

## *Chapter 5. Preparation of Nanoparticles*

## 5.1 Introduction

### \* Keys for NP preparation

- Formation of high-degree supersaturation in narrow time or space
- Suppression of aggregation
- Monodisperse growth- Diffusion-controlled growth/Ostwald ripening

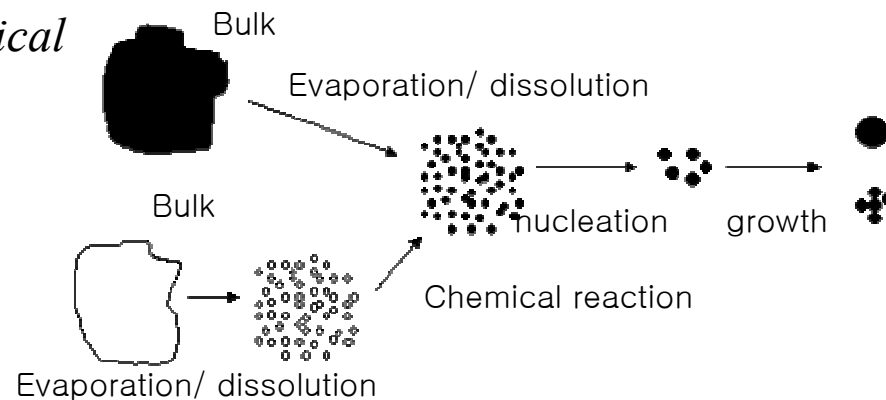
### \* Classification of preparation methods

- In terms of phase of medium for preparation

*Gas phase/ Liquid phase/ Aerosol phase/ Solid phase*

- In terms of method of "monomer" preparation

*Physical/ Chemical*



## ***5.2 Gas-Phase Physical Preparation***

### *Characteristics of gas-phase preparation*

*Formation in less dense and more mobile phase*

- *Requires large- $V$  and high- $T$  process*
- *High equipment cost*
- *exclude additional sintering process*
- *Aggregation: less and weak but still some*
- *Properties: quite different between gas and NP produced*
- *No solubility problems for precursors in gas media*

*Sulfide, nitride, carbide and boride: easily obtainable*

*Less number of chemical species and processes involved*

- *High purity product/ environmentally friendly*
- *No washing, no additional sintering and easier recovery*
- *No effective stabilizers and less controllable*

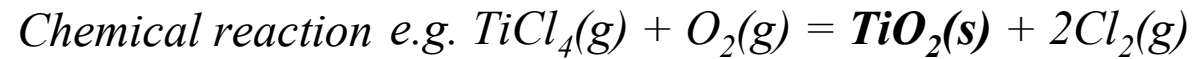
### Gas and Liquid as a medium

	Air	Water
Density (g/cm <sup>3</sup> )	0.001205	0.9982
Viscosity (g/cm/s)	1.809x10 <sup>-4</sup>	0.01009
Kinematic viscosity(cm <sup>2</sup> /s)	0.1501	0.01011
Mean free path of molecules(cm)	6.45x10 <sup>-6</sup>	

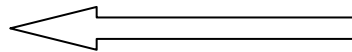
General strategy for gas-phase preparation

- Rapid increase in concentration of vapor molecules by

*Vaporization/Sublimation*



*needs energy*



*Hot wall  
reactor*

- Short duration of nucleation by rapid

*Flame*

*Cooling*

*Laser*

*Expansion*

*Plasma*

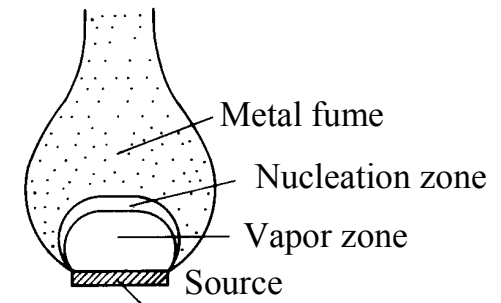
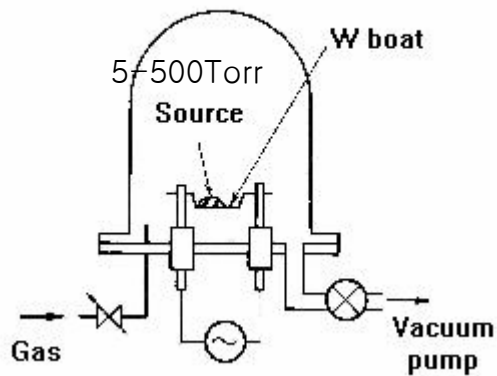
*Dilution*

*Attainment of high but short supersaturation:*

*\* Liquid carbon dioxide expansion, Supercritical expansion*

## *(1) Physical Preparation*

### *Electrically heated generators*



*-Electrical heating for evaporation of bulk materials in tungsten heater into low-pressure inert gas (He, Ne, Xe)*

*-Transported by convection and thermophoresis to cool environment*

*-Subsequent nucleation and growth*

*-Suitable for substances having a large vapor pressure at intermediate temperatures up to about 1700 °C*

*-Disadvantage: the operating temperature is limited by the choice of crucible*

- Evolved to flow process using tubular reactor placed in electrical furnace.
- Requires rapid temperature decrease by the free jet expansion or in a turbulent jet
- Elemental nanoparticles such as Ag, Fe, Ni, Ga, TiO<sub>2</sub>, SiO<sub>2</sub>, PbS

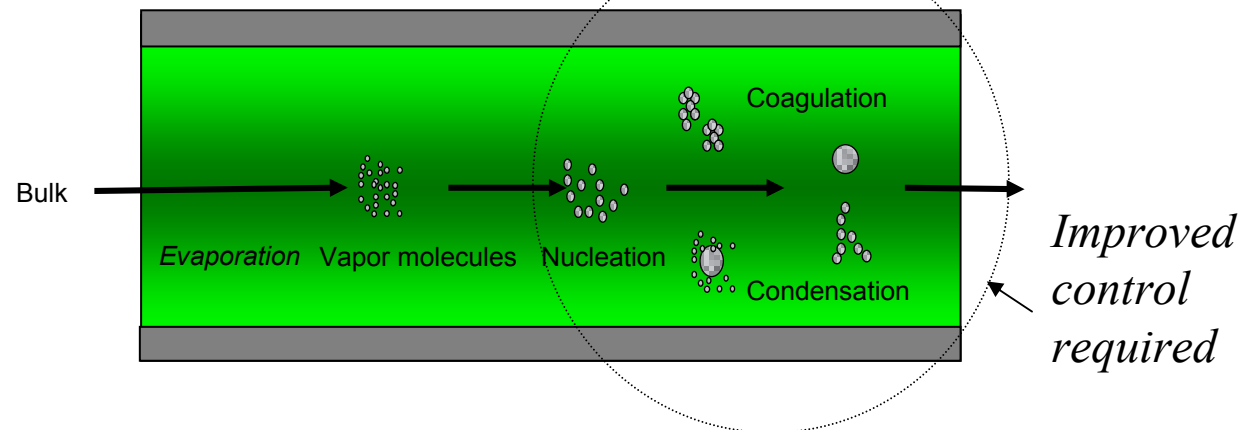
furnace - evaporation



furnace - precursor pyrolysis

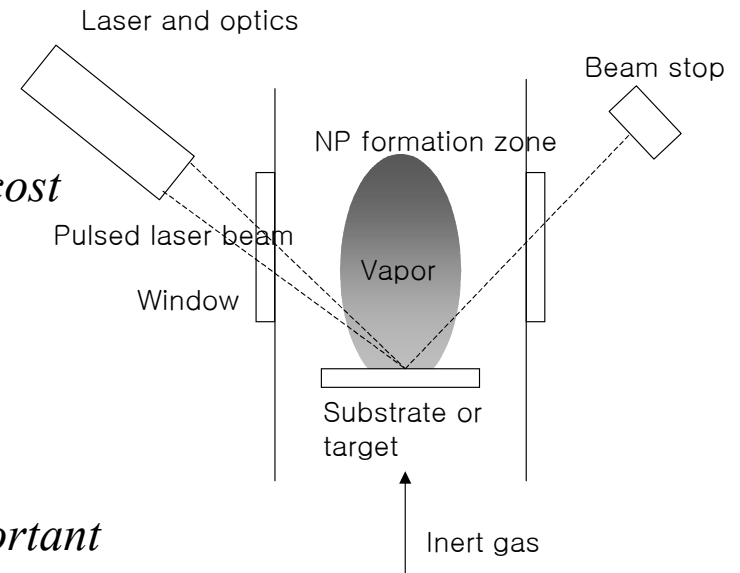


### *Mechanism in flow reactors*



## Laser Processes

- Use of (pulsed) laser instead of electrical heating
- Energy efficiency improved but expensive energy cost



- Wavelength\* and pulse width\*\* of the laser: important

\*Absorption coefficient of the target and cross section of ambient gas \*\*excitation ablation mechanism

- Laser: excimer laser(193, 248, 308nm), Nd:YAG laser(532nm),  
ruby laser and CO<sub>2</sub> laser

- Short pulses: 10-50ns

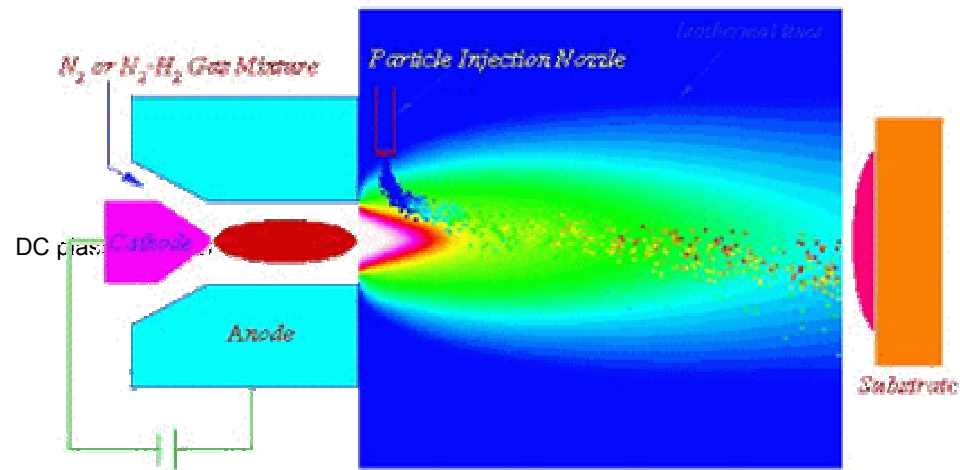
- Production rate: micrograms/pulse → 10-100mg/h at 50Hz

- Small scale production due to high production cost



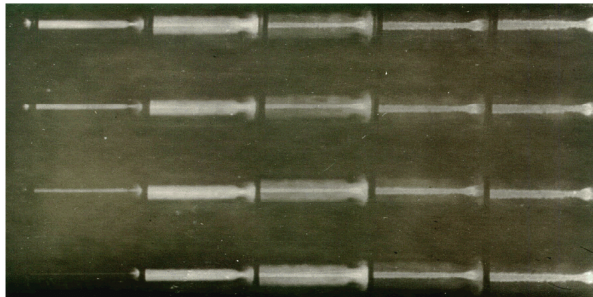
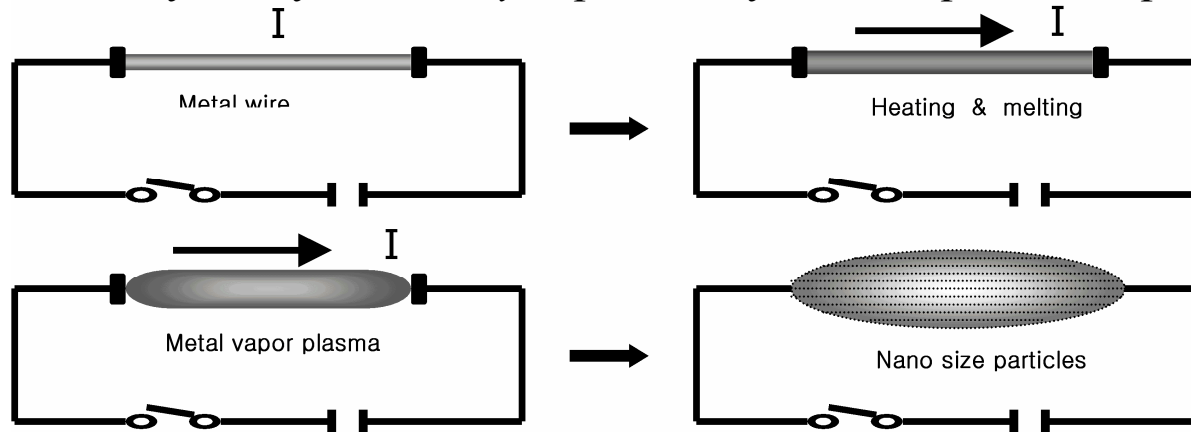
## Arc (DC) plasma

- Spark (arc) discharge
- High current spark across the electrodes produced by breakdown of flowing inert gas vaporizes a small amount of the electrode metals
- $10 \sim 100V$  and electric current density  $10-1000A/cm^2$



## Wire electrical explosion

- *Overheating (resistive, or Joule-heating) of a metal wire through which a strong pulse current flows, followed by explosion of metal vapor so evaporated*



Streak camera photograph of discharge through exploding wire  
(start: left down, end: right up, time interval: 0.1 $\mu$ sec)

- *15kV and 500-800kA through a wire in a few ms at 50bar*
- *Production rate : 1kg/h*
- *Powder consumption : 2kWh/g*

# Sputtering

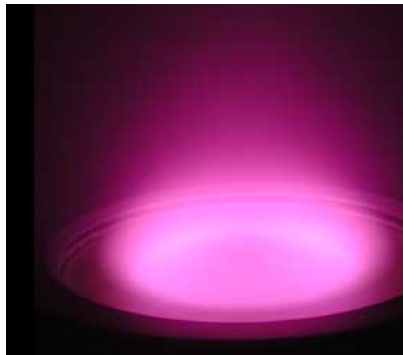
## \* Plasmas

*high-temperature plasma (electrons and ions: high T)*

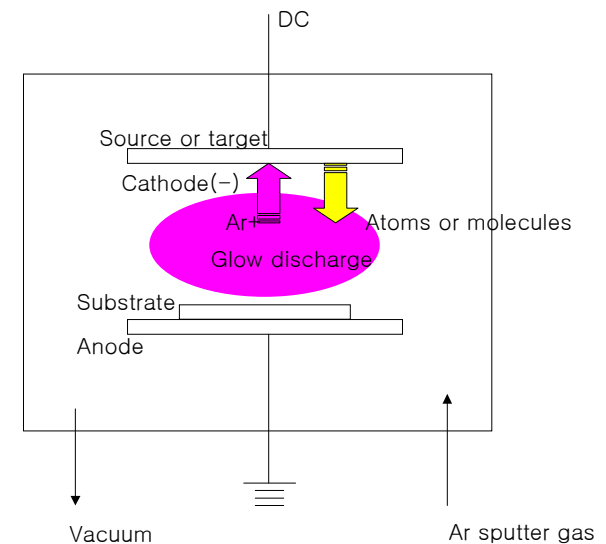
*e.g. arc discharge, AC(RF) plasma*

*low-temperature plasma (electrons: high T but ions: low T)*

*e.g. sputtering, microwave plasma*

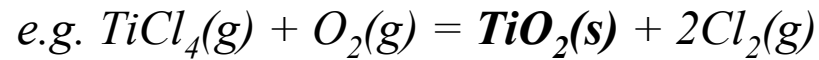


- *Glow discharge to produce energetic particles (ions)*
- *Momentum transfer to a target, resulting in the ejection of surface atoms or molecules to produce the sputtering species*
- *~1mTorr*
- *100-1000V at 10-100Pa and electric current density several mA/cm<sup>2</sup>*



### 5.3 Gas-Phase Chemical Preparation

-Monomers are chemically produced from low-boiling but highly reactive precursors\*



$$\text{Saturation ratio } S = \frac{P_{\text{TiO}_2}}{P_{\text{TiO}_2,0}}$$

- Usually very high at even high temperature...

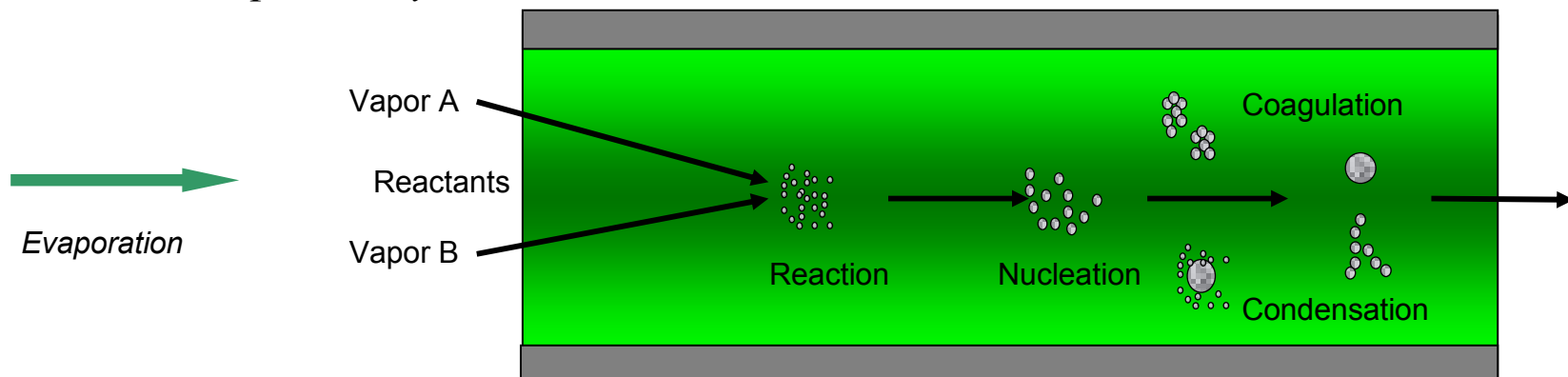
-Supply of energy for chemical reaction

*Electrically heated furnace: hot-wall tubular reactor*

*Flame reactors*

*Laser pyrolysis*

*Thermal plasma synthesis*

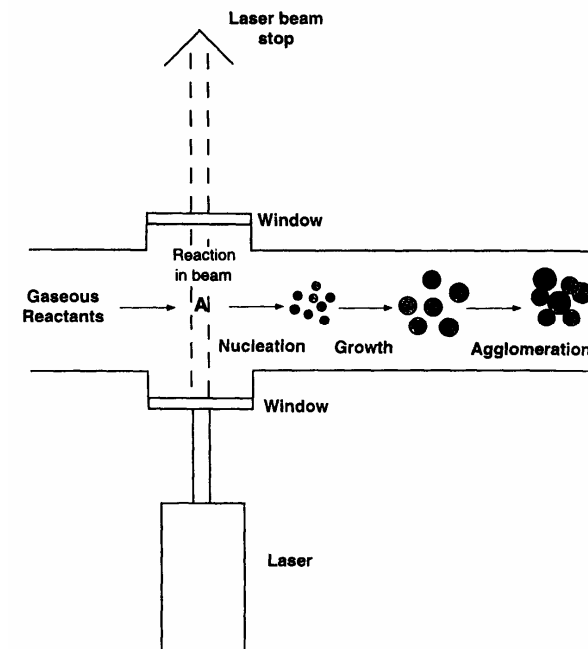
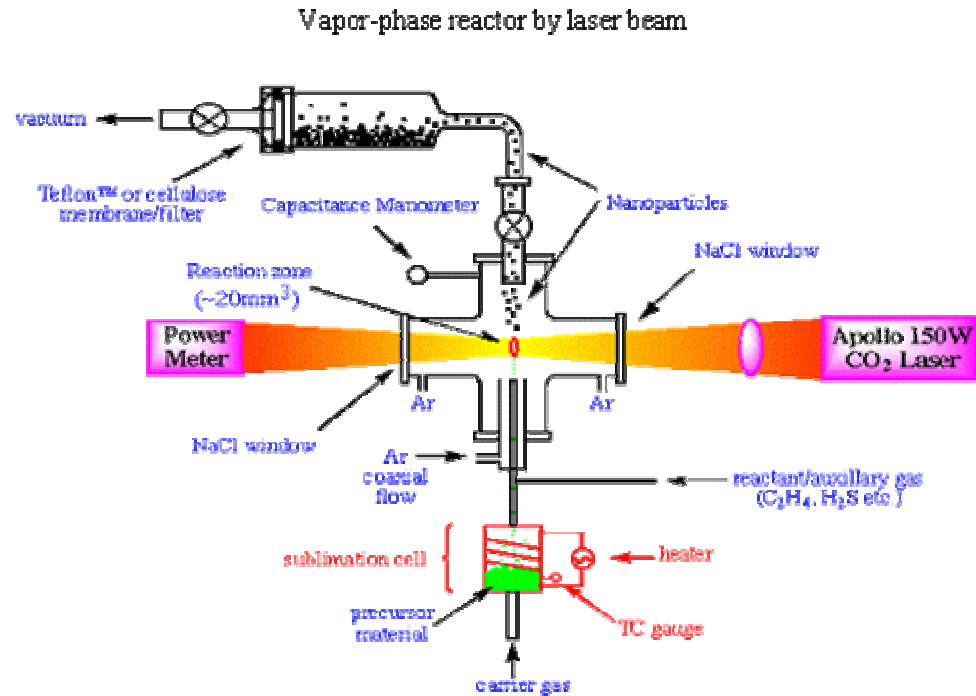


Hot-wall tubular reactor

- Tubular reactor with heating provided through hot wall
- Temperature: directly controllable
- Use of low-boiling precursors such as organometallics or metal carbonyls, followed by its decomposition to yield a condensable material
- Flexibility in producing a wide range of materials
  - can produce composite particles - coated or doped
- <1700°C and low energy efficiency

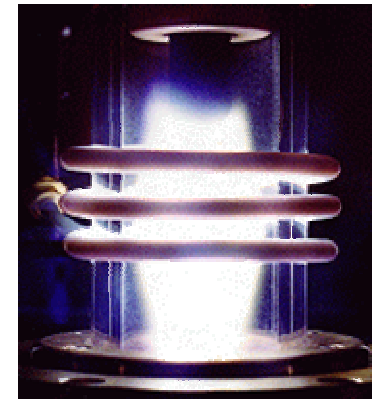
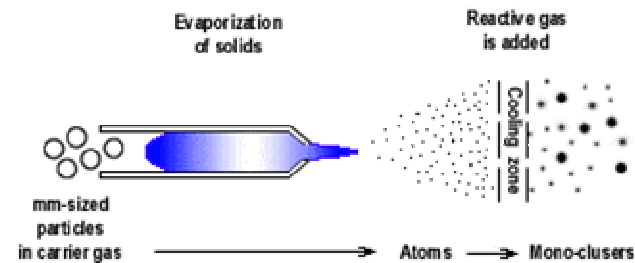
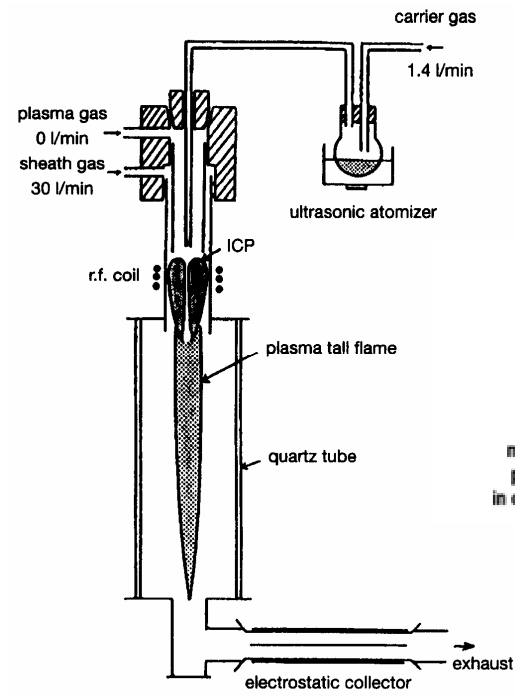
## Laser pyrolysis/ photothermal synthesis

- Spot heating and rapid cooling
- highly localized and efficient
- IR ( $\text{CO}_2$ ) laser: absorbed by precursors or by an inert photosensitizer ( $\text{SF}_6$ )
- Si from  $\text{SiH}_4$ ,  $\text{MoS}_2$ ,  $\text{SiC}$



## Thermal plasma synthesis

- Thermal plasma produced by arc discharge\*, microwaves, laser or high-energy particle beams, or electroless radio frequency (RF) discharge (capacitive or inductive coupling\*\*) \*,\*\* the most widely used ; \*\* time-varying magnetic field at 3 to 30MHz
- Providing 40kW of thermal power(30-40% efficiency) up to 6Nm<sup>3</sup>/h of plasma gases(N<sub>2</sub>, Ar, air)
- Precursors: solid, liquid, gas
- Residence time in the hot zone(10000K) < 1s; cooling rates of 10<sup>6</sup>-10<sup>9</sup>K/s

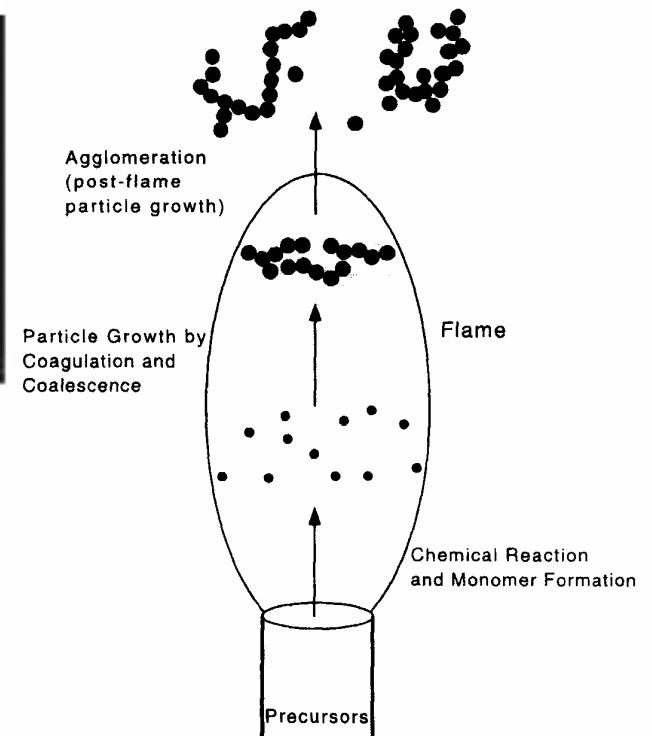


## Flame synthesis

- Requires fuels for combustion as heat supply
- Evaporation and chemical reaction of precursors in a flame produced by fuel combustion
- The most commercially successful process -  $\sim 10^6$  tons/year of carbon black and metal oxides ( $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ )
- Difficult to control the process
- Flame temperature:  $1000\text{-}2400^\circ\text{C}$   
residence time in flame:  $10\text{-}100\text{ms}$

\* Sintering of the particles by laser irradiation

Control of particle aggregation by DC field application





## 5.4 Preparation of Carbon Nanotube

See <http://www.pa.msu.edu/cmp/csc/nanotube.html>

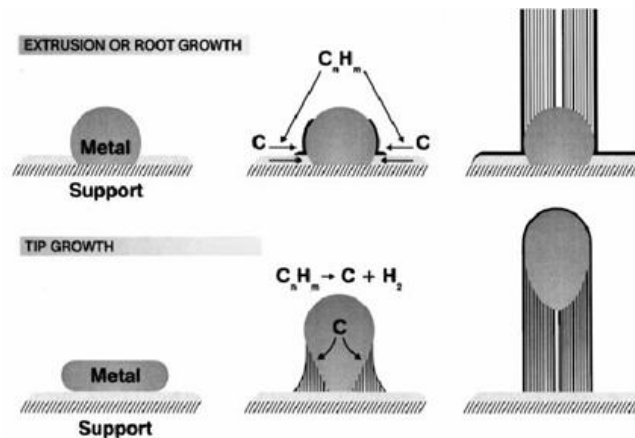
- No commercial equipments
- home-made, low throughput batch reactors

\* Prepared by decomposition of  $C_2H_2$ ,  $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$ , or  $CO$  in nonoxidizing carrier gas

\* Catalysts for SWNT: nanoparticles of  $Fe$ ,  $Co$ ,  $Ni$ ,  $Mo$ \*

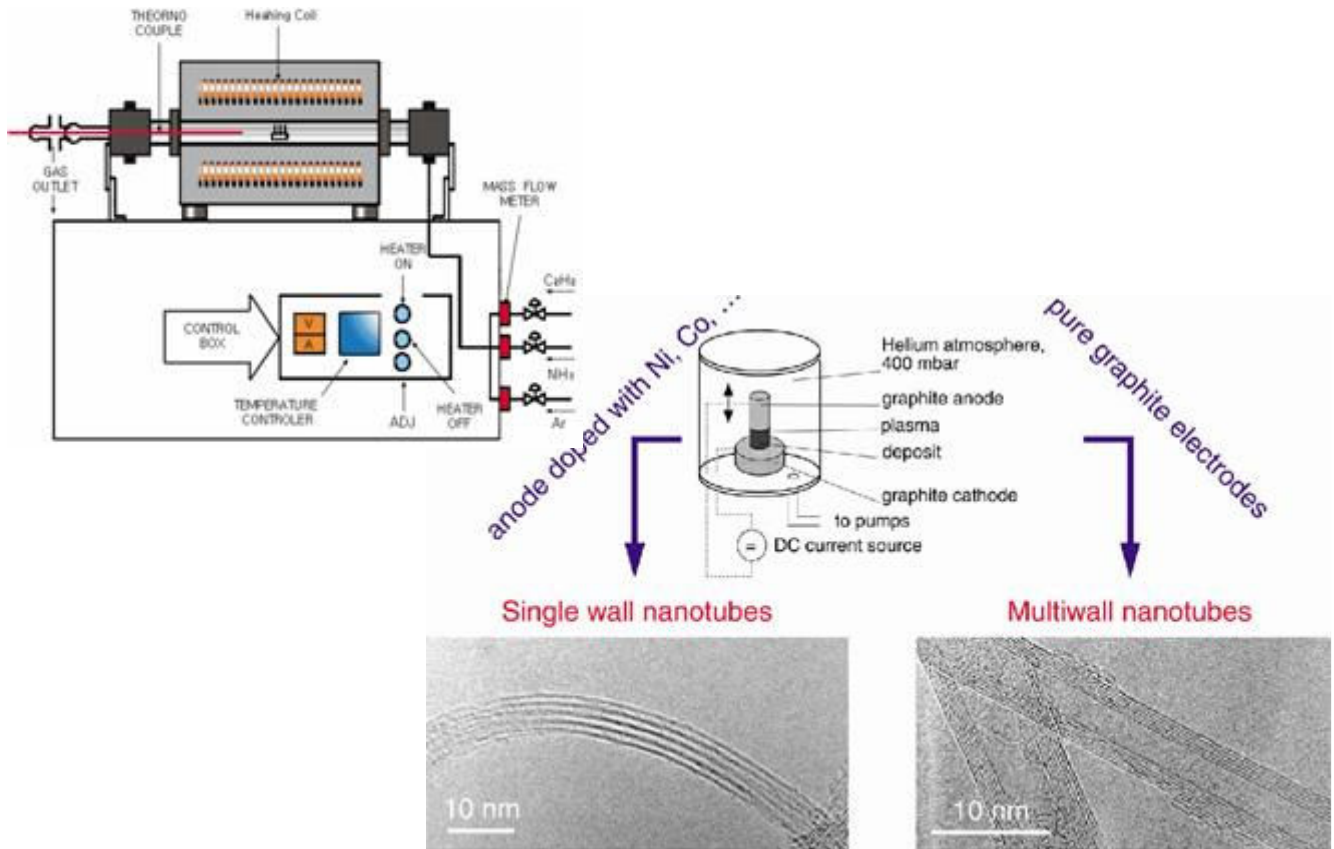
Growth mechanism

- Base growth
- Tip growth



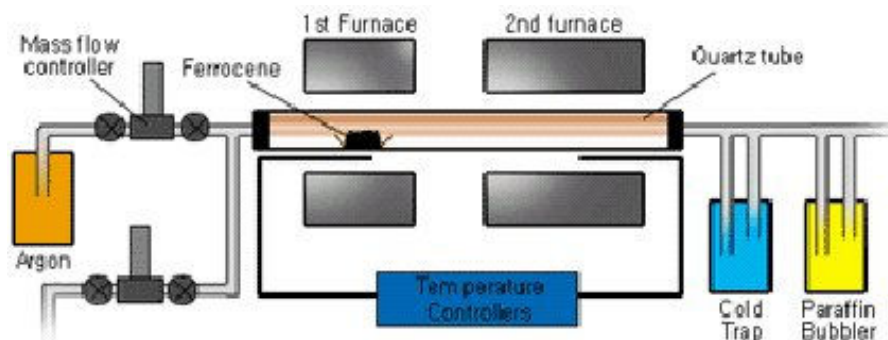
- Laser evaporation

- Thermal CVD reactors



- Plasma reactors

- Vapor-phase growth (Floating catalyst) reactors



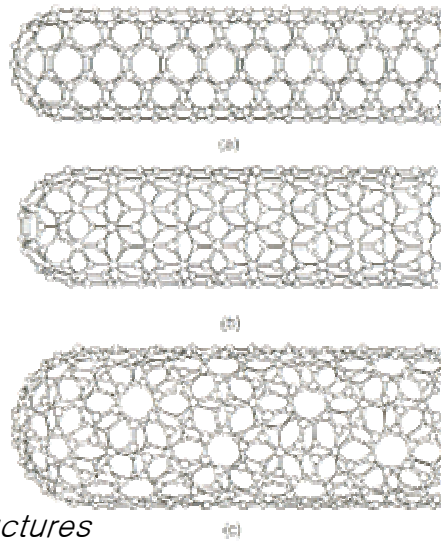
*A summary of the major production methods and their efficiency*

Method	Arc discharge method	Chemical vapour deposition	Laser ablation (evaporation)
Who	Ebbesen and Ajayan, NEC, Japan 1992 <sup>15</sup>	Endo, Shinshu University, Nagano, Japan <sup>53</sup>	Smalley, Rice, 1995 <sup>14</sup>
How	Connect two graphite rods to a power supply, place them a few millimetres apart, and throw the switch. At 100 amps, carbon vaporises and forms a hot plasma.	Place substrate in oven, heat to 600 °C, and slowly add a carbon-bearing gas such as methane. As gas decomposes it frees up carbon atoms, which recombine in the form of NTs	Blast graphite with intense laser pulses; use the laser pulses rather than electricity to generate carbon gas from which the NTs form; try various conditions until hit on one that produces prodigious amounts of SWNTs
Typical yield	30 to 90%	20 to 100 %	Up to 70%
SWNT	Short tubes with diameters of 0.6 - 1.4 nm	Long tubes with diameters ranging from 0.6-4 nm	Long bundles of tubes (5-20 microns), with individual diameter from 1-2 nm.
MWNT	Short tubes with inner diameter of 1-3 nm and outer diameter of approximately 10 nm	Long tubes with diameter ranging from 10-240 nm	Not very much interest in this technique, as it is too expensive, but MWNT synthesis is possible.
Pro	Can easily produce SWNT, MWNTs. SWNTs have few structural defects; MWNTs without catalyst, not too expensive, open air synthesis possible	Easiest to scale up to industrial production; long length, simple process, SWNT diameter controllable, quite pure	Primarily SWNTs, with good diameter control and few defects. The reaction product is quite pure.
Con	Tubes tend to be short with random sizes and directions; often needs a lot of purification	NTs are usually MWNTs and often riddled with defects	Costly technique, because it requires expensive lasers and high power requirement, but is improving

## *Carbon nanotube*

- *long, thin cylinders of carbon, discovered in 1991 by S. Iijima*
- *thought of as a sheet of graphite (a hexagonal lattice of carbon) rolled into a cylinder.*

*\* Three structures of CNT*

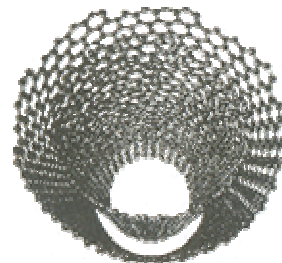


*(a) armchair; (b) zigzag; (c) chiral structures*

*\* Single-walled nanotubes: 2nm in dia, 100 $\mu$ m long*

*- prepared with metal catalysts*

*Multi-walled nanotubes*



## Properties of carbon nanotubes

- *Properties: sensitive to NT structures*

### *(i) Electrical Properties*

- *metallic or semiconducting depending on the diameter and chirality of the tube*

*armchair: metallic*

*chiral: semiconducting*

- *From synthesis*

*2/3: semiconducting; 1/3: metallic in general*

- *quantum confinement effect*

*limited number of electronic states in circumferential directions*

*\* coulomb blockade, single electron tunneling, field effect transistor*

*\* Metallic CNT*

-  $\sim 10^9 \text{ A/cm}^2$   $\therefore$  very few defect

cf. Cu  $\sim 10^6 \text{ A/m}^2$

- very good thermal conductors

factor of 2 more than that of diamond

*\* Magnetoresistance: more conducting under DC magnetic field*

*(ii) Vibrational Properties*

- Two normal modes of vibration

Frequencies: Raman active

depends on nanotube radius

*(iii) Mechanical properties*

$E = 1.28\text{-}1.8 \text{ TPa}$ , very stiff, 10 times that of steel

Tensile strength = 45 billion Pa, 20 times stronger than steel

## Applications

- *Large scale production methods: should be developed.*
- *\$1500/g for SWNT: should be downed to \$20/kg*
- *Field emission and shielding*
- *Computers: field effect transistors (switching components)*  
*10<sup>4</sup> faster, higher density*
- *Fuel cells: anode*  
*Li/H storing*
- *Chemical sensors (as FET)*
- *Catalysts (with metal bonded to CNT)*
- *Mechanical reinforcement (as filler)*

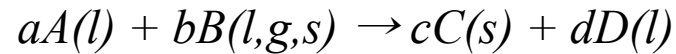
## ***5.5 Liquid-phase Preparation***

<http://neon.cm.utexas.edu/academic/courses/Fall1997/CH380L/yw.html>

- *Physical: solvent removal, crystallization/ not adequate for nanoparticle formation*

*Chemical: liquid involving reaction*

### *(1) Introduction*



- *If C: highly insoluble, high chances to form very small and so many nuclei*

- *Results in giant aggregates composed of nanoparticles due to high density and low mean free path in liquid phase.*

- *Requires to suppress aggregation of the nanoparticles*

*Electrical double layer*

*Surfactants*

*Polymers*



*In general, liquid-phase preparation has advantage*

*-Highly developed*

*-High controllability*

*-Produce very sophisticated products*

*But has disadvantages, too;*

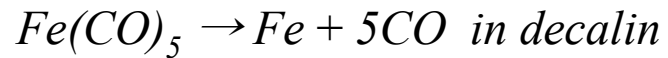
*-more art than technology*

*-requires lots of chemical species and process steps*

*e.g. aging, filtration, washing, drying, sintering (thermal treatment)*

## *(2) Metal nanoparticles*

*- Decomposition: thermal and sonochemical*



$\Delta$

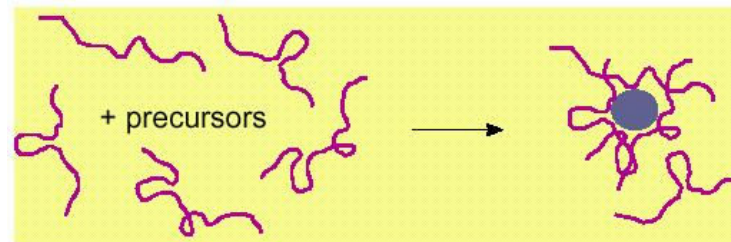
*- Salt reduction*

*Salt + reducing agent with polymer stabilizer in water*



*Supply of energy: thermal, radiation (gamma ray, UV, microwave etc.),*

*ultrasound, electrical*



### *(3) Semiconductors*

*Pyrolysis of organometallic in the presence of polymer stabilizer or capping agent at elevated temperatures*

*CdE (E = S, Se and Te)*

*- Me<sub>2</sub>Cd + (TMS)<sub>2</sub>S/TOPSe/TOPTe in mixed (TOP+TOPO) solution\**

*bis(trimethylsilyl) sulfide selenide telluride      tri-n-octylphosphine oxide*

*at 300°C under Ar environment*

*\* Coordinating solvent (solvent + capping agent)*

*- Followed by rapid cooling (to 180°C): short nucleation*

*gentle reheating(230-260°C): Ostwald ripening*

*selective precipitation: repeated dissolution in 1-butanol and ppt with*

*methanol: classification*

*\* Reaction of salt with gaseous H<sub>2</sub>S*

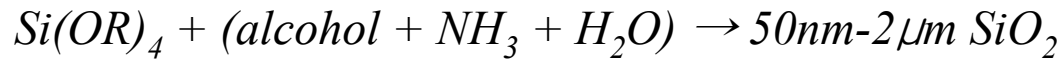
*- Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O or Cd(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O + (NaPO<sub>3</sub>)<sub>6</sub> + NaOH with H<sub>2</sub>S or H<sub>2</sub>Se + PVP*

#### (4) Forced Hydrolysis for Oxides

*Oxides: more stable thermally and chemically*

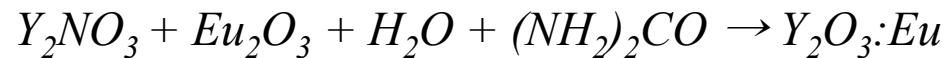
*Ostwald ripening: generally unimportant*

*Hydrolysis and condensation of metal salts with addition of catalysts (acids, bases)*



*Dilution required high supersaturation Ostwald ripening*

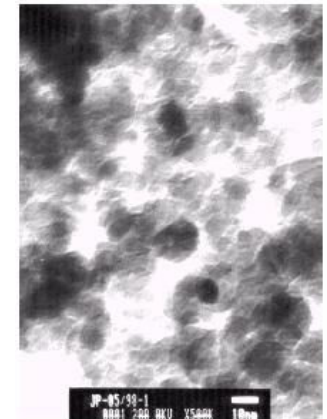
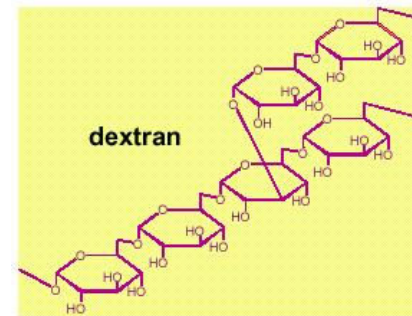
*Diffusional growth*



*Controlled release of OH*



*Iron oxide (left) without (right) with dextran*



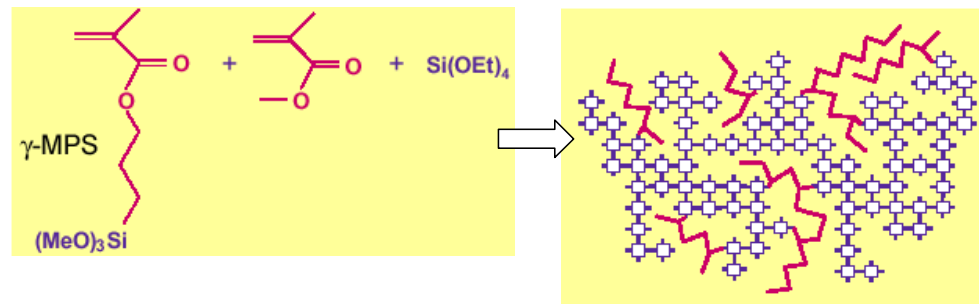
## (5) Suppression of Nanoparticle Aggregation

- In polymer solution

- Polymer: PVP, PVC, PVA, dextran

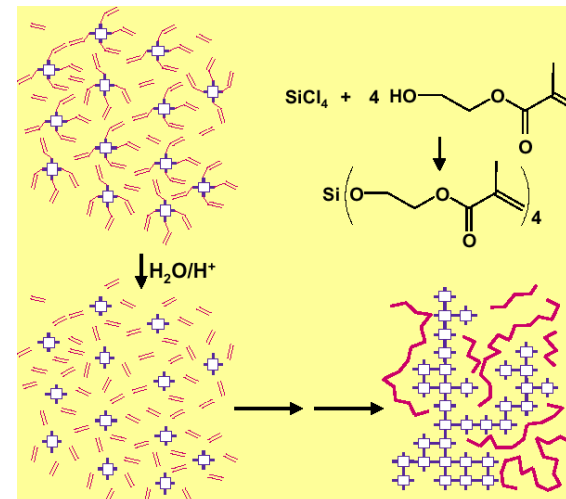
- Surfactants or capping agents: thiophenolate, glutathione peptide

- Simultaneous polymerization of monomers

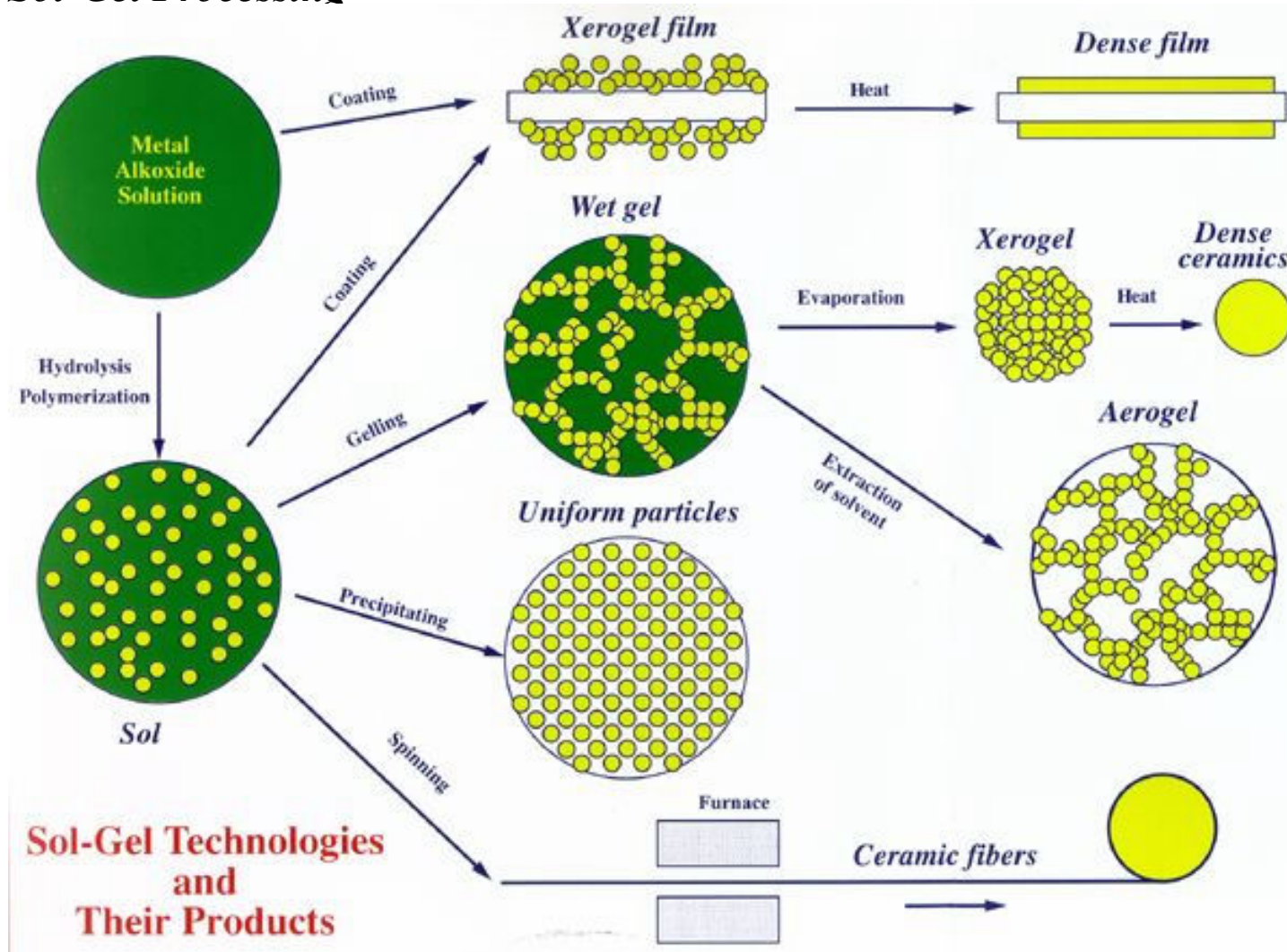


$\gamma\text{-MPS} = \gamma\text{-methacryloyloxypropyl-trimethoxysilane}$

- From a single precursor for NP and polymer



## 5.6 Sol-Gel Processing



*(1) Precursors*

\* *Metal alkoxides,  $M(OR)_Z$ , in organic solvent*

*where  $M = Si, Ti, Zr, Al, Sn, Ce$*

*OR = an alkoxy group*

*Z = the valence or the oxidation state of the metal*

\* *Metal salts (chloride, oxychloride, nitrate..) in aqueous solution*

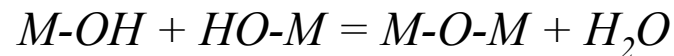
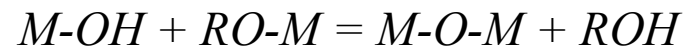
*- much cheaper and easier to handle*

*- reactions: more difficult to control*

*(2) Basic mechanism*

\* *Hydrolysis*       $M-OR + H_2O = M-OH + ROH$

\* *Polycondensation*

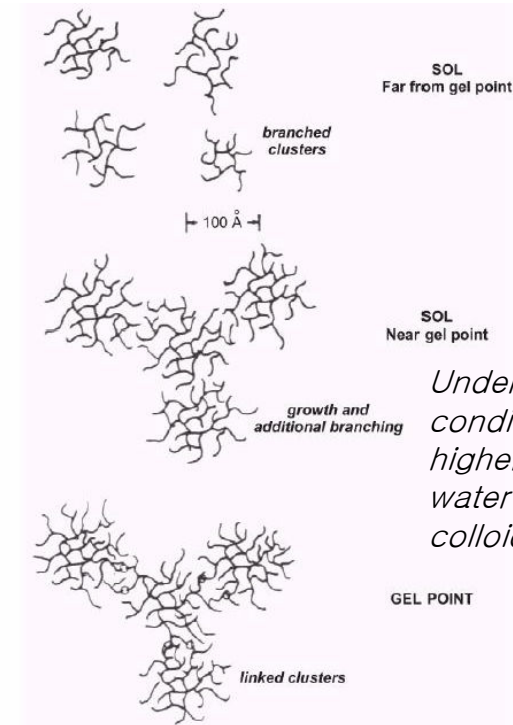
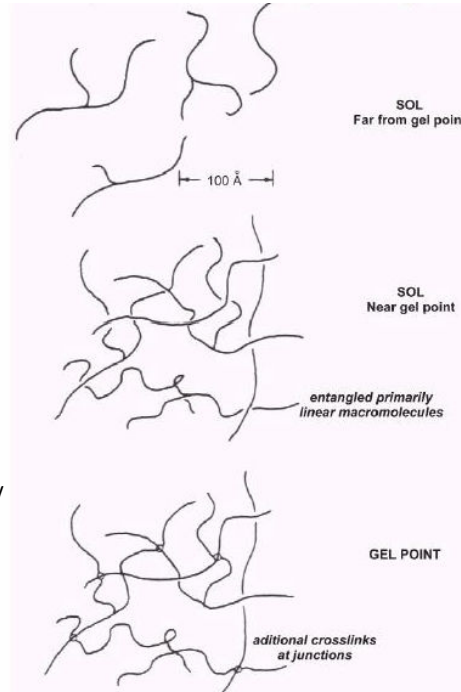


*- Occurs sequentially and in parallel*

### (3) Gel formation

#### Ex. Sol-gel transformation for silica

*Under acid catalyzed conditions : polymeric gel*



### (4) Characteristics of sol-gel processes

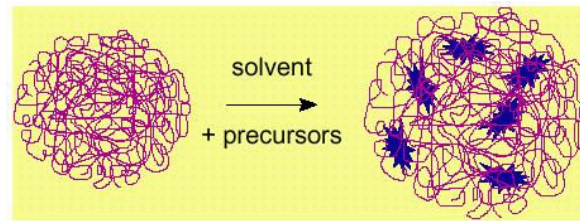
- Low processing temperature
- Molecular-level homogeneity
- Useful in making complex metal oxides, temperature-sensitive organic-inorganic hybrid materials and thermodynamically unfavorable or metastable materials



## 5.7 Confined Growth

### (1) Growth in structured materials

- In polymer matrix



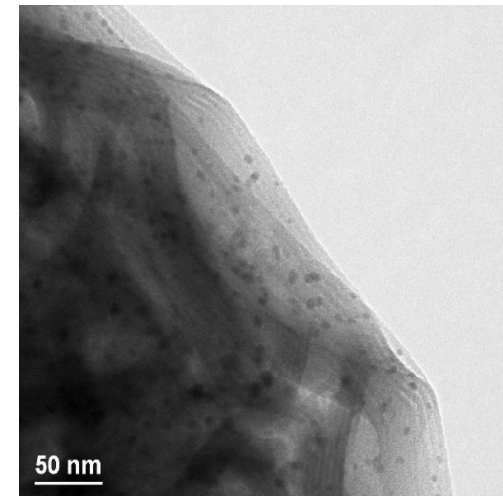
- In layered materials

*e.g. kaolinite*

- In porous materials

*e.g. zeolites, mesoporous silica*

- In carbon nanotubes



## (2) Growth in Microemulsion

### \* Definition

- Surfactants: hydrophilic + hydrophobic groups

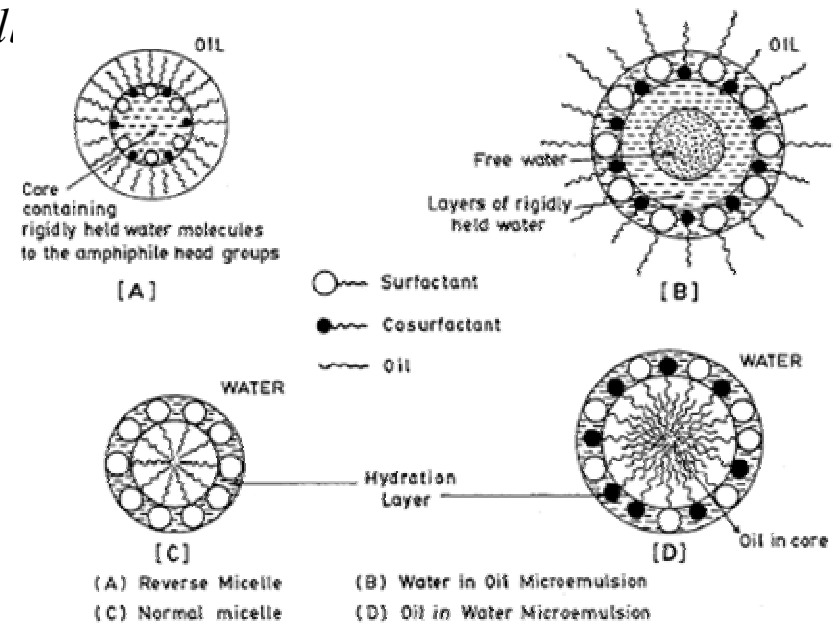
*Anionic/ cationic/ amphiphilic*

- Micelles vs. microemulsions

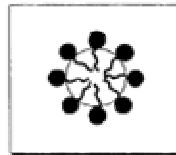
- critical micelle concentration (cmc)

- Emulsion vs. microemulsions

<http://www.responseonline.com/tech/emul.htm>

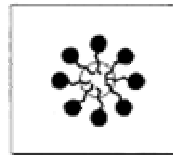


**Emulsion**  
Milky-white opaque



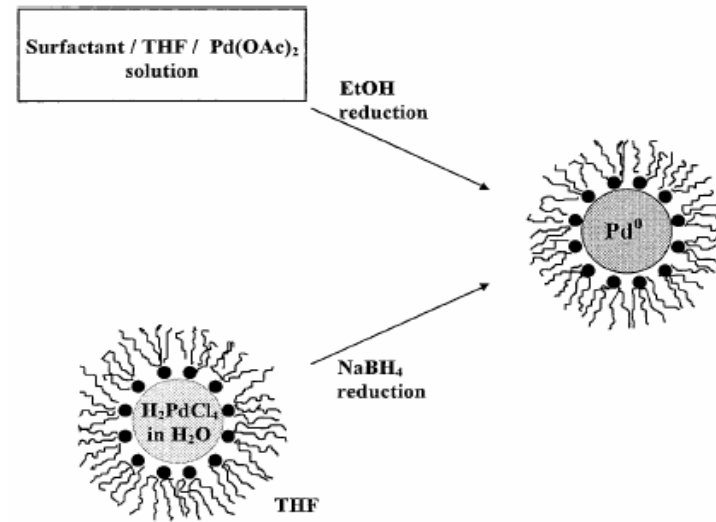
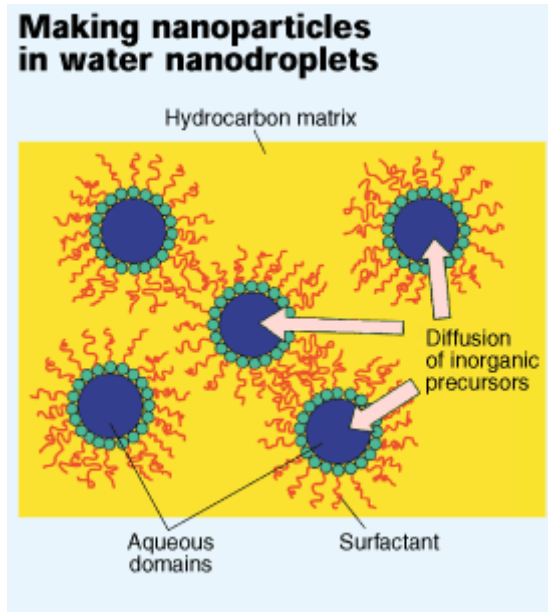
Droplet size:  
500-5000 nm

**Microemulsion**  
Transparent



Droplet size:  
10-80 nm

- Preparation of nanoparticles in microemulsion



## 5.8 Droplet-to-Particle Conversion- Aerosol-phase preparation

### (1) Introduction

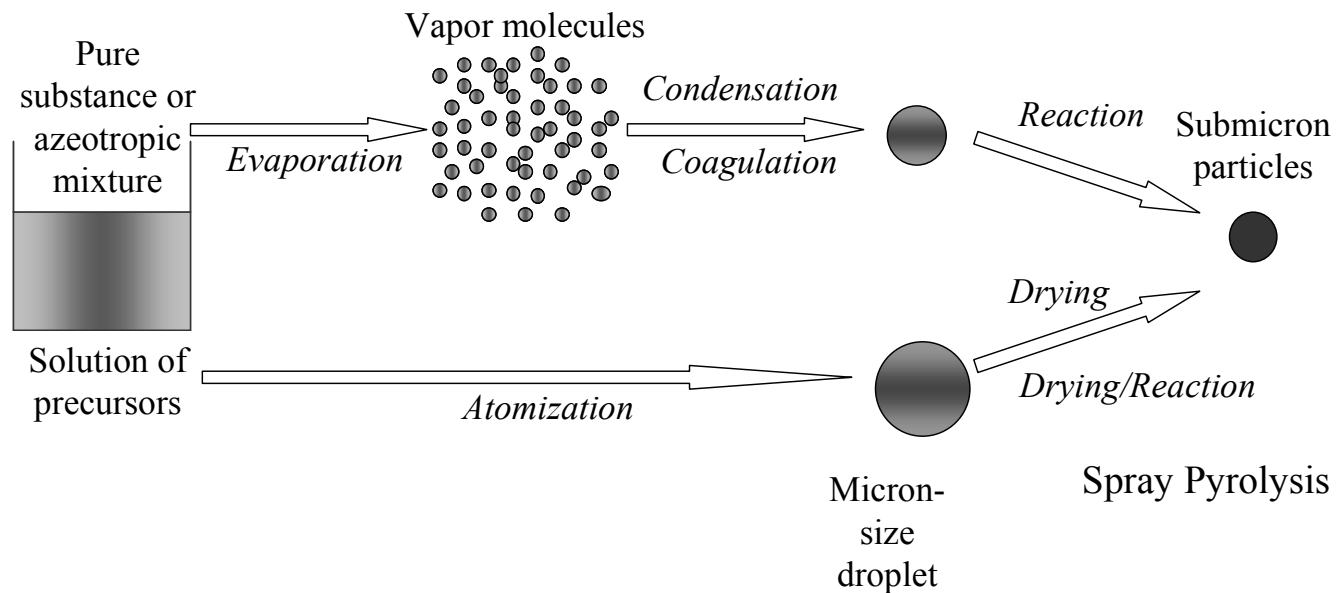
- Confined growth in droplets

cf. microemulsion

### \* Droplet (aerosol) formation

- Evaporation-condensation

- Atomization\*-spray pyrolysis



*\* Advantage of aerosol preparation*

*- Media: both liquid + gas*

*- Use of solution chemistry from well-developed liquid phase process*

*- Use of advantage of gas-phase preparation*

*Continuous, simple processes, less number of chemical species, no sintering process*

*- Gas-to-droplet interaction*

*Evaporation (drying)/condensation, droplet-surface interaction*

*- Confined growth*

*\* Methods of atomization*

*- Disintegration (nebulization) of liquid or suspension by*

*- Pressure atomizer*

*- Two-fluid atomizer*

*- Rotating disk atomizer*

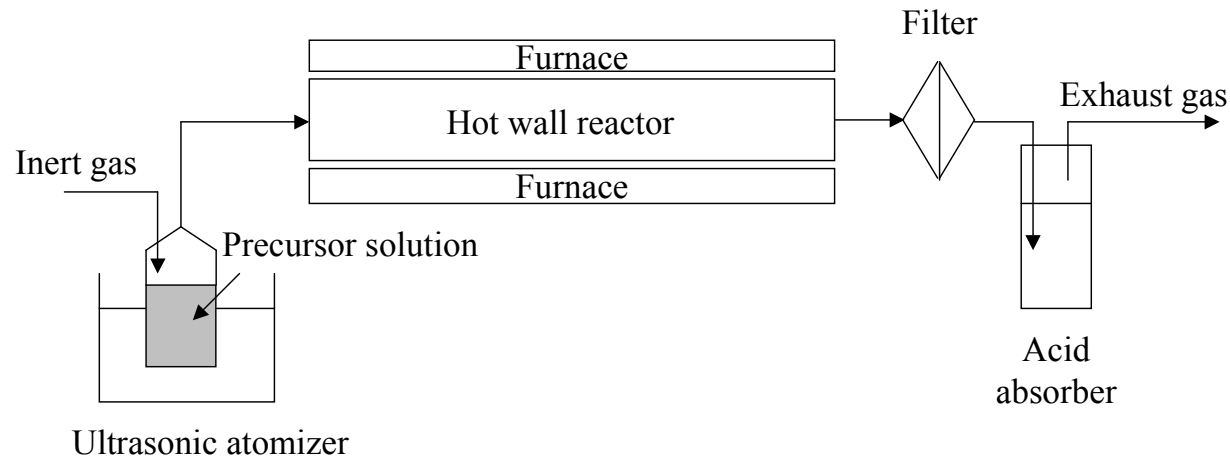
*- Ultrasonic nebulizer\**

*- Electrospray*

## *(2) Conventional Spray Pyrolysis*

*\* Precursors - liquids or solutions*

*\* Equipments*



*\* Mechanism of droplet-to-particle conversion*

*Drying of solvent*

*Solute precipitation*

*Salt-to-product conversion by solid (liquid)-gas reaction*

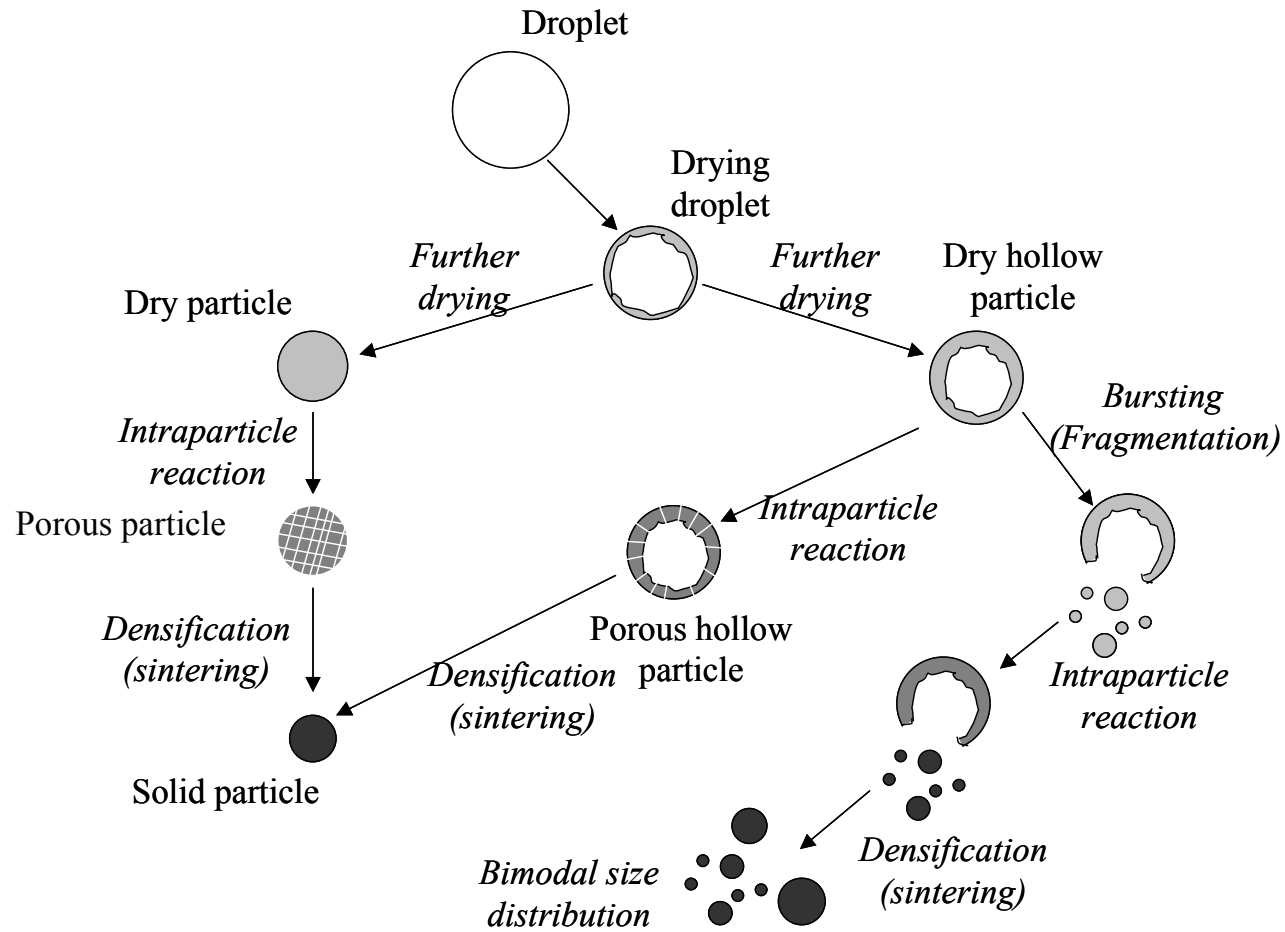
*Nuclei growth by sintering*

*\* Examples: metals, oxides, carbides, sulfides and nitrides*

*\* Various morphologies*

*-Solid, hollow spheres or fragmented particles*

*-Spheres composed of small nuclei with various porosity*



*\* Hollowness of particles*

*Solid dense particles are obtained*

- If center reaches saturation when surface to start precipitate (critical supersaturation)*
- If volume contraction due to density increase is higher than  $\sim 1/16$  by density increase*

*“Percolation theory”*

*\* Characteristics*

- Multicomponent particles: easily prepared*
- Various types of morphology*
- Spherical particles*
- Hard to prepare nanoparticles: inefficient*

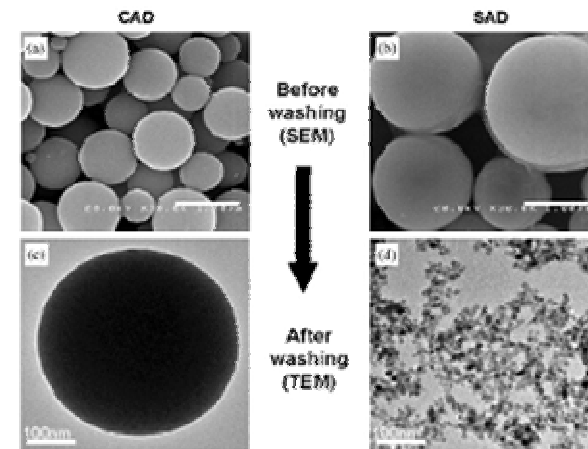
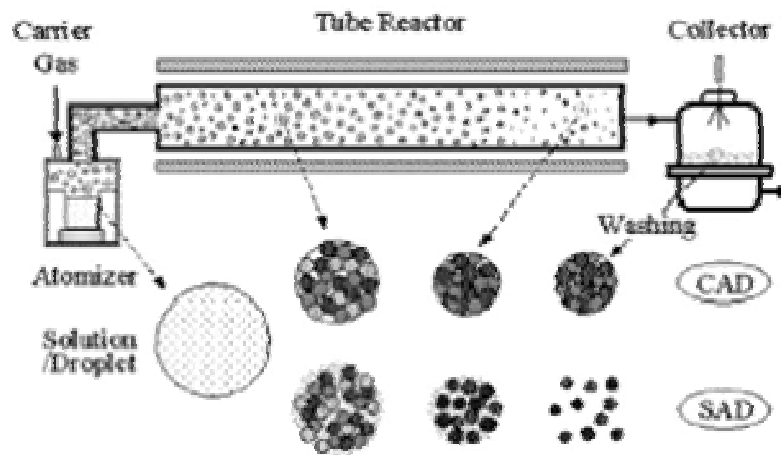


### (3) Assisted Spray Pyrolysis

#### Salt-assisted

\* *Solution of precursor + water-soluble stable salt*

\* *Salts should melt but not decompose in processing temperatures.*



*Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> particles synthesized by CAD and SAD, respectively.*

\* *Nanoparticles form and grow dispersed in salt*

\* *Crystallinity increased due to enhanced solubility and mass transfer of precursors in the melt*

## Polymer-assisted

\* *Solution: metal salt + polymer + water*

\* *Polymers used: PVP, PVA, dextran*

\* *Solvent evaporation, polymer matrix formation and precursor reaction: in sequence*

\* *Nanoparticles: preparable at relatively high precursor concentrations with relatively low concentration of polymer*

*Ex.  $\text{AgNO}_3$  + PVP in water*

