PREPARATION, PROPERTIES
AND
APPLICATIONS
OF
HIGHLY DISPERSED METALLIC PARTICLES

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PREPARATION OF METALLIC PARTICLES

- **Phase 'break down'**
  - Milling/grinding
  - Atomization
- **Phase 'transformation'**
  - Thermolysis/Pyrolysis
  - Reduction
- **Phase 'build-up'**
  - Condensation in gas phase $(Me^0)_g$
  - Condensation in liquid phase $(Me^0)_l$

PHASE 'BREAK DOWN' / MILLING

Size reduction of coarse/agglomerated metallic powders

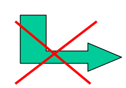
- Mechanical energy (shear, collision)
- Dispersion media (liquid or gas)
- Dispersing agents
- Controlled atmosphere and temperature frequently required

- **Suitable for some applications (mechanical alloying)**
- **Rarely yields highly monodispersed, spherical particles**

PHASE 'BREAK DOWN' / ATOMIZATION

Spraying/pulverization of molten metals

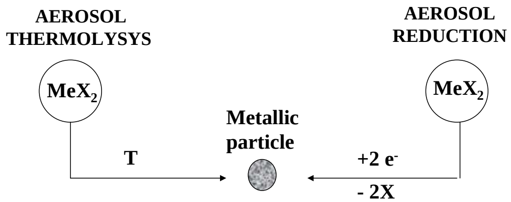
- **Large particles, broad size distributions**



{ **- Monodispersed particles**
- Sub-micrometer size

- **Capable to produce a large variety of alloy powders**
- **Low manufacturing costs**
- **Inert carrier gases may be required**

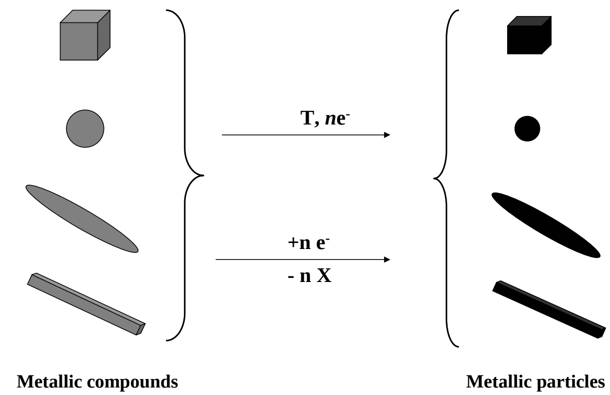
PHASE TRANSFORMATION



- Difficult to control the size distribution of precursor droplets
- Agglomeration of droplets/particles due to collisions

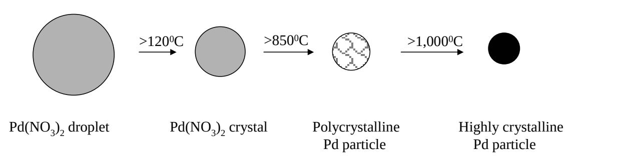
Wide particle size distribution

PHASE TRANSFORMATION



SPRAY PYROLYSIS/AEROSOL THERMOLYSIS

Decomposition of liquid precursors in gas phase

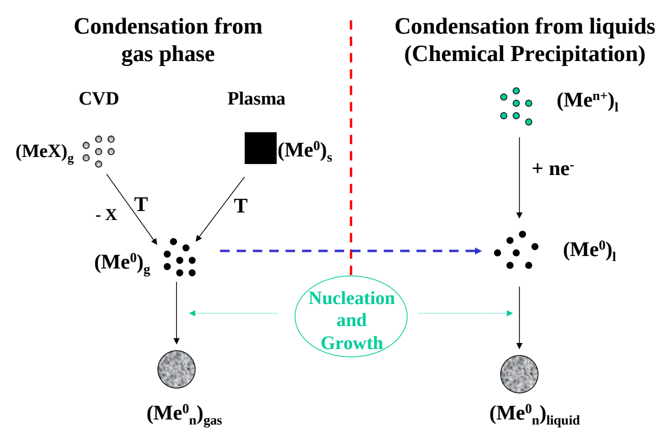


Size, uniformity, and degree of agglomeration of Me particles depends on:

a) Size and size distribution of droplets
- Droplet generation → pneumatic/spraying
  → ultrasonic
- Size control → pressure
  → transducers' frequency, size ~ ν
- Size distribution → various approaches (momentum, gravitation force)

b) Stability of the aerosols (droplets, intermediates, and final particles)
- Laminar flow during the process
- Working below the critical concentration)

PHASE 'BUILD UP' / CONDENSATION



CHEMICAL PRECIPITATION

Metal atoms generated 'via' redox reactions:

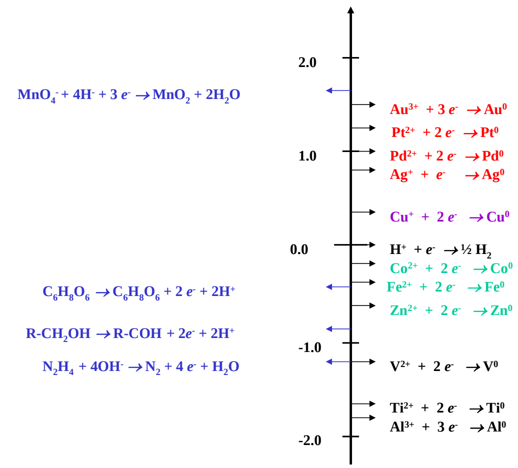
$$Me^{n+} + Red \rightarrow Me^{0} + Ox$$

Driving force:

$$\Delta E^0 = E^0_1 - E^0 2$$

$$\ln K_e = nF \cdot \Delta E^0 / RT$$

ΔE^0 → critical supersaturation
→ nucleation rate



TAILORING ΔE^0

$Ag^+ + 1e^- \rightarrow Ag^0$	$E^0 = +0.799V$

- **Precipitation** $Ag^+ + Cl^- \rightarrow AgCl$ $K_{sp} = 1.82 \times 10^{-10}$

$AgCl + 1e^- \rightarrow Ag^0 + Cl^-$

$E^0_{AgCl} = E^0_{Ag+} - 0.059/1 \log[Cl^-]/K_{sp} = 0.799 - 0.059(\log[Cl^-] - \log K_{sp}) = 0.222V$

AgI	$K_{sp} = 3.0 \times 10^{-17}$	$E^0 = -0.152V$
Ag_2S	$K_{sp} = 6.3 \times 10^{-50}$	$E^0 = -0.710V$

- **Complexation** $Ag^+ + 2NH_3 \rightarrow Ag[NH_3]_2^+$ $pK_f = 10^{-7.4}$

$Ag[NH_3]_2^+ + 1e^- \rightarrow Ag^0 + 2NH_3$

$E^0_{Ag[NH3]2} = E^0_{Ag+} - 0.059/1 \log[Ag^+][NH3]^2/[Ag(NH3)2]^+ = 0.799 - 0.059(pK_f) = 0.373V$

$Ag(SO_3)_2^{3-} + 1e^-$	$\rightarrow Ag^+ + 2SO_3^{2-}$	$pK_f = 8.68$	$E^0 = 0.430V$
$Ag(S_2O_3)_2^{3-} + 1e^-$	$\rightarrow Ag^+ + 2S_2O_3^{2-}$	$pK_f = 13.46$	$E^0 = 0.010V$
$Ag(CN)_2^- + 1e^-$	$\rightarrow Ag^+ + 2CN^-$	$pK_f = 19.85$	$E^0 = -0.290V$

- **Concentration**

$E = E^0 - 0.059 \log [Ag^0]/[Ag^+] = 0.799 + 0.059 \log[Ag^+]$
$[Ag^+] = 10^3 M$ $E^0 = 0.777V$

TAILORING ΔE^0

- **Effect of the pH**

→ Whenever H^+ or OH^- species are involved in the reaction

Examples

a) $C_6H_6O_6 + 2e^- + 2H^+ \rightarrow C_6H_8O_6$ $E^0 = -0.244V$

$E^0 = E^0 - 0.059/2 \log[C_6H_8O_6]/[H^+]^2[C_6H_6O_6] = -0.244 - 0.059\,(pH)$

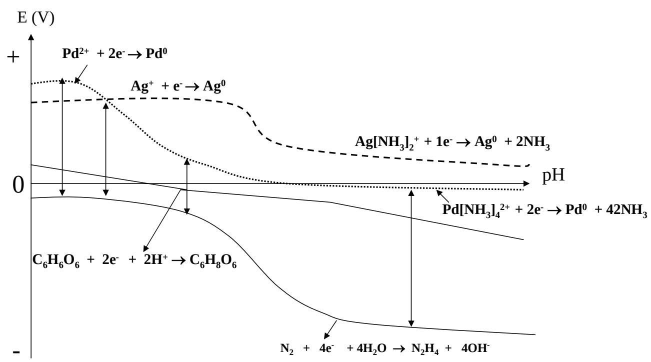
$[H^+] \uparrow$, pH $\downarrow$ ⇒ $C_6H_8O_6$ less strong reductant

b) $N_2 + 4e^- + 4H_2O \rightarrow N_2H_4 + 4OH^-$ $E^0 = -1.160V$

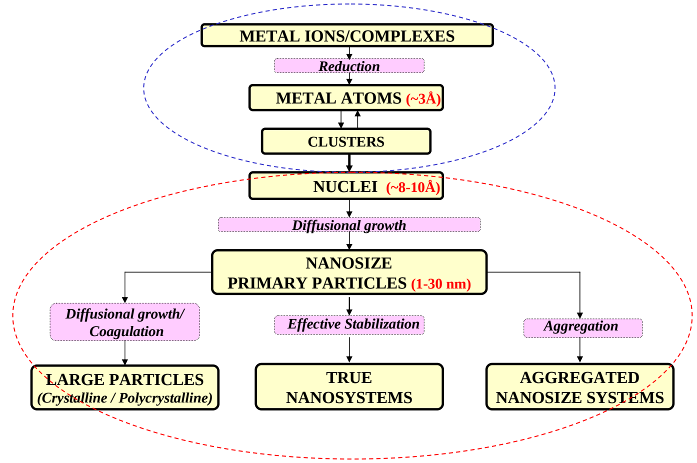
$E^0 = E^0 - 0.059/4 \log 1/[OH^-]^4 = -1.160 + 0.059\,(14 - pH)$

$[H^+] \uparrow$, pH $\downarrow$ ⇒ Hydrazine becomes a less strong reductant

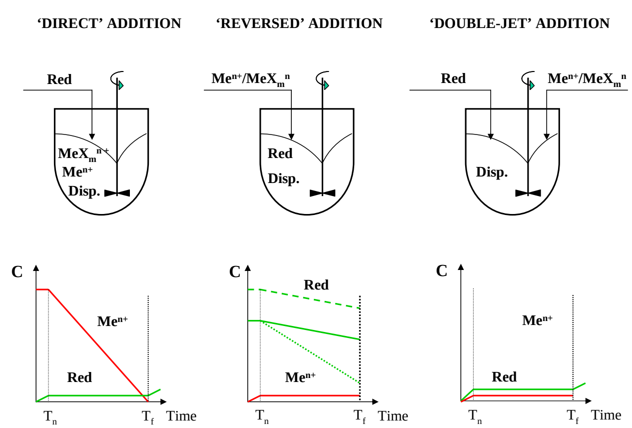
REDOX DIAGRAMS



CONDENSATION FROM LIQUID PHASE



EXPERIMENTAL



CRITICAL PROPERTIES

- **Particle size and size distribution**
- **Internal structure**
- **Particle morphology**
- **Internal composition**
- **Surface properties**

PREPARATION OF NANOSIZE METALLIC PARTICLES

a) **Generate a large number of nuclei**

b) **Involve a large fraction (*f*) of atoms in the nucleation step**

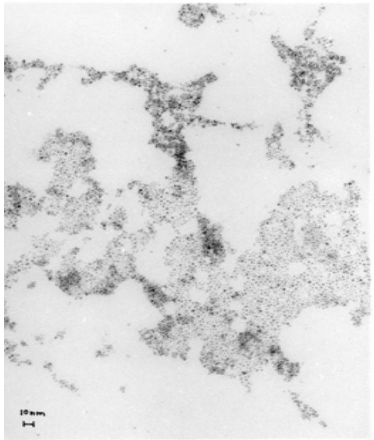
Final size in the nanosize range $R_p = r_n \times (100/f)^{1/3}$

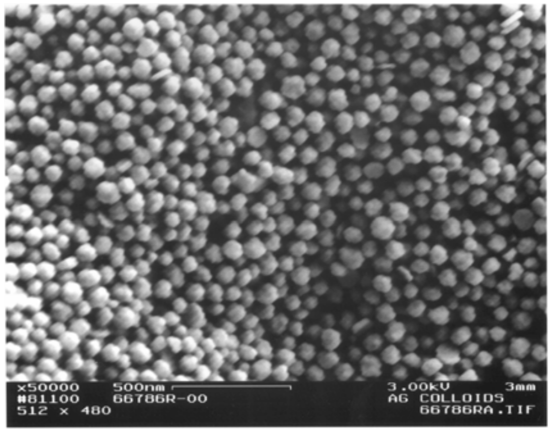
→ Provide high supersaturation (large ΔE)
→ Use suitable dispersion media
→ Work in dilute systems
→ Use surfactants

c) **Prevent the aggregation of primary particles**

→ Maximize electrostatic repulsive forces (dilute systems)
→ Minimize/screen attractive forces (dispersing agents)

Platinum Particles (~ 2.0 nm)





Nanosize Silver Particles (~90 nm)

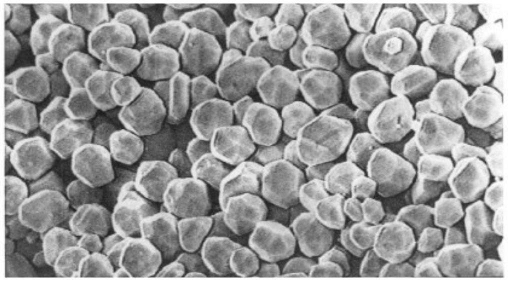
PREPARATION OF LARGE PARTICLES

A. CRYSTALLINE → diffusion growth

- Slow nucleation (small ΔE, strong metallic complexes)
- Slow addition of precursors in the system
- Use of seeds
- Very effective stabilization

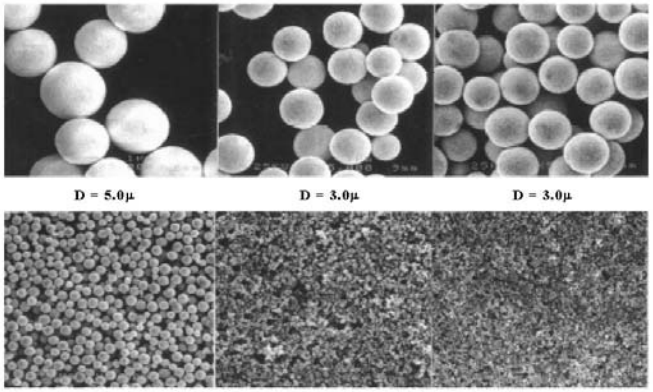
B. POLYCRYSTALLINE PARTICLES → aggregation

- Control the attractive/repulsive forces by adjusting:
    - Ionic strength
    - pH
    - Activity of the dispersant/protective colloid
- More versatile in controlling the size of the particles



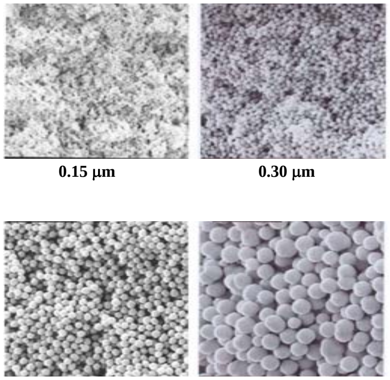
CRYSTALLINE GOLD POWDER

MONODISPERSED GOLD



D = 5.0μ D = 3.0μ D = 3.0μ

D = 0.8μ D = 0.2μ D = 60nm

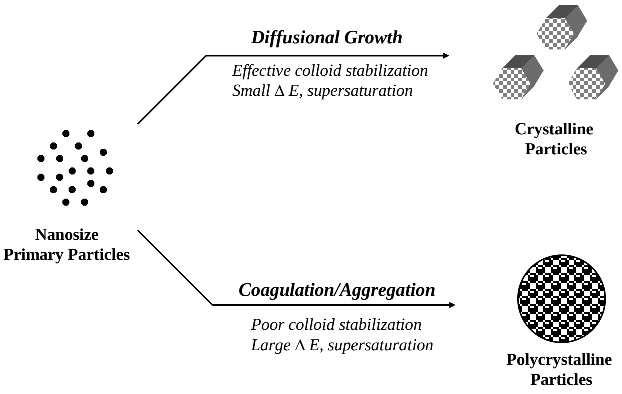


0.15 μm 0.30 μm

0.5 μm 1.0 μm

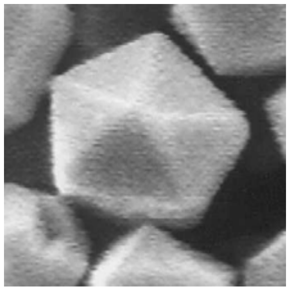
AgPd Spherical Alloy Particles

INTERNAL PARTICLE STRUCTURE



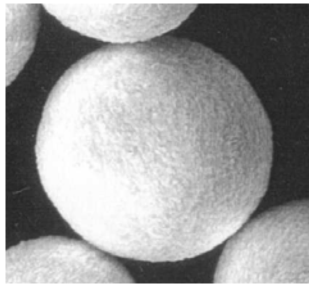
INTERNAL PARTICLE STRUCTURE

Crystalline Monodispersed Gold



2 μm

Polycrystalline Monodispersed Gold



2 μm

IMPORTANCE OF PARTICLE STRUCTURE

A. Electronics/Thick film

Due to the absence of internal grain boundaries, highly crystalline particles of PM yield dense, continuous, thinner, and more conductive 'fired' films.

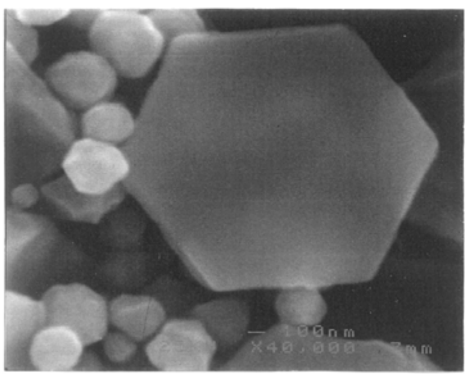
B. Electronics/Oxidation of base metals

Highly crystalline base metals (Cu, Ni) are more resistant against oxidation when used as precursors for thick film conductors.

C. Medicine/Biology

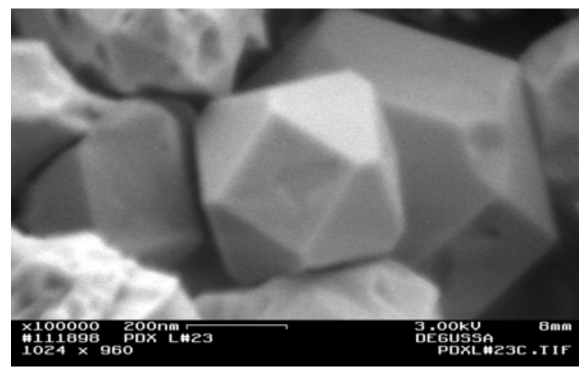
Highly crystalline, dense gold particles are more effective as carriers of drugs/vaccines through biological tissues.

PARTICLE MORPHOLOGY



Hexagonal Gold platelets

PARTICLE MORPHOLOGY



Crystalline Pd Particles

INTERNAL COMPOSITION

Bimetallic particles → electronics (wide range of properties attainable)
→ catalysis (enhanced catalytic activity)

•Core/Shell structure

$E^0_1 \neq E^0_2$ → the most electropositive element will form the core
→ the most electronegative element will form the shell

⇒ Precipitation order can be tailored by appropriate complex formation

- **'Solid solutions'/Alloys**

$E^0_1 \cong E^0_2$ → similar reduction rates
$\Delta E^0_1, \Delta E^0_2 >>$ → fast reactions

⇒ Uniformly mixed crystalline lattices

SURFACE PROPERTIES

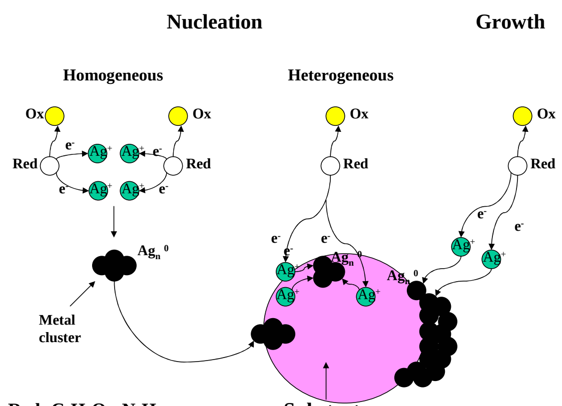
IMPACT

- **Dispersibility in liquids**
- **Self assembly properties**
- **Sintering characteristics**
- **Catalytic activity**
- **Adhesion properties**
- **Corrosion**

TAILORING SURFACE BEHAVIOR

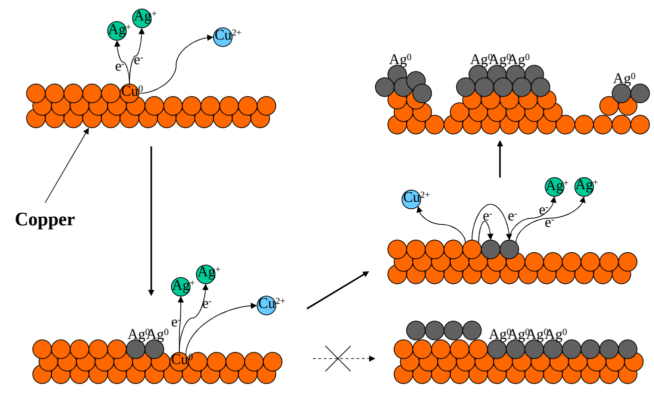
- **Selection of precipitation environment (reductant, dispersant, solvent)**
- **Subsequent surface treatment (performed on either wet or dry powders)**
  - Coating with organic compounds
  - Coating with inorganic compounds
  - Coating with metals

ELECTROLESS PLATING



Red: $C_6H_8O_6$, N_2H_4

ELECTRODISPLACEMENT



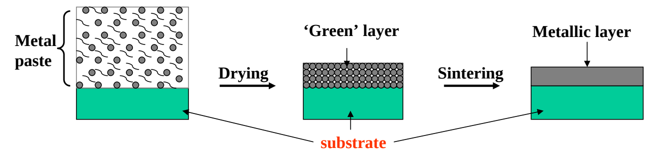
APPLICATIONS OF MONODISPERSED METALLIC PARTICLES

- **Electronics**
- **Catalysis**
- **Biology and medicine**
- **Pigments**
- **Obscurant smokes**
- **Nonlinear optics**
- **Transparent conductive coatings**
- **Ferromagnetic fluids**
- **High density magnetic storage**

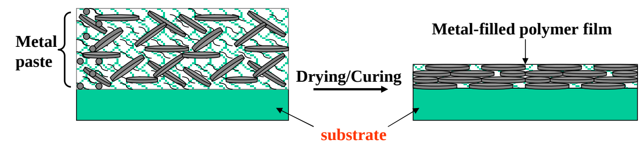
THICK FILM TECHNOLOGY

Conductive layers

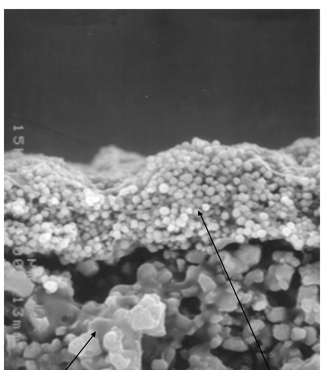
a) 'Fired'/Sintered films



b) 'Non-Fired' films



ULTRATHIN METALLIC LAYERS



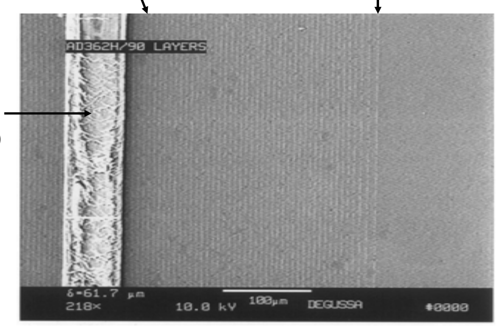
Dielectric Tape   1.0 μm   Electrode film

SECTION THROUGH A MLCC

(Up to 800 alternative layers)

dielectric layers (~ 6 μm)   **metallic layers (~ 1 μm)**

Human hair (~ 60 μm)

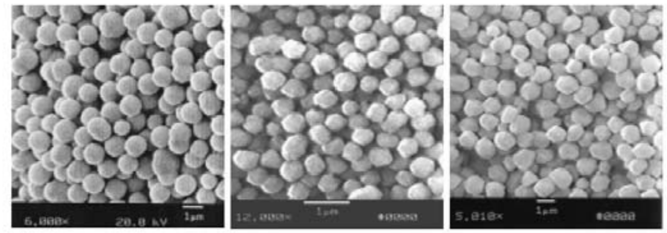


HIGH PERFORMANCE METAL POWDERS

- **Spherical**
- **Monodispersed**
- **Size : 0.1 - 1.0 μm**
- **Non-agglomerated particles**
- **Easily dispersible**
- **Controlled composition (metals ratio, impurities)**
- **Highly crystalline**
- **Controlled sintering behavior**

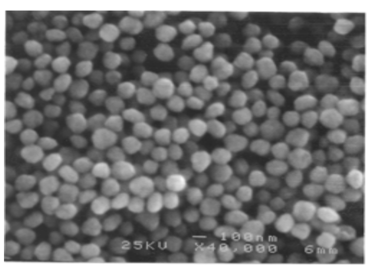
MONODISPERSED METAL POWDERS

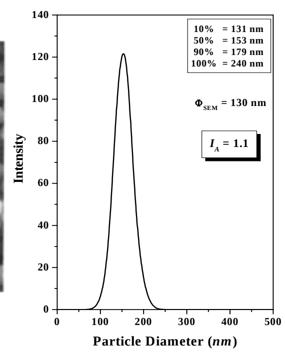
Ag/Pd **Ni** **Cu**



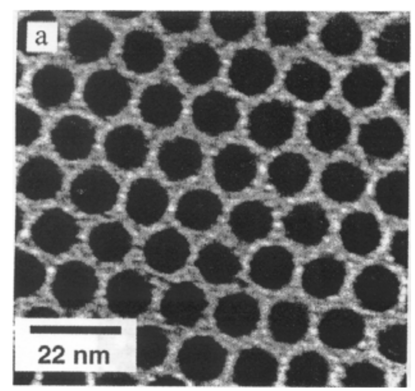
2.0 μm **1.0 μm** **2.0 μm**

ULTRATHIN METALLIC FILMS



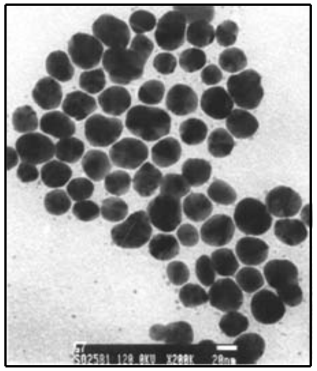


Monodispersed AgPd Particles



Monodispersed Co particles

Monodispersed Ag Particles

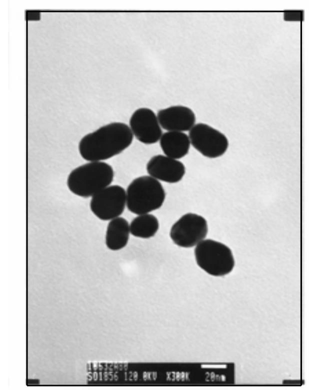


50 nm

Applications

- Antimicrobial activity
  - Antimicrobial coatings
  - Water purification
- SPR Biosensing
- Transparent conductive coatings
  - Coating of CRT screens
  - Potential replacement for ATO

Monodispersed Nanosize Gold Particles



50 nm

Applications:

- Medicine and Biology
  - Delivery of anti-tumor drugs
  - Vaccine delivery
  - Biosensing and bioassays (SPR)
- Pigments for functional glasses

NANOSIZE METALS IN CATALYSIS

Decreasing particle size → larger specific surface area
→ larger fraction of surface atoms

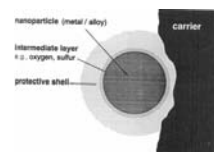
Benefits : → Increased catalytic activity
→ Significant cost reduction

Difficulties : → Separation of reaction products
→ Propensity for sintering

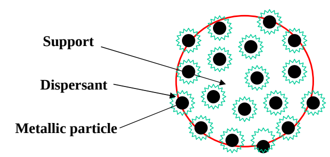
Supported metal catalysts

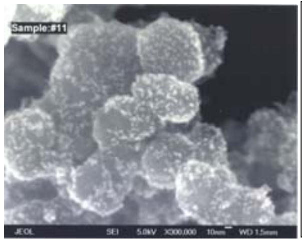
SUPPORTED METALLIC CATALYSTS

- 'Adhesion technique'

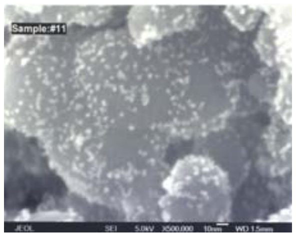


- 'On-support' precipitation



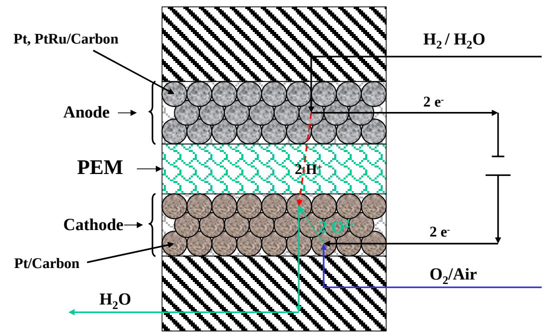


Pt/Ru/C Catalyst For PEM Fuel Cells



PEM FUEL CELLS

Electrodes:
- 2.0 – 3.0 nm Pt and Pt/Ru particles supported on carbon
- Up to 60% metal loading



CONCLUSIONS

- **Chemical precipitation is a versatile technique capable to yield non-agglomerated monodispersed metallic particles with:**

  - wide range of modal diameters (1 nm to several microns)
  - controlled internal structure and morphology
  - controlled composition
  - controlled surface characteristics

Materials for many existing and emerging fields of high technology

CHALLENGE:

Assembly of fine particles (nanoparticles) into ordered mono, bi, and three-dimensional complex structures structures