Chapter 9. Assembly and Consolidation of Nanoparticles

9.1 Introduction

* Use of nanoparticles

    - Dispersed state: paints, filler, cosmetics, homogenous or dispersed catalysts

    - Consolidated state

        -porous: catalysts, sensor, electrodes(directly, or indirectly)

        -densified: ultrahard alloy, fine ceramics, ceramic engines

        -ordered: electronic, optical, optoelectronic devices

* Consolidation:

    - size enlargement of nanoparticles

* Methods of consolidation

    - forming by using templates usually

        3-D: die casting, extrusion, spray drying

        2-D: deposition on substrate surface

        1-D: use of linear template, particle dipoles*

Source of consolidation

Particle-to-particle interaction or particle-to-substrate interaction

- Long-range force for consolidation

- Brownian motion

- capillary force

- fluid force (inertia, shear)

- external force (electrical, pressure, gravitational)

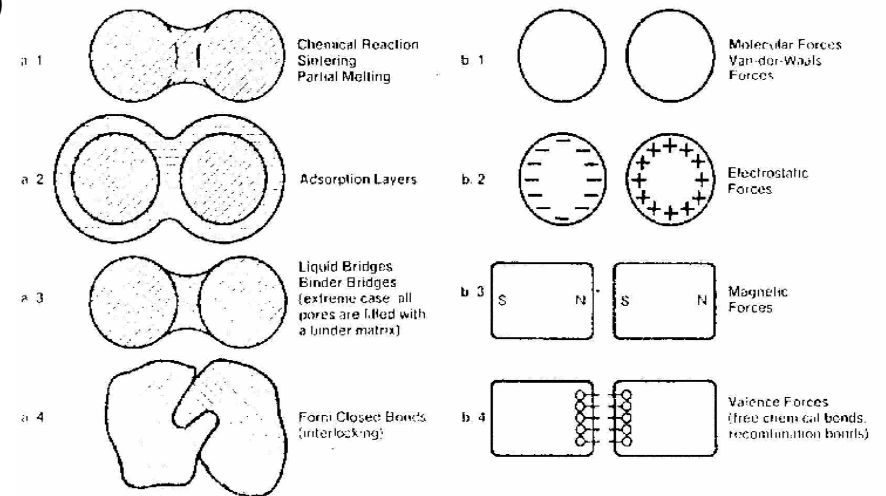*- Ultimate consolidation (short-range force)*

- van der Waals' force

- liquid bridge

- chemical bond

(usually via surface modifier)

Ultimate densification

- Sintering

## 9.2 Mechanical Forming

(1) Pressure forming

- Pressing of masses through openings of sieves, rollers, or dies

- Solid bridges : formed by compressive deformation at the point of contact

- Dry or moist binder and lubricants : used for powders which are difficult for compaction

* Methods

- Die compaction

- Roll compaction

- Extrusion

Die compaction process
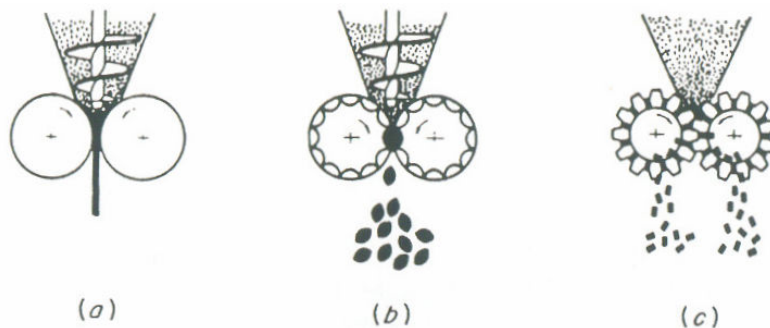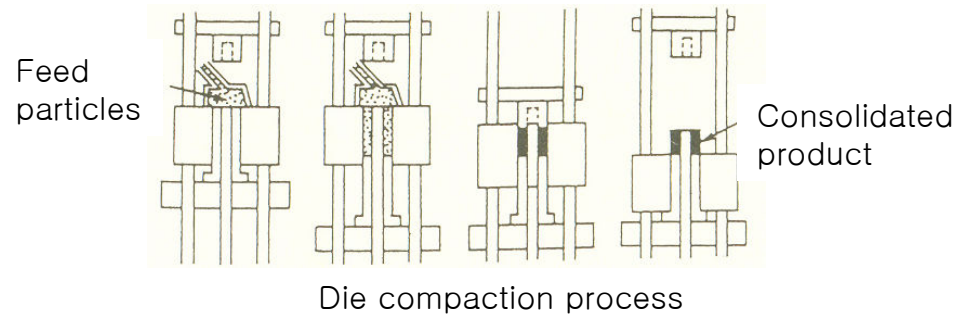
Roller, a:compaction; b:briquetting; (c) pelleting
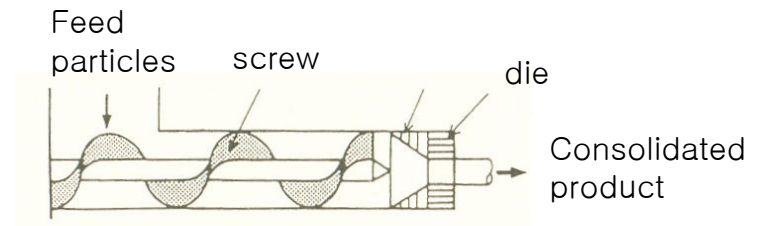
Extruder

(2) Granulation

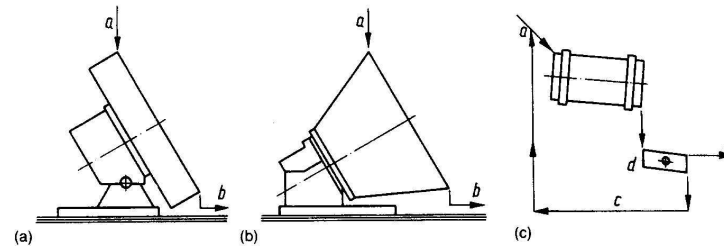** Granulation process:*

      wetting   →   growth   →   granule consolidation

         nucleation/coalescence/layering

   - Interparticle collision by tumbling, mixing and turbulent motion

   - Often requires moisture or other binding agents

   - Not very strong agglomeration without after-treatment (drying, sintering)

* Methods of granulation

   - Tumbling type

   - Agitation type

   - Fluidization type

Tumbling-type granulators (a) disc (b) cone (c) drum
   a.Feed+water(binder); b.green agglomerates; c.recycle
   a.Feed+water(binder); b.green agglomerates; c.recycle
   (undersize); d.sieve
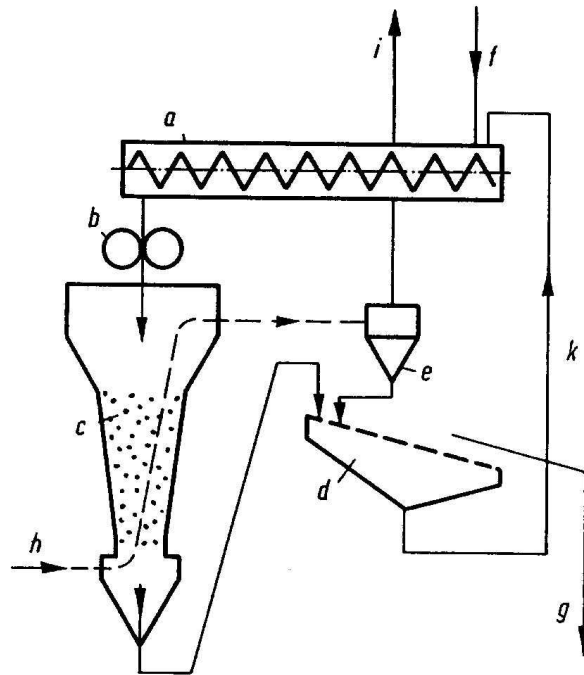
Fluidized−bed granulator
a.mixing screw, b.distributing rolls, c.venturi fluidizer, d.sieve,
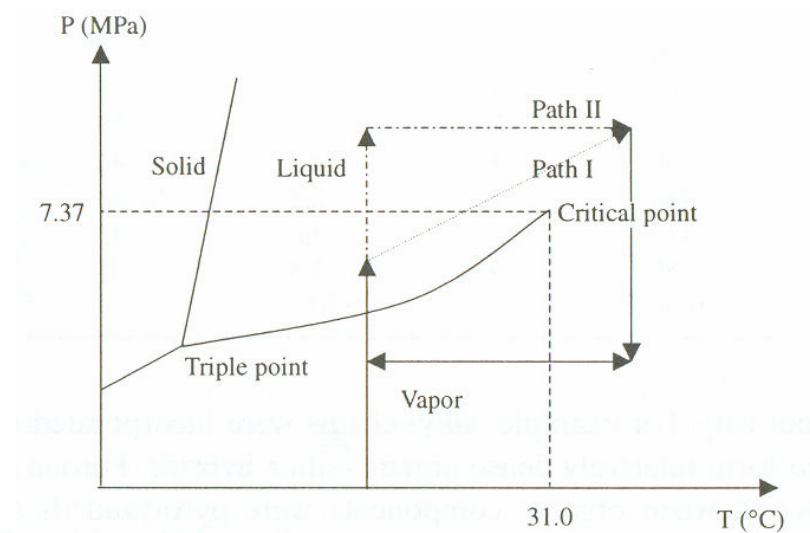e.cyclone, f.feed, g.granulates, h.hot gas, i.exhaust air,
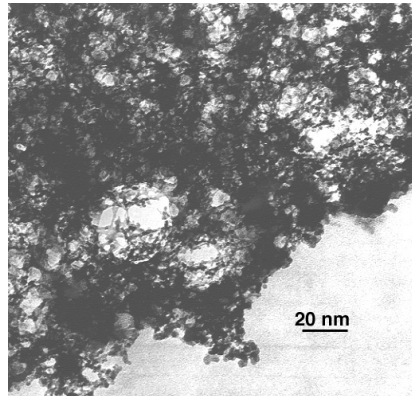k.recycled undersize

9.3 Porous Structure Materials by Sol-gel-drying Processes

(1) Aerogels and xerogels

* Drying

   - due to capillary force in the pores $p_c = -\sigma_{lv} \cos\theta \left(\dfrac{1}{R_1} + \dfrac{1}{R_2} \right)$

   under ambient conditions $\rightarrow$ collapsed dried gel $\rightarrow$ xerogel

* Supercritical drying $\rightarrow$ aerogels

20 nm

- Critical points

Solvents	Formula	T_c (°C)	P_c (MPa)
Water	H_2O	374.1	22.04
Carbon dioxide	CO_2	31.0	7.37
Freon 116	$(CF_3)_2$	19.7	2.97
Acetone	$(CH_3)_2O$	235.0	4.66
Nitrous oxide	N_2O	36.4	7.24
Methanol	CH_3OH	239.4	8.09
Ethanol	C_2H_5OH	243.0	6.3

- *Solvent exchange*

- *Characteristics of aerogels*

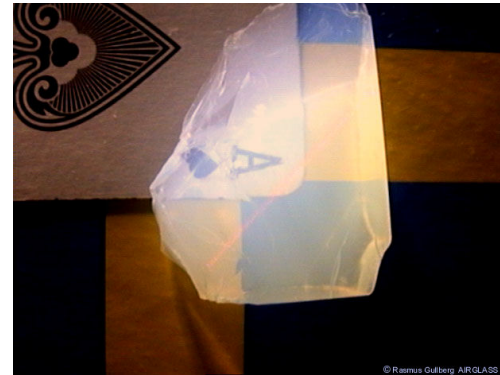   *Porosity: 75-99%*

    Specific surface area: ~ >1,000m^2/g

   *cf. porosity of xerogel: 1-50%*

    - very light, transparent

    - used in catalysts, sensor, electrodes, thermally and/or electrically insulating

materials

(2) Mesoporous materials

 - starting from precursor+ solvent+ catalyst+ surfactant

 - aligning surfactant molecules during solvent evaporation

 - hydrolysis and condensation like sol-gel process on head side of the alignment

hexagonal

Cylindrical type micelle

lamellar

TiO2 mesoporous structure made with urea

20 nm
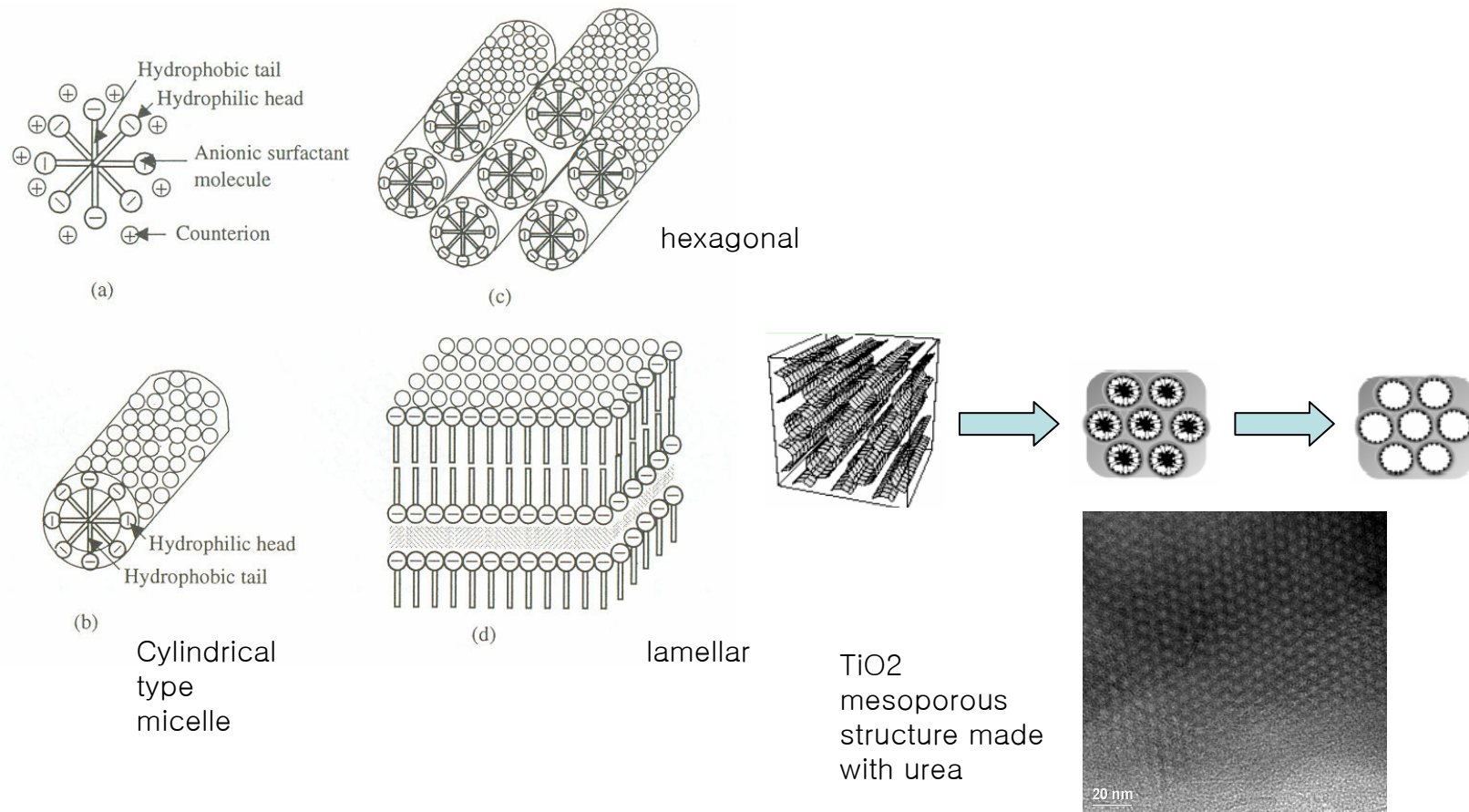
(3) Sol-derived films

    - simultaneous evaporation and gel formation

    - crack formation possible by rapid drying and incompatibility between coating and

    substrate

Spin coating

   - delivery of sol onto the substrate center $\rightarrow$ *spin-up* $\rightarrow$ *spin-off* $\rightarrow$ *evaporation*

   - Uniform films for Newtonian fluid

   - Thickness

$$H = \left(1 - \frac{\rho_A{}^0}{\rho_A}\right)\left(\frac{3\mu e}{2\rho_A{}^0 \omega^2}\right)$$

where ρ_A, $\rho_A{}^0$ *present and initial mass of volatile solvent per unit volume*

       μ *: viscosity of liquid*

       e: evaporation rate

       ω *: angular velocity*

Dip coating

- evaporation and gel formation
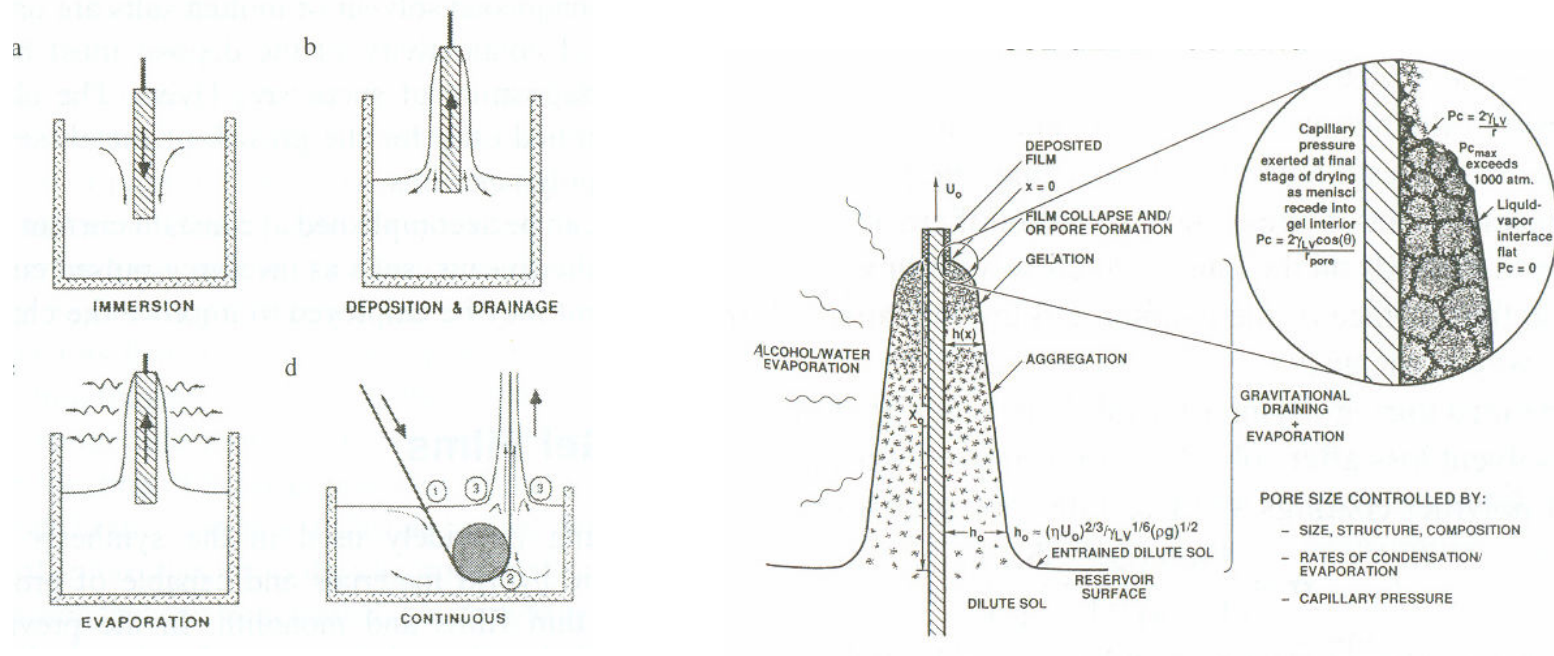
- thickness
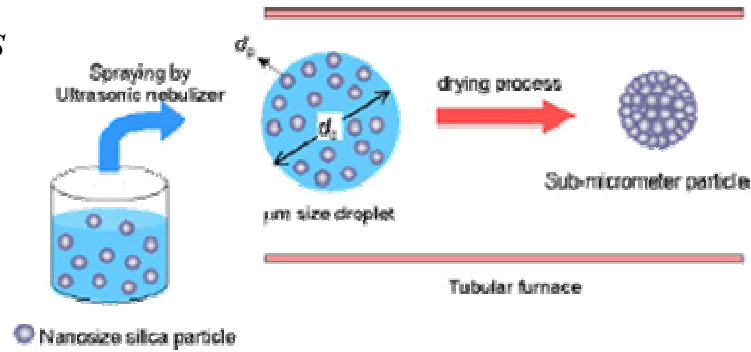
$$H = c_1 \left(\frac{\mu U_0}{\rho g} \right)^{1/2}$$

where U_0 : withdrawal speed of the substrate
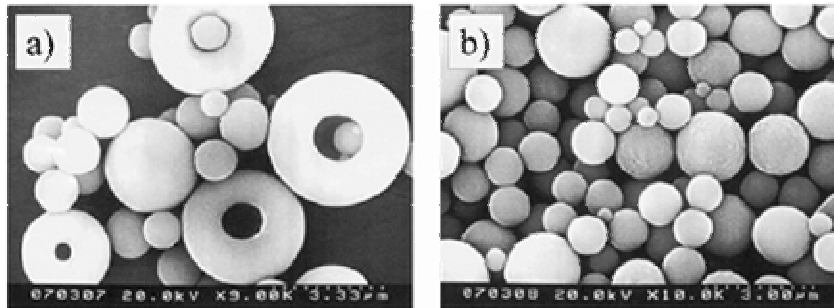
ρ *: density of coating*

c_1 *: constant*

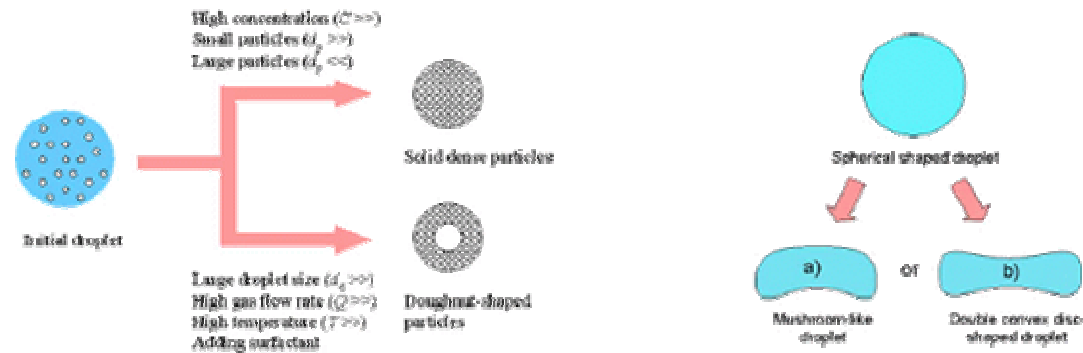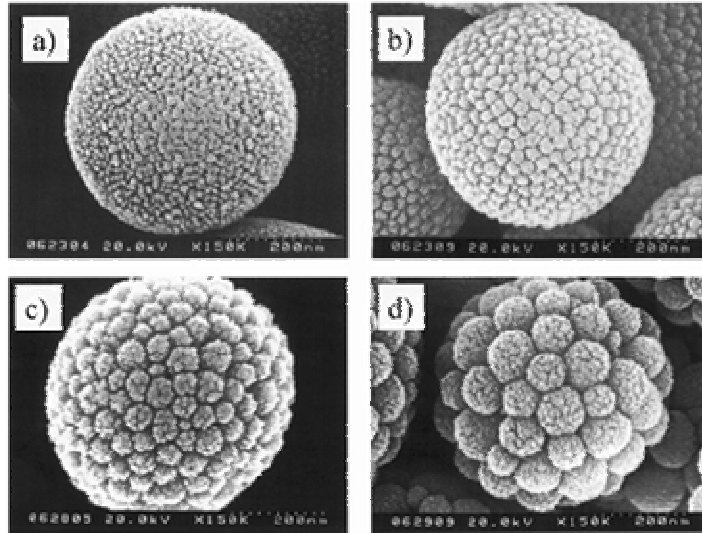# 9.4 Sol spray drying method

(1) Spherical porous materials

- *Morphology of dried aggregates*

SEM photographs of dried silica particles obtained without (a) and with (b) diffusion dryer placed before reactor inlet.

- *Hierarchical structures*

Effect of primary particle size on morphology of final particles. Experimental condition: (a) CS-1, (b) CS-2, (c) CS-3 and (d) CS-4, at 200.C.
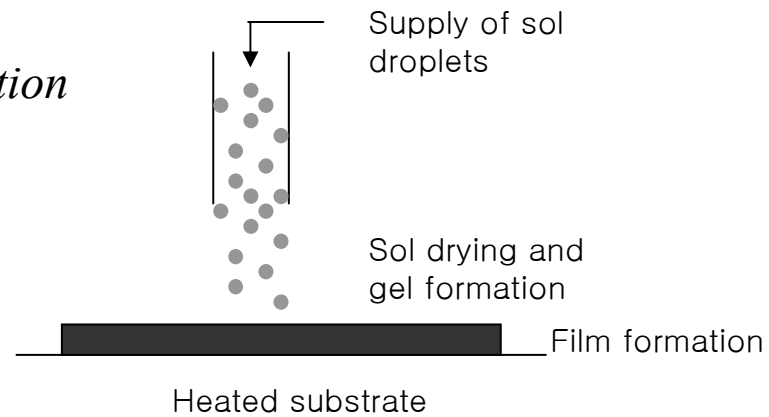
Physical properties of colloidal silica suspension

Sample	Nominal particle diameter, d_f (nm)	Suspension pH
CS-1	4-6	9-10
CS-2	20-30	8.5-9.5
CS-3	40-60	9-10
CS-4	70-100	9-10

- *Also produces mesoporous structures*

(2) Sol-spray deposition

  - Ordinary spray deposition

Supply of sol droplets

Sol drying and gel formation

Film formation

Heated substrate

 - Electrospray deposition

Bubble Injector

N₂

Liquid Reservoir

High Voltage Power Supply

Capillary

Primary Droplets

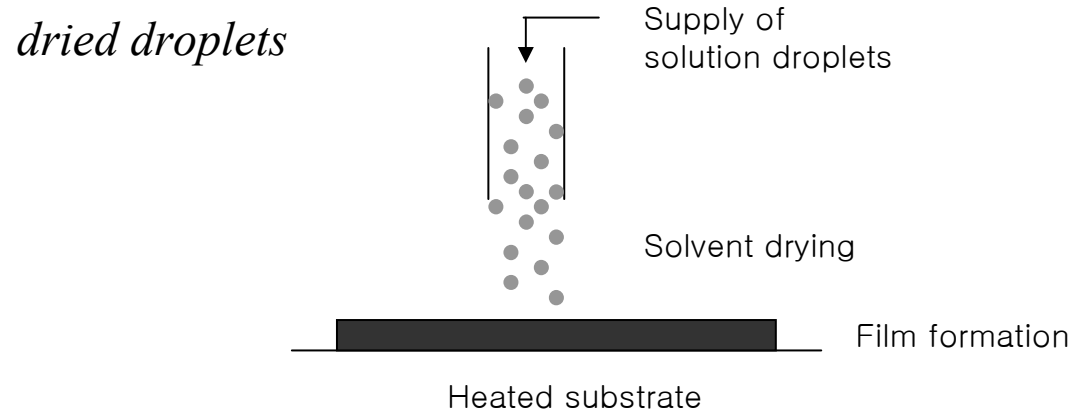Satellite Droplets

Ground Electrode

Substrate

Electrometer

20 μm

2 μm
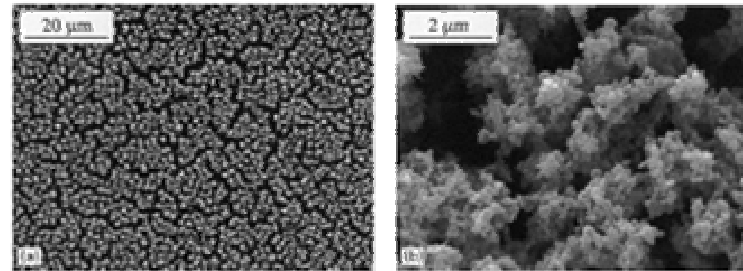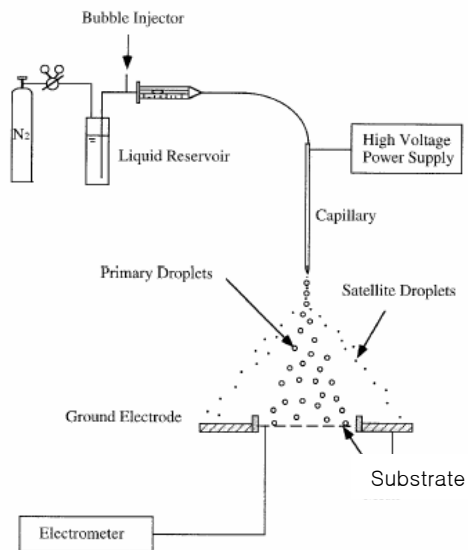
SEM micrographs (with two magnifications) of a ZrO2 thin film deposited at 220ºC on an Al plate substrate (flow rate: 0.8 ml/ h)

  - enhancement of deposition efficiency

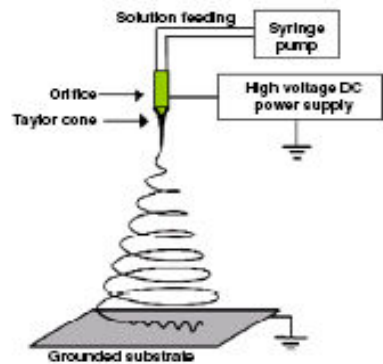## (3) Chemical aerosol deposition

- spray $\rightarrow$ solvent evaporation $\rightarrow$ deposition

- deposition occurred mainly by diffusion of solute molecules and/or partially

dried droplets

Supply of solution droplets

Solvent drying
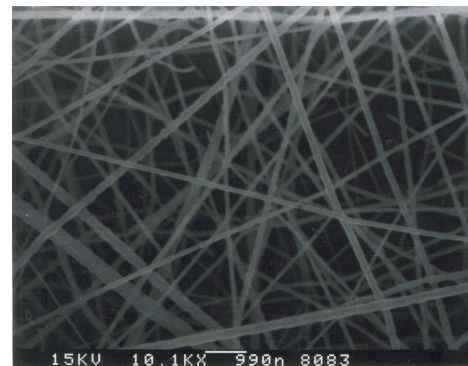
Film formation
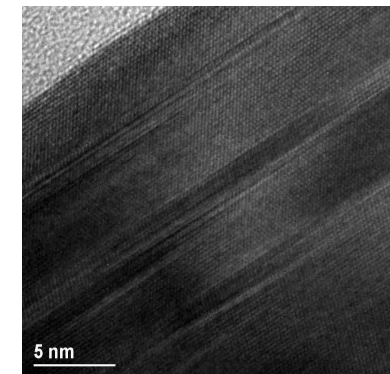
Heated substrate

(4) Electrospinning

- electrospray of linear polymer+ precursor solution followed by calcination
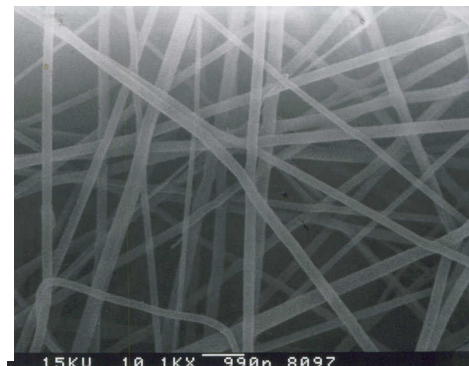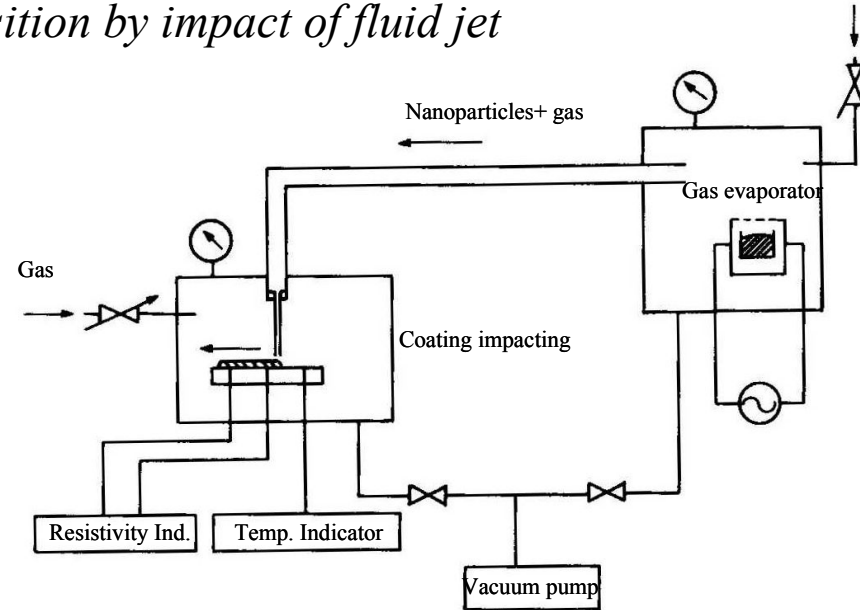

Before calcination   After calcination

9.5 Direct deposition in fluid

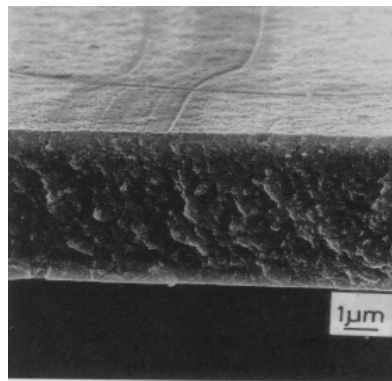*(1) Electrophoresis of sols*

- *Movement of surface charged particles*

- *packing density <74%*

- *depends on particle concentration, zeta potential, applied electric field*

- *slow arrival of nanoparticles onto the surface results in high packing density…*
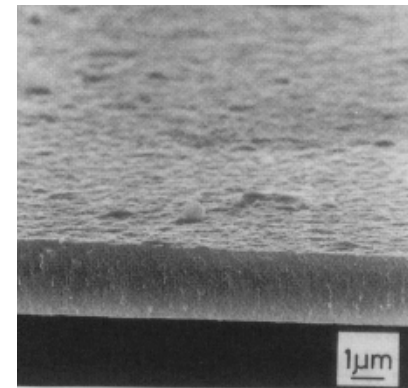
(2) Impaction of nanoparticle beams

- particle deposition by impact of fluid jet

Gas evaporator

Nanoparticles+ gas

Gas

Coating impacting
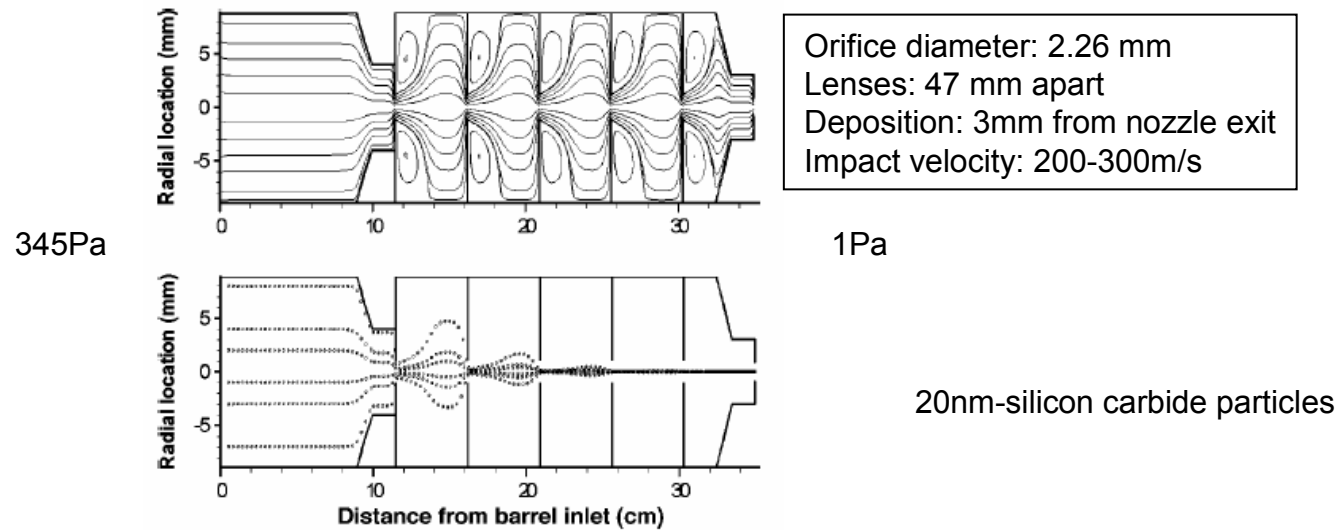
Resistivity Ind.

Temp. Indicator

Vacuum pump

- use of vacuum

Ag film

Cu film

- *Cascade hypersonic impactors*

Orifice diameter: 2.26 mm
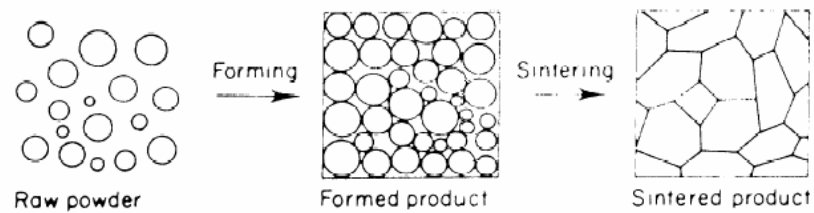Lenses: 47 mm apart
Deposition: 3mm from nozzle exit
Impact velocity: 200-300m/s

345Pa

1Pa

Predicted flow streamlines (top) and particle trajectories (bottom) in the aerodynamic lens assembly.

20nm-silicon carbide particles

400μm 65X

F. Di Fonzo, A. Gidwani, M. H. Fan, D. Neumann, D. I. Iordanoglou, J. V. R. Heberlein, P. H. McMurry, and S. L. Girshicka), N. Tymiak and W. W. Gerberich, and N. P. Rao, Appl. Phys. Lett., Vol. 77, No. 6, 7 August 2000

200μm 100X

Application → MEMS
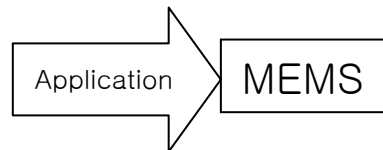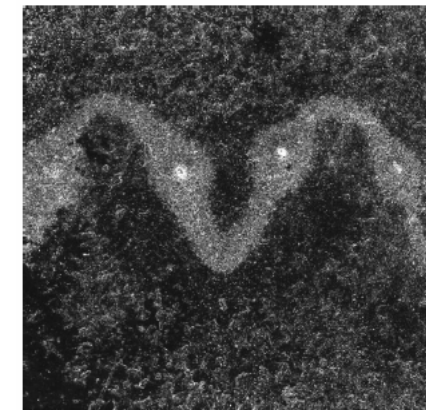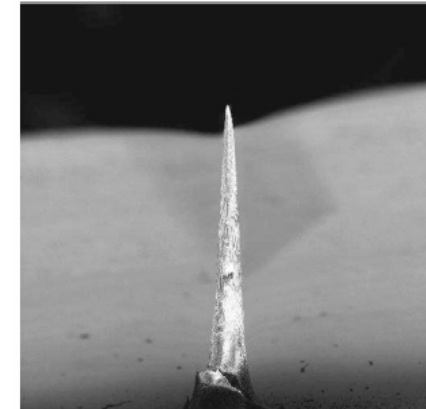
9.6 Formation of dense structure: sintering

Raw powder → Forming → Formed product → Sintering → Sintered product

* Driving force of sintering:

- Reduction in overall surface energy :Reduction in surface area relative to its volume

* Four stages of sintering

Stage	Process	Surface Area Loss	Densification	Coarsening
Adhesion	Contact formation	Minimal, unless compacted at high pressures	None	None
Initial	Neck growth	Significant, up to 50% loss	Small at first	Minimal
Intermediate	Pore rounding and elongation	Near total loss of open porosity	Significant	Increase in grain size and pore size
Final	Pore closure, final densification	Negligible further loss	Slow and relatively minimal	Extensive grain and pore growth

(1) Mechanism of sintering

- Surface transport: neck growth without shrinkage or densification

$$\frac{\Delta l}{l} = 0$$

where Δl : increase in length of particle

l: initial length of particle

- surface diffusion: lowest activation energy, predominant at low temperature

- vapor diffusion: evaporation from convex surface to concave surface

- bulk transport: net particle movement leading to shrinkage and densification

Accompanying shrinkage in dimension

*- **lattice** diffusion: dominant for crystalline materials*

*- **cross grain boundary** diffusion: dominant for crystalline materials*

*- **viscous flow:** dominant for amorphous materials*

* Reactive sintering: solid-to-solid (solid phase) reaction
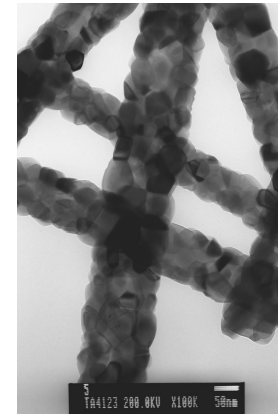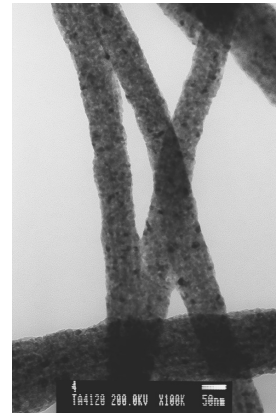
- Formation of interface product layer

e.g. Pozzolanic reaction : $SiO_2 + Ca(OH)_2$ in water at elevated pressure

(2) Sintering of nanoparticles

* Advantages of nanoparticle sintering

   *- **High rate of sintering***

   - Lowering of sintering temperature

*- Addition of nanoparticles **accelerates the***

   sintering of larger particles

Sintering of TiO2 nanofiber with respect to temperature

From left to right: 400, 600, 800°C

 e.g. W+ 0.1-0.5% of Ni nanoparticles; sintering temperature to 1200~1300ºC.

* Disadvantages of nanoparticle sintering

*- **Aggregation** results in formation of pores, change in required dimension or*

   deformation of the sintered body.

☞ *High-pressure sintering/ Fast-firing/ Plasma-assisted sintering*

   Chemical modification of the nanoparticle surface

9.7 Ordered consolidation by self assembly

Self assembly: a process by which components spontaneously assemble without the requirement of external energy or information

(1) Building blocks

- *Ordinary sols*

- *Monolayer protected (passivated) nanoparticles*

    - *alkanethiol*

    - *sulfide or sulfur containing biomaterials (DNA, proteins)*

    - *Assembly: used for electronic, optoelectronic devices, biological chips…*

- *Colloidal crystals(>100nm)*

    - *Monodisperse submicron particles (silica, latex)*

    - *Assembly: used for photonic crystals, catalysts, sensors, electrodes…*

Self assembly of templates → Simultaneous or subsequent infusion (growth) of metal or metal precursors → Template removal by calcination
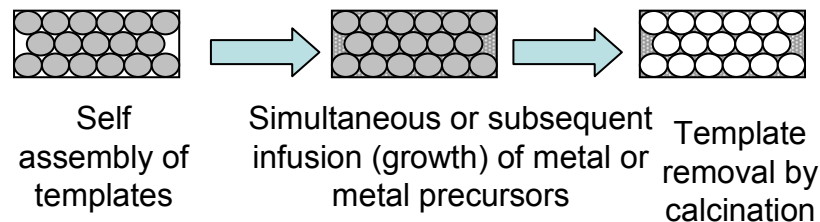
(2) 1-D assembly

Pore filling

* Ordered pores

   - Anodized aluminum membrane

      made by anodic oxidation of aluminum sheet in acid solutions...

   - Capillary membranes: polycarbonate films bombarded by neutron beams

* Filling: capillary force, electrophoresis, pressure, chemical vapor deposition,
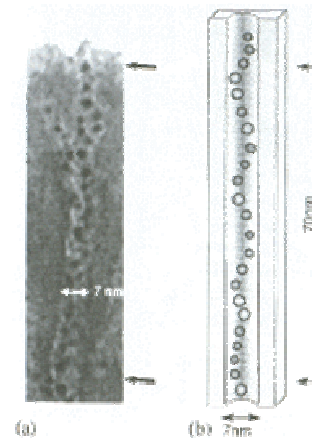
   centrifugation

   - high wettability, chemical inertness against pore wall, shrinkage control
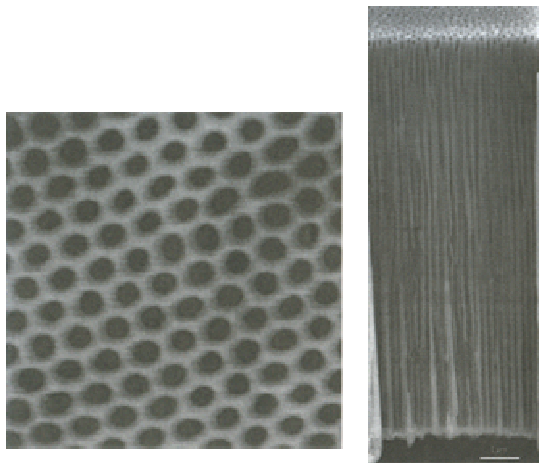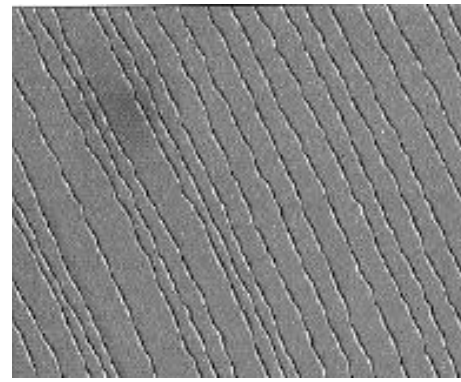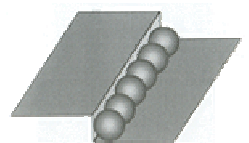

Alumina surface anodized in acids

TiO2 nanowires from its sol−alumina removed

Wire of surface−modified Au_{55} particles d=4.2nm

Deposition or attachment onto existing line templates

- *Along line defect*

    - *Defined steps on crystalline surfaces*

- *Existing nanowires*

- *Linear polymers*

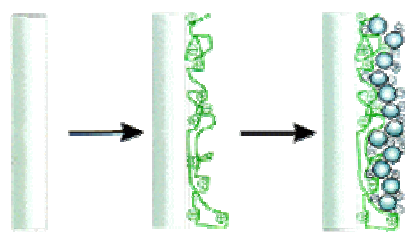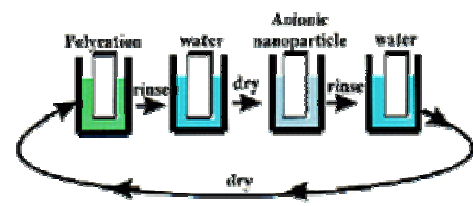Copper wire 3nmwide and 50nm apart on astepped Mo(110) surface—STM

(3) 2-D assembly
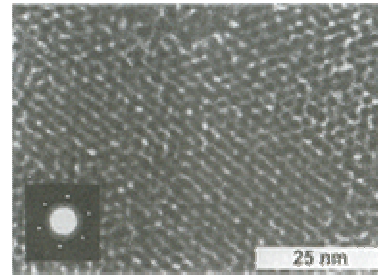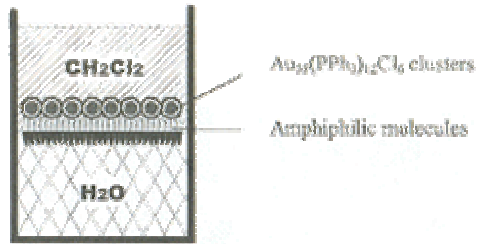
* Deposition of building blocks by
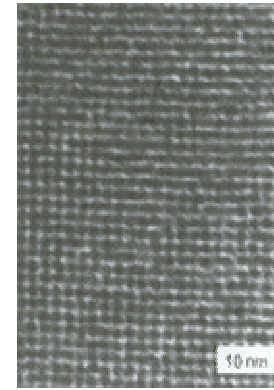
- *Electrophoresis*

- *Electrostatic force*
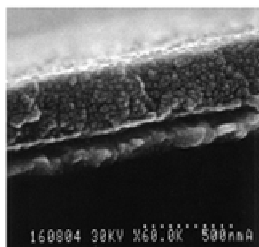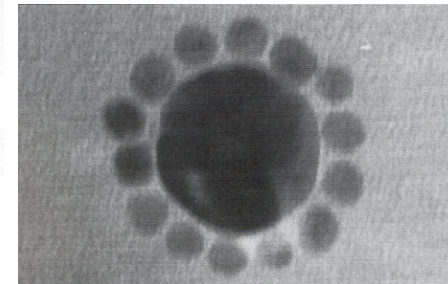

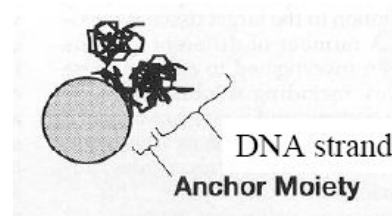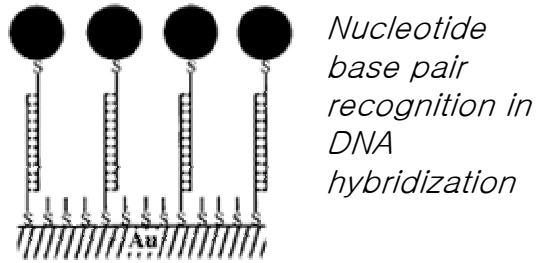SnO_2 self-assembled nanoparticles – gas sensor
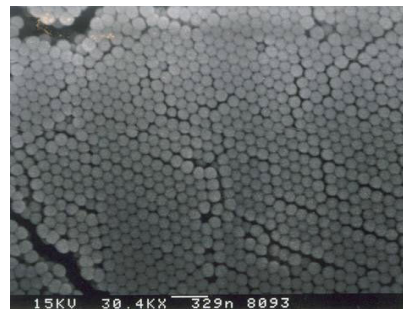
- *Bond linkage*

Hexagonal monolayer on Poly(vinylpyrrolidone)

Arranged squares on poly(ethyleneimine)

Nucleotide base pair recognition in DNA hybridization

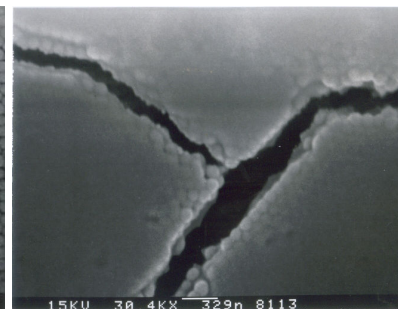DNA strand
Anchor Moiety

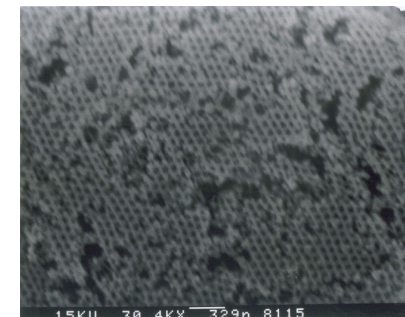30nm-gold particle linked with 8-nm gold particles via DNA linkage

- *Gravity filtration*
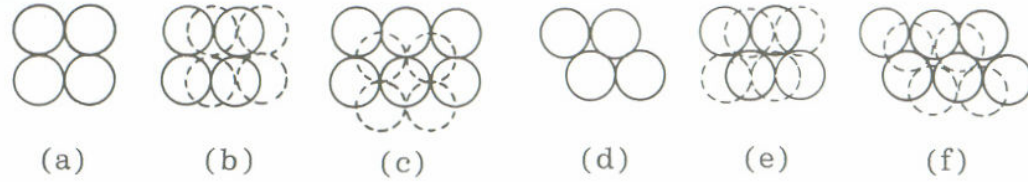
- *Dip coating*

Dip coating of polystyrene latexes

TTIP dip-coating

After calcination

Regular packing of equal spheres

(a)   (b)   (c)   (d)   (e)   (f)

Types of packing	Figures	Volume of unit cell	Void volume of unit cell	Void fraction	Packing fraction	Coordination number
Cubic	(a)	D_p^3	$0.48D_p^3$	0.4764	0.5236	6
Ortho-rhombic	(b),(d)	$0.87D_p^3$	$0.34D_p^3$	0.3954	0.6046	8
Tetragonal-sphenoidal	(e)	$0.75D_p^3$	$0.23D_p^3$	0.3019	0.6981	10
Rhombo-hedral	(c),(f)	$0.41D_p^3$	$0.18D_p^3$	0.2595	0.7405	12

D_p, diameter of equal spheres.