

# **Nanoparticle Technology**

## **Lecture 06: 2-D Nanostructures Fabrication**

## Lecture 06: table of contents

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- 2      Fundamentals of heterogeneous nucleation**
- 3      Fundamentals of film growth on substrate**
- 4      Fabrication methods and case study**

# **Introduction to 2-D nanostructures fabrication**

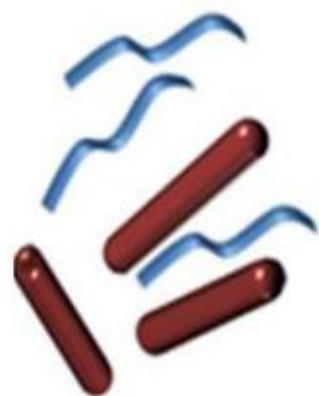
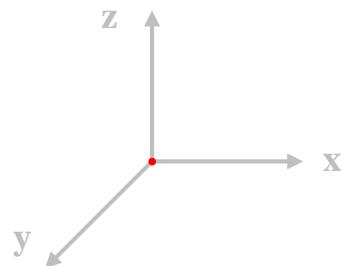
# Nanoparticle Technology

## Classification of nanomaterials

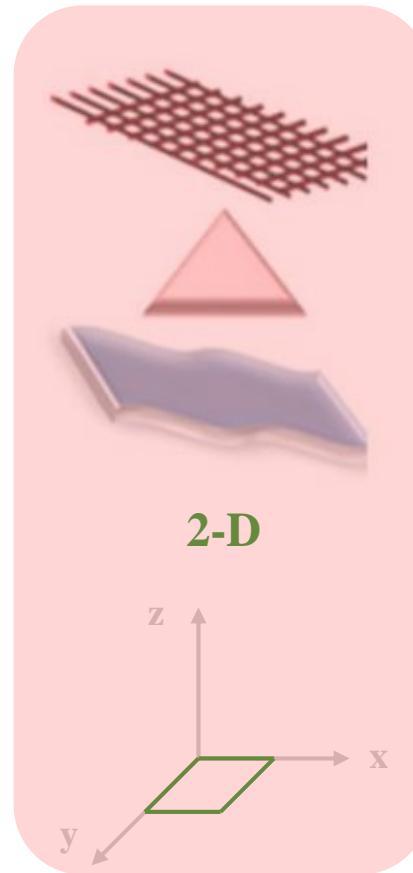
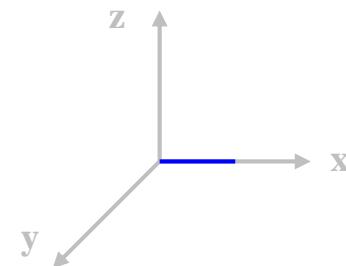
### Dimensional classification



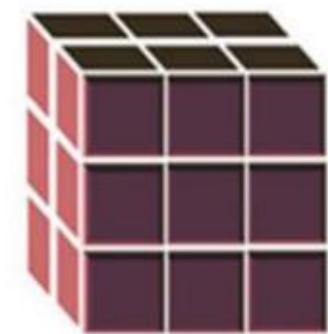
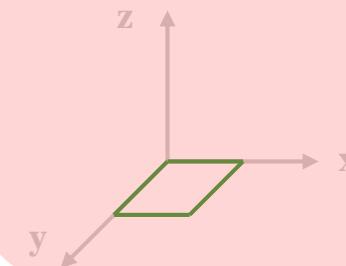
**0-D**



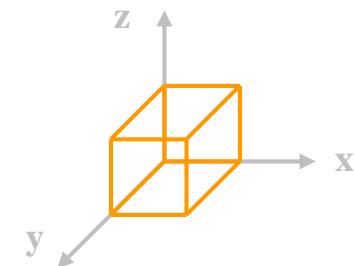
**1-D**



**2-D**



**3-D**

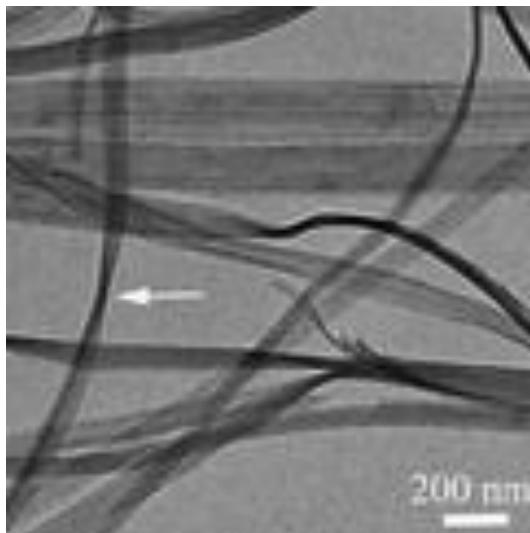


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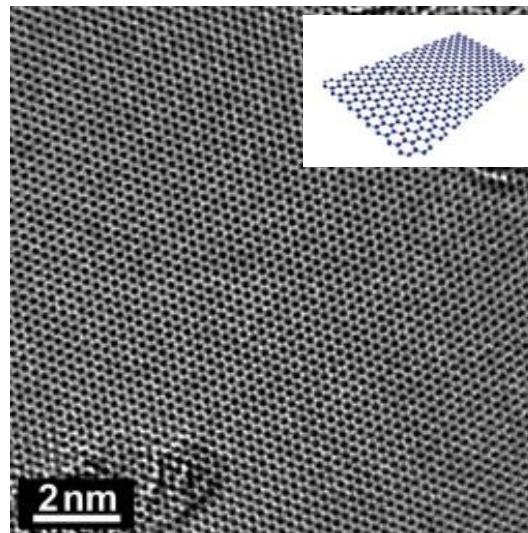
## Classification of nanomaterials

### Two-dimensional (2-D) structures

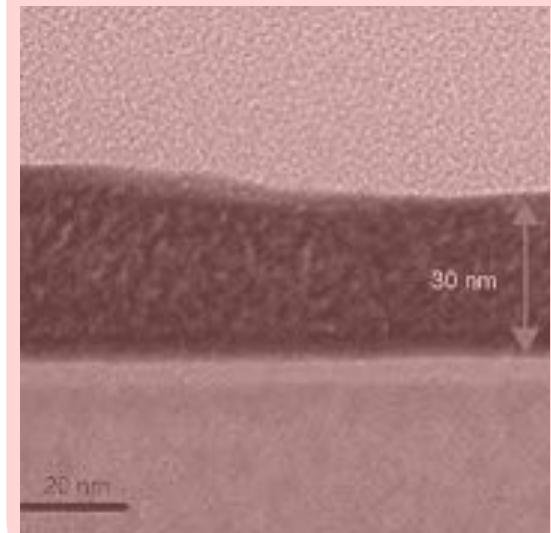
- Nanobelts -



- Graphene -



- Thin film -



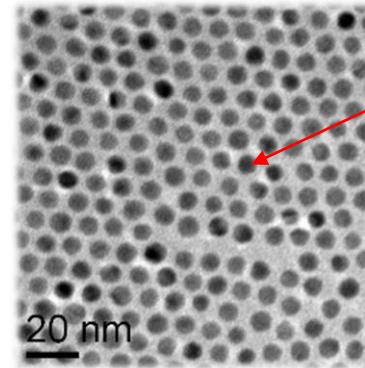
# Nanoparticle Technology

## Nucleation: homogeneous vs. heterogeneous



Solution

Homogeneous  
nucleation

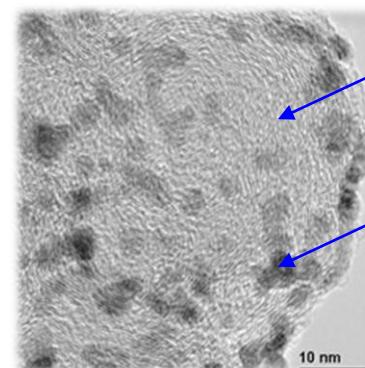


Nanoparticle

+ Carbon powder



Heterogeneous  
nucleation



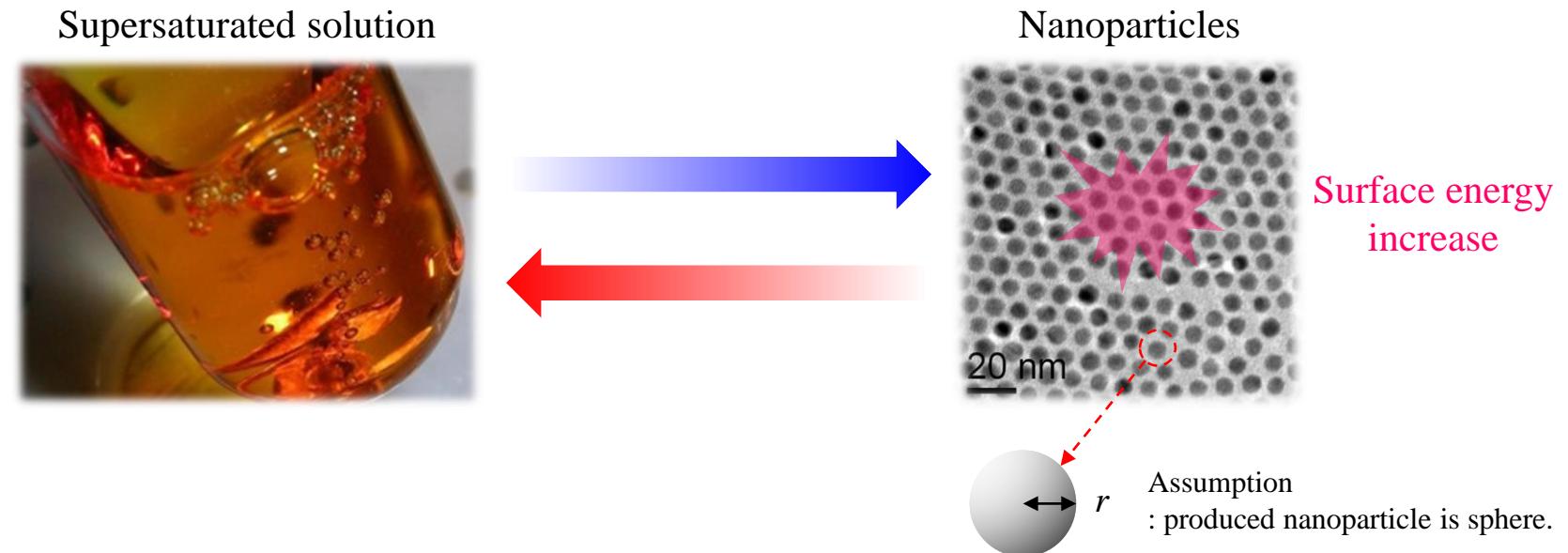
Carbon

Nanoparticle

# Fundamentals of heterogeneous nucleation

# Nanoparticle Technology

## Homogeneous nucleation (lecture 04)

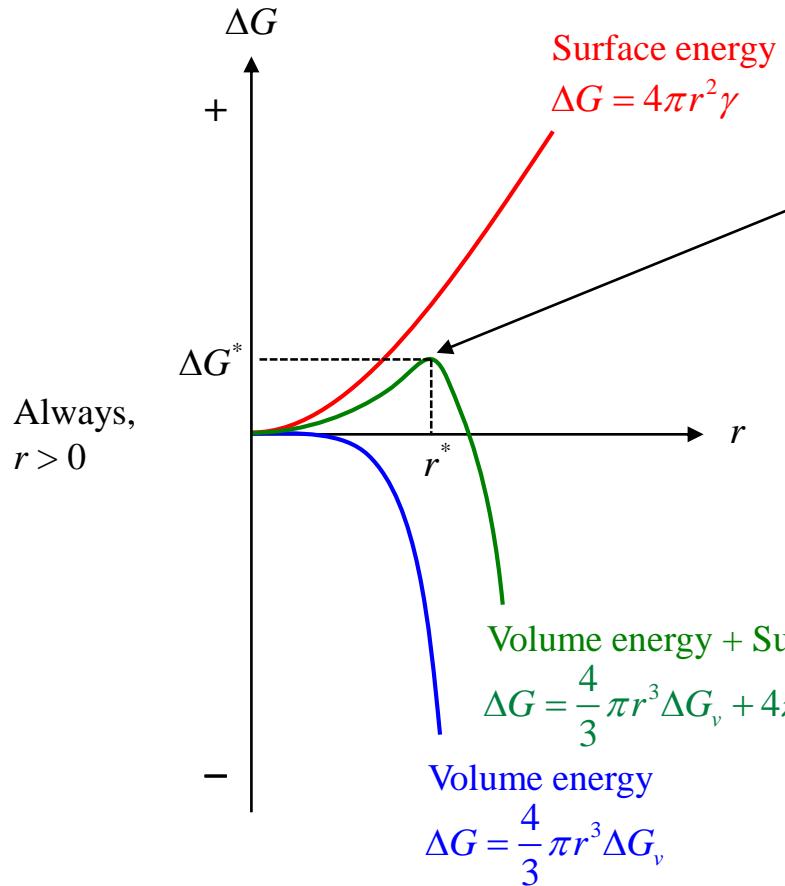


$$\Delta G = \frac{4}{3} \pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

Volume energy      Surface energy  
(minus)                (plus)

# Nanoparticle Technology

## Homogeneous nucleation (lecture 04)



Always,  
 $r > 0$

Surface energy

$$\Delta G = 4\pi r^2 \gamma$$

$r^*$ : critical radius of nucleation

When  $r = r^*$ ,  $d(\Delta G)/dr = 0$

$$\frac{d(\Delta G)}{dr} = 4\pi r^2 \Delta G_v + 8\pi r \gamma$$

$$4\pi (r^*)^2 \Delta G_v + 8\pi r^* \gamma = 0$$

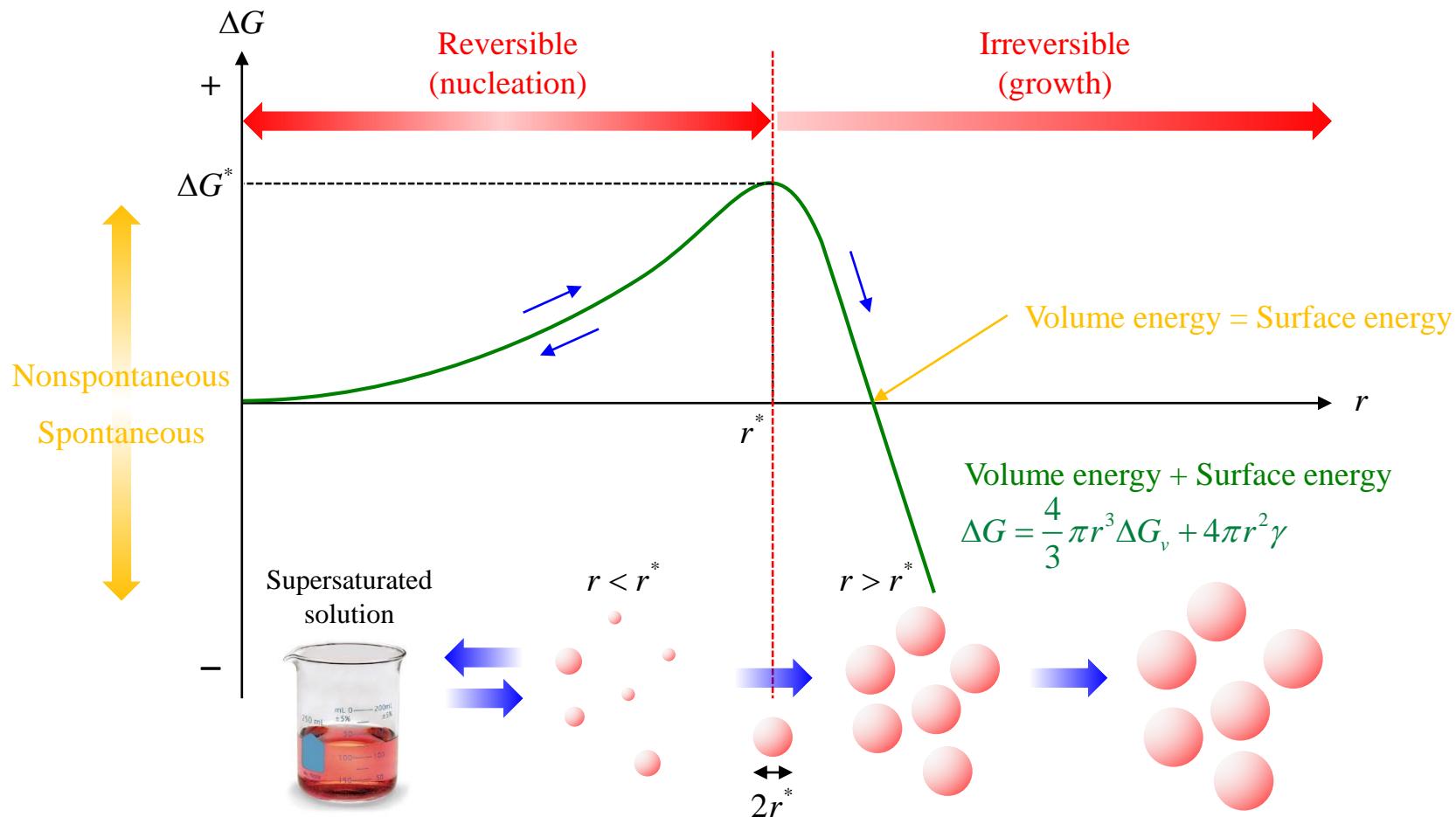
Critical radius of nucleation  $r^*$  is...

$$r^* = -2 \frac{\gamma}{\Delta G_v} = \left( \frac{2V_m}{kT} \right) \frac{\gamma}{\ln \sigma}$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} = \left( \frac{16\pi V_m^2}{3k^2 T^2} \right) \frac{\gamma^3}{(\ln \sigma)^2}$$

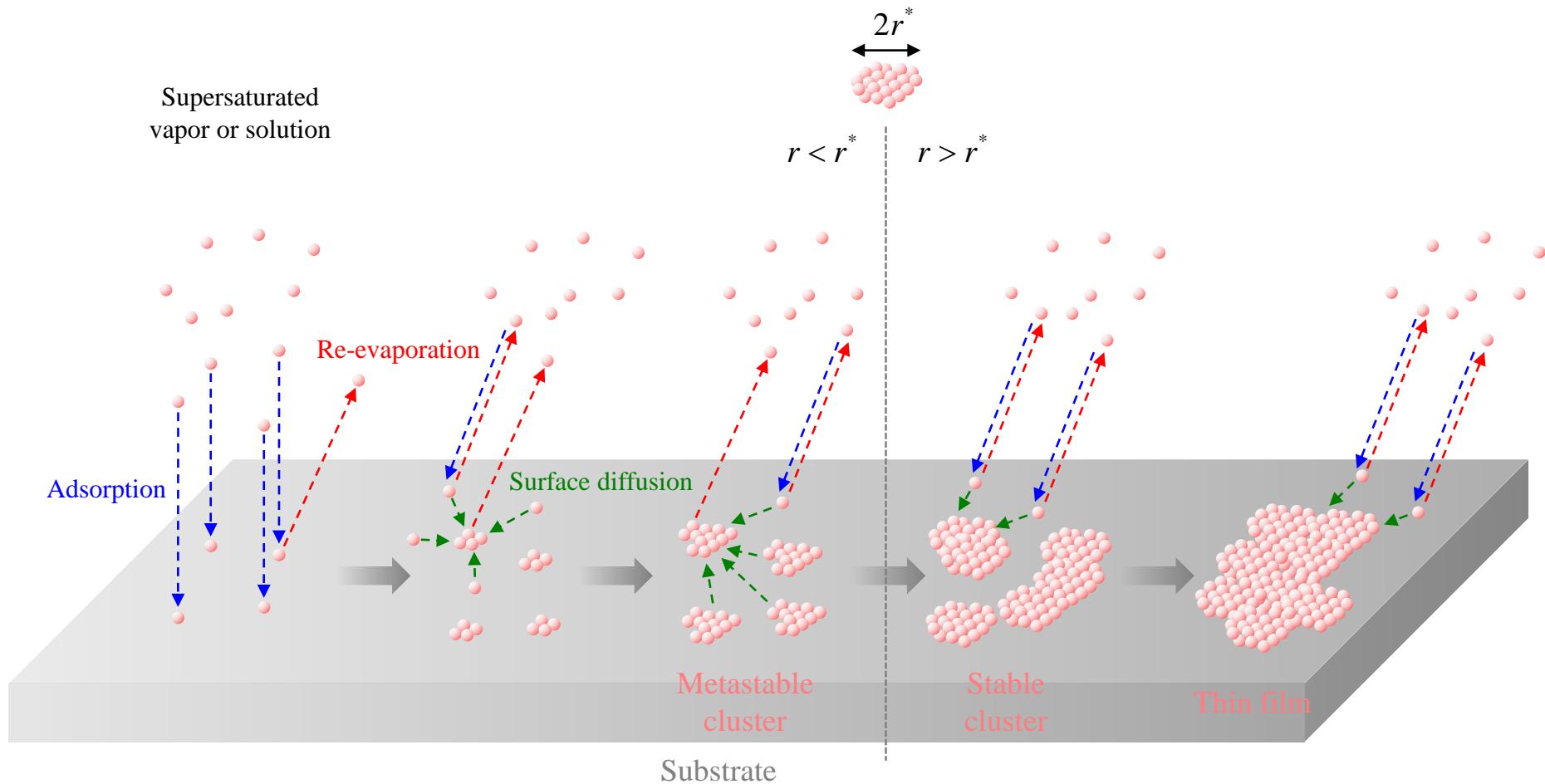
# Nanoparticle Technology

## Homogeneous nucleation (lecture 04)



# Nanoparticle Technology

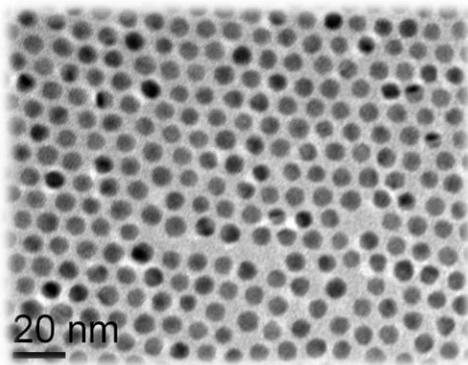
## Heterogeneous nucleation (thin film formation)



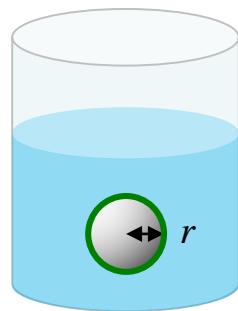
# Nanoparticle Technology

## Surface energy: homogeneous vs. heterogeneous

Homogeneous

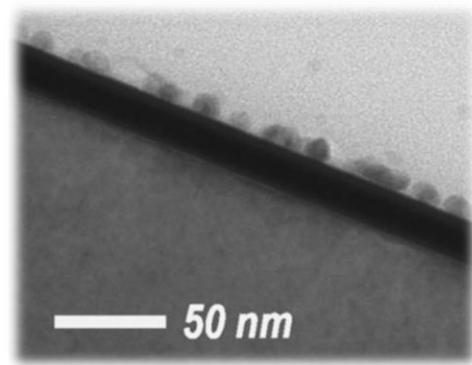


Liquid  
(solution)

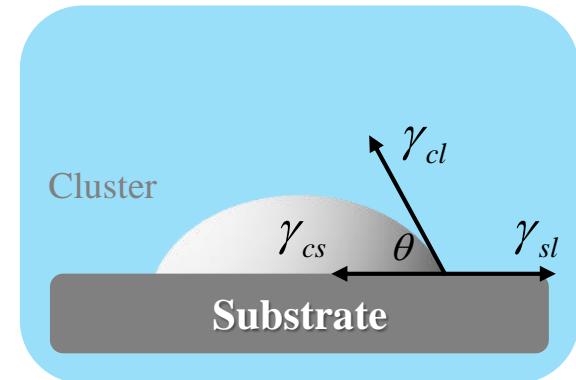


$$\text{Surface energy} : 4\pi r^2 \gamma_{sl}$$

Heterogeneous



Liquid  
(solution)

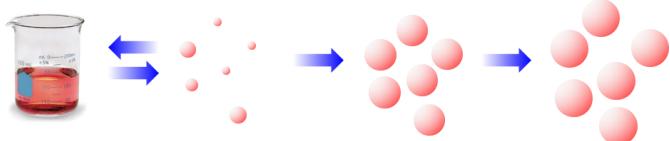


$$\gamma_{sl} = \gamma_{cs} + \gamma_{cl} \cos \theta$$

# Nanoparticle Technology

## Nucleation: homogeneous vs. heterogeneous

### Homogeneous nucleation



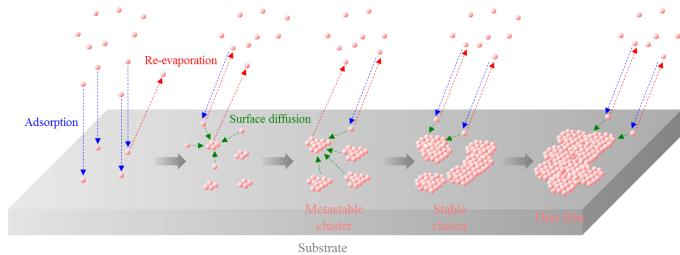
$$\Delta G_{Homo} = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

$$r_{Homo}^* = -2 \frac{\gamma}{\Delta G_v}$$

$$\Delta G_{Homo}^* = \frac{16\pi\gamma_{sl}^3}{3(\Delta G_v)^2}$$

$$\Delta G_{Homo}^* f(\theta) = \Delta G_{Hetero}^*$$

### Heterogeneous nucleation



$$\Delta G_{Hetero} = a_3 r^3 \Delta G_v + a_1 r^2 \gamma_{cl} + a_2 r^2 \gamma_{cs} - a_2 r^2 \gamma_{sl}$$

$$r_{Hetero}^* = -2 \frac{(a_1 \gamma_{cl} + a_2 \gamma_{cs} - a_2 \gamma_{sl})}{3 a_3 \Delta G_v} \quad a_1 = 2\pi(1 - \cos \theta)$$

$$a_2 = \pi \sin^2 \theta \quad a_2 = \pi \sin^2 \theta$$

$$a_3 = 3\pi(2 - 3\cos \theta + \cos^2 \theta)$$

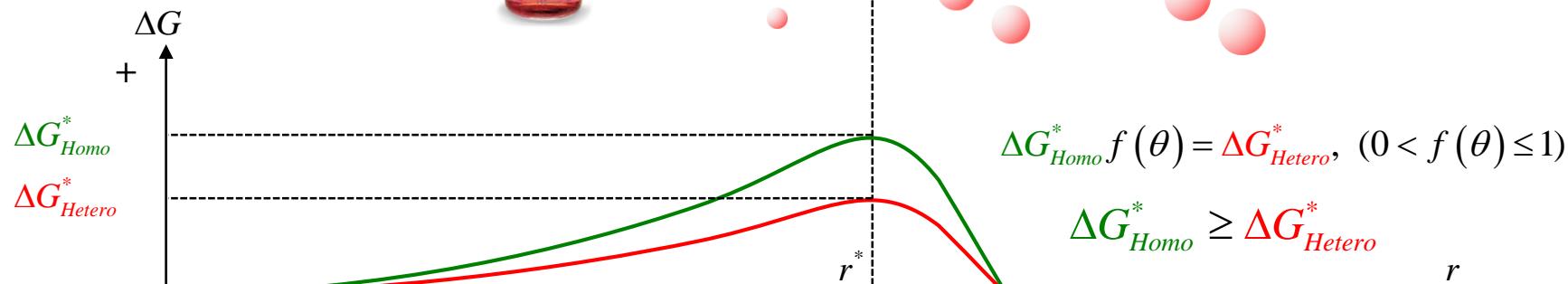
$$\Delta G_{Hetero}^* = \frac{16\pi\gamma_{sl}^3}{3(\Delta G_v)^2} \times \left( \frac{2 - 3\cos \theta + \cos^3 \theta}{4} \right)$$

$$\text{Shape factor: } f(\theta) = \left( \frac{2 - 3\cos \theta + \cos^3 \theta}{4} \right)$$

# Nanoparticle Technology

## Nucleation: homogeneous vs. heterogeneous

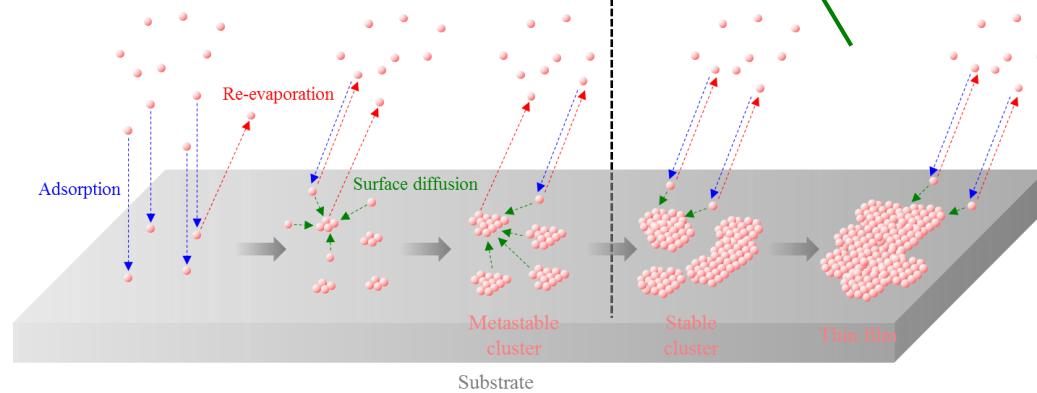
Homogeneous nucleation



$$\Delta G_{Homo}^* f(\theta) = \Delta G_{Hetero}^*, \quad (0 < f(\theta) \leq 1)$$

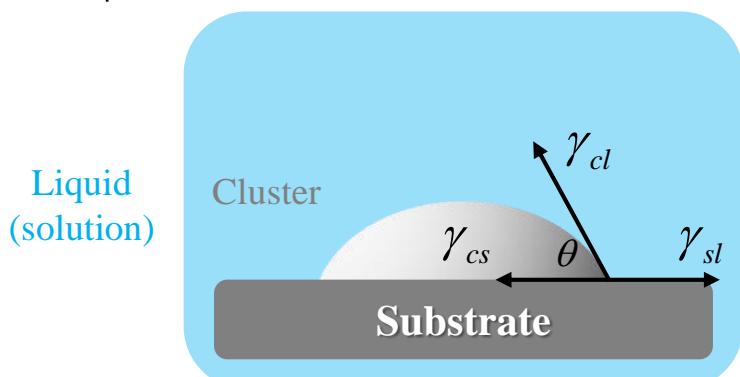
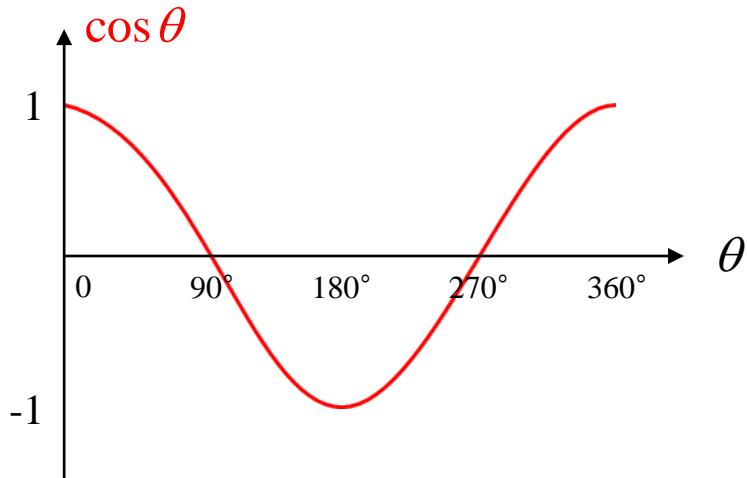
$$\Delta G_{Homo}^* \geq \Delta G_{Hetero}^*$$

Heterogeneous nucleation



# Nanoparticle Technology

## Nucleation: homogeneous vs. heterogeneous



$$\gamma_{sl} = \gamma_{cs} + \gamma_{cl} \cos \theta$$

$$\Delta G_{Homo}^* f(\theta) = \Delta G_{Hetero}^*$$

$$f(\theta) = \left( \frac{2 - 3 \cos \theta + \cos^3 \theta}{4} \right)$$

$$\theta = 10^\circ, \quad f(10^\circ) = \left( \frac{2 - 3 \cos 10^\circ + \cos^3 10^\circ}{4} \right) = 0.001$$

$$\theta = 90^\circ, \quad f(90^\circ) = \left( \frac{2 - 3 \cos 90^\circ + \cos^3 90^\circ}{4} \right) = 0.5$$

$$\theta = 180^\circ, \quad f(180^\circ) = \left( \frac{2 - 3 \cos 180^\circ + \cos^3 180^\circ}{4} \right) = 1$$

# Nanoparticle Technology

## Nucleation: homogeneous vs. heterogeneous

$$\Delta G_{Homo}^* f(\theta) = \Delta G_{Hetero}^* \quad f(\theta) = \left( \frac{2 - 3\cos\theta + \cos^3\theta}{4} \right)$$

Liquid (solution)

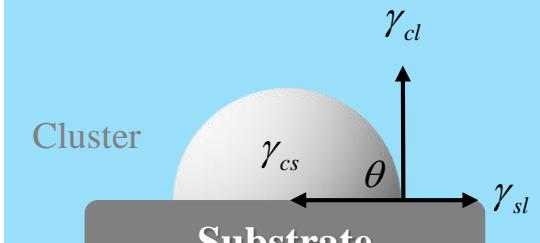


$$\theta = 10^\circ, \quad \cos 10^\circ = 0.985$$

$$f(10^\circ) = \left( \frac{2 - 3 \times 0.985 + 0.985^3}{4} \right) = 0.001$$

$$\Delta G_{Homo}^* \times 0.001 = \Delta G_{Hetero}^*$$

Liquid (solution)

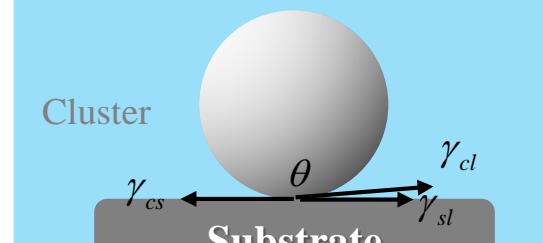


$$\theta = 90^\circ, \quad \cos 90^\circ = 0$$

$$f(90^\circ) = \left( \frac{2 - 3 \times 0 + 0^3}{4} \right) = 0.5$$

$$\Delta G_{Homo}^* \times 0.5 = \Delta G_{Hetero}^*$$

Liquid (solution)



$$\theta = 180^\circ, \quad \cos 180^\circ = -1$$

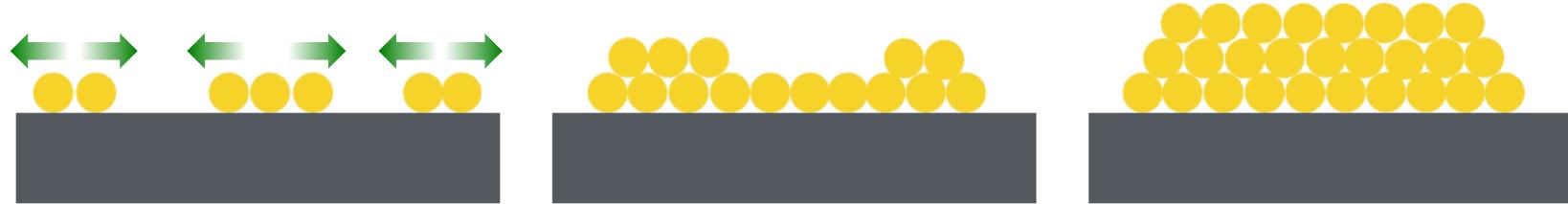
$$f(180^\circ) = \left( \frac{2 - 3 \times (-1) + (-1)^3}{4} \right) = 1$$

$$\Delta G_{Homo}^* = \Delta G_{Hetero}^*$$

# Fundamentals of film growth on substrate

## Film growth mechanism 1

### Layer-by-layer growth (Frank-van der Merwe)



- Film atoms strongly bound to substrate than to each other.
- Generally highest crystalline quality
- Fast surface diffusion

## Film growth mechanism 2

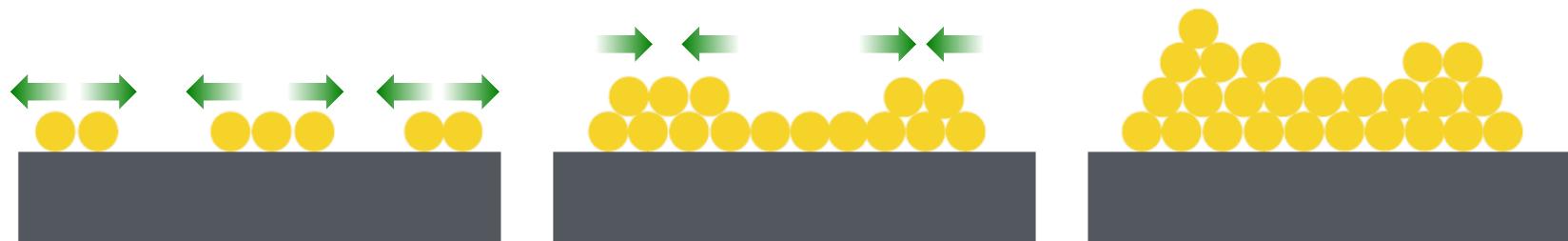
### Island growth (Volmer-Weber)



- 3-dimensional islands are formed.
- Film atoms more strongly bound to each other than to substrate.
- Slow surface diffusion

## Film growth mechanism 3

### Mixed growth (Stranski-Krastanov)



- At initial stage, layer-by-layer growth is dominant.
- 3-dimensional islands are formed at late stage.

# Nanoparticle Technology

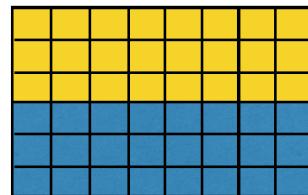
## Lattice difference between film and substrate

### Single crystal case

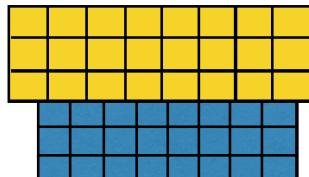
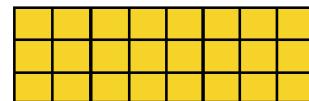
Film



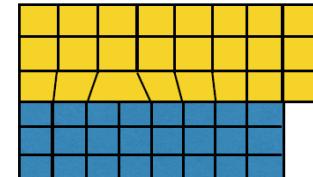
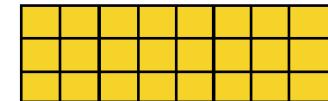
Substrate



Matched



Strained

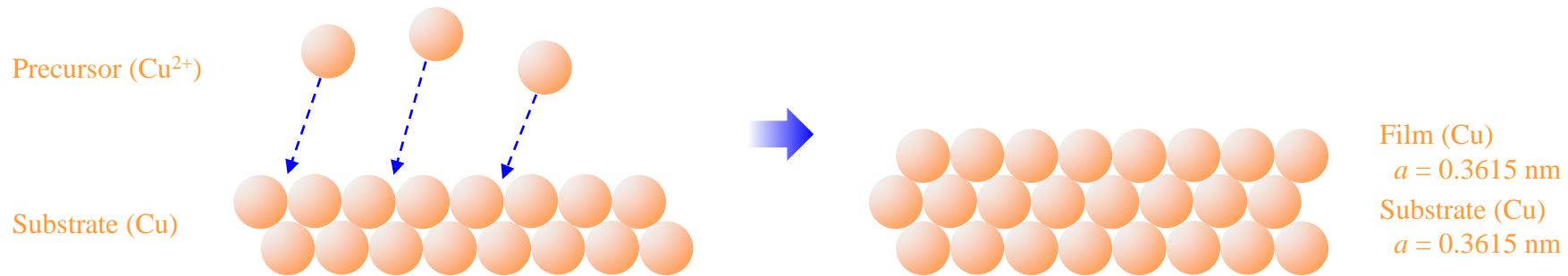


Relaxed

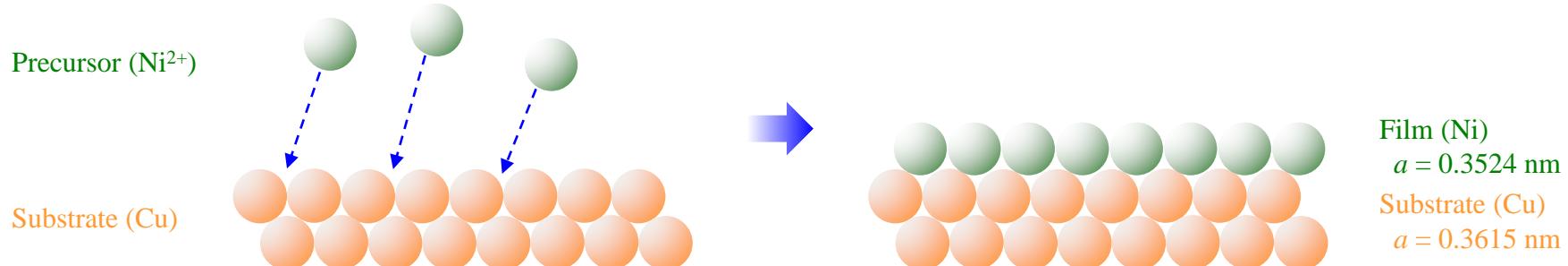
# Nanoparticle Technology

## Lattice difference between film and substrate

### Matched



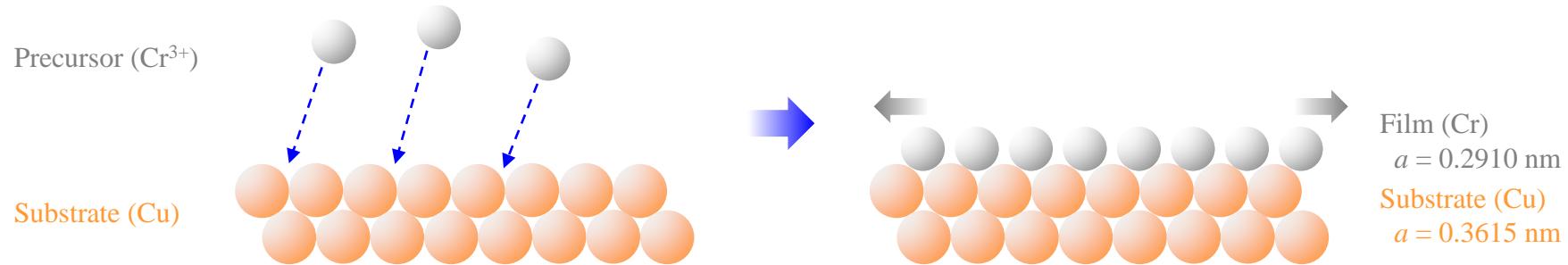
### Mostly matched



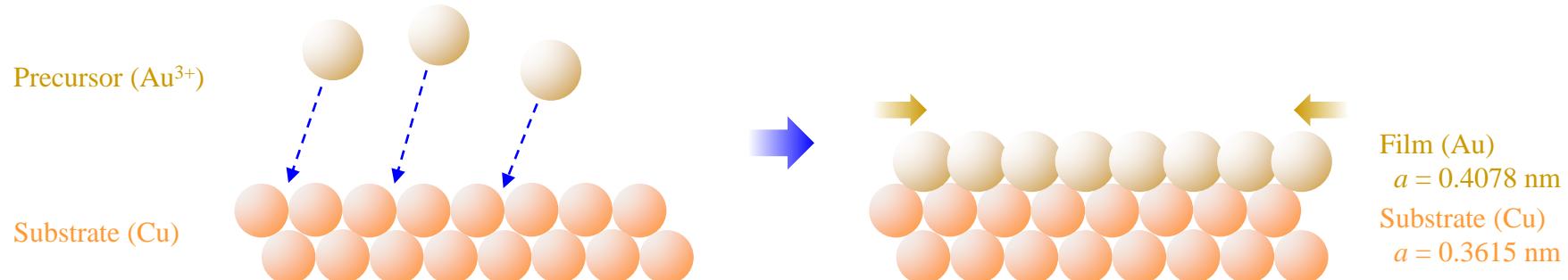
# Nanoparticle Technology

## Lattice difference between film and substrate

### Strained (expansion)



### Strained (compression)



# Nanoparticle Technology

## Electronegativity difference between film and substrate

### Lattice parameter

Film (Au)  
 $a = 0.4078 \text{ nm}$

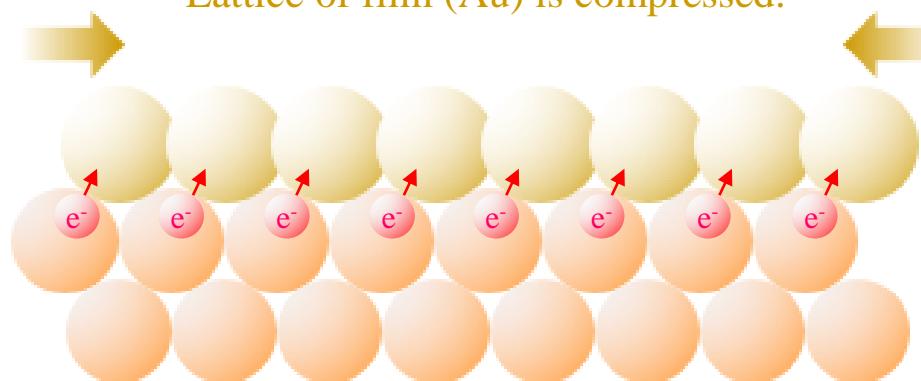
Substrate (Cu)  
 $a = 0.3615 \text{ nm}$

Lattice of film (Au) is compressed.

### Electronegativity

Film (Au)  
2.54

Substrate (Cu)  
1.90

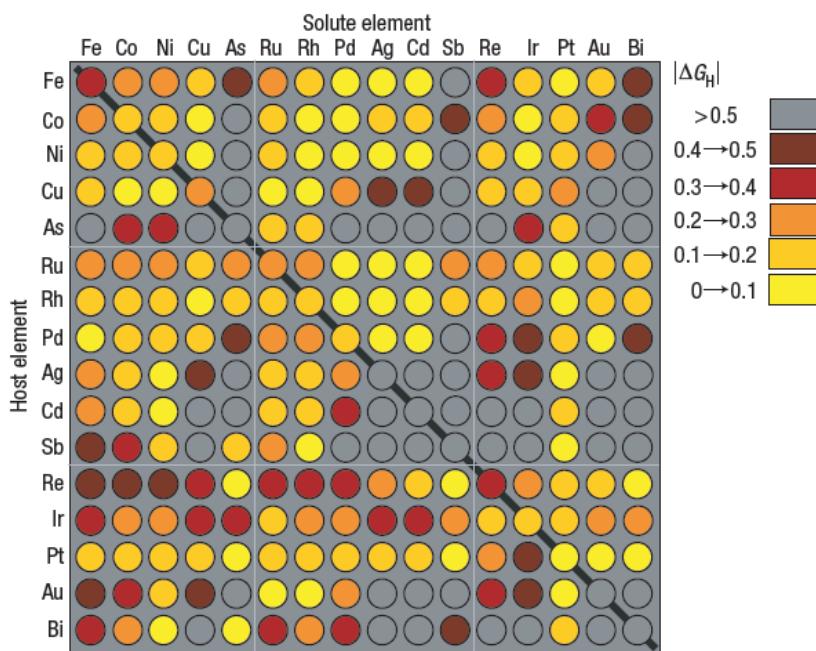


**In heterogeneous film growth, difference of lattice parameter and electronegativity (between film and substrate) generates the bimetallic effect.**

# Nanoparticle Technology

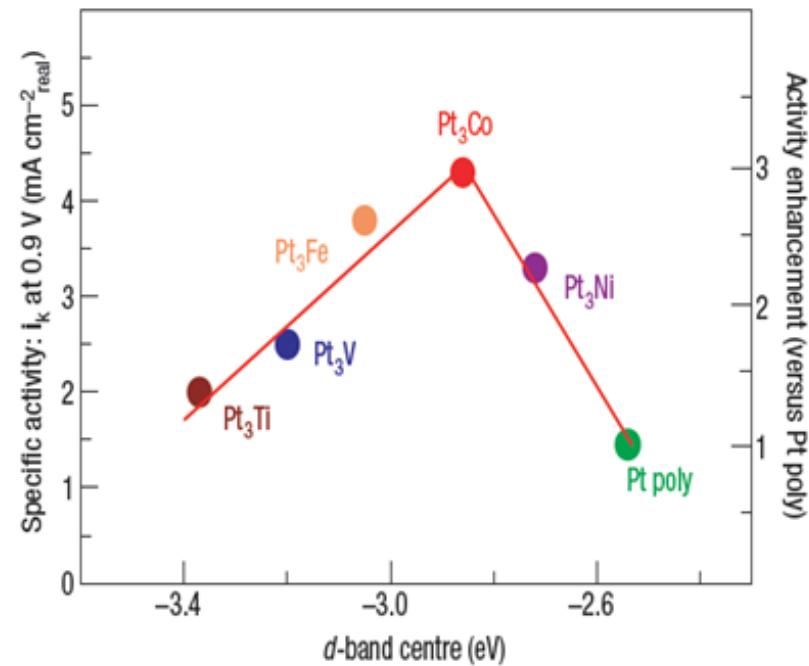
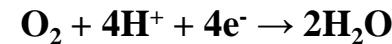
## Bimetallic effect

### Hydrogen adsorption



[*Nat. Mater.*, **5** (2006) 909-913.]

### Oxygen reduction reaction

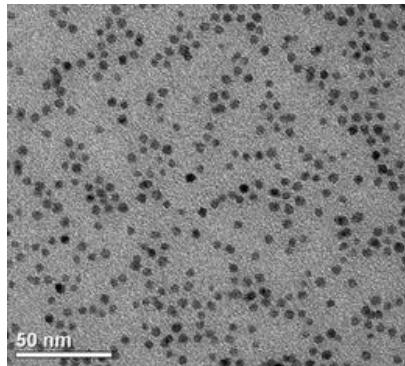


[*Nat. Mater.*, **6** (2007) 241-247.]

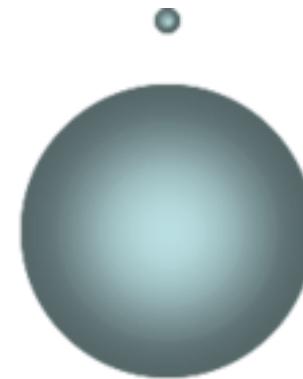
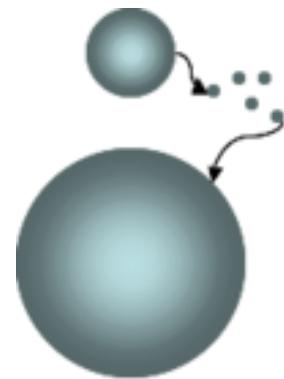
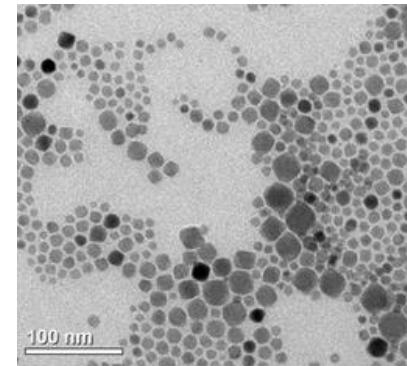
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## Ostwald ripening

- Ostwald ripening of Pd nanoparticles



300 °C for 80 min



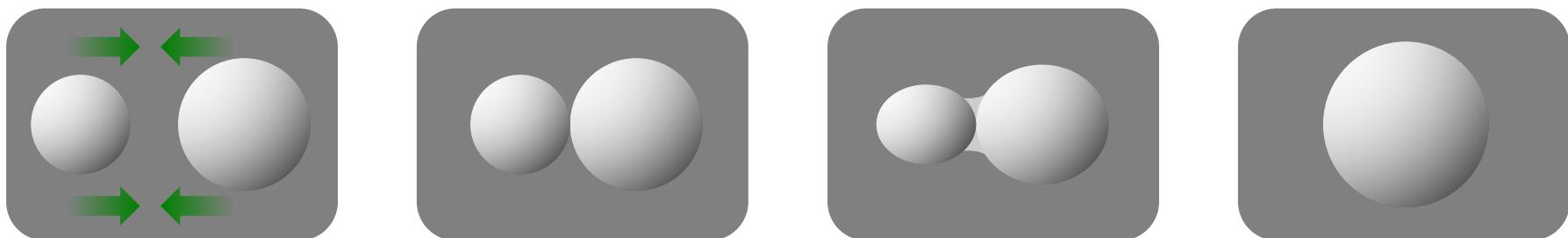
# Nanoparticle Technology

## Coalescence of nuclei

Side view



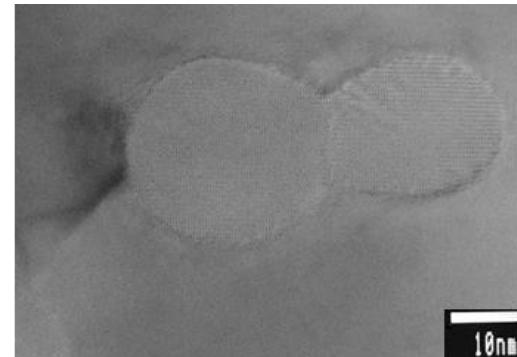
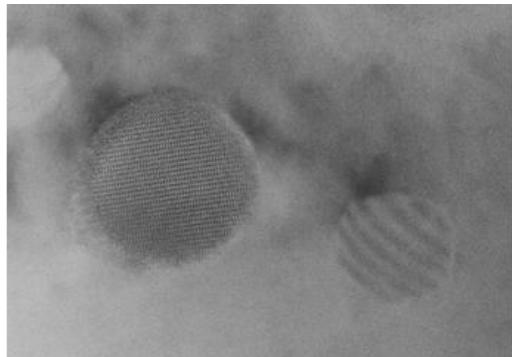
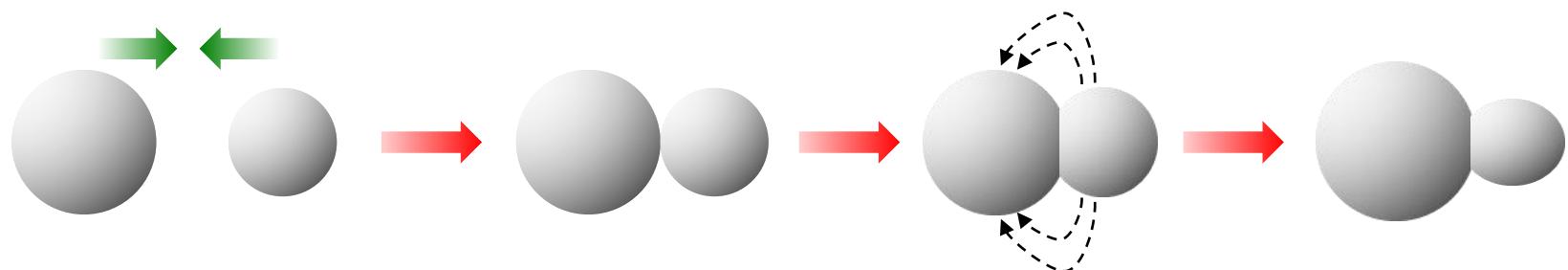
Coalescence



Top view

# Nanoparticle Technology

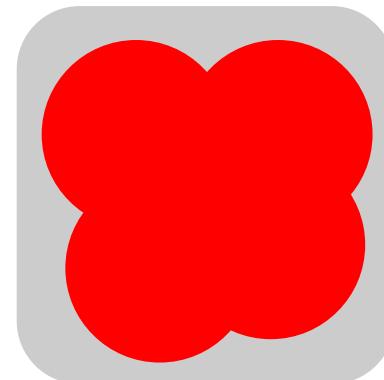
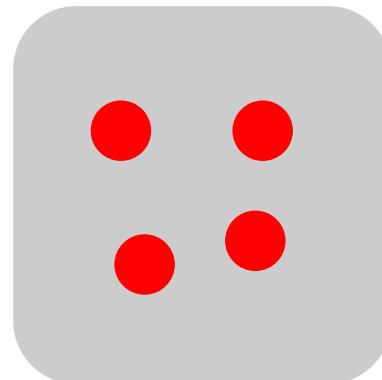
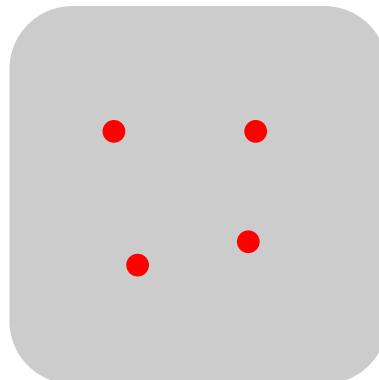
## Coalescence of nuclei



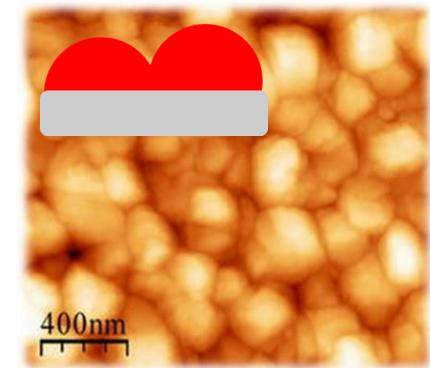
# Nanoparticle Technology

## Nucleation density and film roughness

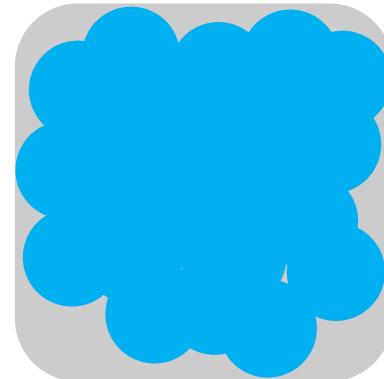
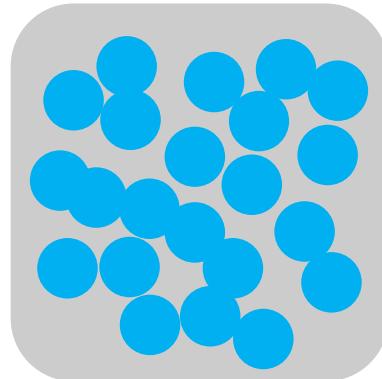
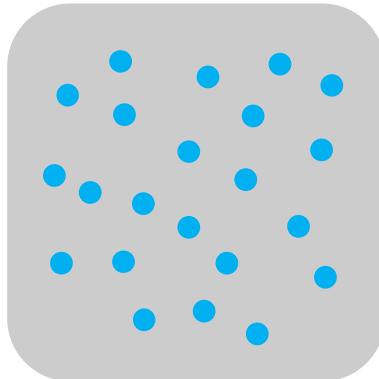
Low nucleation density



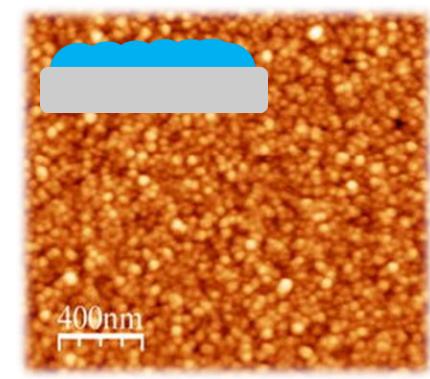
Rough film



Growth and coalescence



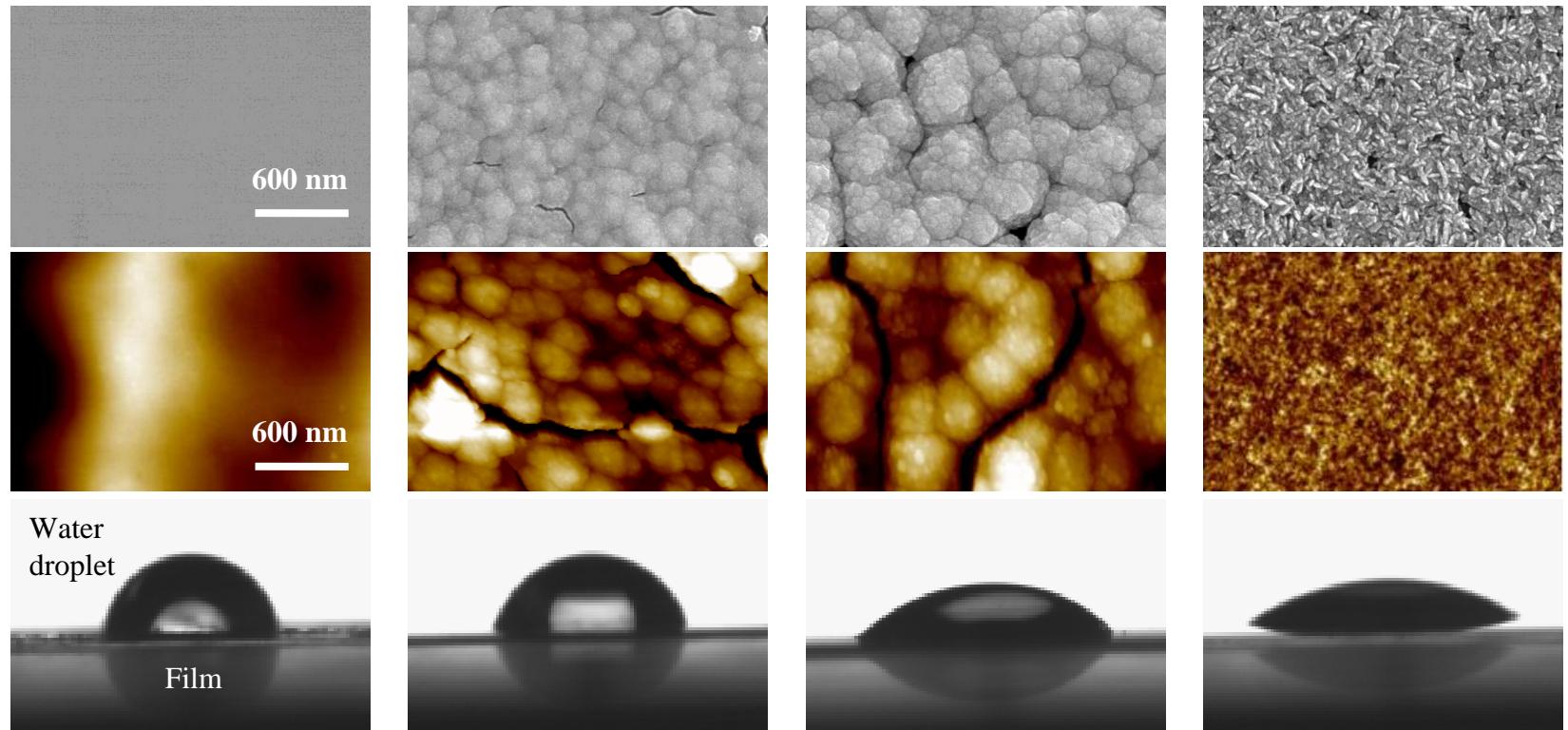
Smooth film



High nucleation density

# Nanoparticle Technology

## Roughness effect



Wenzel's law: hydrophilic films get more hydrophilic when the film roughness increase.

# Fabrication methods and case study

# Nanoparticle Technology

## Fabrication methods

### Nanomaterial fabrication methods

#### Physical methods

Ball milling

Inert gas condensation

Arc discharge

Ion sputtering

Laser ablation

Spray pyrolysis

Flame pyrolysis

Thermal evaporation

Pulsed laser deposition

Molecular beam epitaxy

#### Chemical methods

Chemical reduction synthesis

Solvothermal synthesis

Photochemical synthesis

Electrochemical synthesis

Sonochemical synthesis

Micelles and microemulsions

Chemical vapor deposition

Sol-gel process

#### Lithographic techniques

Photolithography

Electron-beam lithography

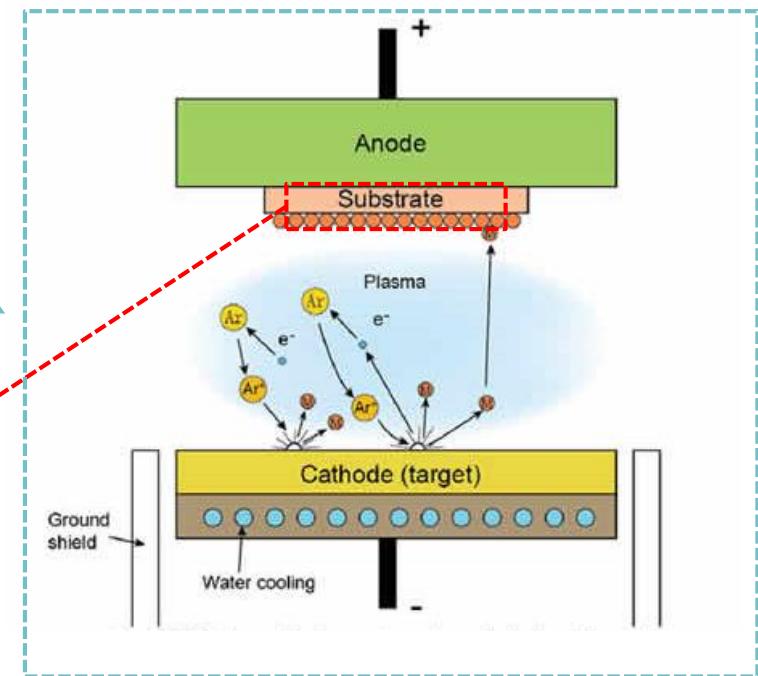
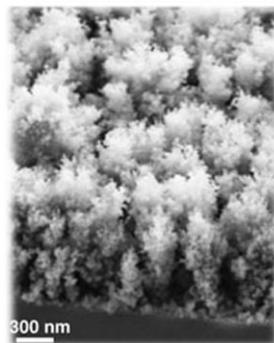
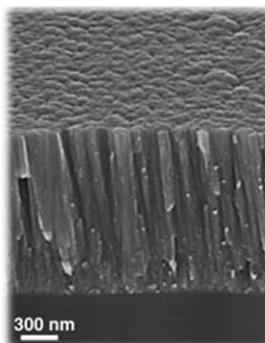
Focused ion beam lithography

Nanoimprint lithography

## Fabrication methods 1: physical methods

### Ion sputtering: direct current (DC) sputtering

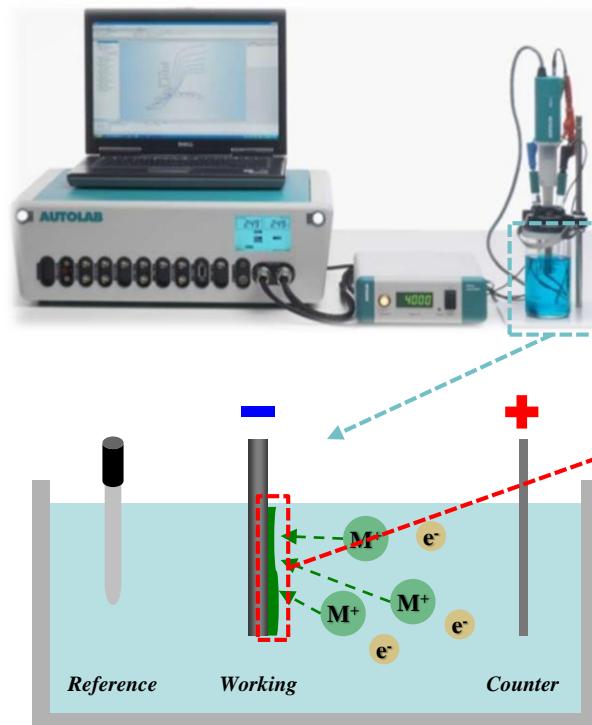
- Argon is ionized by a strong potential difference, and these ions are accelerated to a target. After impact, target atoms are released and travel to the substrate, where they form layers of atoms in the thin film.



## Fabrication methods 2: chemical methods

### Electrochemical synthesis: electrodeposition

- Metal ions in solution can be electrochemically reduced by negative applied potential on the surface of substrate (working electrode).



- Electrodeposited thin films -

