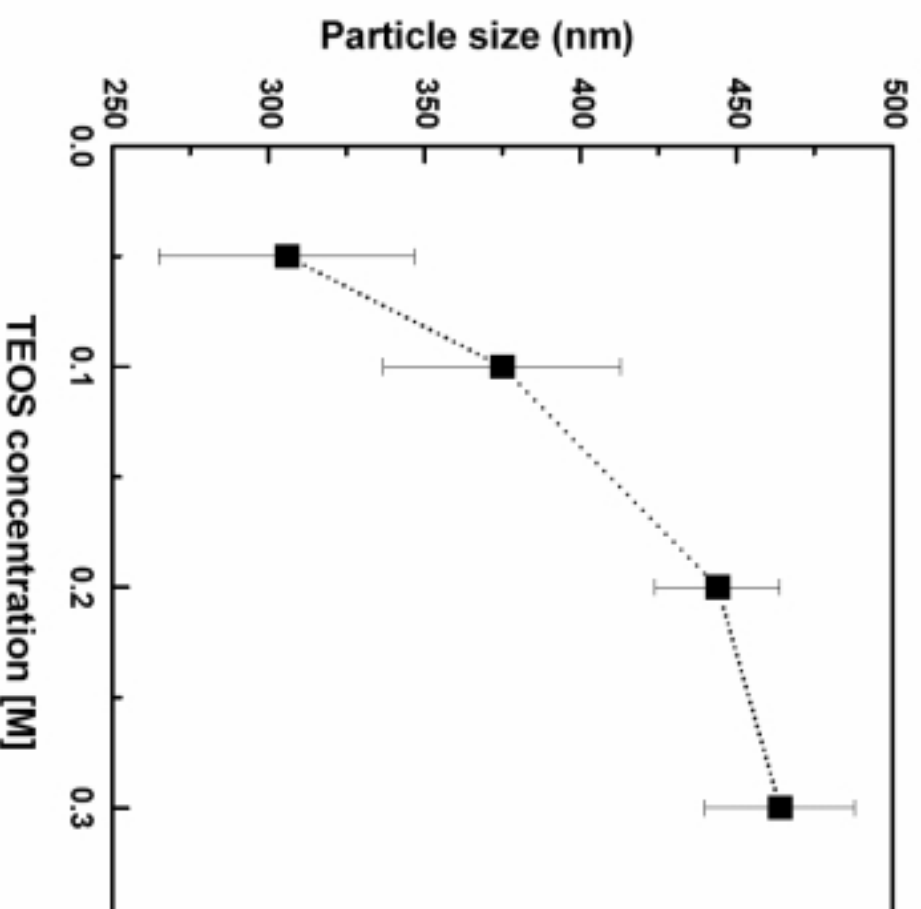


# Monodispersed $\text{SiO}_2$ From TEOS

- Stober Method



- Particle size vs. TEOS Conc.



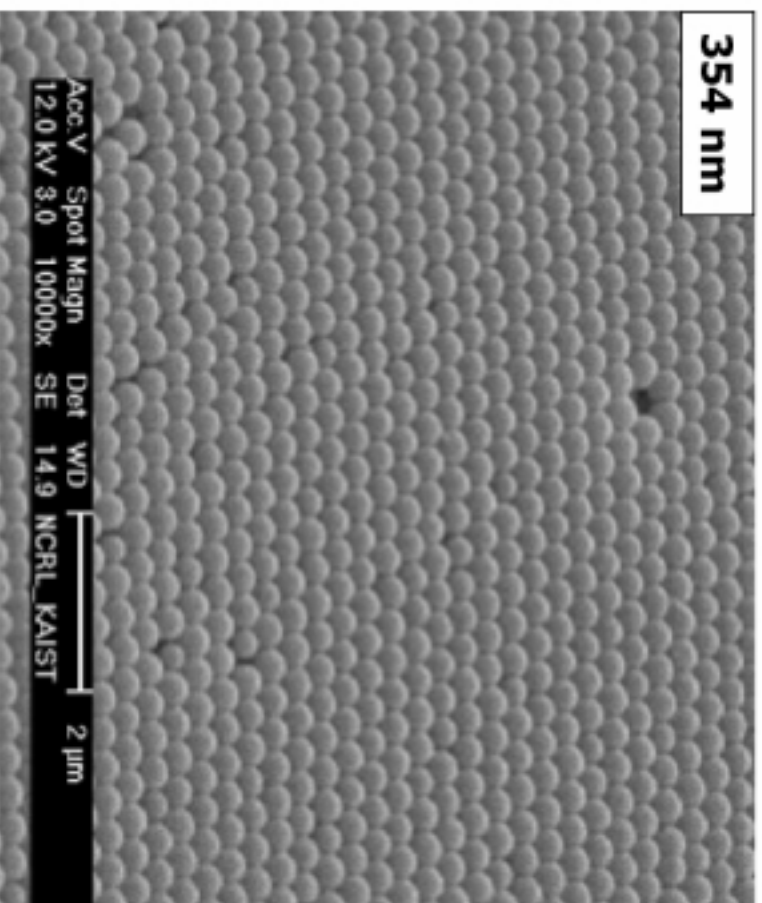
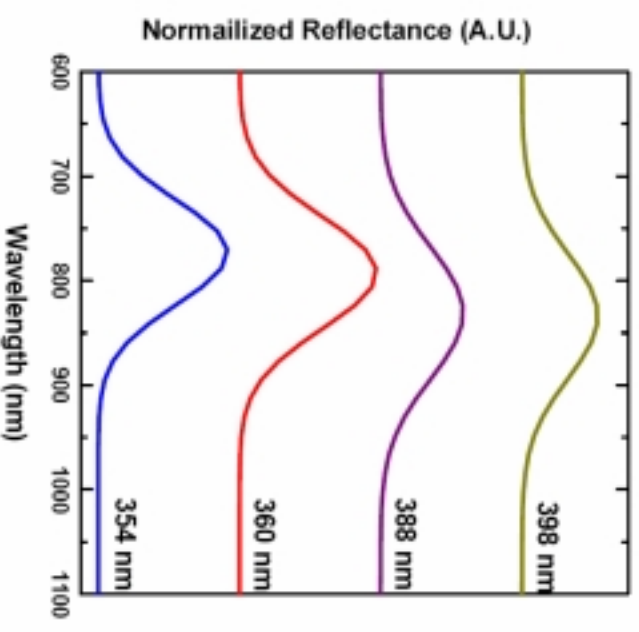
- $\text{H}_2\text{O}/\text{EtOH}=0.2$ ,  $[\text{NH}_3]=0.7\text{M}$ ,  $22^\circ\text{C}$
- TEOS : Tetraethoxyorthosilicate

- Conc. of TEOS  $\uparrow \rightarrow$  Particle size  $\uparrow$



# Photonic Crystal

- Reflectance vs. Particle size



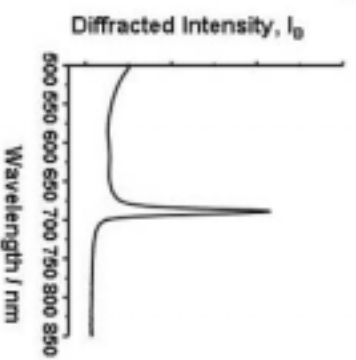
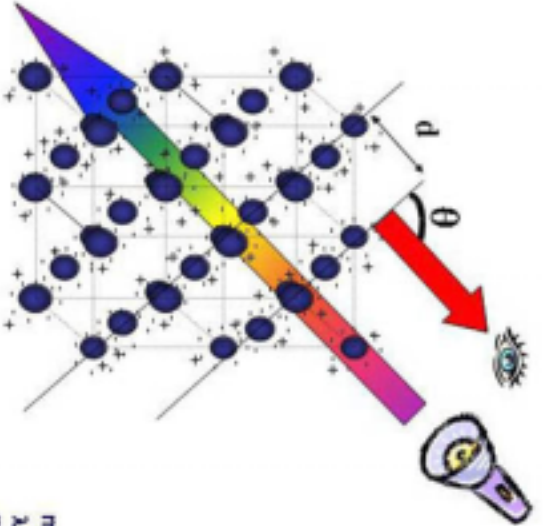
- Bragg's Law

$$\lambda_{\text{Bragg}} = 2n_{\text{eff}}d_{111}$$

$$n_{\text{eff}} = \sqrt{n_{\text{SiO}_2}^2 \times f + n_{\text{air}}^2 \times (1-f)}$$

$$d_{111(\text{FCC})} = \sqrt{2/3}D \quad f = \text{filling ratio}$$

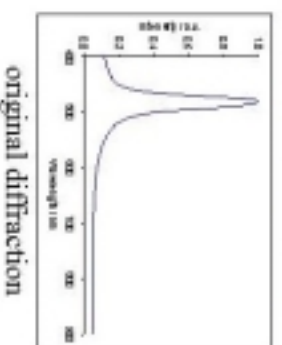
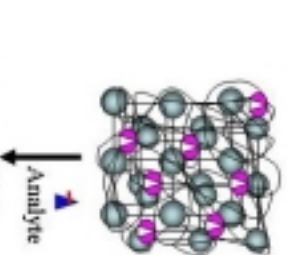
## Bragg Diffraction



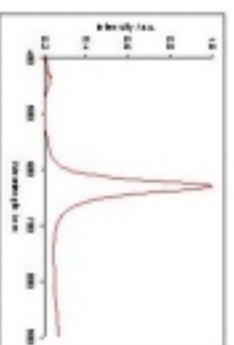
$$m\lambda = 2nd \sin \theta$$

$m$  = order of diffraction  
 $\lambda$  = diffracted wavelength  
 $n$  = refractive index of system  
 $d$  = spacing between diffracting planes  
 $\theta$  = Bragg glancing angle

## IPCCA: Chemical Sensing Material

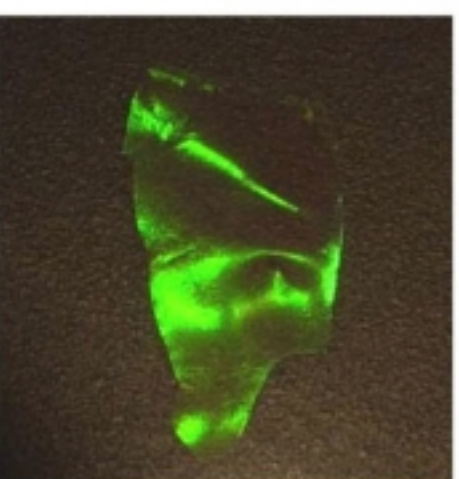
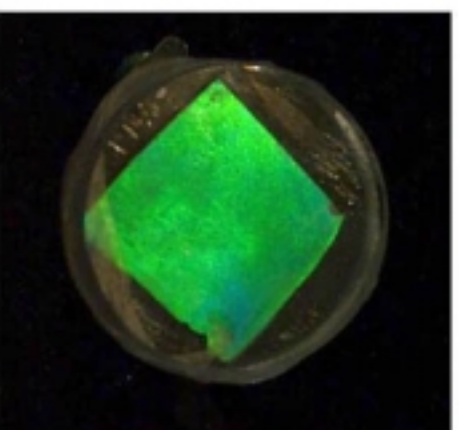


original diffraction



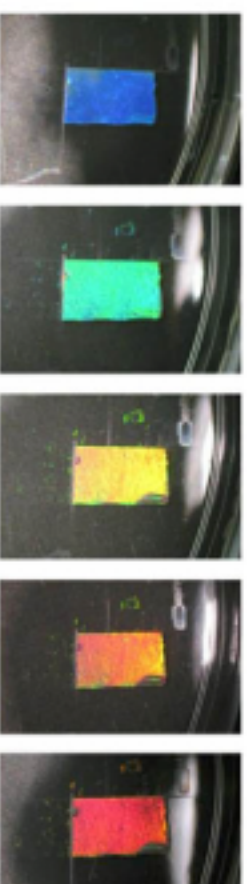
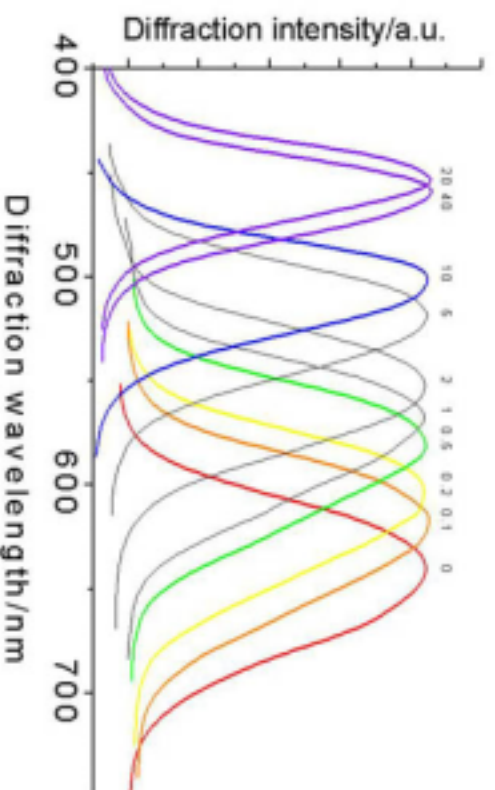
final diffraction

## Diffraction from CCA and PCCA



CCA

PCCA



# Hydrothermal Synthesis

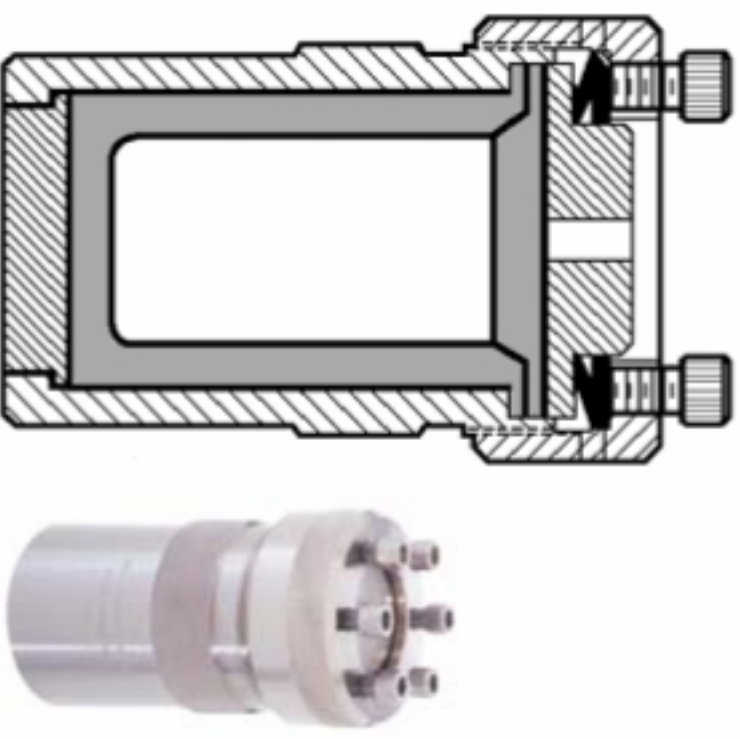
## • Development of Hydrothermal Processing

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- |  |   |
|--|---|
| 1. Crystal synthesis and Growth  | Oxide, Sulfide, Fluoride... (1978 ~)                                |
| 2. Controlled Fine Crystals, Size, Composition, Size, Shape              | PZT, $\text{ZrO}_2$ , $\text{BaTiO}_3$ , HAp, ferrite (1978 ~)      |
| 3. Crystallized Thin/Thick Films   | $\text{BaTiO}_3$ , $\text{SrTiO}_3$ , $\text{LiNbO}_3$ (1989 ~)     |
| 4. Etching, Corrosion, Polishing   | Oxide, Nitride, Carbide   |
| 5. Combined with Electrical, Photo-, Radio-, Mechano-processing          | Synthesis, Modification, Coating                                    |
| 6. Organic and Biomaterials<br>Non-aqueous solution<br>Continuous system | Hydrolysis, Extraction, Polymerization,<br>Synthesis, Decomposition |
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# Hydrothermal Reactor

- High Temperature & High Pressure
- Mediate Temperature





## Advantage

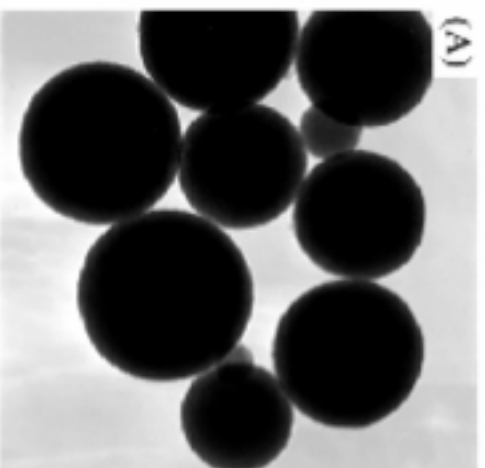
- **No post-heat treatment (aggregation ↓)**  
→ **No milling process (impurity ↓)**
- **Complex chemical composition**
- **Controllable of particle size & shape**
- **Relatively cheap raw materials**

The method, hydrothermal synthesis, is carried out using autoclaves. The autoclave must be treated under 200 degree Celsius because the internal Teflon container is not durable over the temperature. A weighed amount of starting materials and water is mixed and sealed in the autoclave. The autoclave is kept in a temperature-controlled oven for planned time. Internal pressure depends on the temperature.

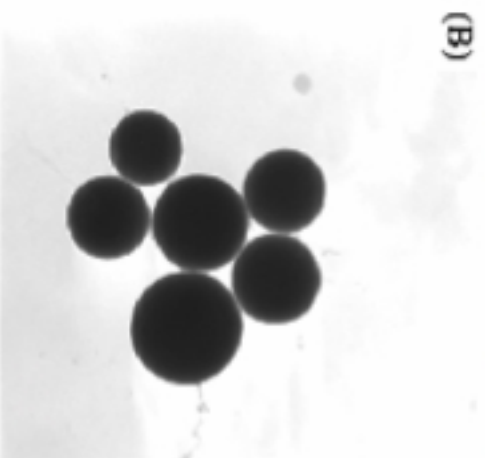


# Perovskite Nanoparticles

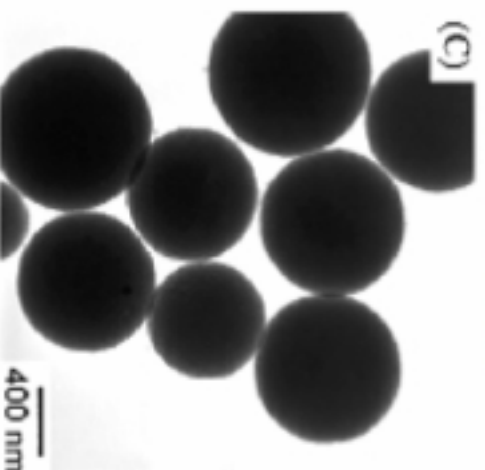
- Thermal Hydrolysis of Metal Salt (microwave heating)



$\text{TiO}_2$  Gel



$\text{ZrO}_2$  Gel



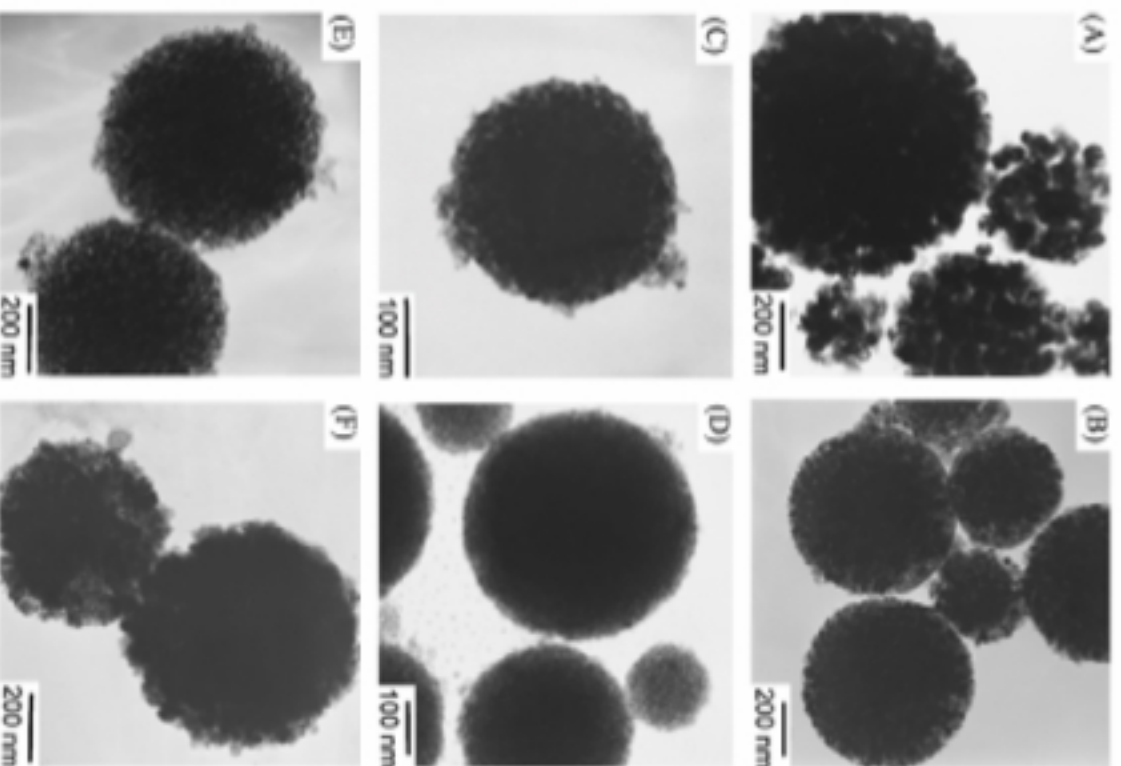
$\text{ZrTiO}_4$  Gel



## Hydrothermal Crystallization

- Adding Pb, Ba, Sr source
- pH control
- Temperature & holding time

# Perovskite Nanoparticles



(A)  $\text{BaTiO}_3$

(B)  $\text{SrTiO}_3$

(C)  $\text{PbTiO}_3$

(D)  $\text{PbZrO}_3$

(E)  $\text{Pb}(\text{Ti}_{0.5}\text{Zr}_{0.5})\text{O}_3$

(F)  $\text{Ba}(\text{Ti}_{0.5}\text{Zr}_{0.5})\text{O}_3$

# Solvothermal Synthesis

## Solvothermal Synthesis

Solvothermal synthesis utilizes a solvent under pressures and temperatures above its critical point **to increase the solubility of solid and to speed up reaction** between solids

- Most materials can be made soluble in **proper solvent** by heating and pressuring the system close to its critical point
- Easily control a solubility of solute  
→ Lower supersaturation state

**1 Dimensional Nanostructure !**

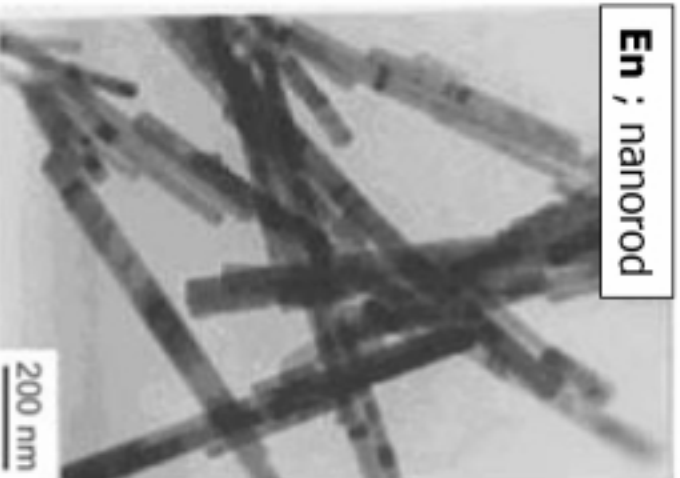
# Solvothermal Synthesis

- Semiconductor nanoparticles (CdE (E = S, Se, Te))

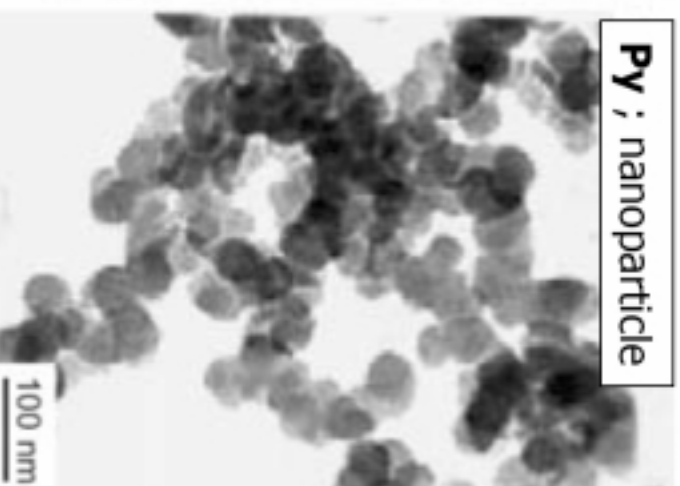


- Ethylenediamine
- Pyridine

**En** ; nanorod



**Py** ; nanoparticle

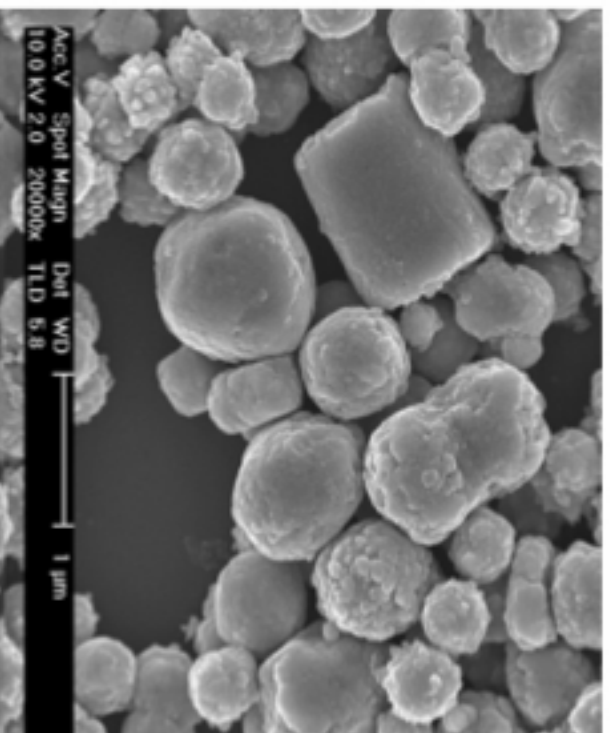


# Introduction – Reduction in Solution

## <Reduction in Solution>



Reducing agent



- Random shape
- Random size
- Broad size distribution



- Heterogeneous Nucleation
- Additive (dispersant, complex agent)



# Reducing agent

## • Guidelines for the choice of reducing agents

**Table 1** Guidelines for the choice of reducing agents and reaction conditions in the precipitation of metal particles

Metal species	$E^0/V$	Reducing agent	Conditions	Rate
$Au^{3+}, Pt^{4+}, Pd^{2+}, Ag^+, Rh^3+, Hg^{2+}, Ir^{3+}$	$\geq +0.7$	Organic acids, alcohols, polyols Aldehydes, sugars Hydrazine, $H_2SO_3$ , $H_3PO_2$ $NaBH_4$ , boranes, hydrated $e^-$	$\geq 70^\circ C$ $< 50^\circ C$ Ambient Ambient Ambient	Slow Moderate Fast Very fast
$Cu^{2+}, Re^{3+}, Ru^{3+}$	$< +0.7$ and $\geq 0$	Polyols Aldehydes, sugars Hydrazine, hydrogen $NaBH_4$ $NaBH_4$	$> 120^\circ C$ $70-100^\circ C$ $< 70^\circ C$ Ambient	Slow Slow Moderate Fast
$Cd^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, In^{3+}, Sn^{2+}, Mo^{3+}, W^{6+}$	$< 0$ and $\geq -0.5$	Polyols Hydrazine, hydroxylamine $NaBH_4$ , boranes <sup>14,60</sup> Hydrated $e^-$ , radicals $NaBH_4$ , boranes <sup>14</sup>	$> 180^\circ C$ $70-100^\circ C$ Ambient Ambient	Slow Slow Fast Very fast
$Cr^{3+}, Mn^{2+}, Ta^{5+}, V^{2+}$	$< -0.6$	Hydrated $e^-$ , radicals	$T, P > \text{ambient}$ Ambient	Slow Fast

# How to control the particles

- **Processing parameter**

Temperature, Concentration , pH, Chemical composition ... etc.

- **Seed (Heterogeneous Nucleation)**

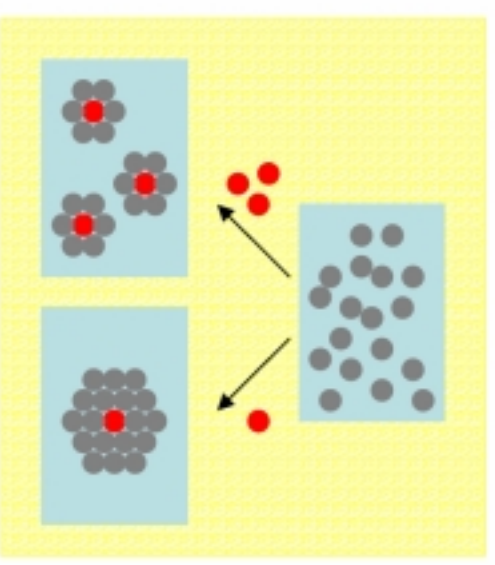
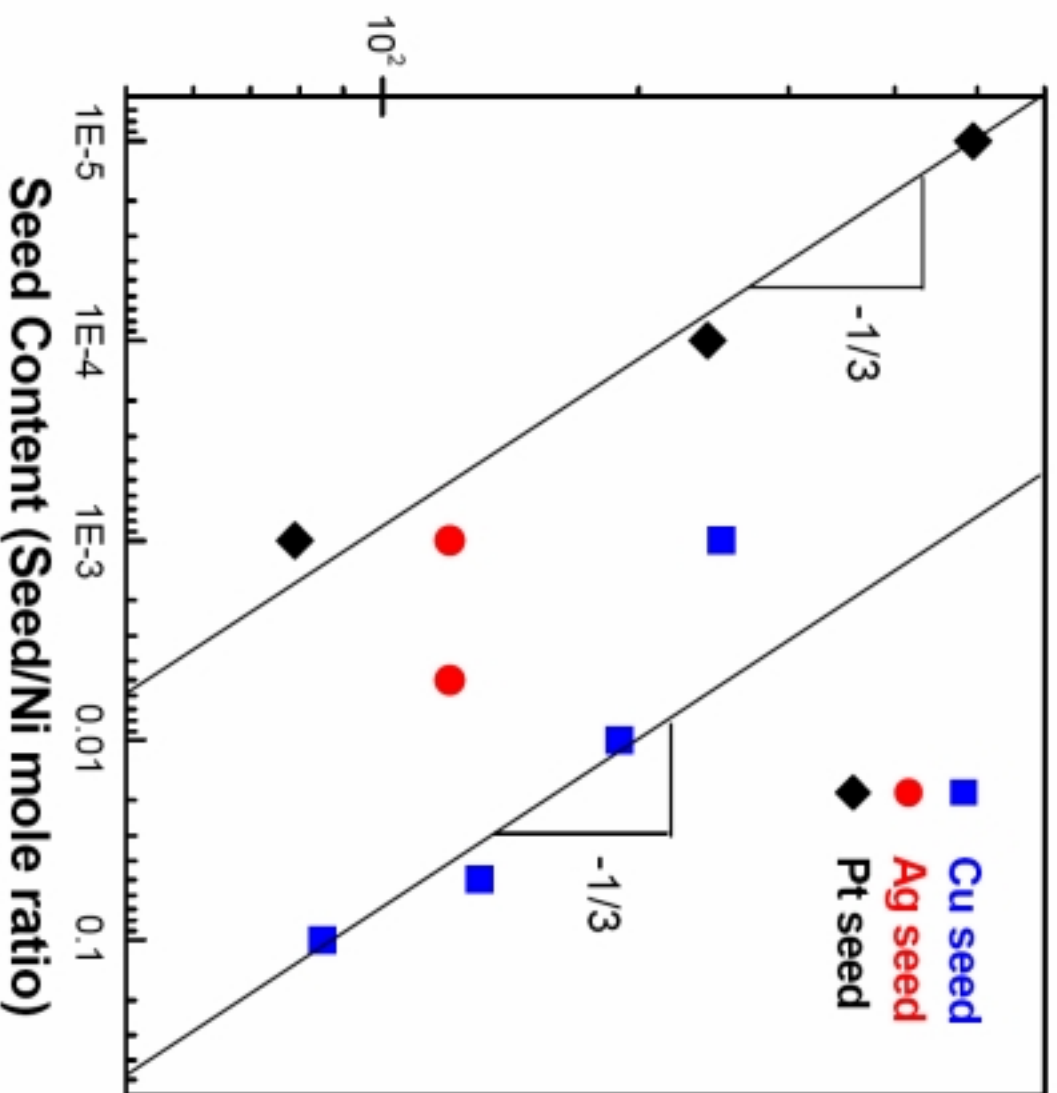
- **Complex agent**

**Table 2** Changes in the redox potential of  $\text{Ag}^+$  ion as a result of complex formation

Redox system	$-\log K_p$	$E_0/\text{V}$
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}^0$	—	+0.799
$[\text{Ag}(\text{NH}_3)_2]^+ + \text{e}^- \rightarrow \text{Ag}^0$	7.2	+0.38
$[\text{Ag}(\text{SO}_3)_2]^{3-} + \text{e}^- \rightarrow \text{Ag}^0 + 2 \text{SO}_3^{2-}$	8.7	+0.29
$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-} + \text{e}^- \rightarrow \text{Ag}^0 + 2 \text{S}_2\text{O}_3^{2-}$	13.4	+0.01
$[\text{AgI}_4]^{3-} + \text{e}^- \rightarrow \text{Ag}^0 + 4 \text{I}^-$	15.0	-0.09
$[\text{Ag}(\text{CN})_3]^{2-} + \text{e}^- \rightarrow \text{Ag}^0 + 3 \text{CN}^-$	22.2	-0.51

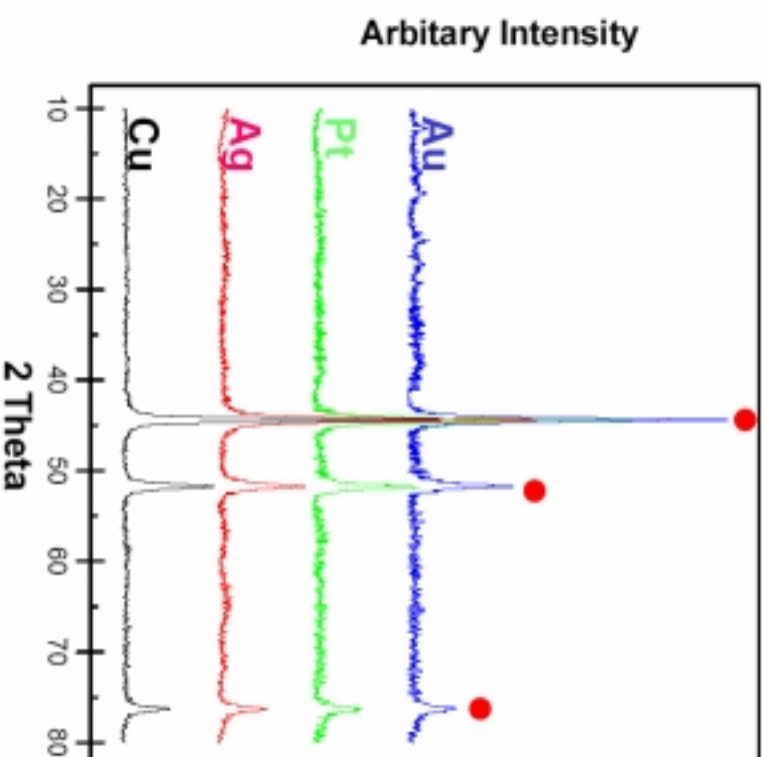
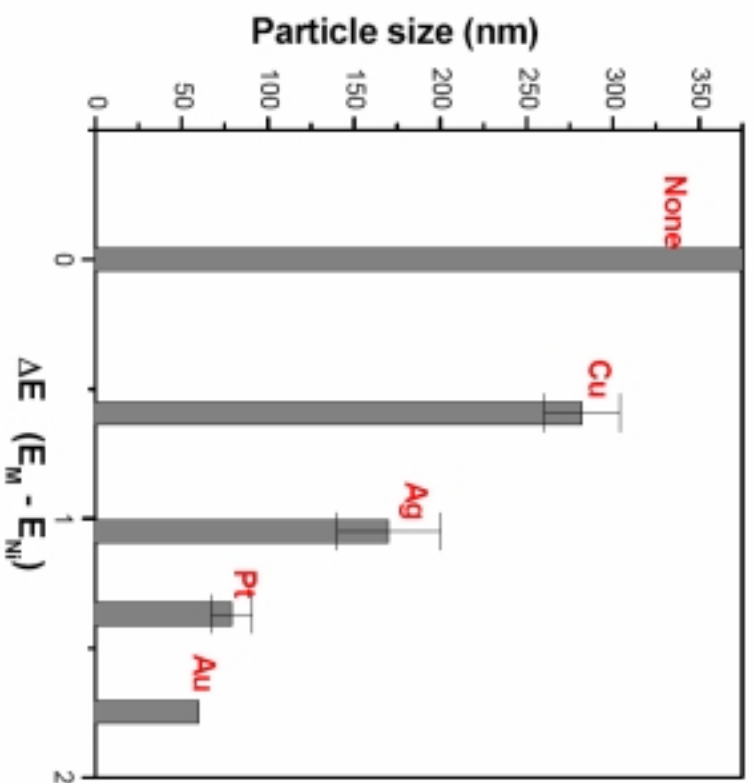
# Heterogeneous Nucleation (1)

<Seed concentration Vs. particle size>



$$d_m = A [\text{Seed}]^{-\frac{1}{3}}$$

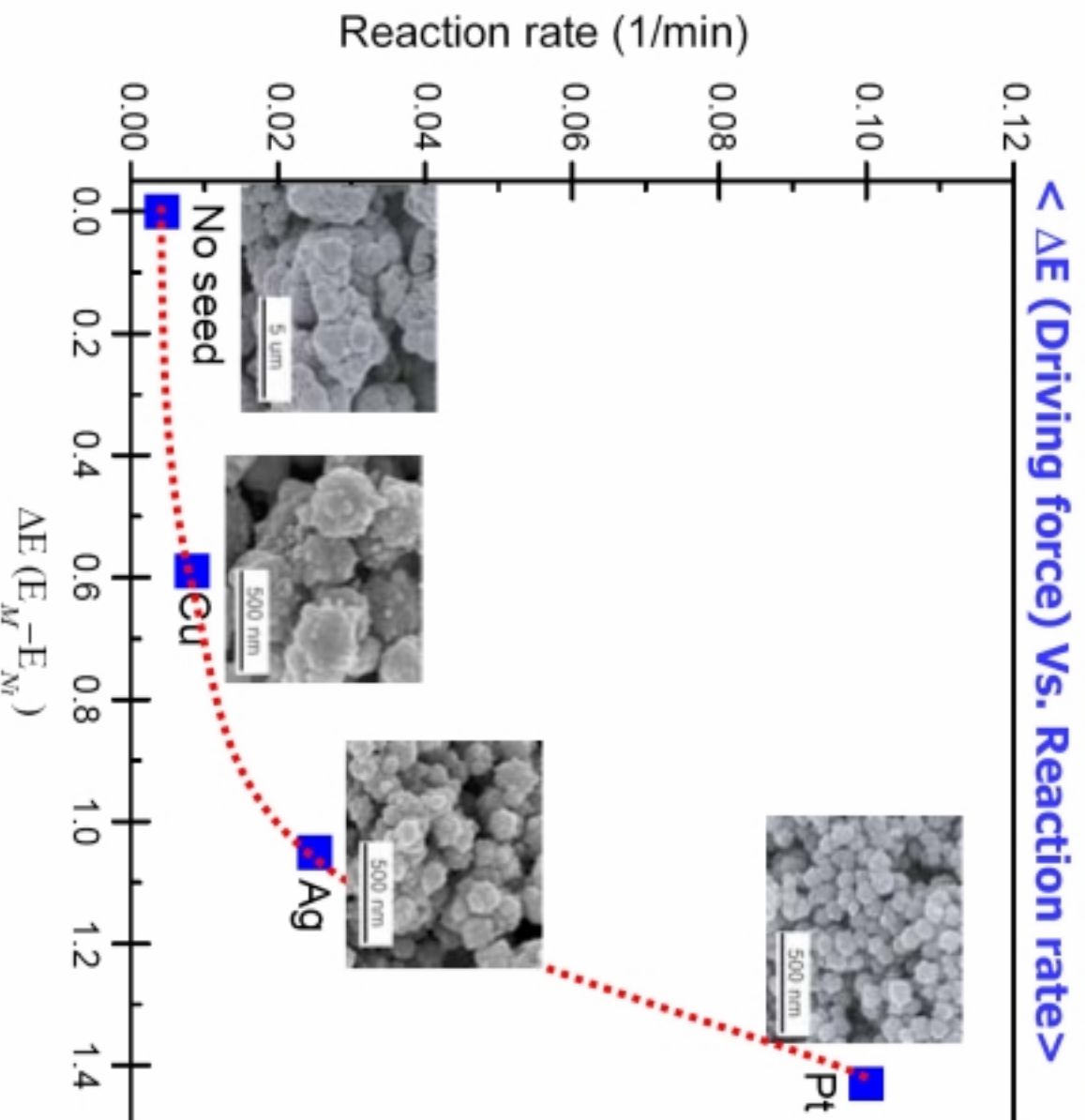
# Heterogeneous Nucleation (2)



Seed	Vs SHE (eV)	Ni Particle Size(nm)
Cu	+0.34	282
Ag	+0.80	170
Pt	+1.18	90
Au	+1.50	$\approx 60$



# Heterogeneous Nucleation (3)

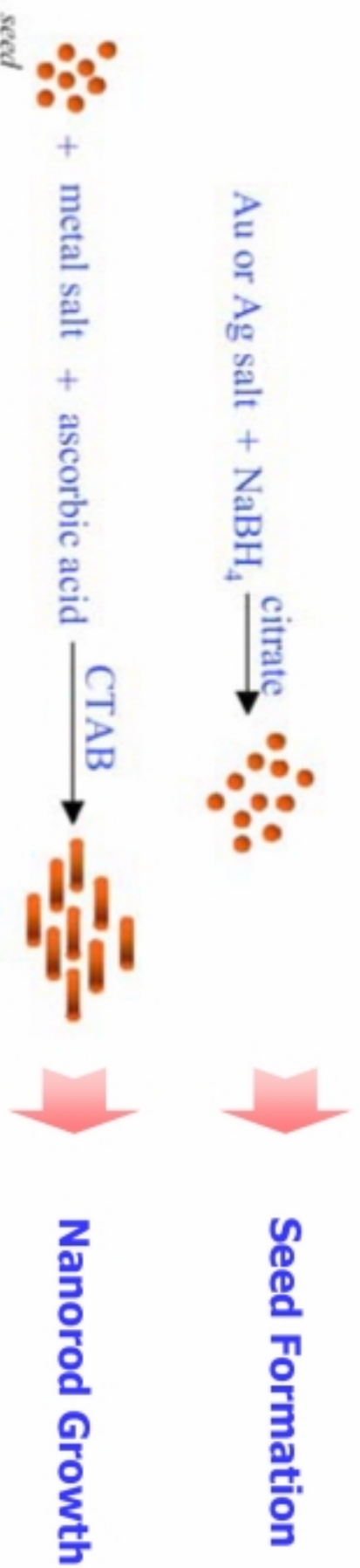


- Driving Force :  $\Delta E$   
→ Redox potential
- Reaction :  $\Delta E > 0$
- $\ln K_e = nF\Delta E/RT$

# Seed-Mediated Growth in Solution

## • Formation mechanism

Seed-mediated growth for gold and silver

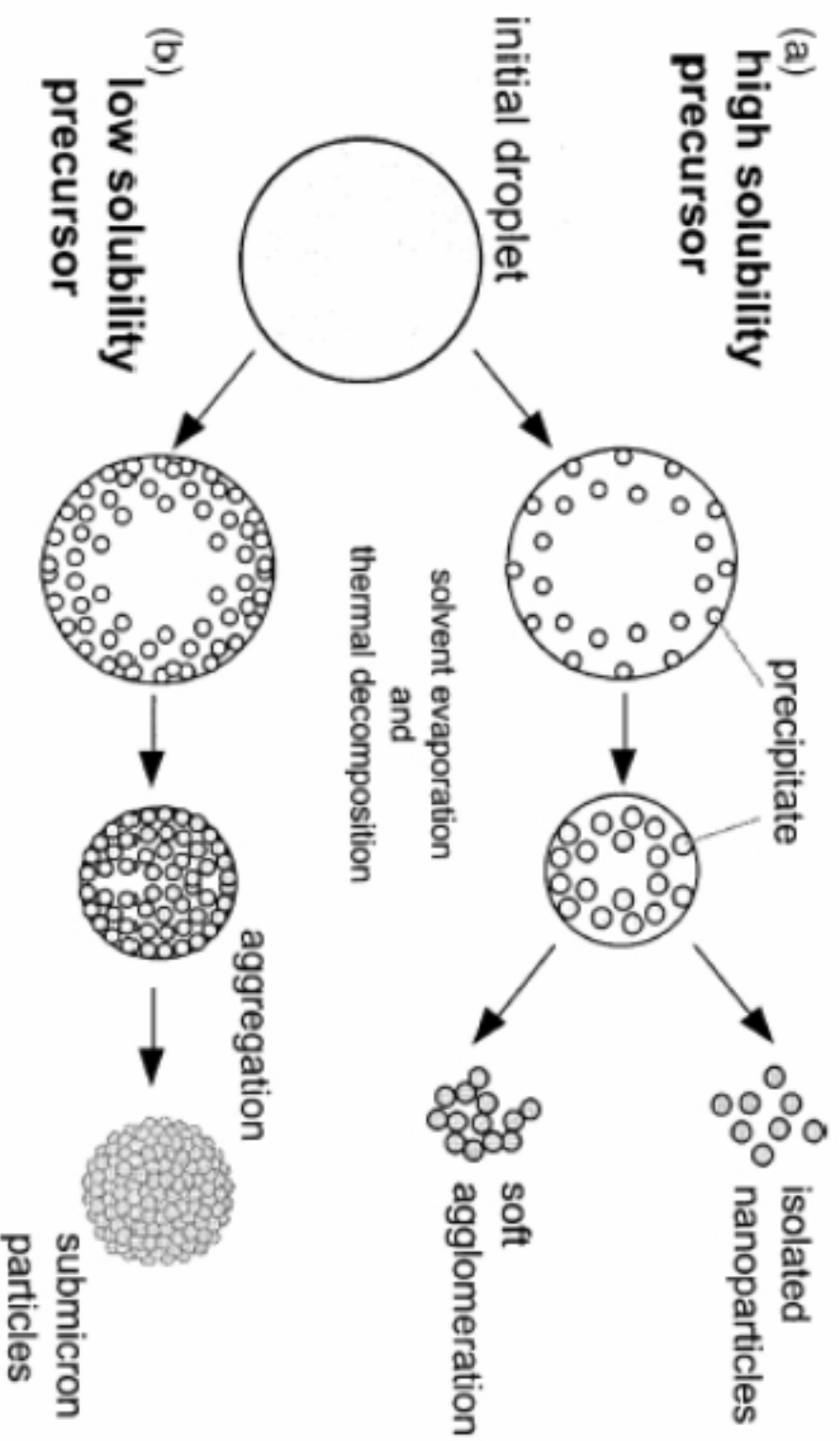


- $\text{NaBH}_4$  ; Strong reducing agent
- Citrate ; capping agent (inhibit particle growth)
- Ascorbic acid ; Weak reducing agent
- CTAB ; Rod like template

# Synthesis Techniques

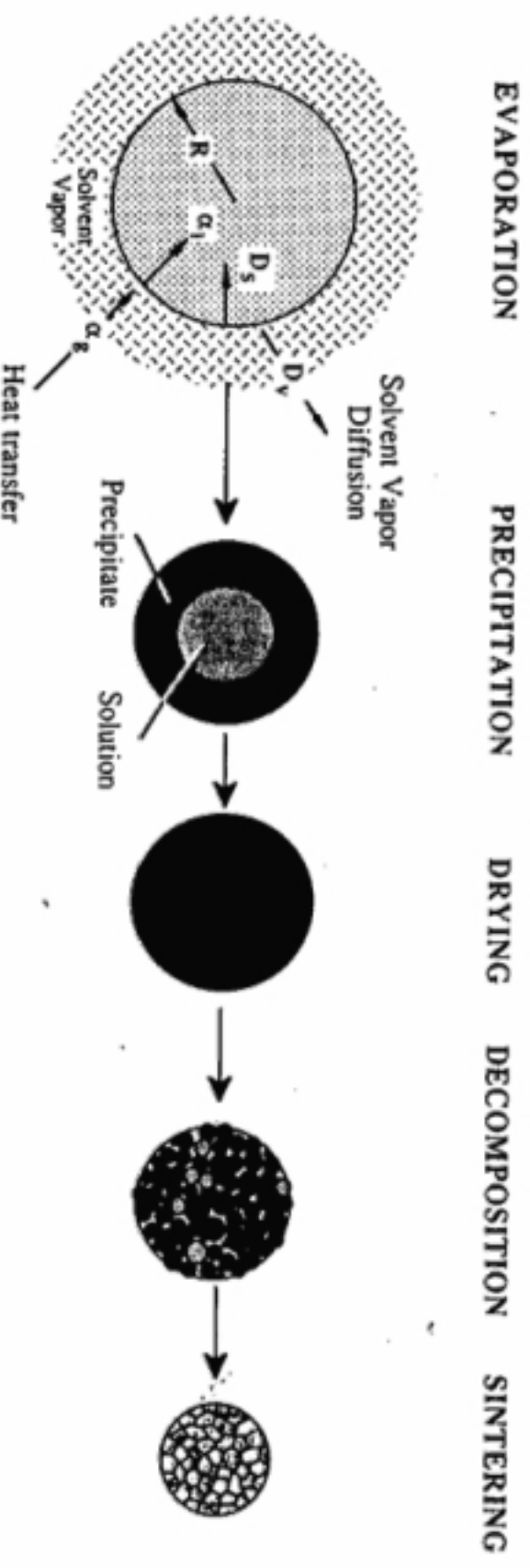
- **Mechanical:** **Milling**
- **Chemical:** **Chemical vapor reaction**  
**Spray pyrolysis**  
**GNP (Glycine Nitrate Process)**
- **Physical:** **Evaporation-Condensation**

# Spray pyrolysis





# Spray pyrolysis



## Stages of Spray Pyrolysis Process

## Considerations

- The **precursor must be dissolved** in the liquid, but **must not reacted with it**.
- The **product must not dissolve** in the liquid, and **must not react with the liquid**.
- There must be **large volume change (decrease)** for the reaction precursor production.
- Transport of the leaching agent in the liquid and the fugitive compound formed must be sufficiently rapid.

## NiO Nanoparticle

Temperature increase

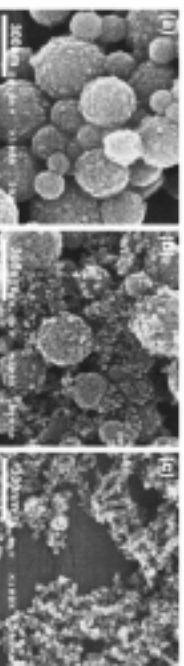


Fig. 3. NiO particles prepared from nitrate precursor at different temperatures: (a) 400 °C, (b) 500 °C, (c) 600 °C. Other conditions: operating pressure, 40 Torr; starting solution concentration, 0.15 mol/L; carrier gas flow rate, 2 l/min; glass fiber size, 3.5  $\mu$ m.

Fiber expansion generator



## Experimental variables

- (substrate temperature)
- ambient temperature
- chemical composition of carrier gas and/or environment
- (nozzle to substrate distance)
- droplet radius
- solution concentration
- solution flow rate

## NiO Nanoparticle

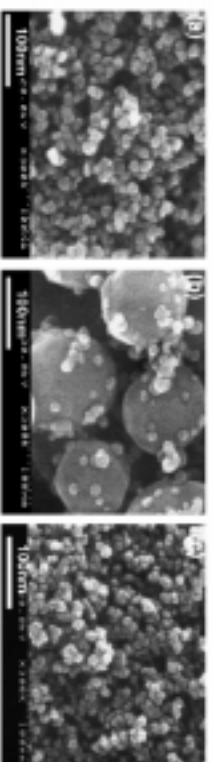
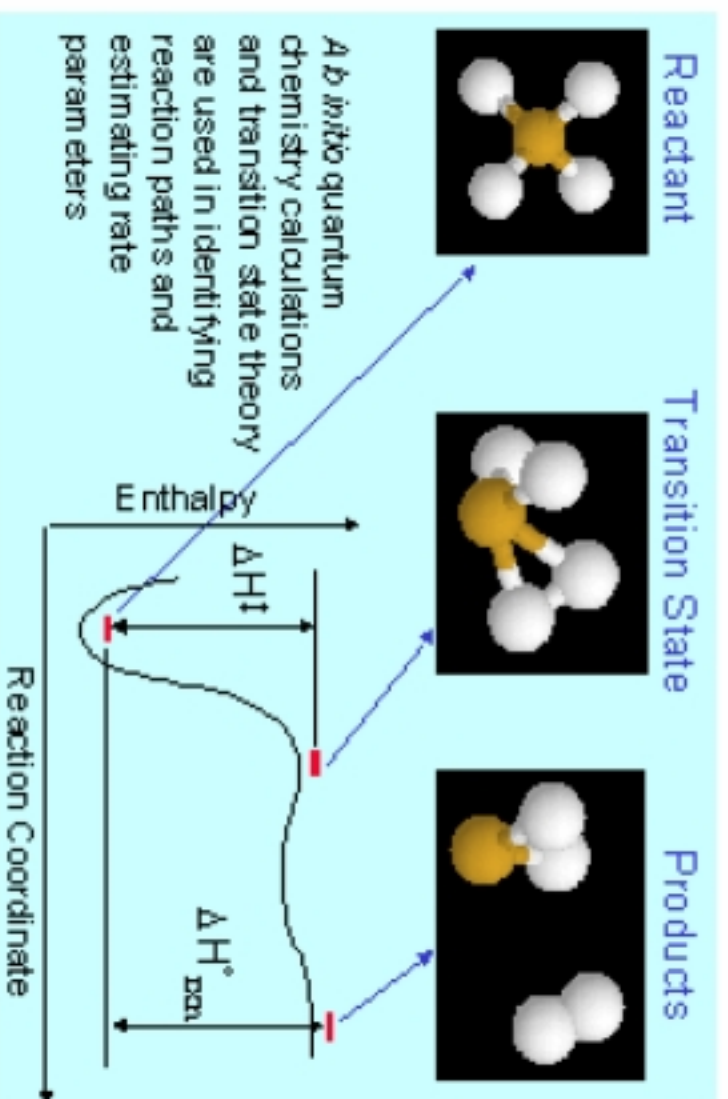
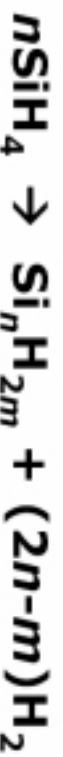


Fig. 5. NiO particles prepared at different residence time: (a) 0.02 s, (b) 0.2 s, (c) 0.5 s using 3.5  $\mu$ m glass fiber. Other conditions: nitrate precursor operating pressure, 40 Torr; starting solution concentration, 0.15 mol/L.

## Particle nucleation:



## Overall reaction:



# Advantage & Disadvantage

## Advantage

- No Liquid Byproducts
- No Post Processing treatment
- Low-Temperature Synthesis
- High Homogeneity
- Easy Achieved

## Disadvantage

- Sensitivity for Atmosphere Condition
- Expensive of Raw Materials
- Use of Toxic Systems



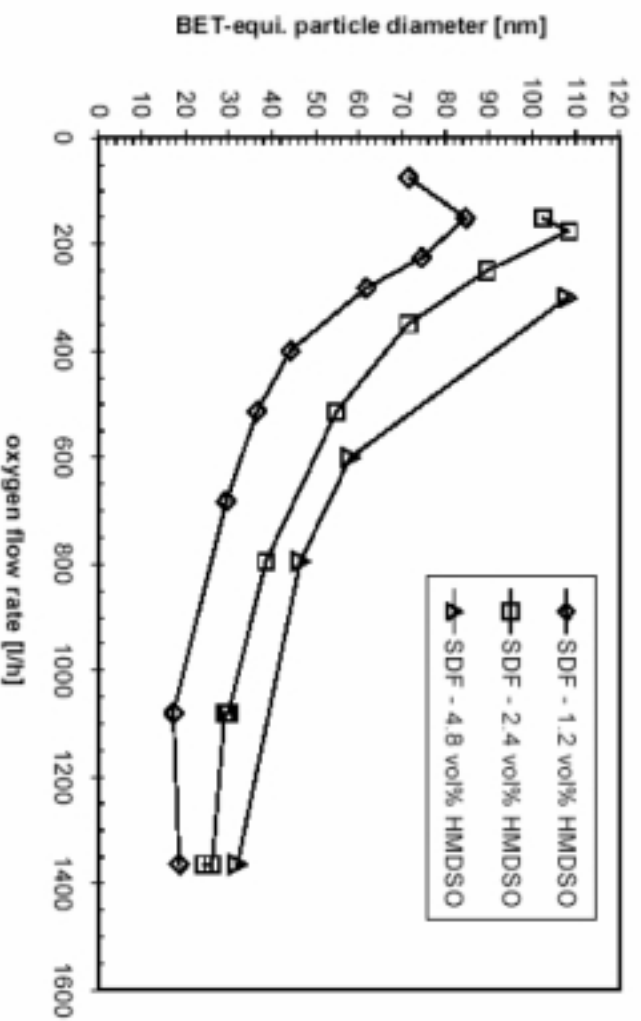
## Starting Materials

Si precursor:	Hexamethyldisiloxane
Oxidizer:	Oxygen
Fuel Gas:	Methane

↓  
**Flame Hydrolysis**

↓  
**SiO<sub>2</sub> nanoparticles**

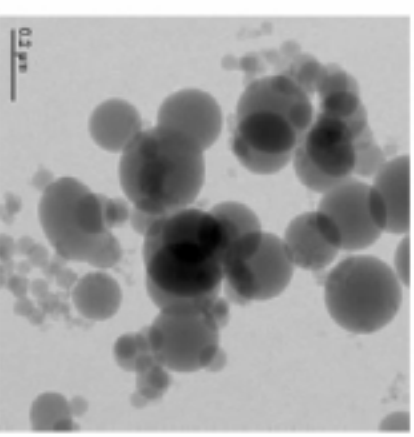
# Size Control



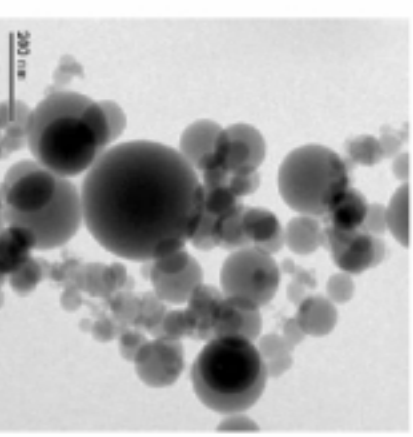
Higher precursor conc.

Bigger particles

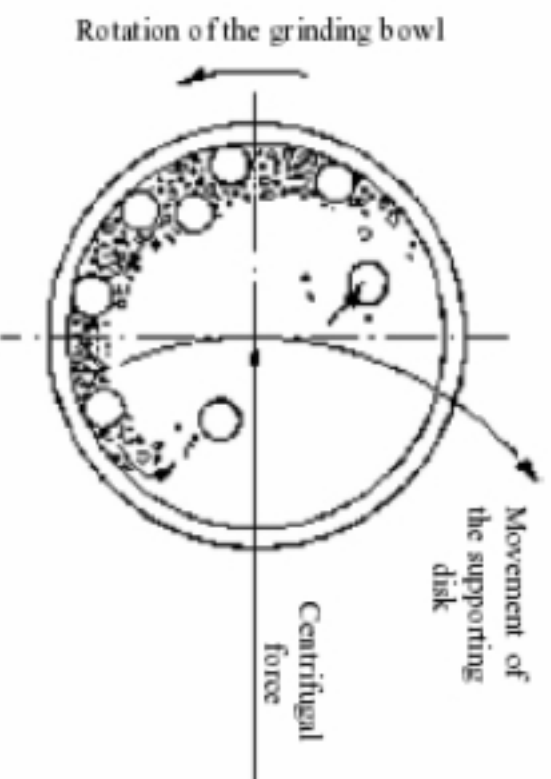
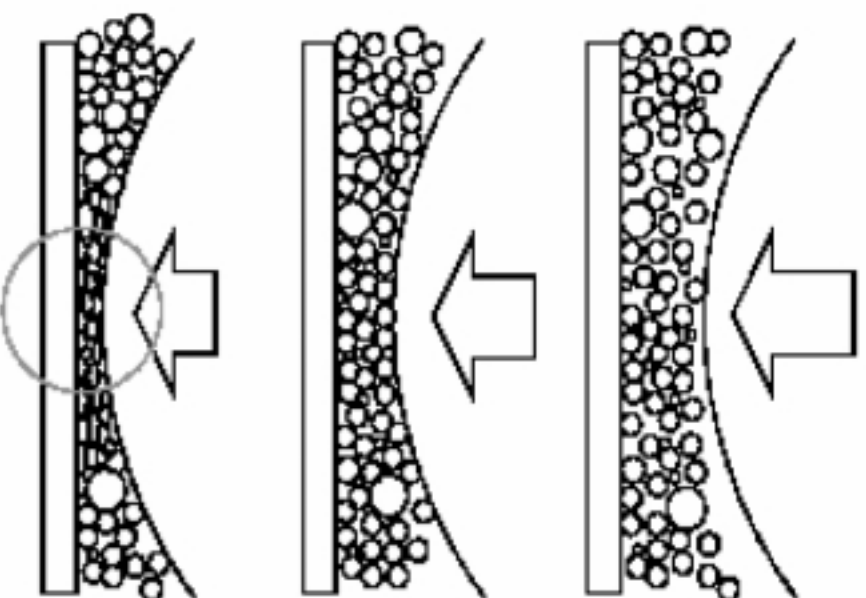
Precursor conc 2.4 vol%



Precursor conc 4.8 vol%



# Mechanochemical Process



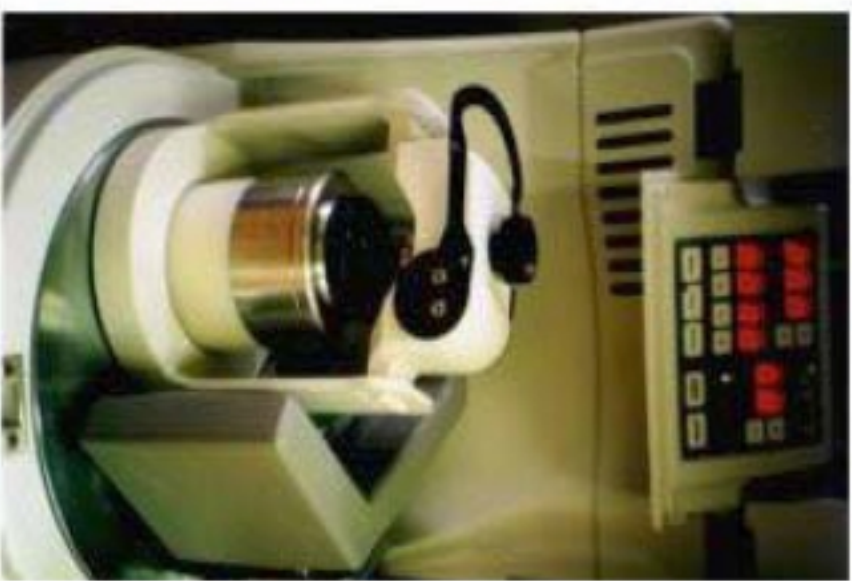
**From the viewpoint of changes of free energy Mechanical activation changes the amount of accumulated energy**

# Mechanical activation devices

Vibrating mill

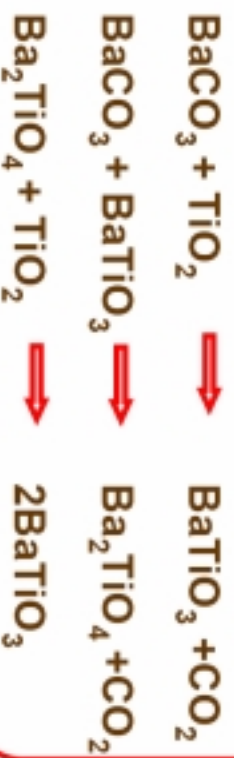


Planetary mill





# Reaction Kinetics



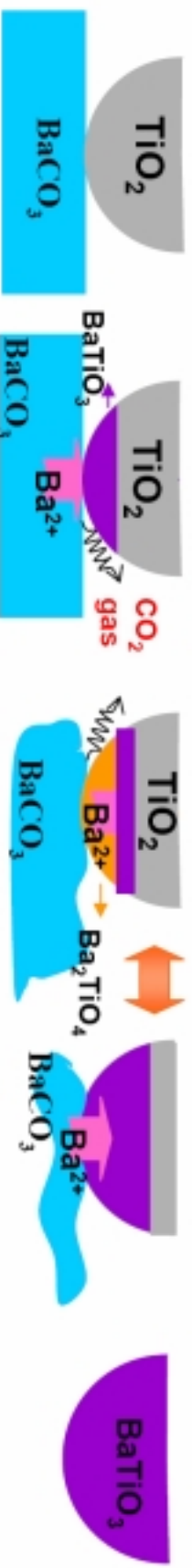
Smaller  $\text{TiO}_2$  particle

- Increase Kinetics

Milling of  $\text{BaCO}_3$

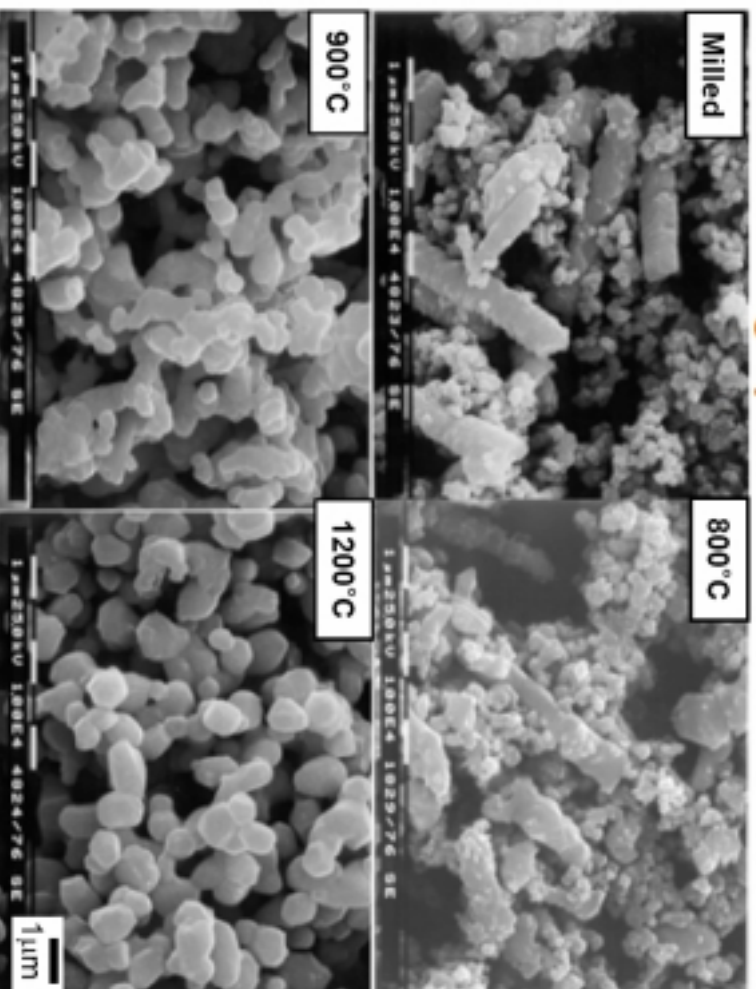
- Mechanical Activation

## ● Schematic Diagram

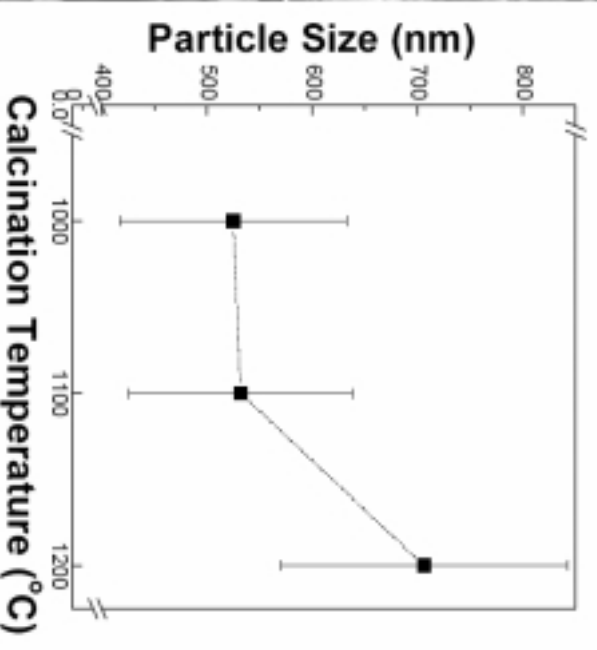


# Particle Morphology

## SEM Micrographs



## Particle Size



● **Just milled powder**  
 $\text{TiO}_2$ : Smaller spherical  
 $\text{BaCO}_3$ : Large rod-like

● **900°C**  
 No elongated shape  
 Average particle size ↑

● **800°C**  
 Starting Ba Diffusion  
 No  $\text{Ba}_2\text{TiO}_4$  phase

● **1200°C**  
 Single phase  $\text{BaTiO}_3$   
 Shape similar to  $\text{TiO}_2$

● **Particle Size Increase**  
 with temperature

● **Reaction completed at**  
**1200°C**

# Polymeric Nanoparticles

- **Emulsion Polymerization**

The "ingredients" for an emulsion polymerization include 1) a water soluble initiator, 2) a chemical emulsifier, and 3) a monomer that is only slightly soluble in water, or completely immiscible.

The two differences between emulsion and suspension polymerization are: 1) that a suspension polymerization is a mechanical process, and must have a stabilizing agent until the droplets are far apart, and 2) the emulsion polymerization is a chemical process which requires a surfactant to make the monomer "emulsify."

Disadvantage- the surfactant is a soap and it contaminates the polymer.

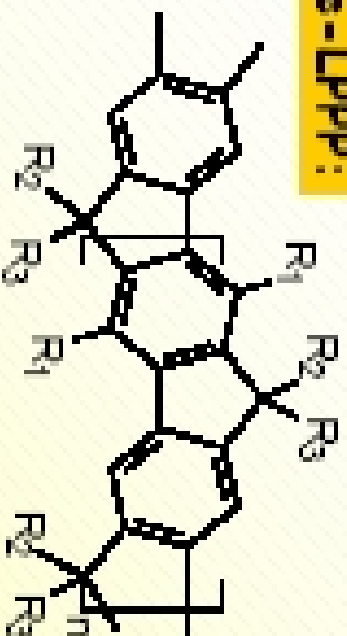
Advantage- better heat control; the size of the emulsion polymer is usually 0.05 to 5 microns, and the size of the droplets is usually in the 10- 1000 micron diameter range.

Water-soluble initiators are used rather than monomer-soluble initiators. The end product is usually a stable latex--an emulsion of polymer in water rather than a filterable suspension.

Overview of Polymeric Nanoparticles (PNP) Applications

Application	Material	Purpose
Cancer Therapy	Polyalkylcyanoacrylate nanoparticles with anticancer agents, Oligonucleotides	Targeting, Reduce Toxicity, Increase uptake, Improve stability
Intracellular Targeting	Polyalkylcyanoacrylate/polyester nanoparticles with anti-parasitic, antibacterial or antiviral agents	Target reticuloendothelial systems for intracellular infection
Prolonged Systemic Circulation	Polyesters with adsorbed polyethylene glycols, pluronics or derivatized polyesters	Prolong systemic drug effect, Avoid uptake by the reticuloendothelial system
Vaccine Adjuvant	Polymethyl methylacrylate nanoparticles with vaccines, Oral and intra-muscular immunizations	Enhance immune response, Alternate acceptable adjuvant
Peroral Absorption	Polymethyl methylacrylate nanoparticles with proteins and therapeutic agents	Enhance bioavailability, Protect from gastrointestinal enzymes
Ocular Delivery	Polyalkylcyanoacrylate nanoparticles with steroids, Anti-inflammatory agents, Antibacterial agents for glaucoma	Improve retention of drug/reduce washout
Other Applications	Polyalkylcyanoacrylate nanoparticles with peptides, Nanoparticles with adsorbed enzymes, Polyalkylcyanoacrylate nanoparticles for transdermal applications, Nanoparticles with radioactive or contrasting agents	Cross blood-brain barrier, Enzyme immunoassays, Improve absorption, Imaging

**Me-LPPP:**



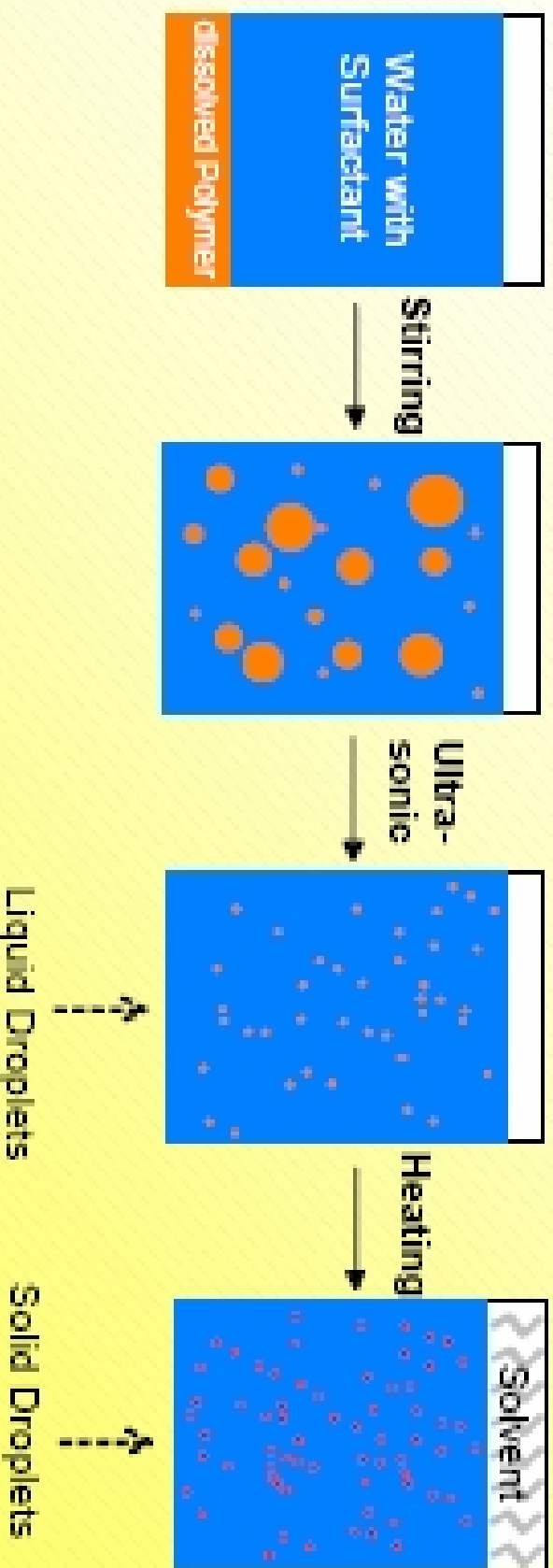
(-R1: hexyl, -R2: methyl, -R3: 4-decylphenyl)

**PF:**



PF 2tB: (-R1: alkyl: 2-ethylhexyl)

PF11112: (-R1: 3,7,11-trimethyldodecyl)



So far, the size of the particles could be controlled between 70-250nm. The solid contents of the miniemulsions used for the experiments are typically in the range of 4-10%.