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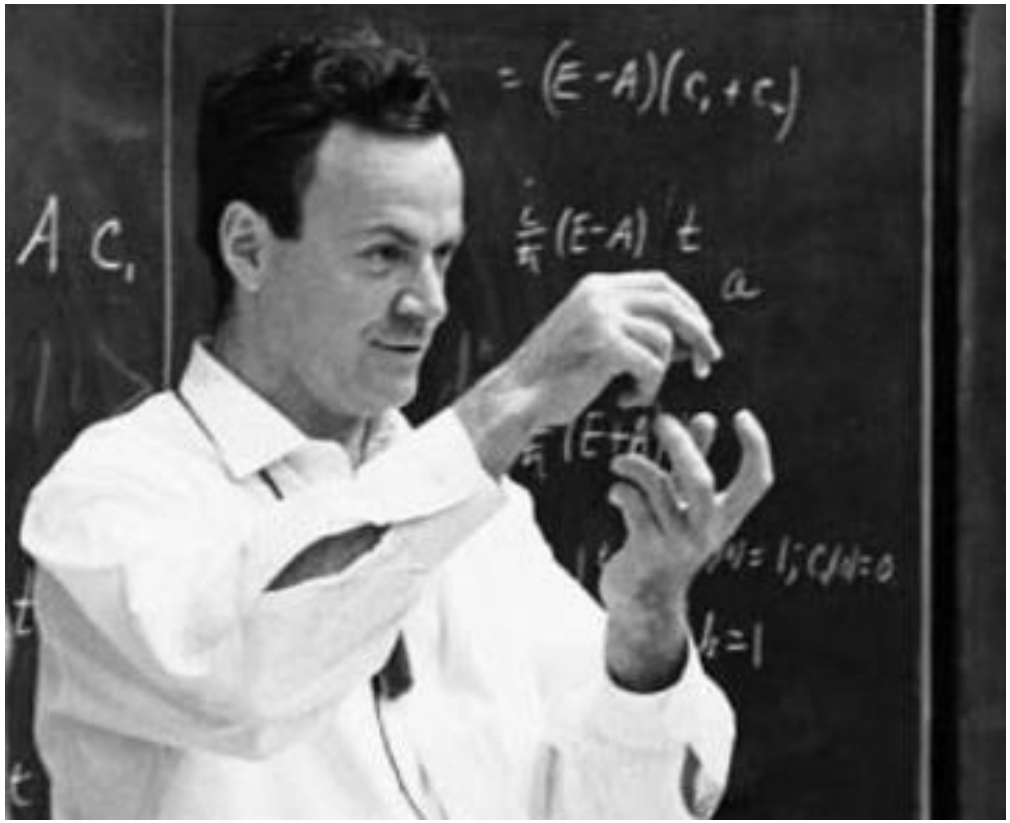
SQF5850

Tópicos em Nanociência e Nanotecnologia


USP
PÓS
GRADUAÇÃO

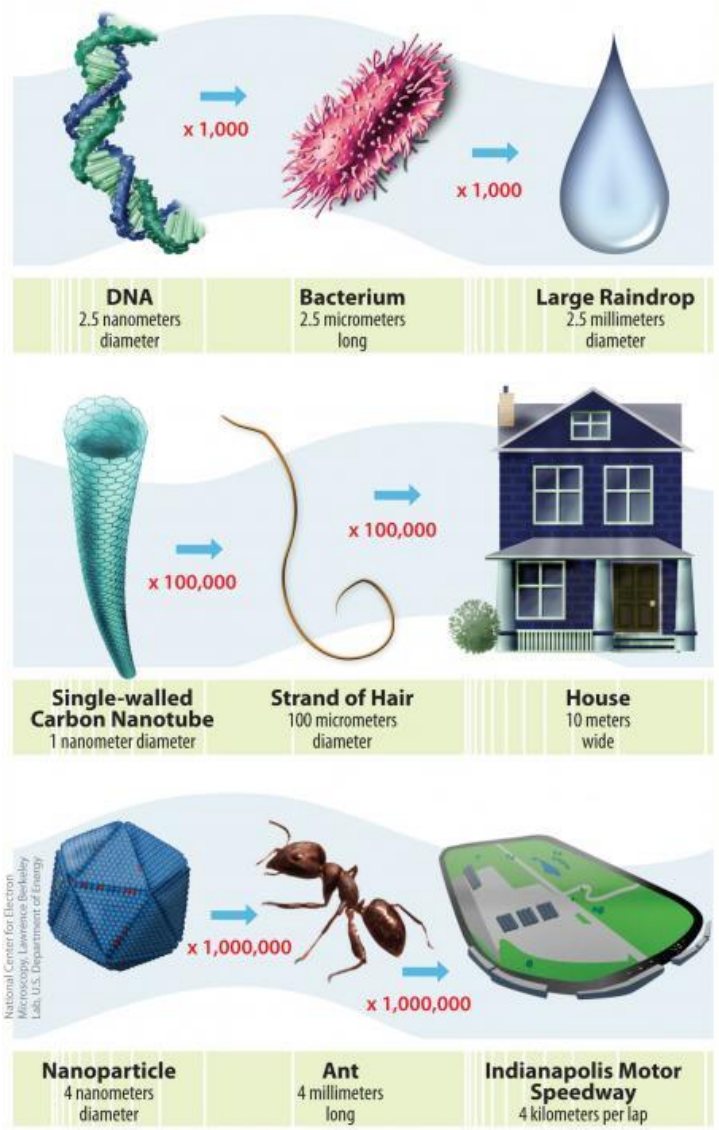
NANOSCIENCE AND NANOTECHNOLOGY



The ideas and concepts behind nanoscience and nanotechnology started with a talk entitled **“There’s Plenty of Room at the Bottom”** by physicist Richard Feynman at an American Physical Society meeting at the California Institute of Technology (CalTech) on December 29, 1959, long before the term nanotechnology was used.

http://www.nano.gov

NANOSCIENCE AND NANOTECHNOLOGY



http://www.nano.gov

(Nano) Material, Science, Technology ….

Matter and Energy are manifestations of the universe they exist in a variety of forms and interact with each other in many ways.

Nano means 10^{-9}. (Nanometer is one thousand Millionth of a Meter)

To understand how small one nm is let us see few comparisons

1. A **Red blood cell** is approximately **7000nm** wide.
2. Water Molecule is almost **0.3nm** across.
3. Human hair which is about **80,000nm** wide

Nano Material

1. Nano Materials could be defined as the materials with at least one of its dimensions in the range of a Nano meter.

2. Thus the material need not be so small that it cannot be seen, it can be a large surface or a long wire whose thickness is in the scale of Nanometers.

3. Materials that are Nano scale in one dimension are layers, such as a Thin films or Surface coatings.

4. Materials that are Nano Scale in two dimensions include Nano wires and Nano tubes.

5. Materials that are Nano scale in three dimensions are particles for example precipitates, colloids and quantum dots (Small particles of Semiconductor Materials)

Nano Science

Nano Science can be defined as the study of phenomena and manipulation of materials at Atomic, Molecular and Macromolecular scales where properties differ significantly from those at a larger scale.

Nano Science is the study and understanding of properties of Nano Particles.

Why properties of Nano Materials are different ?

The properties of Nano Materials are very much different from those at a larger scale.
Two principal factors cause the properties of Nano Materials to differ significantly from other materials.

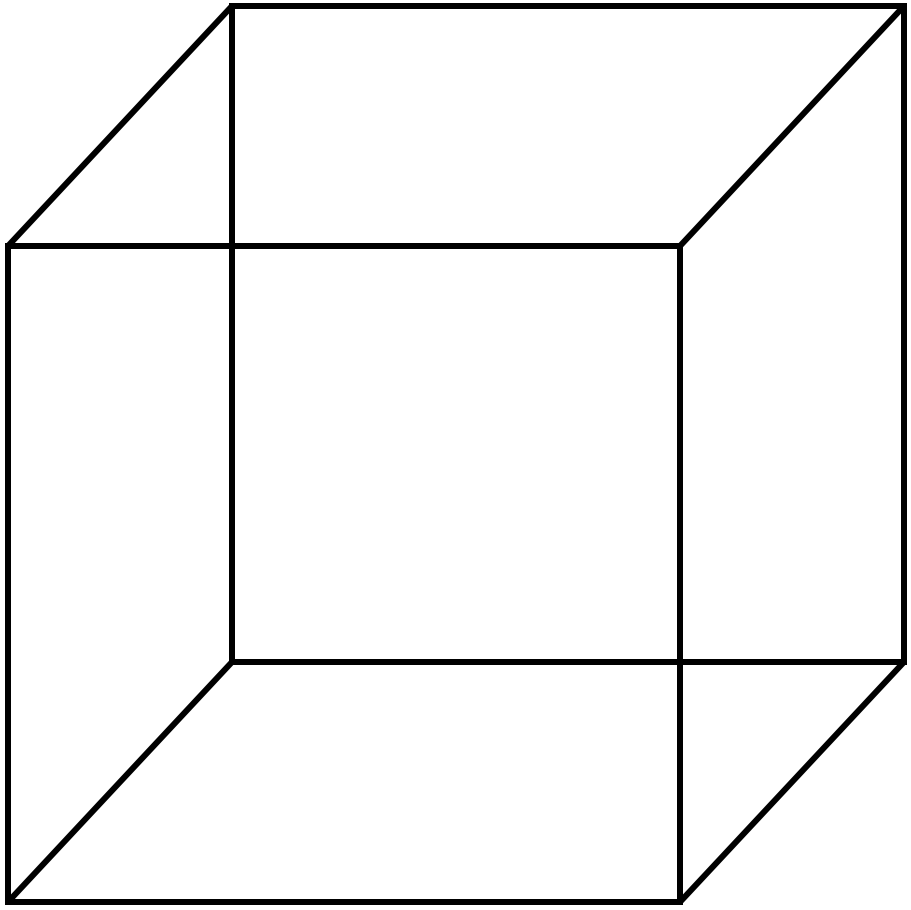
1. Increased relative surface area.

2. Quantum confinement effect.
   These factors can charge or enhance properties such as reactivity , strength and electrical characteristics.

Increase in a Surface Area to Volume ratio

Nano Materials have a relatively larger Surface area when compared to the same volume or mass of the material produced in a larger form.

Let us consider a Sphere of radius “r”.
Its Surface Area $=4\pi r^{2}$.
Its volume= $4/3\pi r^{3}$
Surface Area to Volume Ratio= 3/r.
Thus when the radius of the Sphere decreases , its Surface to Volume ratio increases.



$$surface\ \ area = 6 \times 1m^2 \Rightarrow 6m^2$$

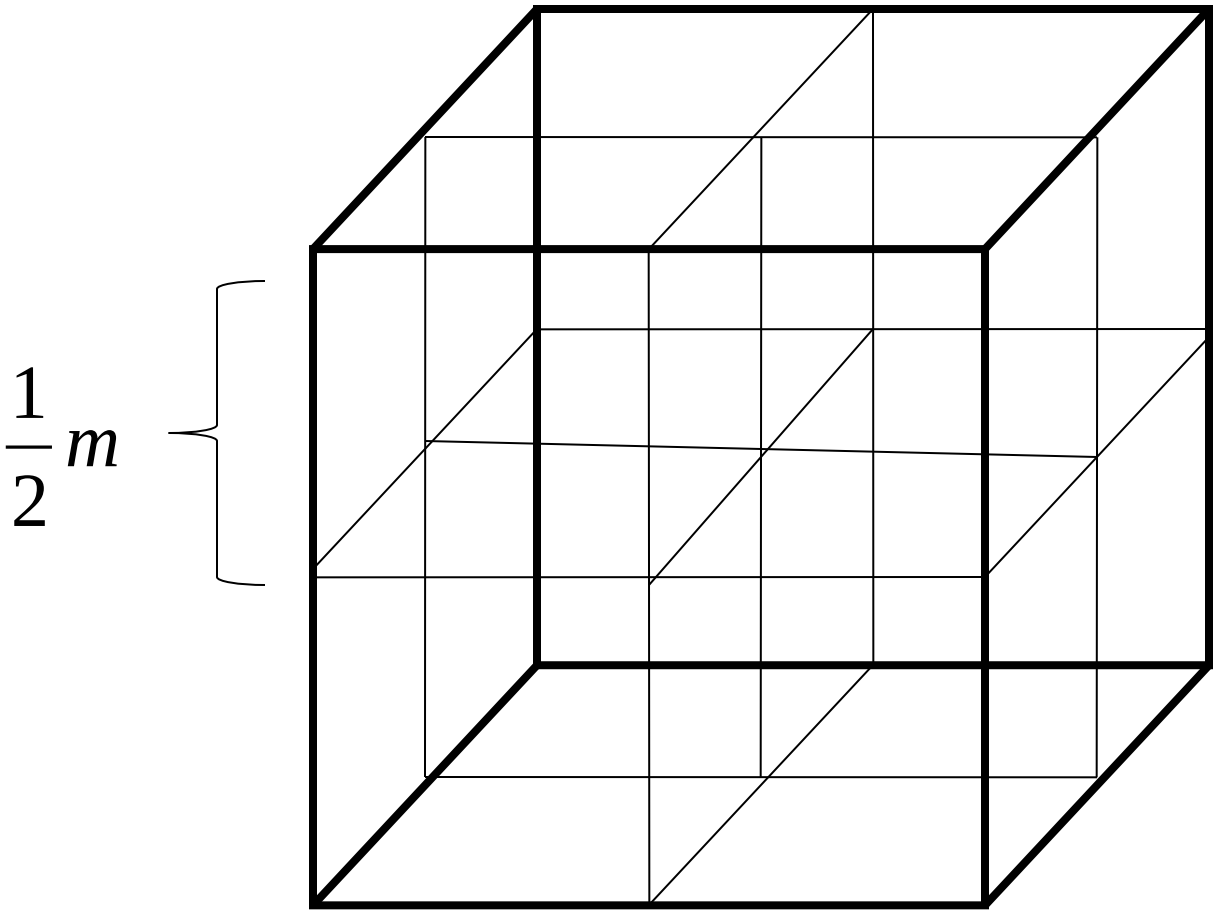
Let us consider one Cubic Volume shown in figure its the Surface Area is $6m^2$.

When it is divided into eight pieces its Surface Area becomes $12m^{2,}$ similarly When the same volume is divided into 27 pieces its Surface Area becomes $18m^{2.}$

Thus we find that when the given volume is divided into smaller pieces the Surface Area increases.

Hence as particle size decreases a greater proportion of atoms are found at the surface compared to those inside.

Nano particles have a much greater surface area per given volume compared with larger particles. It makes materials more Chemically reactive.



$$surface\ area = 6 \times (\frac{1}{2}m)^2 \times 8 = 12m^2$$

Quantum Confinement

In Nano Crystals, the Electronic energy levels are not continuous as in the bulk but are discrete (finite density of states), because of the confinement of the electronic Wave function to the physical dimensions of the particles. This phenomenon is called Quantum confinement and therefore Nano Crystals are also referred to as quantum dots (QDs).

Overview of Quantum Confinement

History: In 1970 Esaki & Tsu proposed fabrication of an artificial structure, which would consist of alternating layers of 2 different semiconductors with

Layer Thickness

$\approx$ 1 nm = 10 Å = 10^{-9} m $\equiv$ *SUPERLATTICE*

- ***PHYSICS:*** The ***main idea*** was that introduction of an ***artificial periodicity*** will "fold" the Brillouin Zones into smaller BZ's **$\equiv$ "mini-zones".**

$\Rightarrow$ The idea was that this would **raise the conduction band minima**, which was needed for some device applications.

- **Modern growth techniques** (starting in the 1980's), especially **MBE** & **MOCVD**, make fabrication of such structures possible!
- For the same reason, it is also possible to fabricate **many other kinds** of artificial structures on the scale of nm

(nanometers) ≡ "Nanostructures"

Superlattices = **"2 dimensional"** structures
Quantum Wells = **"2 dimensional"** structures
Quantum Wires = **"1 dimensional"** structures
Quantum Dots = ***"0 dimensional"*** structures!!

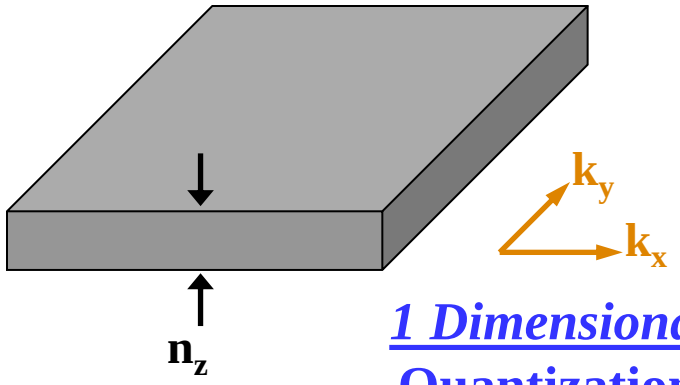
- Clearly, it is not only the electronic properties of materials which can be drastically altered in this way. Also, vibrational properties (phonons). Here, only electronic properties & only an overview!
- For many years, quantum confinement has been a fast growing field in both theory & experiment! It is at the forefront of current research!
- Note that I am not an expert on it!

Quantum Confinement in Nanostructures: Overview

Electrons *Confined in 1 Direction*:

Quantum Wells (thin films)**:**

⇒ **Electrons** can easily move in ***2 Dimensions*!**

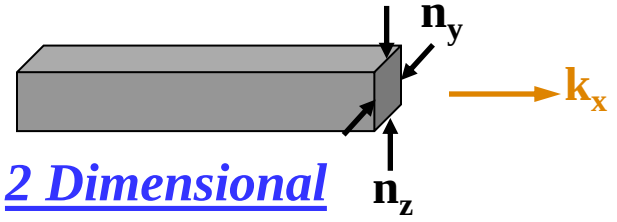


***1 Dimensional* Quantization!**

Electrons *Confined in 2 Directions*:

Quantum Wires:

⇒ **Electrons** can easily move in ***1 Dimension*!**

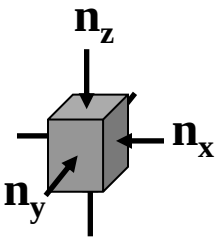


***2 Dimensional* Quantization!**

Electrons *Confined in 3 Directions*:

Quantum Dots:

⇒ **Electrons** can easily move in ***0 Dimensions*!**



***3 Dimensional* Quantization!**

Each further confinement direction changes a continuous k component to a discrete component characterized by a quantum number n.

– Consider the 1st Brillouin Zone for the infinite crystal. The maximum wavevectors are of the order

$$\mathbf{k_m \approx (\pi/a)}$$

a = lattice constant. The potential **V** is periodic with period **a**. In the almost free e^- approximation, the bands are free e^- like except near the Brillouin Zone edge. That is, they are of the form:

$$\mathbf{E \approx (\hbar k)^2/(2m_o)}$$

So, the **energy at the Brillouin Zone edge** has the form:

$$\mathbf{E_m \approx (\hbar k_m)^2/(2m_o)}$$

or

$$\mathbf{E_m \approx (\hbar \pi)^2/(2m_o a^2)}$$

- ***SUPERLATTICES*** ≡ Alternating layers of material. Periodic, with periodicity **L** (layer thickness). Let $\mathbf{k_z}$ = wavevector perpendicular to the layers.
- In a superlattice, the potential **V** has a ***new periodicity*** in the **z** direction with periodicity **L >> a**

⇒ In the **z** direction, the Brillouin Zone is much smaller than that for an infinite crystal. The maximum wavevectors are of the order: $\mathbf{k_s \approx (\pi/L)}$

⇒ At the BZ edge in the **z** direction, the energy has the form:

$$\mathbf{E_s \approx (\hbar\pi)^2/(2m_oL^2) + E_2(k)}$$

$\mathbf{E_2(k)}$ = the 2 dimensional energy for **k** in the **x,y** plane.

Note that: $\mathbf{(\hbar\pi)^2/(2m_oL^2) << (\hbar\pi)^2/(2m_oa^2)}$

Primary Qualitative Effects of Quantum Confinement

- Consider ***electrons confined along 1 direction*** (say, **z**) to a layer of width **L:**

Energies

- The ***energy bands are quantized*** (instead of continuous) in k_z & shifted **upward.** So k_z **is quantized:**

$$k_z = k_n = [(n\pi)/L],\ n = 1, 2, 3$$

- So, in the effective mass approximation (**m***), ***the bottom of the conduction band is quantized*** (like a particle in a **1 d** box) & shifted:

$$E_n = (n\hbar\pi)^2/(2m^*L^2)$$

- ***Energies are quantized!*** Also, the ***wavefunctions are 2 dimensional Bloch functions*** (***traveling waves***) for **k** in the **x,y** plane & ***standing waves in the z direction*****.**

Quantum Confinement Terminology

Quantum Well ≡ QW

= A single layer of material **A** (layer thickness **L**), sandwiched between 2 **macroscopically large layers** of material **B**. Usually, the bandgaps satisfy:

$$E_{gA} < E_{gB}$$

Multiple Quantum Well ≡ MQW

= Alternating layers of materials **A** (thickness **L**) & **B** (thickness **L′**). In this case:

$$L' >> L$$

So, the e^- & e^+ in one **A** layer are independent of those in other **A** layers.

Superlattice ≡ SL

= Alternating layers of materials **A** & **B** with similar layer thicknesses.

Brief Elementary Quantum Mechanics & Solid State Physics Review

- **Quantum Mechanics of a Free Electron:**
  - The **energies are continuous**: $\mathbf{E = (\hbar k)^2/(2m_o)}$ (1d, 2d, or 3d)
  - The **wavefunctions are traveling waves**:

$$\psi_k(x) = A\, e^{ikx} \quad \text{(1d)} \qquad\qquad \psi_k(r) = A\, e^{ik\bullet r} \quad \text{(2d or 3d)}$$

- **Solid State Physics: Quantum Mechanics of an Electron in a Periodic Potential in an infinite crystal :**
  - The **energy bands are (approximately) continuous**: $E = E_{nk}$
  - At the bottom of the conduction band or the top of the valence band, in the effective mass approximation, **the bands can be written:**

$$E_{nk} \cong (\hbar k)^2/(2m^*)$$

  - The **wavefunctions are Bloch Functions =** ***traveling waves***:

$$\Psi_{nk}(r) = e^{ik\bullet r}\, u_{nk}(r); \quad u_{nk}(r) = u_{nk}(r+R)$$

Some Basic Physics

- **Density of states** (DoS)

$$DoS = \frac{dN}{dE} = \frac{dN}{dk}\frac{dk}{dE}$$

in 3D:

$$N(k) = \frac{\text{k space vol}}{\text{vol per state}}$$

$$= \frac{4/3\pi k^3}{(2\pi)^3/V}$$

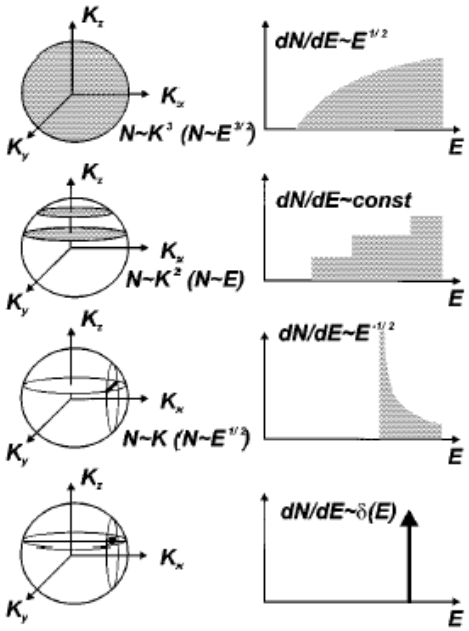


Fig. 1. Density of states for charge carriers in structures with different dimensionalities.

Structure	Degree of Confinement	$\frac{dN}{dE}$
Bulk Material	0D	$\sqrt{E}$
Quantum Well	1D	1
Quantum Wire	2D	$1/\sqrt{E}$
Quantum Dot	**3D**	**δ(E)**

QM Review: The 1d (infinite) Potential Well

("particle in a box") In all QM texts!!

- We want to solve the **Schrödinger Equation for:**

  $x < 0, V \to \infty$; $0 < x < L, V = 0$; $x > L, V \to \infty$

  $$\Rightarrow -[\hbar^2/(2m_o)](d^2\psi/dx^2) = E\psi$$

- Boundary Conditions:

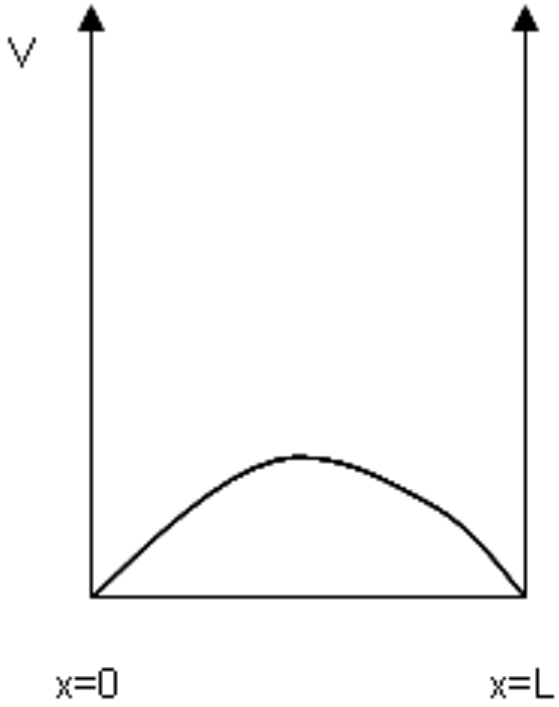
  $\psi = 0$ at $x = 0$ & $x = L$ ($V \to \infty$ there)

- Energies:

  $$E_n = (\hbar n\pi)^2/(2m_oL^2), \quad n = 1,2,3$$

  Wavefunctions:

  $$\psi_n(x) = (2/L)^{1/2}\sin(n\pi x/L)$$ (a standing wave!)



Qualitative Effects of Quantum Confinement:

Energies are quantized & ψ changes from a traveling wave to a **standing wave**.

In 3Dimensions…

- For the **3D infinite potential well**:

$$\Psi(x, y, z) \sim \sin\left(\frac{n\pi x}{L_x}\right)\sin\left(\frac{m\pi y}{L_y}\right)\sin\left(\frac{q\pi z}{L_z}\right),\ \mathrm{n, m, q = integer}$$

$$\text{Energy levels} = \frac{n^2h^2}{8mL_x^{\,2}} + \frac{m^2h^2}{8mL_y^{\,2}} + \frac{q^2h^2}{8mL_z^{\,2}}$$

Real Quantum Structures aren't this simple!!

- In **Superlattices & Quantum Wells,** the potential barrier is obviously not infinite!
- In **Quantum Dots**, there is usually ~ **spherical confinement**, not rectangular.
- The simple problem only considers a single electron. But, in **real structures, there are many electrons** & also **holes!**
- Also, there is often **an effective mass mismatch** at the boundaries. That is ***the boundary conditions we've used are too simple***!

Properties of Nano Materials

Nano Materials have properties that are different from those of bulk materials.
Most Nano structure materials are Crystalline in nature and they posses unique properties.

Physical Properties of Nano Particles

Crystal structure of Nano particles is same as bulk structure with different lattice parameters.

The inter atomic spacing decreases with size and this is due to long range electrostatic forces and the short range core-core repulsion.

The Melting point of Nanoparticles decreases with size.

Chemical Properties

The Electronic structure of Nanoparticles is dependent on its size and the ability of Nano cluster to react, depends on cluster size.

The large Surface area to volume ratio the variations in geometry and the electronic structure of Nano particles have a strong effect on catalytic properties.

Electrical properties

The electronic structure of Nano materials is different from its bulk material.

The density of the energy states in the conduction band changes.

When the energy spacing between two energy levels is more than K_BT , energy gap is created.

Nano clusters of different sizes will have different electronic structures and different energy level separations.

The Ionization potential at Nano sizes are higher than that for the bulk materials

Magnetic Properties

The Magnetic Moment of Nano particles is found to be very less when compared them with its bulk size.

Nanoparticles made of semiconducting materials Germanium , Silicon and Cadmium are not Semiconductors.

Applications of Nanomaterials

Chemical Industry:

Fillers for point systems
Coating Systems based on Nano composites.
Magnetic fluids.

Automotive Industry:

Light weight construction
Painting
Catalysts
Sensors

Medicine

Drug delivery systems
Active agents
Medical rapid tests
Antimicrobial agents and coatings.
Agents in cancer therapy.

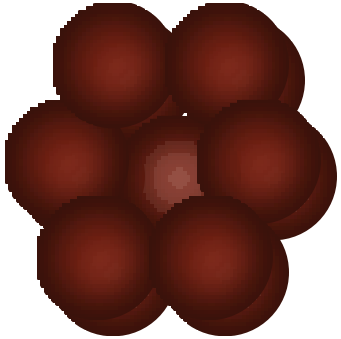
Electronic Industry

Data memory
Displays
Laser diodes
Glass fibers
Filters
Conductive, antistatic coatings.

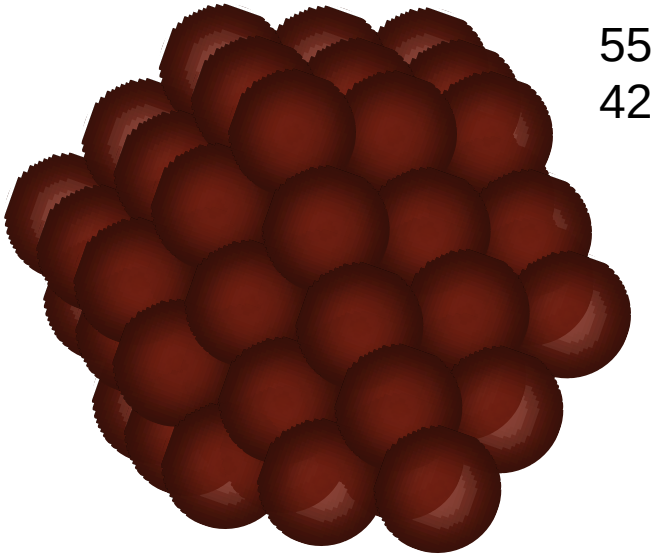
Energy Sources
Fuel cells
Solar cells
Batteries
capacitors.

Cosmetics
Sun protection creams
Tooth paste

Átomos e Nanopartículas



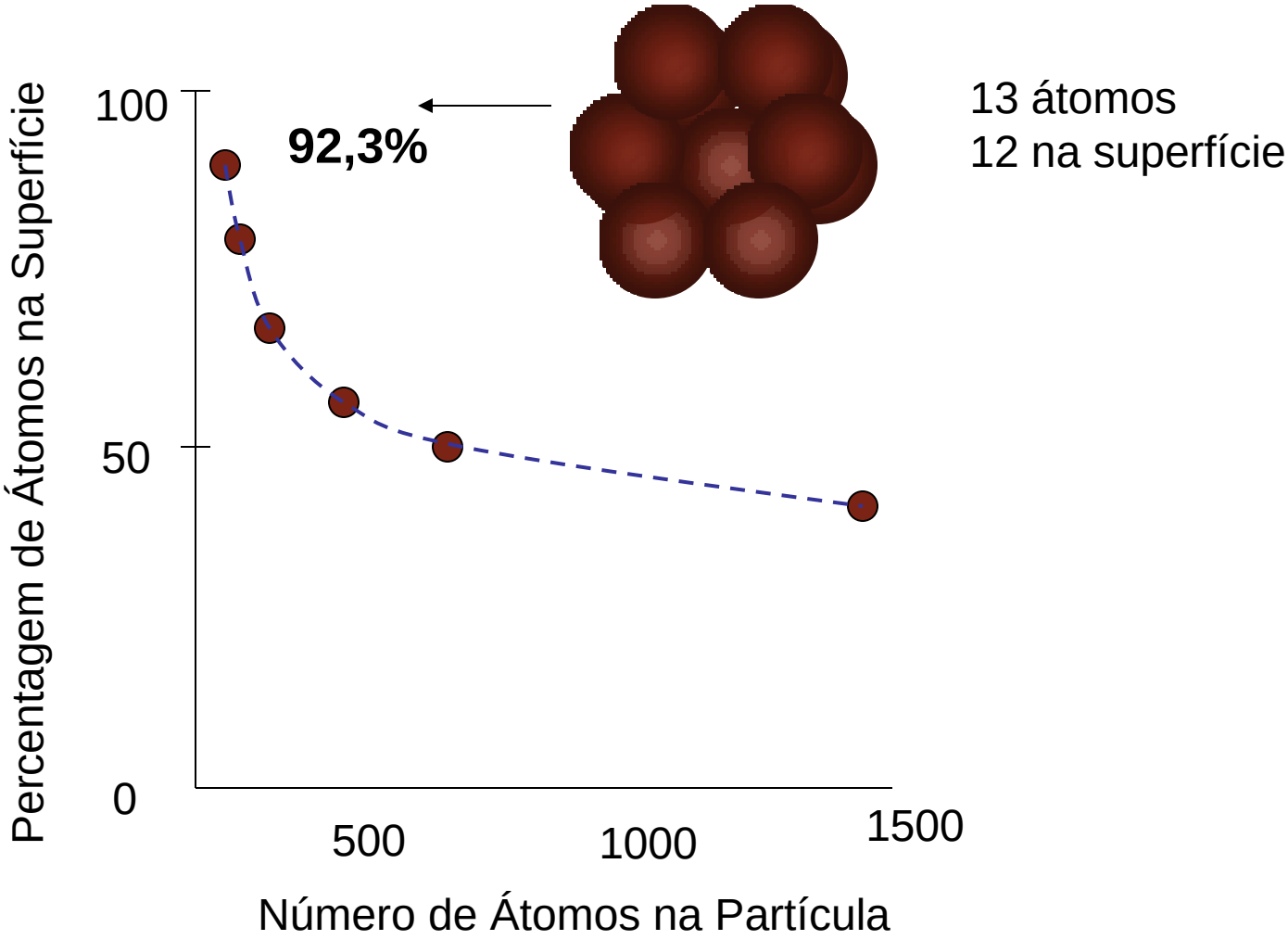
13 átomos
12 na superfície



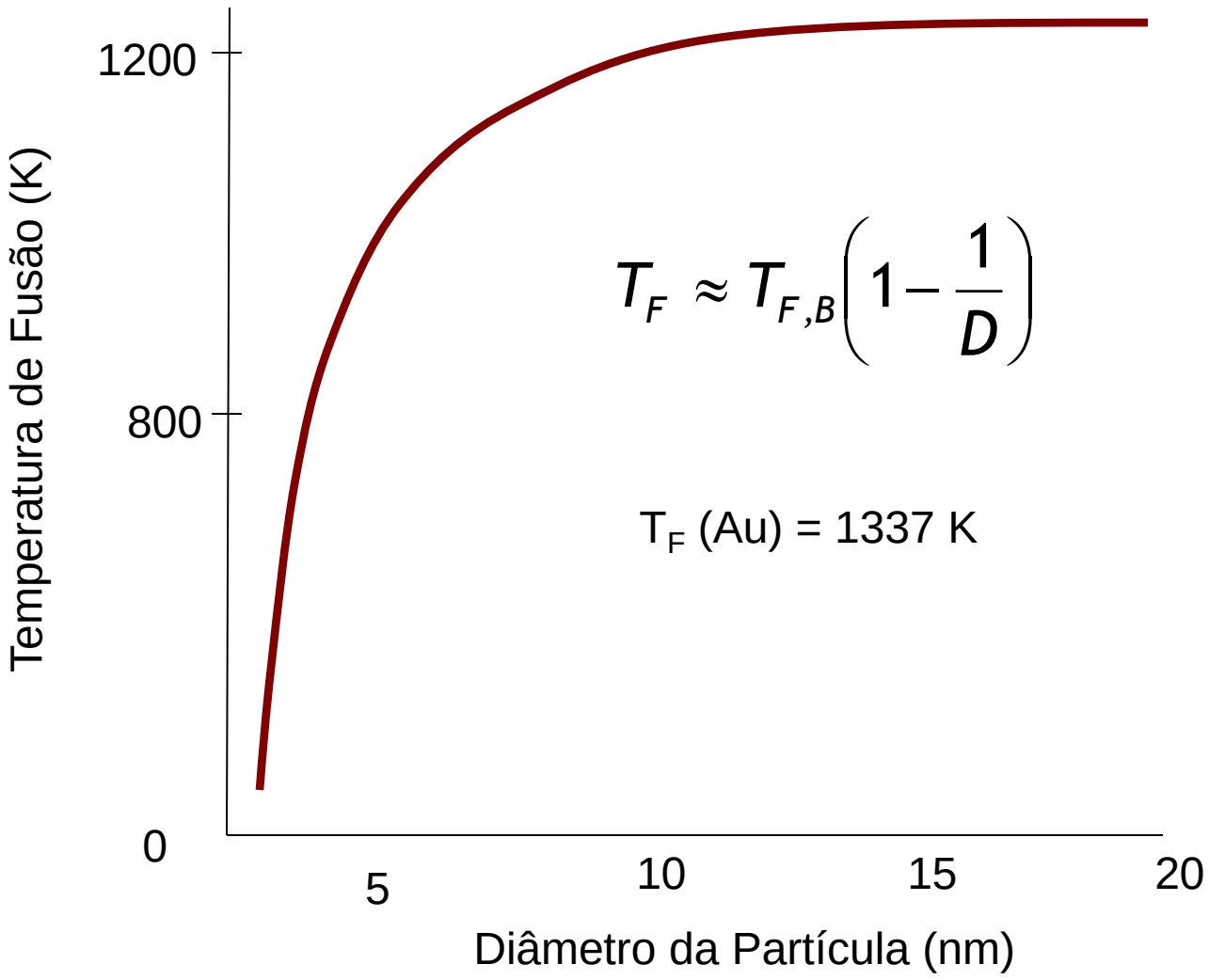
55 átomos
42 na superfície

147 átomos
93 na superfície

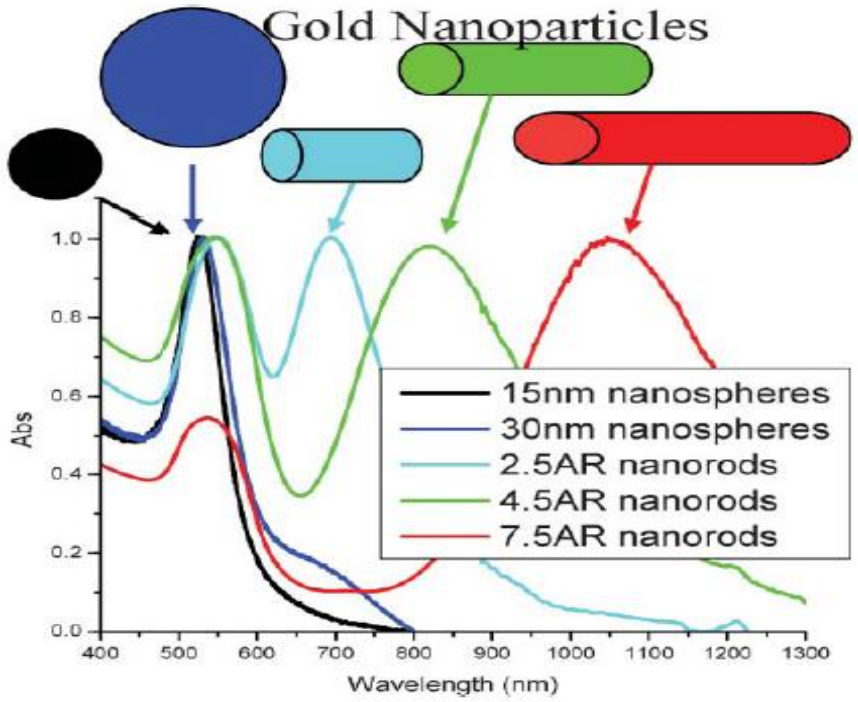
Átomos e Nanopartículas



Temperatura de Fusão



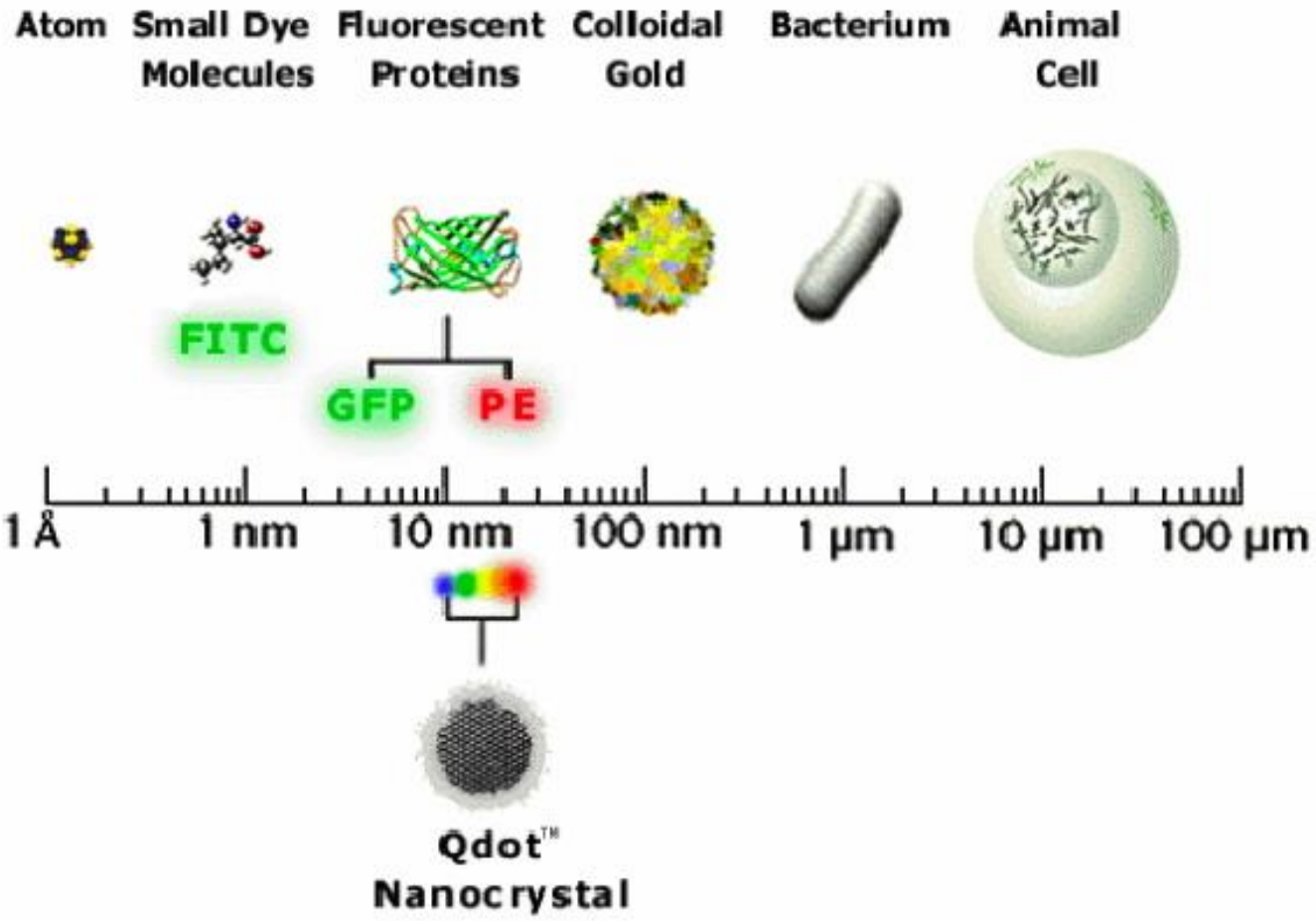
Optical



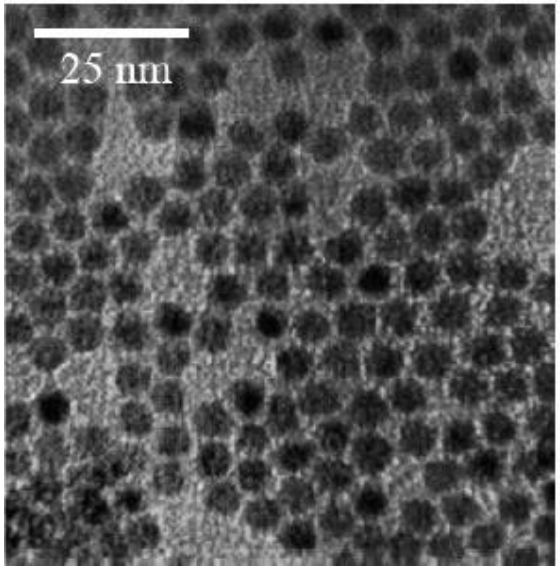
S. Eustis, M. A. El-Sayed, *Chem. Soc. Rev.* **2006**, 35, 209-217

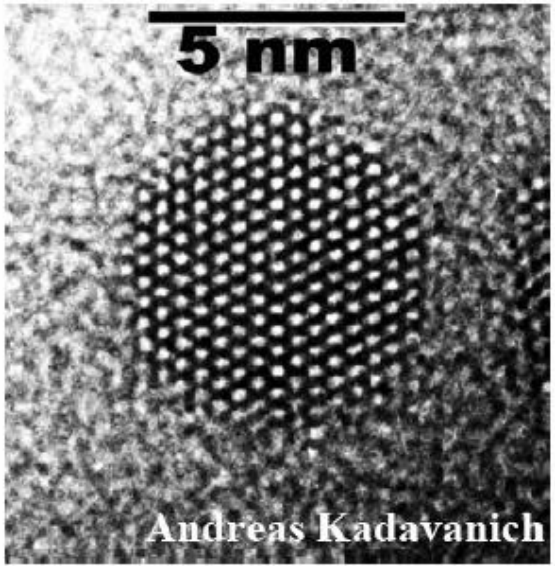
Nanoparticles

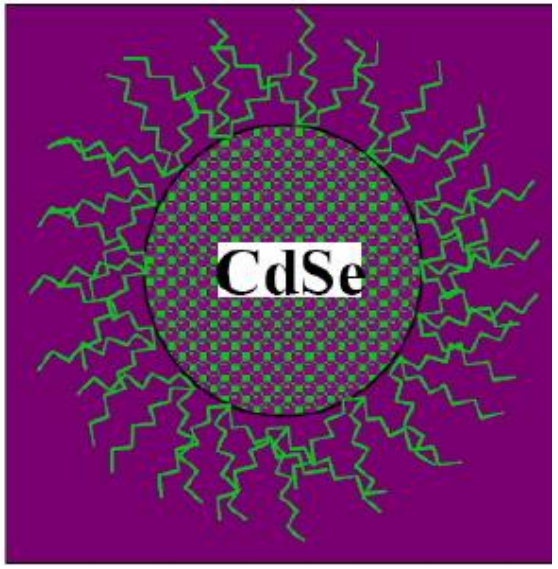
Relative Sizes



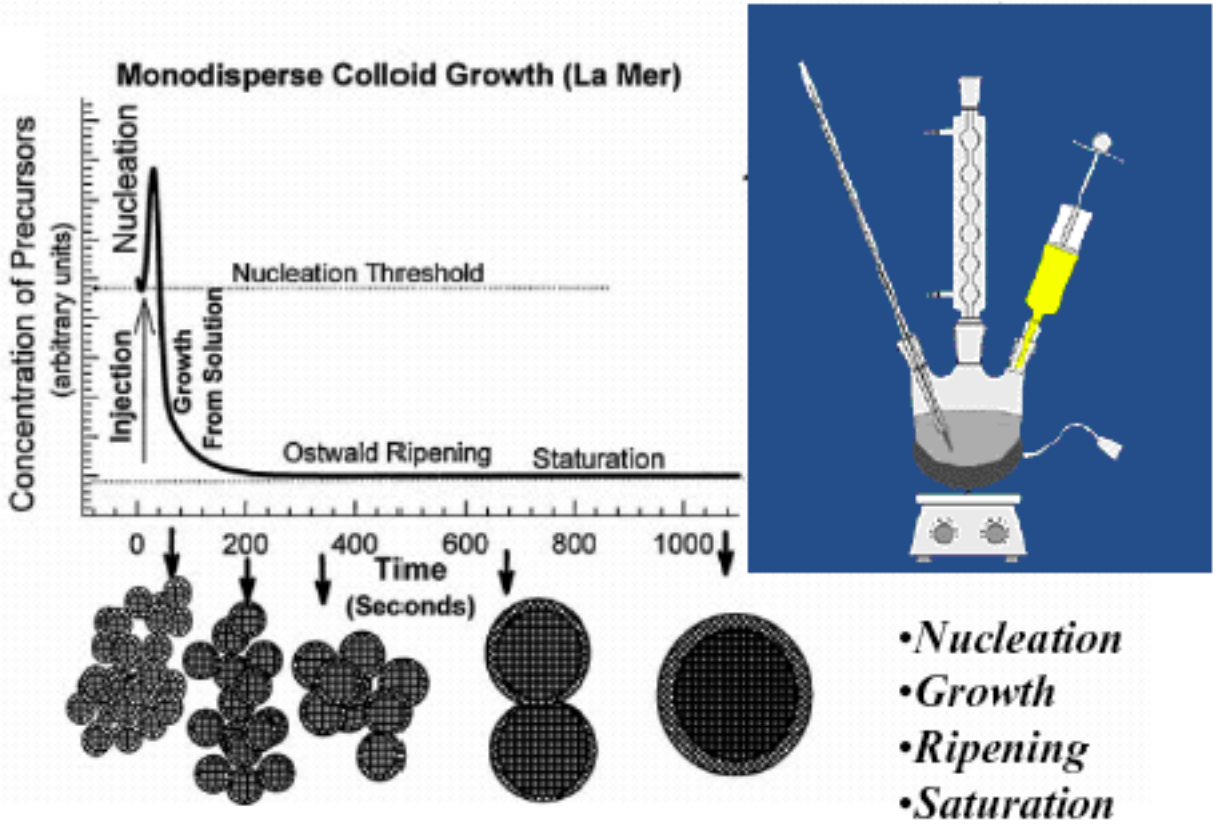
Images of Nanoparticles



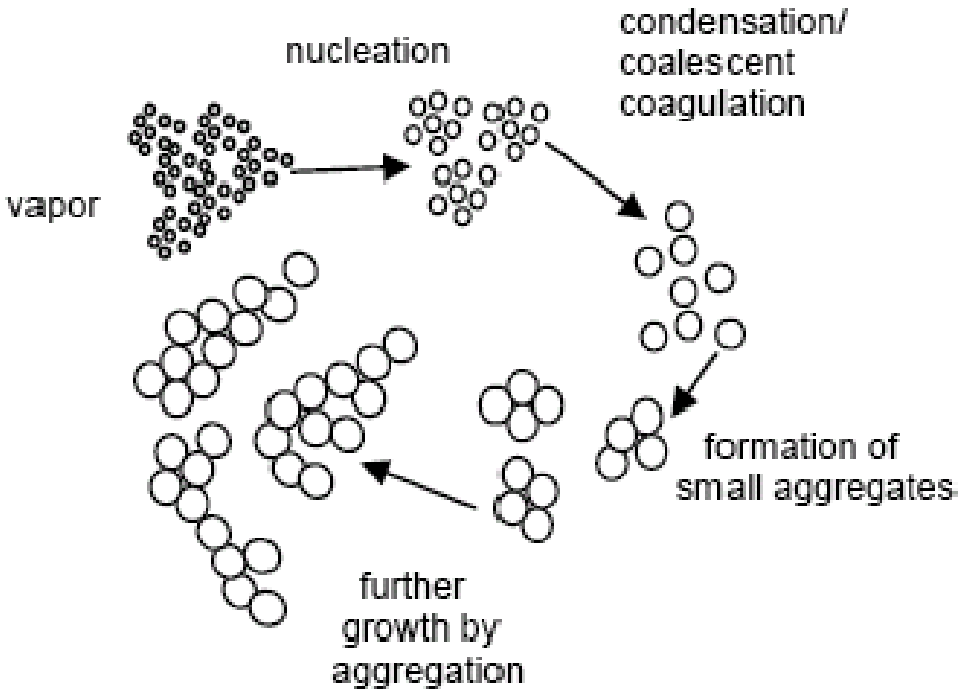




Monodisperse QD Synthesis

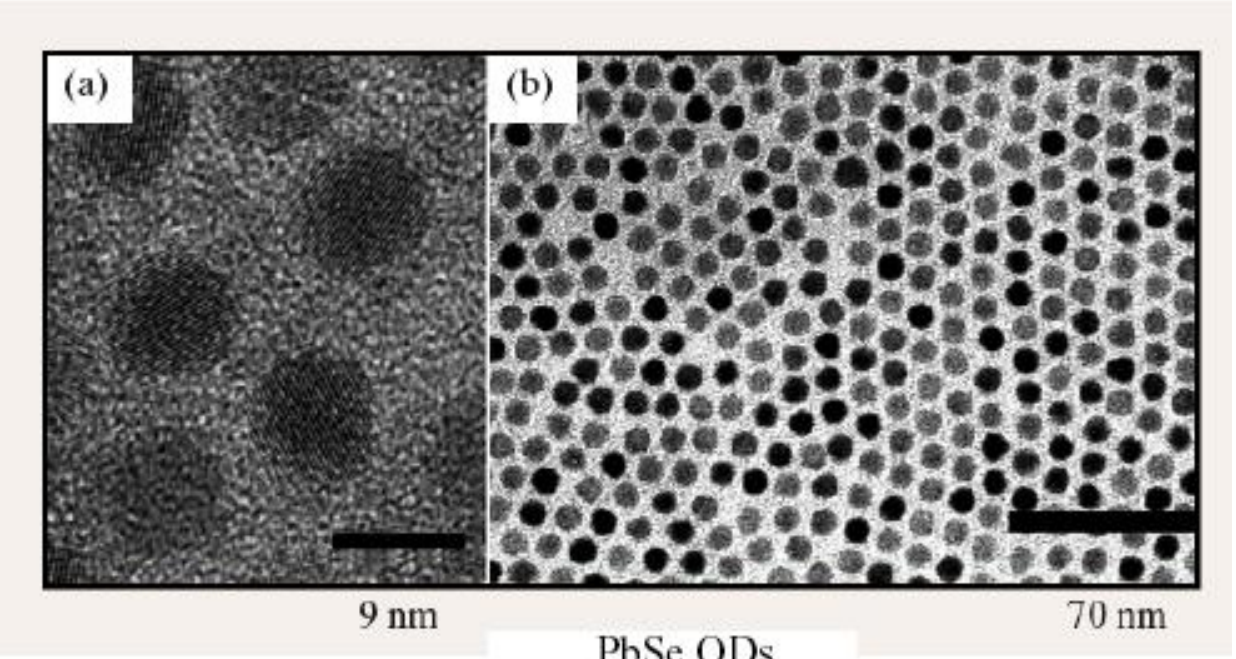


Nanoparticle Growth



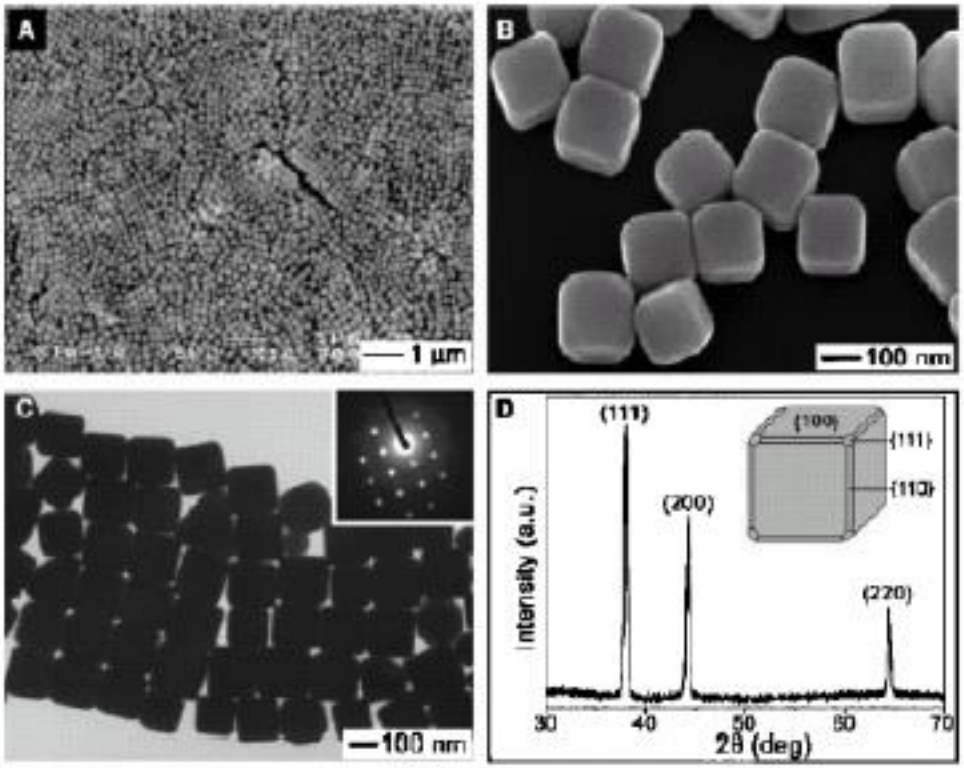
Nanospheres

Monodisperse Nanoparticle (spheres)

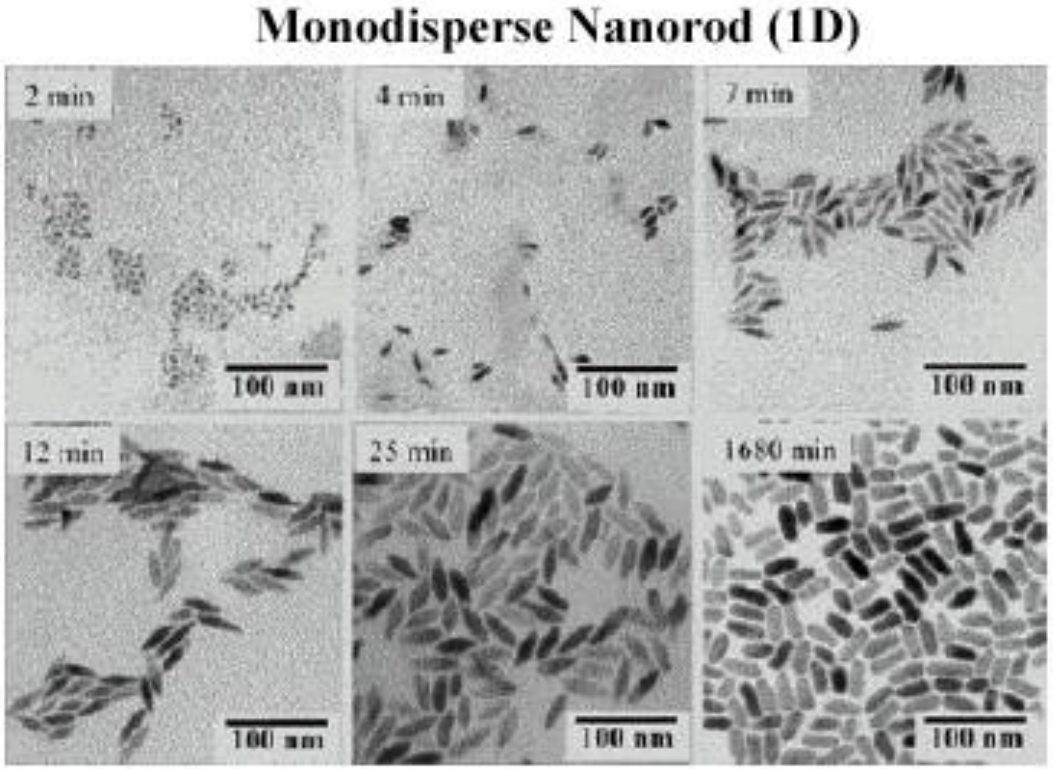


Nanocubes

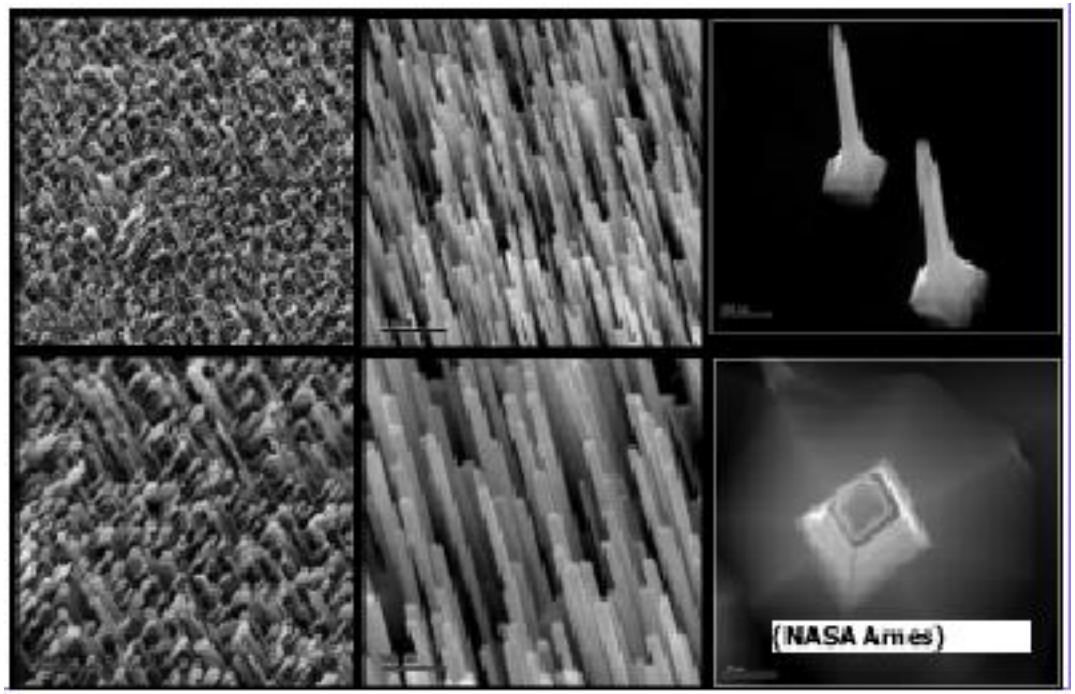
Monodisperse silver nanocubes



Nanorods

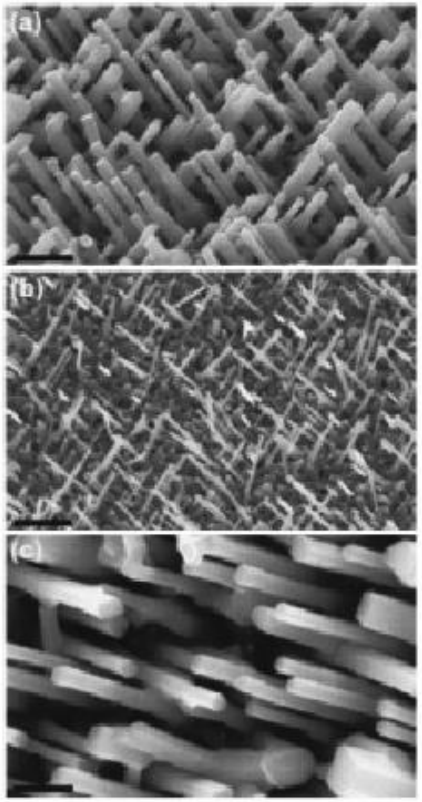

Monodisperse Nanorod (1D)
2 min
100 nm
4 min
100 nm
7 min
100 nm
12 min
100 nm
25 min
100 nm
1680 min
100 nm

Nanorods

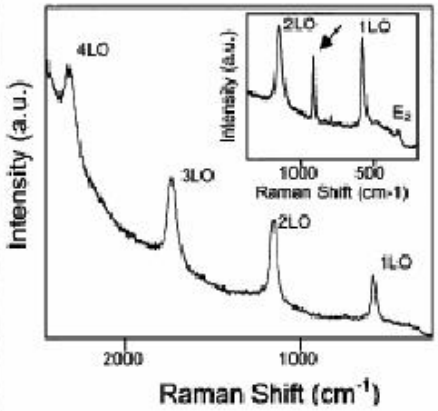


Nanowires

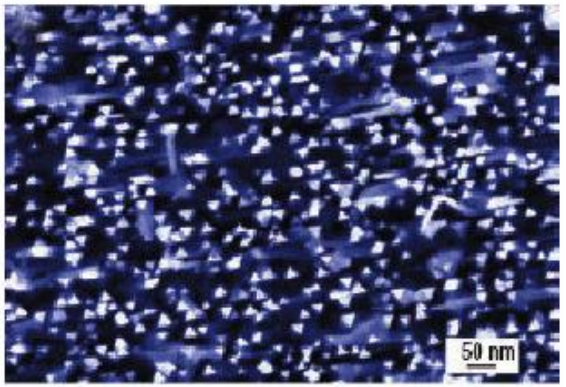
ZnO NWs

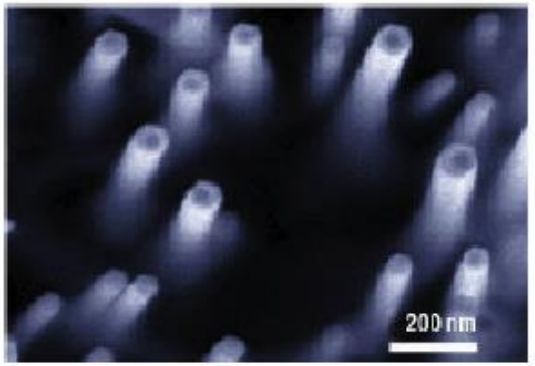


(Ng et al, APL, 82, 2003)



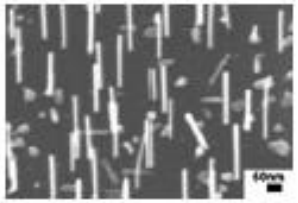
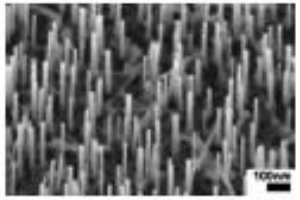
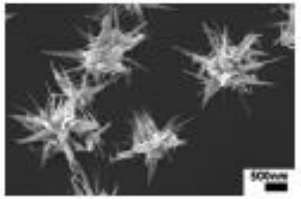
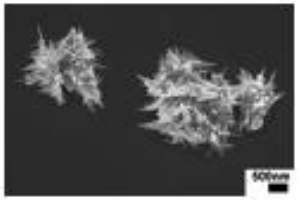
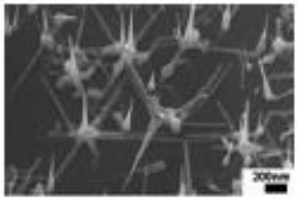
GaN NWs





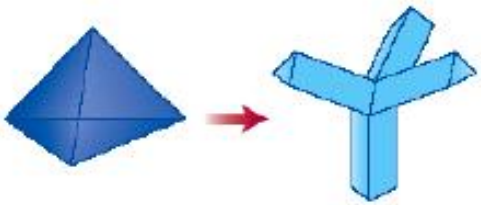
Kuykendall et al, Nature Materials, 2004

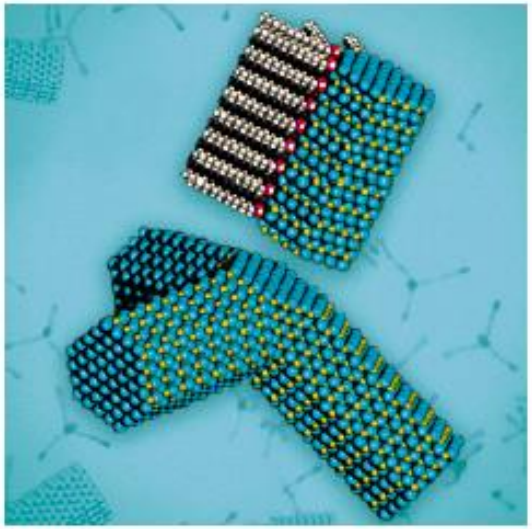
Differences from Growth

	20 nm Au	60 nm Au	120 nm Au
InAs NW on (111) Si (11.6% mismatch)			
InP NW on (111) Si (8.1% mismatch)			
InP NW on (111) GaAs (4.1% mismatch)			

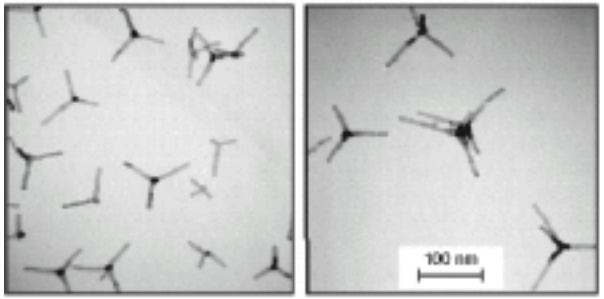
Nanotetrapods

Nanotetrapods (3D)

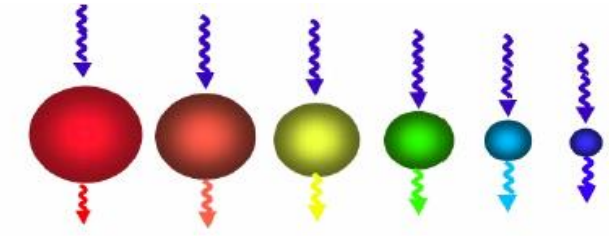


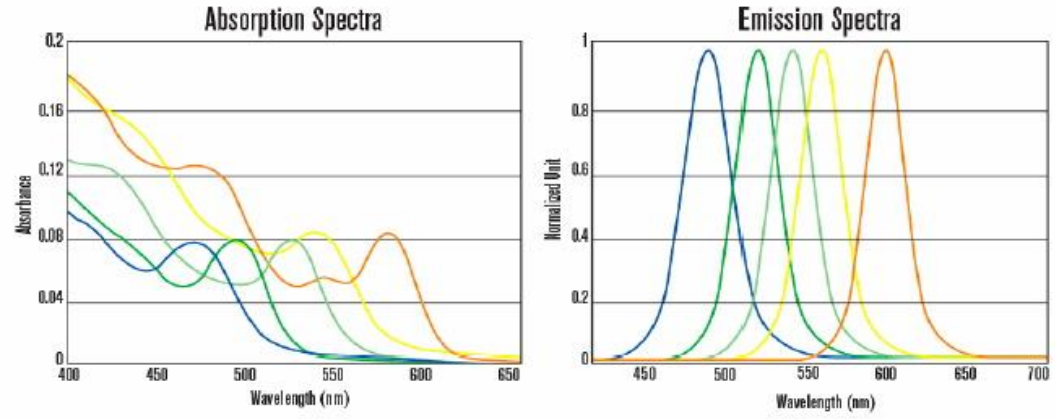


Growth



Absorption and Emission



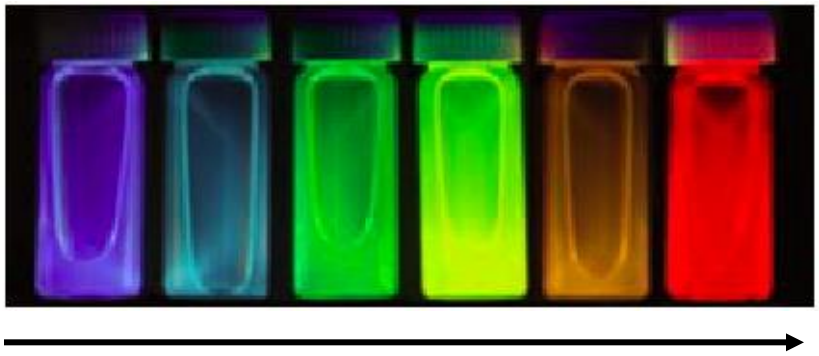


Size of Nanoparticles

Size of quantum dots can be used to tune color and emission wavelength

Quantum Confinement: size of particle smaller than de Broglie wavelength of electron and hole

Emission from Colloidal CdSe
Quantum Dots Dispersed in Hexane



Size: ~2 nm to 8 nm

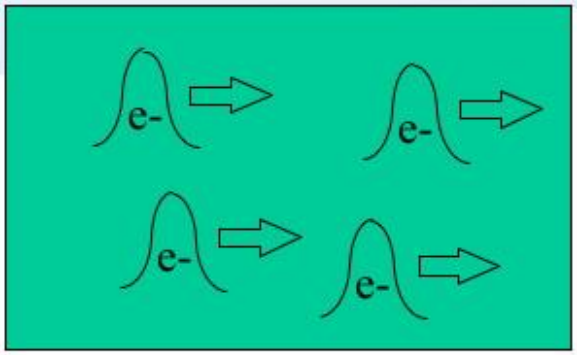
Example 1

Find the de Broglie wavelength for an electron moving at the speed of $5.0 \times 10^6\ m/s$ (mass of an electron is $9.1 \times 10^{-31}\ kg$).

SOLUTION

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.63 \times 10^{-34}\ J \cdot s}{(9.1 \times 10^{-31}\ kg)(5.0 \times 10^6\ m/s)} = 1.46 \times 10^{-10}\ m$$

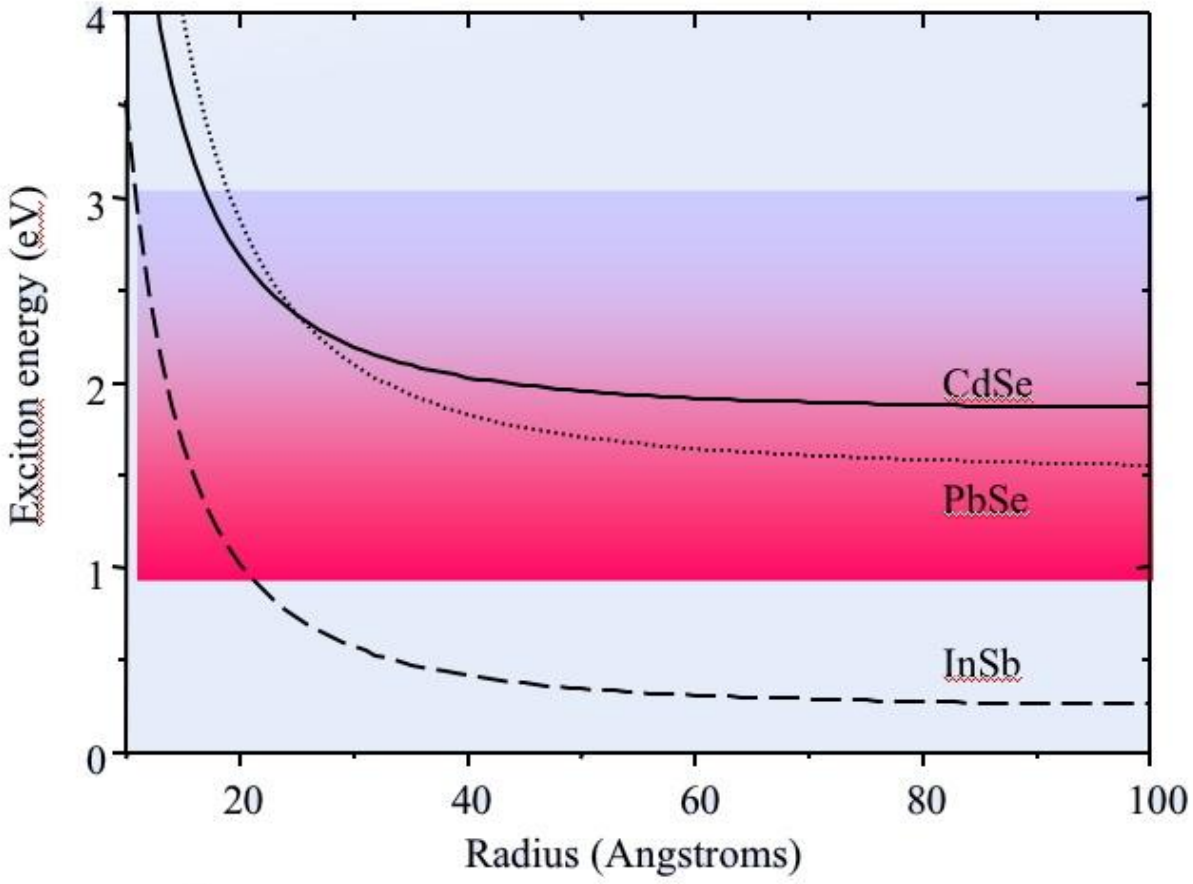
Quantum Confinement



Charges in semiconductors are a certain “size”: they are really waves.

Semiconductor	Wavelength of Fundamental Excitation
Silicon	~ 20 nm
CdSe	~ 6 nm
Gallium Arsenide	~ 10 nm

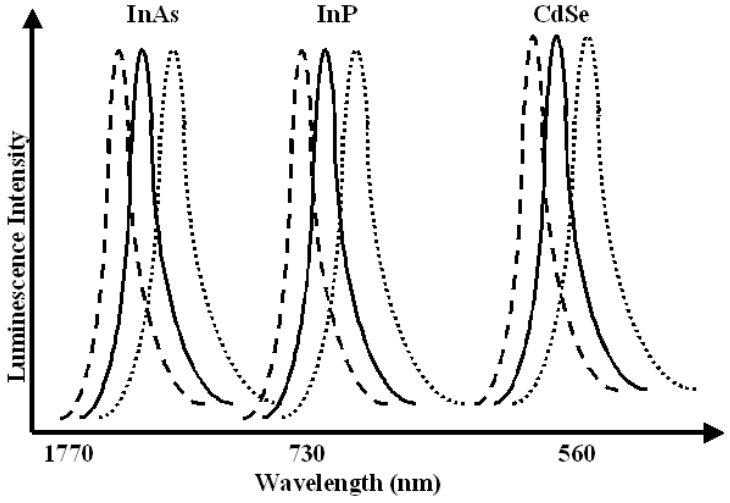
Exciton Energy



Size Dependence

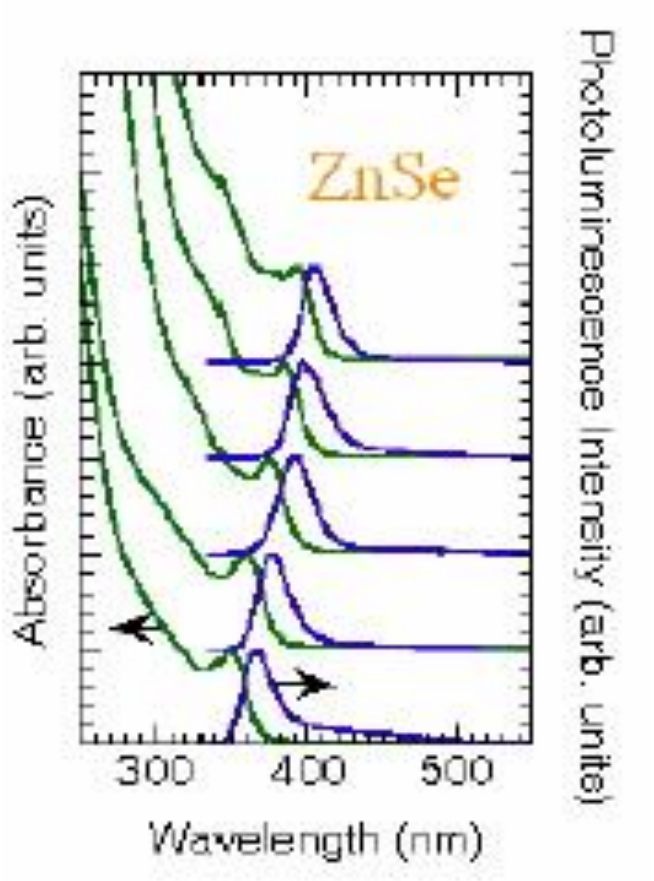
The most important optical feature of quantum dots is that their absorption/emission spectra shifts to shorter wavelengths as the size becomes smaller.

The luminescence spectra for InAs, InP and CdSe Quantum Dots is shown below.



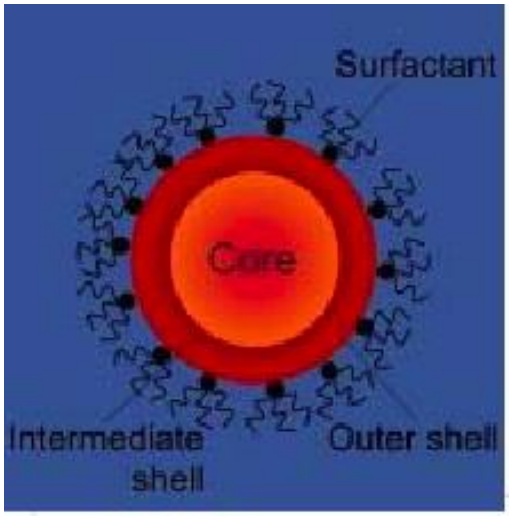
The size decreases from left to right

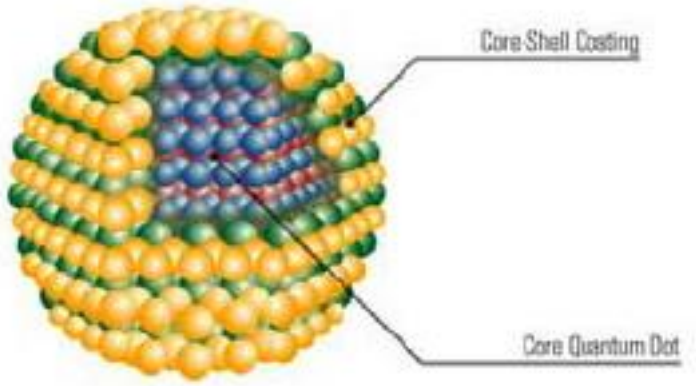
ZnSe Absorption and Emission

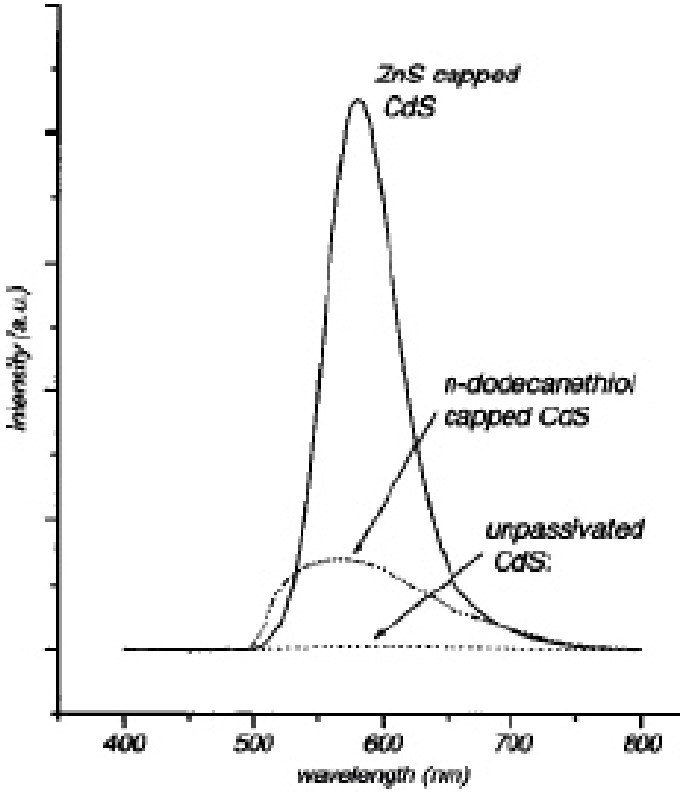


Size increases

Core-Shell Materials



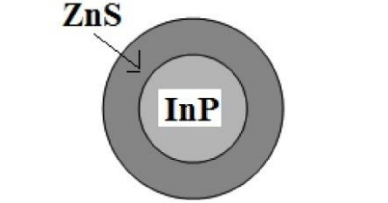




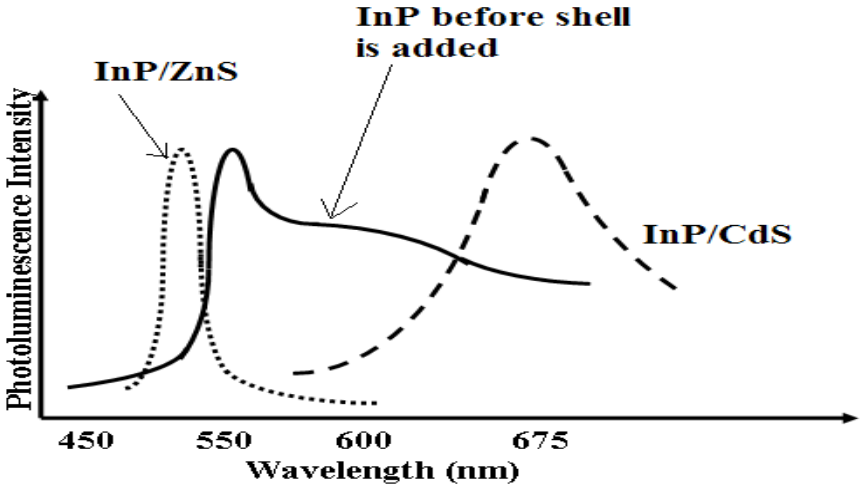
Appl. Phys. Lett., 82, 2003, 1966

Effect of Shell

Core-Shell Quantum Dot refers to a Quantum-Dot surrounded by a shell of higher band-gap semiconductor.



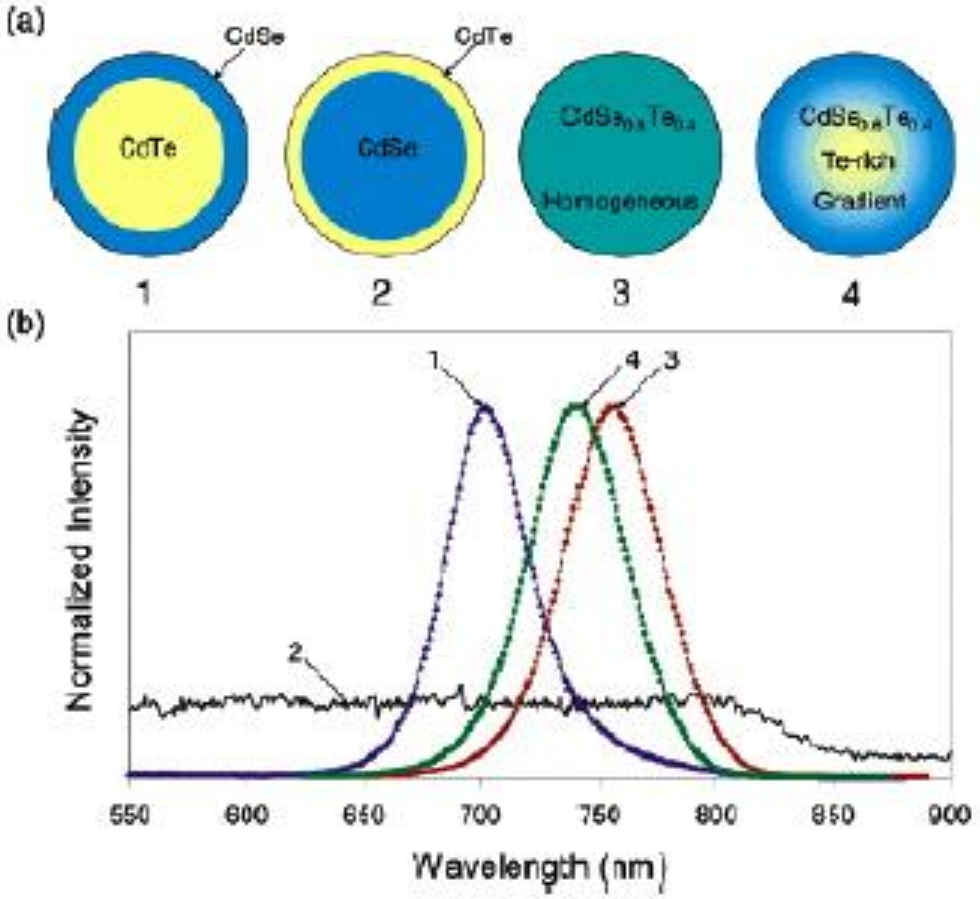
Core-Shell Quantum Dot



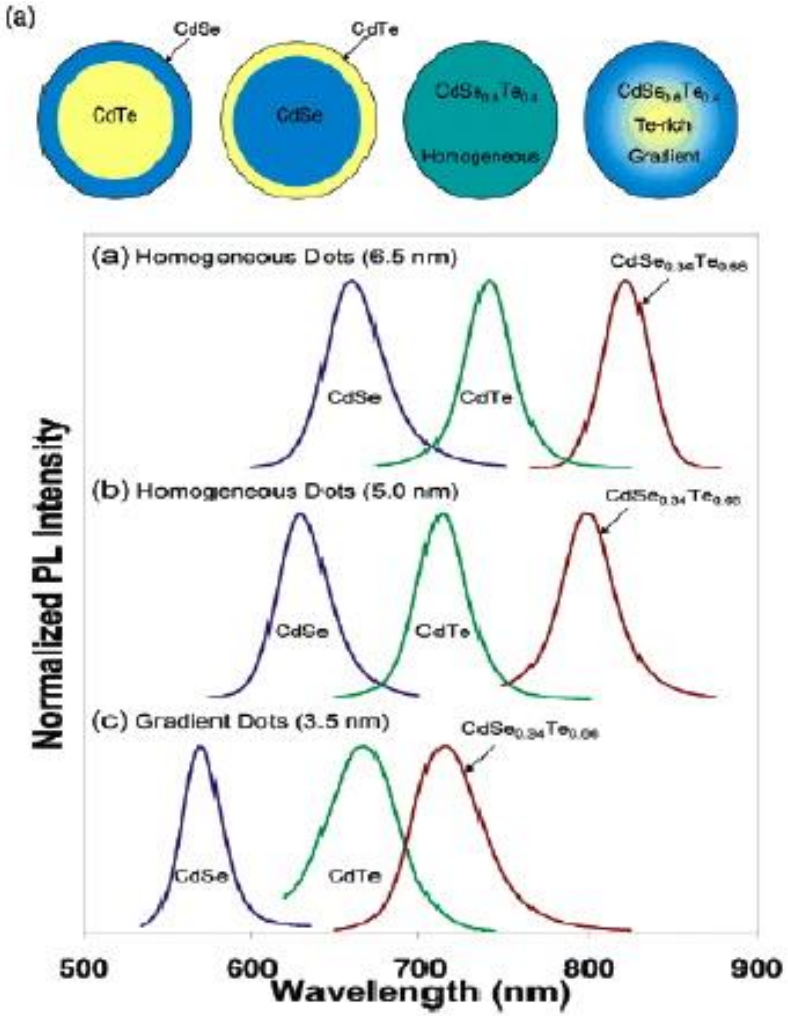
Photoluminescence from Quantum Dots

Covering the surface of a Quantum Dot reduces non-radiative decay of electrons close to the surface and thus enhances luminescence intensity.

Mixed Materials



Mixed Materials

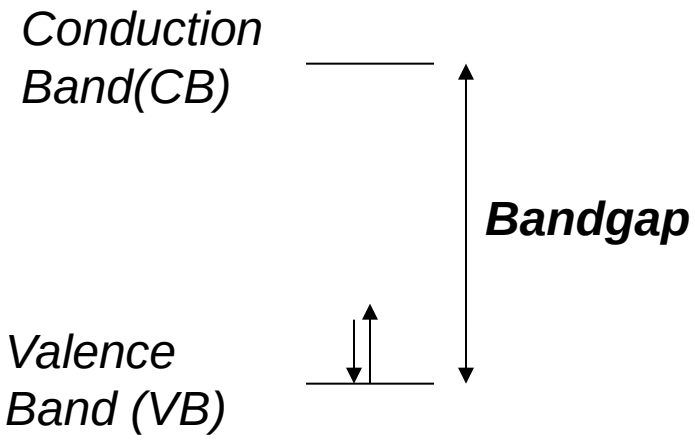


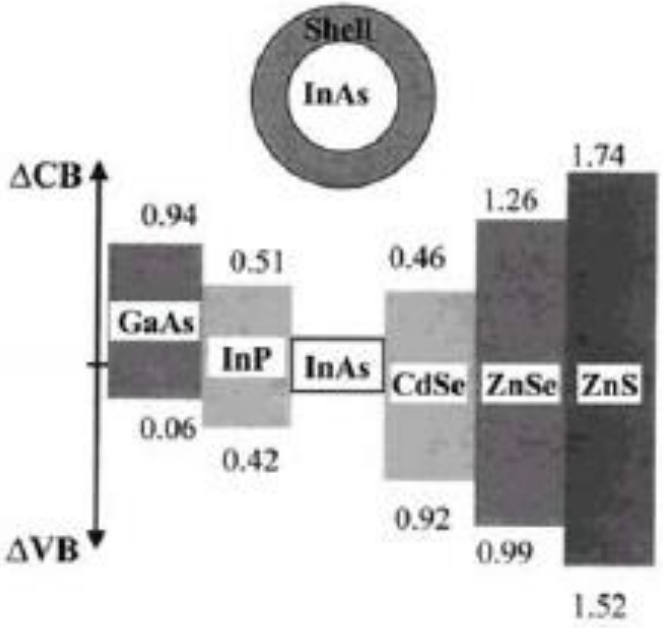
Core Shell Materials

Semiconductor nanoparticles coated with a second material of wider bandgap usually results in dramatic improvement in luminescence efficiency

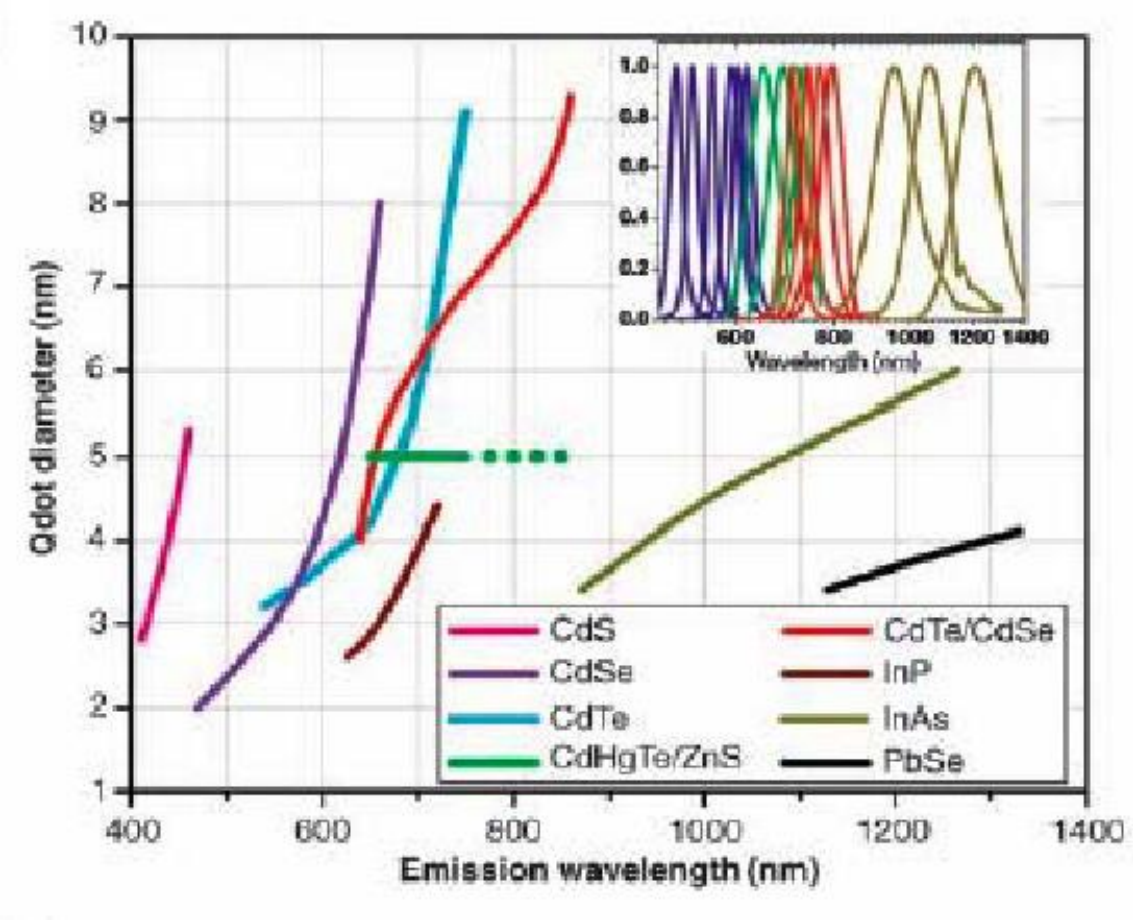
- Si/SiO_2
- $CdS/Cd(OH)_2$, CdSe/ZnSe, CdSe/ZnS,CdS/HgS/CdS, CdSe/CdS
- InAs/GaAs, InAs/InP, InAs/CdSe, InAs/ZnSe, InAs/ZnS

Changes to Bandgap





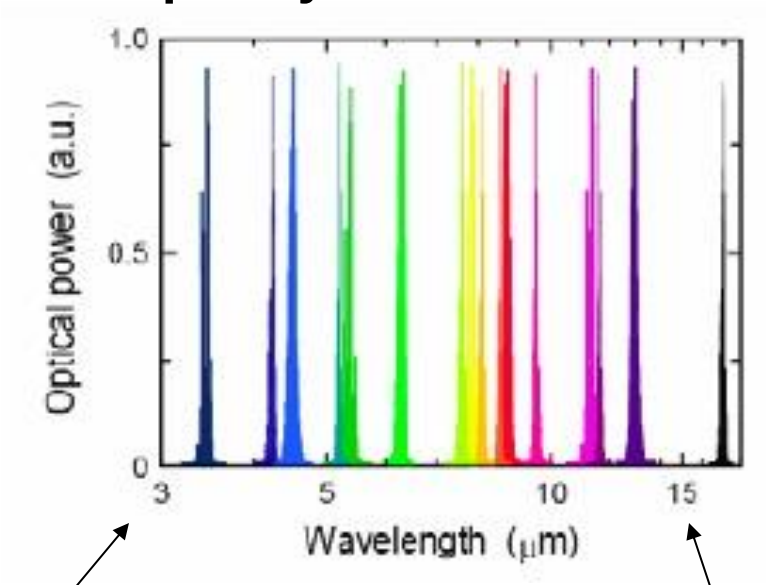
Wavelength Range



Quantum Confined Lasers

Semiconductor layers also exhibit quantum confinement and can be used to coherently add intra-band emission from multiple layers

QC lasers cover entire mid-infrared range (3.4 - 17 μm) by tailoring layer thickness of the same material



3,000 nm
3,333 cm^{-1}

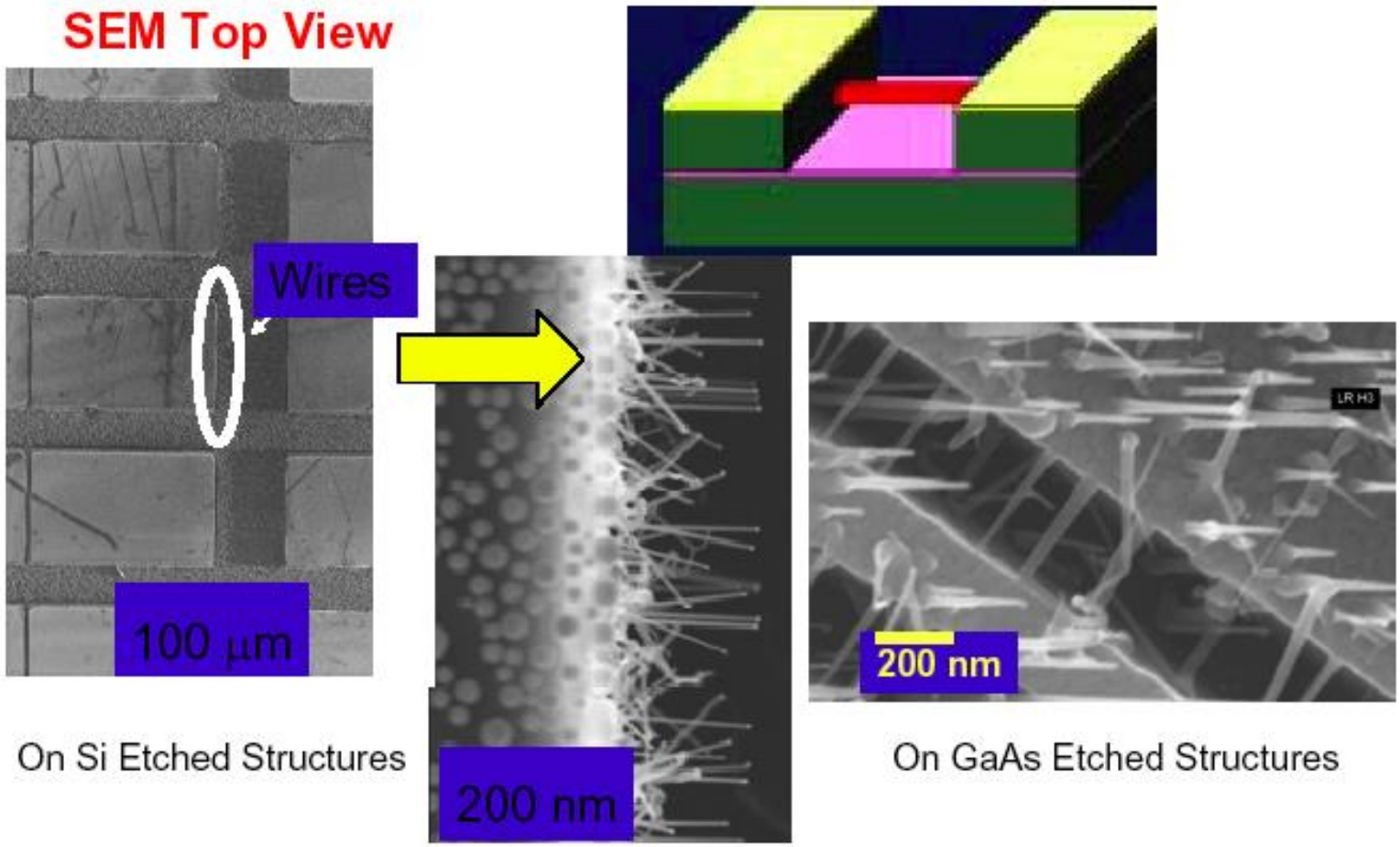
15,000 nm
667 cm^{-1}

In plastics

Colloidal solutions of CdSe/ZnS core-shell nanocrystals.

CdSe/ZnS core-shell nano-crystals in a polymer matrix

Nanoelectronics

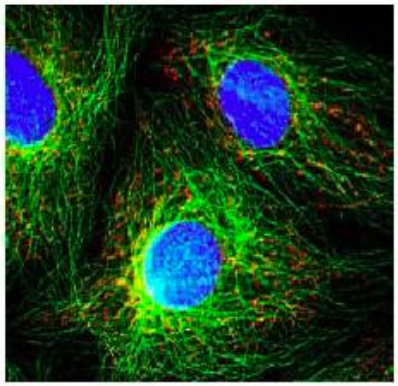


On Si Etched Structures

On GaAs Etched Structures

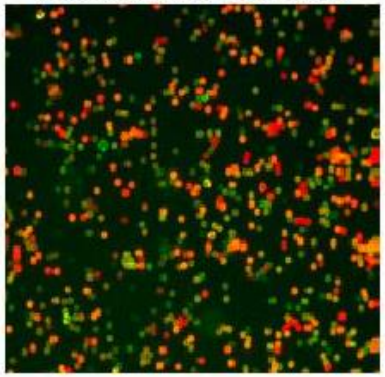
Biological Applications

Bio-labeling



- Detection reagents for microscopy
- DNA chips
- flow cytometry
- immunoassays, …

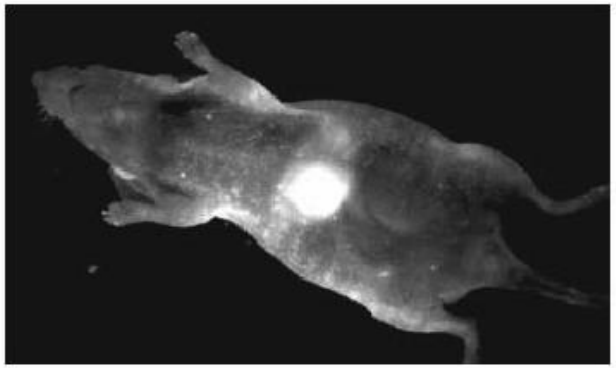
QBead™ encoded beads



Platform for Multiplexed assays:

- proteomics
- genotyping
- gene expression)

Future applications



- Live cell imaging
- *in vivo* imaging,…

Strong luminescence and photostability

Nanoparticles in Solar Cells

TiO_2 nanoparticles

Ru(II) complex to absorb photons and transfer electron to conduction band of TiO_2

I^-/I_3 redox relay

Nanoscale Confinement of Matter or Quantum-Confined Materials

Quantum-confined materials refer to structures which are constrained to nanoscale lengths in one, two or all three dimensions. The length along which there is Quantum confinement must be small than de Broglie wavelength of electrons for thermal energies in the medium.

Thermal Energy, $E = \frac{mv^2}{2} = kT$ **de Broglie Wavelength,** $\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2mkT}}$

Material	Electron effective mass	Hole effective mass
Group IV		
Si (4.2K)	1.08 m_e	0.56 m_e
Ge	0.55 m_e	0.37 m_e
III-V		
GaAs	0.067 m_e	0.45 m_e
InSb	0.013 m_e	0.6 m_e
II-VI		
ZnO	0.19 m_e	1.21 m_e
ZnSe	0.17m_e	1.44 m_e

For T = 10 K, the calculated λ in GaAs is 162 nm for Electrons and 62 nm for Holes

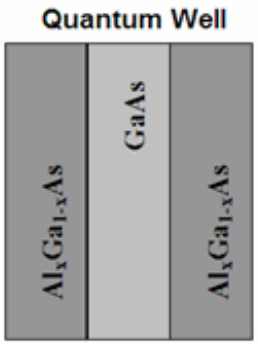
For effective Quantum-confinement, one or more dimensions must be less than 10 nm. Structures which are Quantum-confined show strong effect on their Optical Properties. Artificially created structures with Quantum-confinement on one, two or three dimensions are called, Quantum Wells, Quantum Wires and Quantum Dots respectively.

Density of States for Quantum-Confinement

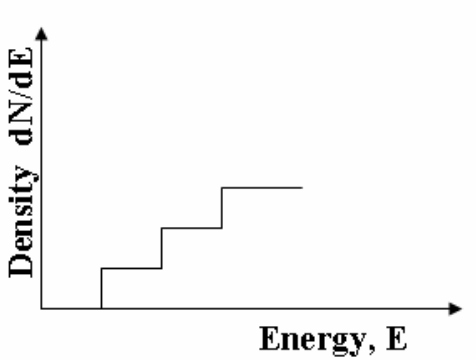
Quantum Well: 1D Confinement

Due to 1-D confinement, the number of continuous energy states in the 2-D phase space satisfy

$$2mE_{2D} = p_x^2 + p_y^2$$



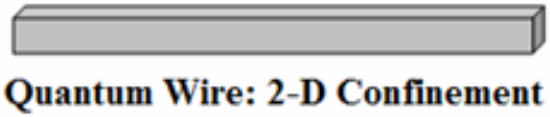
Density of States



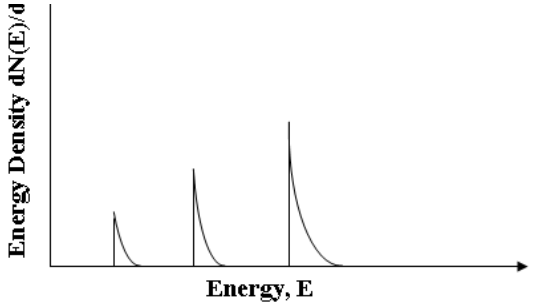
Quantum Wire: 2D Confinement

2D confinement in X and Z directions. For wires (e.g. of InP, CdSe). with rectangular cross-section, we can write:

$$E_{n_1,n_2,k_y} = E_C + \frac{n_1^2 h^2}{8m_e^* L_x^2} + \frac{n_2^2 h^2}{8m_e^* L_z^2} + \frac{h^2 k_y^2}{8\pi^2 m_e^*}$$



Quantum Wire: 2-D Confinement

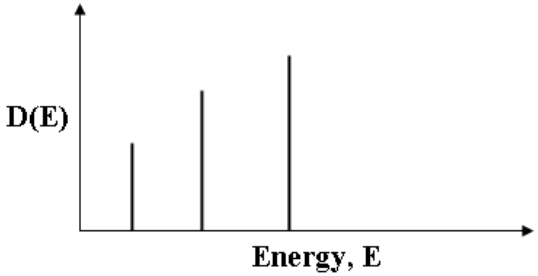


Quantum Dot: 3D Confinement

For a cubical box with the discrete energy levels are given by:

$$E_{n_1,n_2,n_3} = E_C + \frac{h^2}{8m_e^*}\left(\frac{n_1^2}{L_x^2} + \frac{n_2^2}{L_y^2} + \frac{n_3^2}{L_z^2}\right)$$

Quantum Dot: 3-D Confinement



Tópicos da Aula

- Rotas Sintéticas: Caminho Top-down (TD) e Caminho Bottom-up (BU)

- Síntese de Nanopartículas Metálicas: Parâmetros Termodinâmicos e Cinéticos

- Agentes Estabilizantes e Fatores que Alteram a Estrutura e Distribuição das Nanopartículas

Caminho Top-down

Síntese de Nanomateriais

Caminho Top-down (TD)

Em TD, a síntese é baseada em atrito ou desgaste de um material pré-selecionado.

Materiais ***bulk*** com grandes volumes podem ser desgastados até tamanhos reduzidos.

Exemplos:

- Nanolitografia, onde o laser é utilizado para produzir nanocavidades em um substrato.
- Síntese de NPs metálicas

Desvantagens (NPs metálicas**):** materiais não uniformes, baixa homogeneidade e alto grau de contaminação.

Caminho Bottom-up

Caminho Bottom-up (BU)

Dimensão do nanomaterial:

Ordem 0, 0D : pontos quânticos e nanopartículas (NP)

Ordem 1, 1D: nanofios, nanotubos, nanofitas, nanobastonetes, etc.

Ordem 2, 2D: filmes nanoestruturados (filmes finos)

Ordem 3, 3D: diamante, estruturas em blocos, matrizes porosas

Caminho Bottom-up: Materiais OD

Nanomateriais de dimensão 0 (zero)

Caminho Bottom-up (BU)

O caminho BU tem sido o mais utilizado, onde a síntese do nanomaterial 0D é baseada em dois processos progressivos, a **nucleação** e o **crescimento (também chamado de *subsequent growth*)**.

Nucleação: Por exemplo, métodos de **supersaturação** podem ser utilizados, onde a energia livre de formação do nanomaterial é proporcional a concentração do soluto precursor e inversamente proporcional ao volume atômico.

Surface Processes in Materials Growth & Processing

When a growing sample is nearly in equilibrium with vapor, nucleation and growth is mainly governed by *thermodynamics*

Homogeneous nucleation: solid (or liquid) clusters nucleated in a supersaturated vapor of pressure P_0

Thermodynamic driving force --- free energy change per unit volume of condensed phase:

$$\Delta G_v = -nkT \ln (P_0 / P_\infty)$$

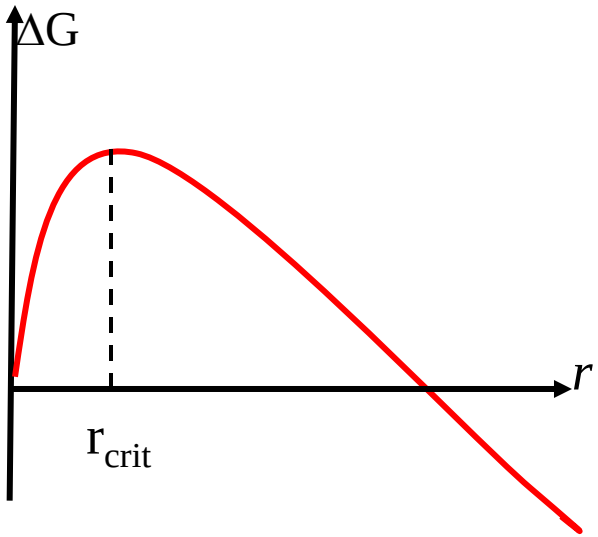
(P_∞: equilibrium vapor pressure over solid, n: solid atomic density)

Formation of spherical cluster of radius r: energy increase due to surface energy $4\pi r^2\gamma$, so total energy change:

$$\Delta G_{homo}(r) = (4\pi r^3/3)\Delta G_v + (4\pi r^2)\gamma$$

Critical cluster radius: $$r_{crit} = -\frac{2\gamma}{\Delta G_v}$$

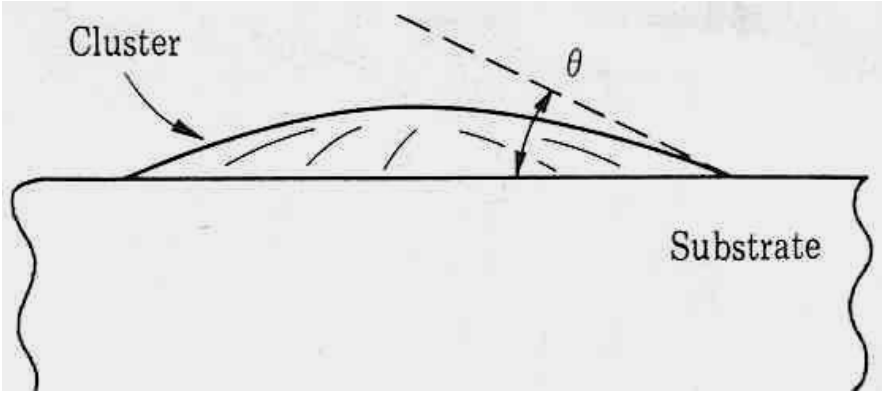
Energy barrier: $$\Delta G_{crit} = \frac{16\pi\gamma^3}{3\Delta G_v^2}$$



When $r > r_{crit}$, the cluster becomes thermodynamically stable

Heterogeneous nucleation: clusters are formed on a substrate (Cluster/substrate interface energy γ_{int}, substrate surface energy γ_s)

Truncated sphere of contact angle:



$$\theta = \cos^{-1}[(\gamma_s - \gamma_{int})/\gamma]$$

When $\gamma_s \geq \gamma_{int} + \gamma$, $\theta = 0$, *complete wetting*

When $\gamma_{int} \geq \gamma_s + \gamma$, $\theta = 180^\circ$, spherical ball without any wetting

Free energy barrier for stable nucleation:

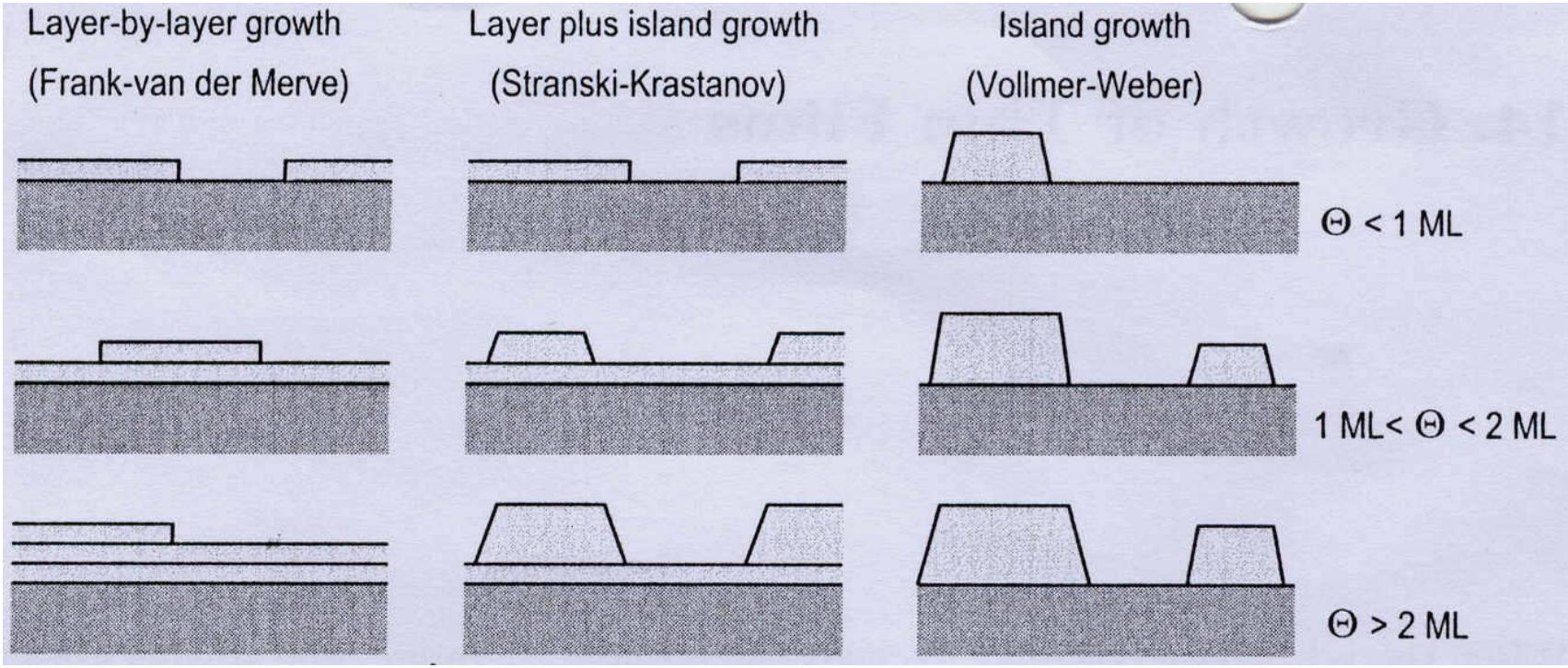
$$\Delta G_{het} = \Delta G_{homo}(2 + \cos\theta)(1 - \cos\theta)^2/4$$

Hetero-nucleation barrier is significantly lower than that of homo-nucleation in general!

Epitaxy: Crystalline film growth on a crystalline substrate in a unique lattice orientation relationship

Growth proceeds as atomic layers stacking up sequentially

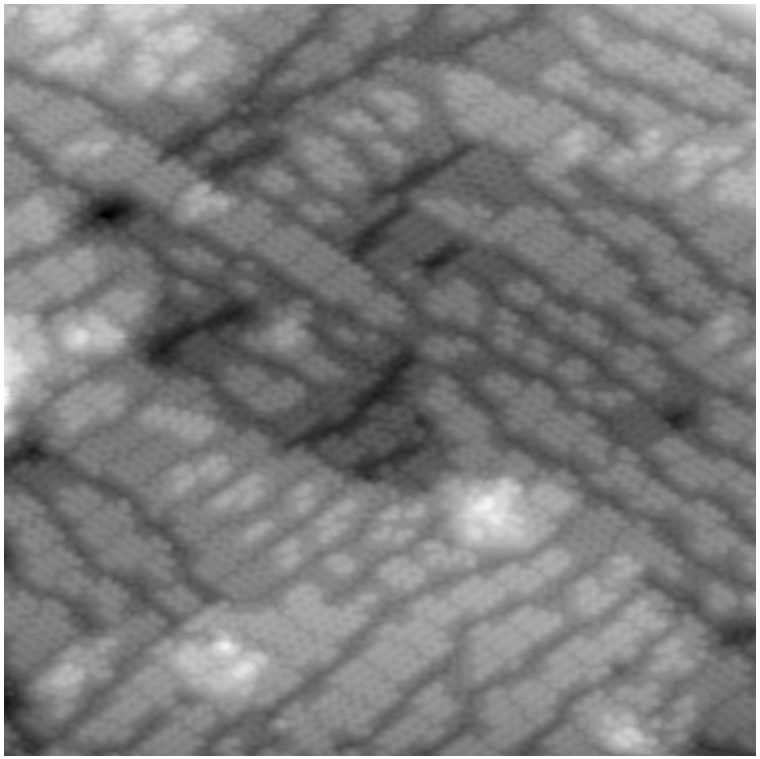
Three growth modes



$\gamma_{int} \leq \gamma_s - \gamma_f$ $\gamma_{int} \leq \gamma_s - \gamma_f$ with misfit $\gamma_{int} \geq \gamma_s - \gamma_f$

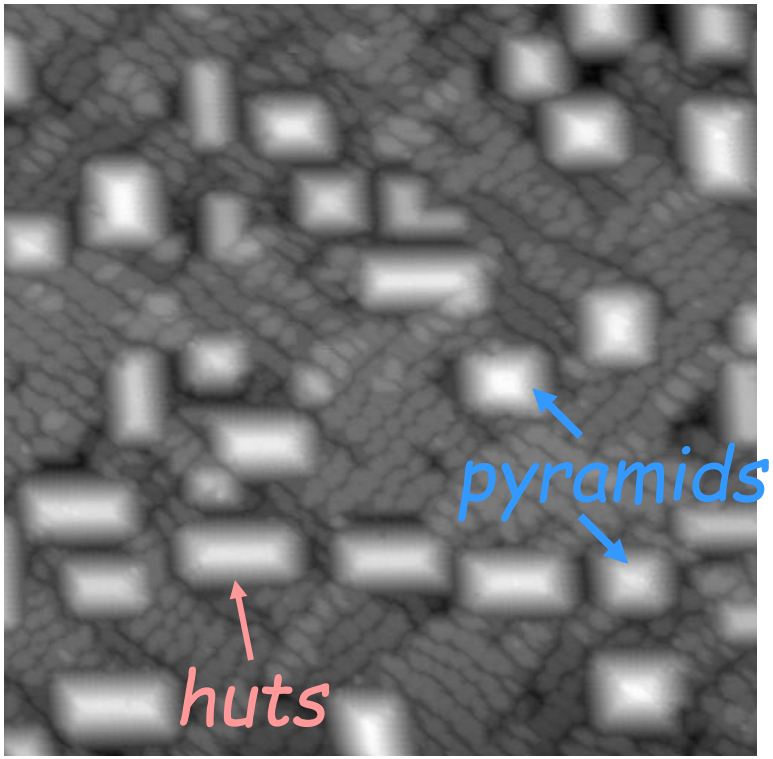
Stranski-Krastanov growth of Ge on Si(001)

4% lattice mismatch between Ge & Si



Wetting layer

~ 2.5 ML Ge, 475 °C, $(44nm)^2$

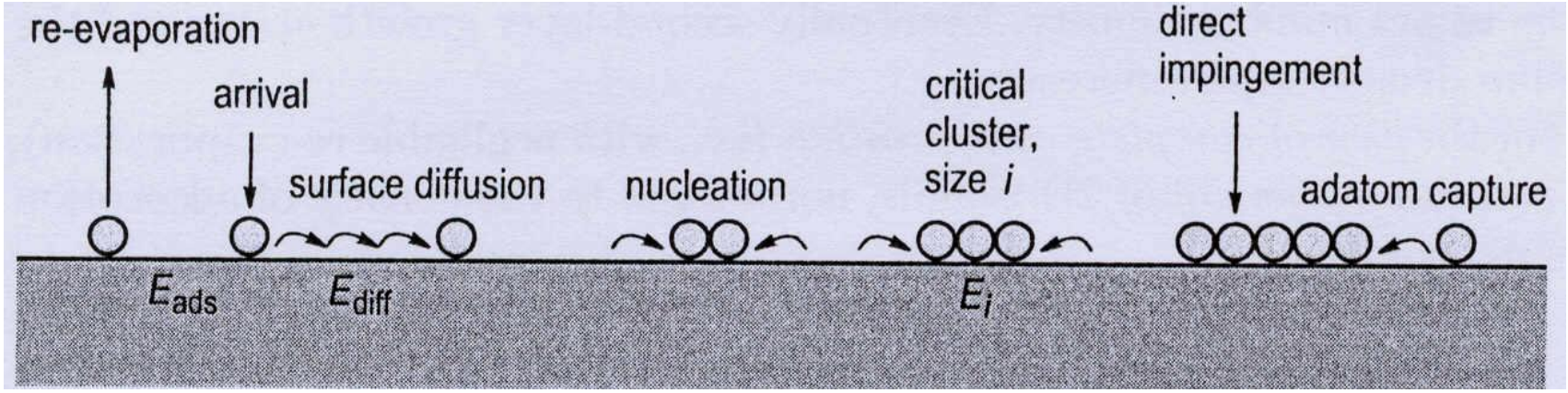


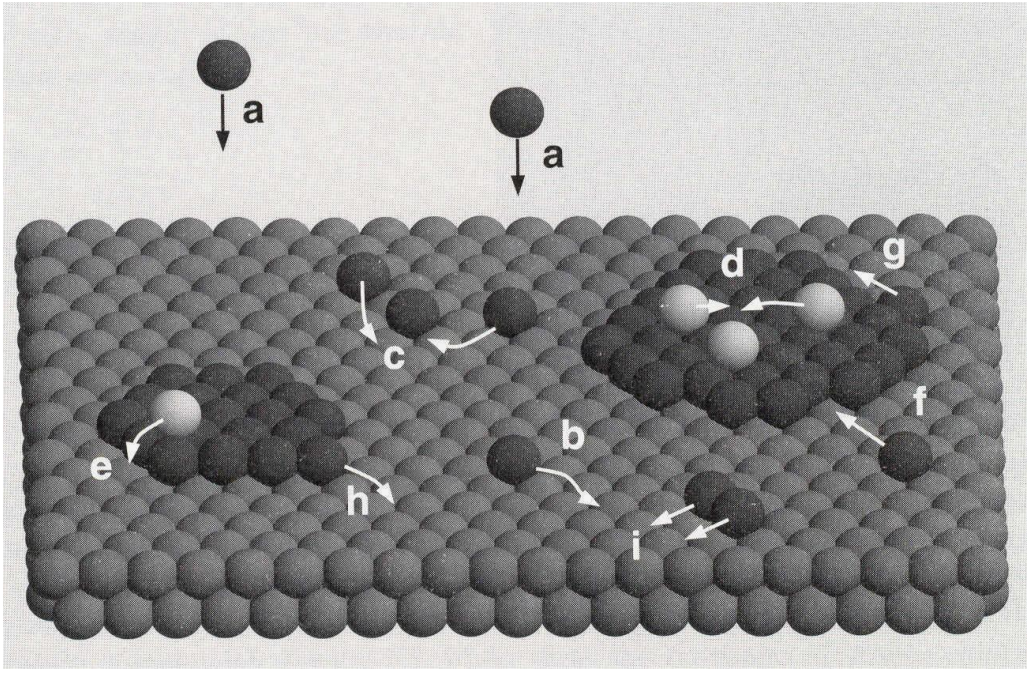
3D islands formation

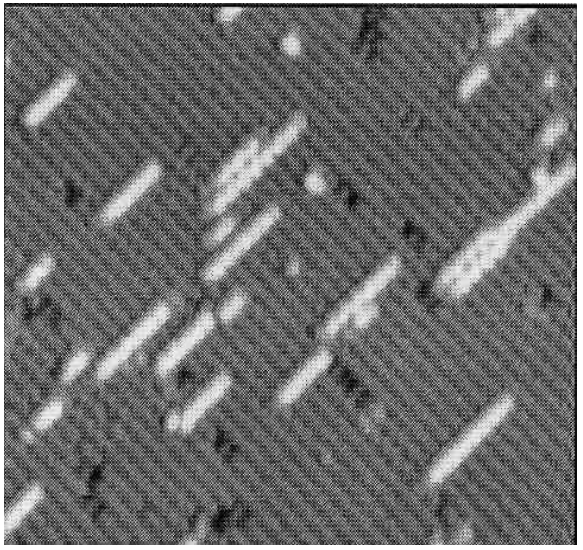
~ 3.5 ML Ge, 475°C, $(110nm)^2$

Atomic Processes in Nucleation & Growth

Adsorption, diffusion, incorporation, nucleation, desorption, coarsening

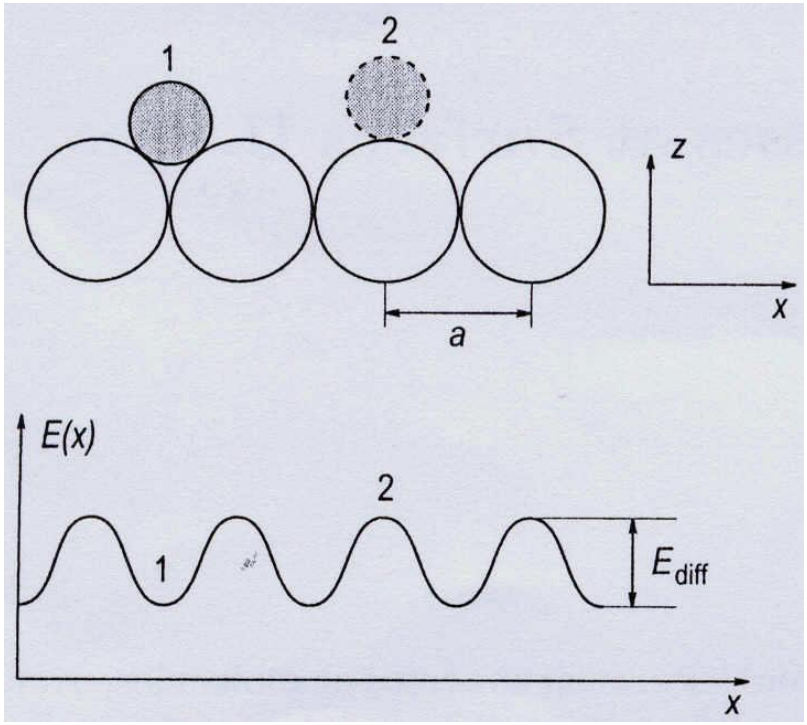






Si islands on Si(001)

Atomic Diffusion on Terrace

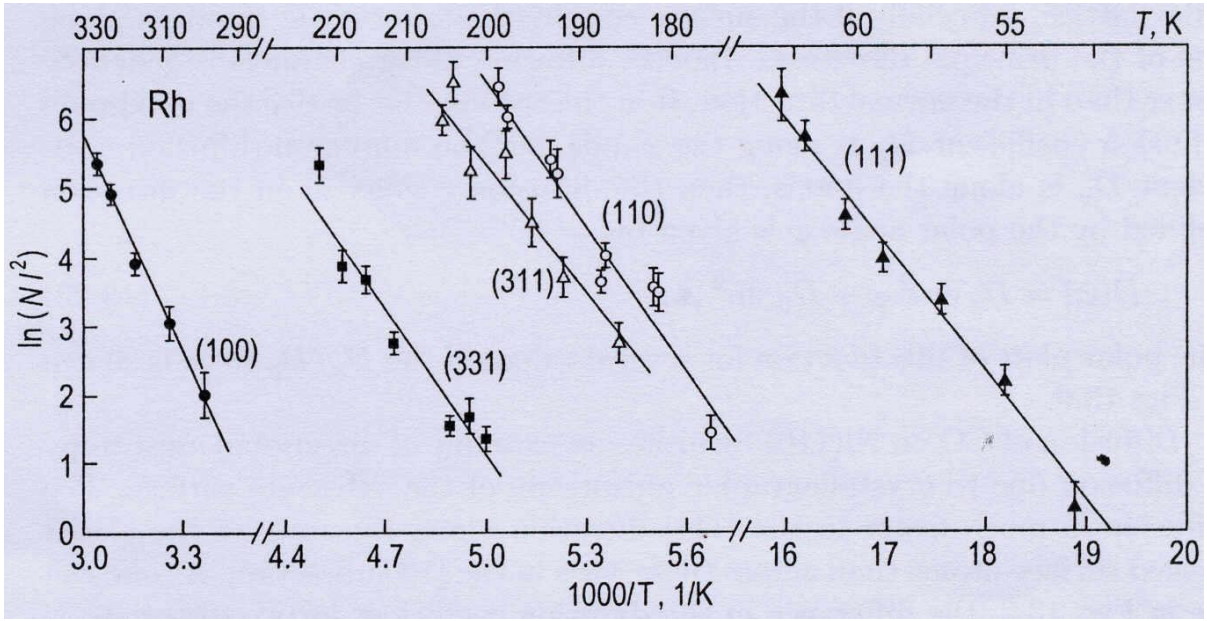


Thermal activated process, hopping frequency:

$$\nu = \nu_0 \exp(-E_{diff} / kT)$$

Diffusivity:

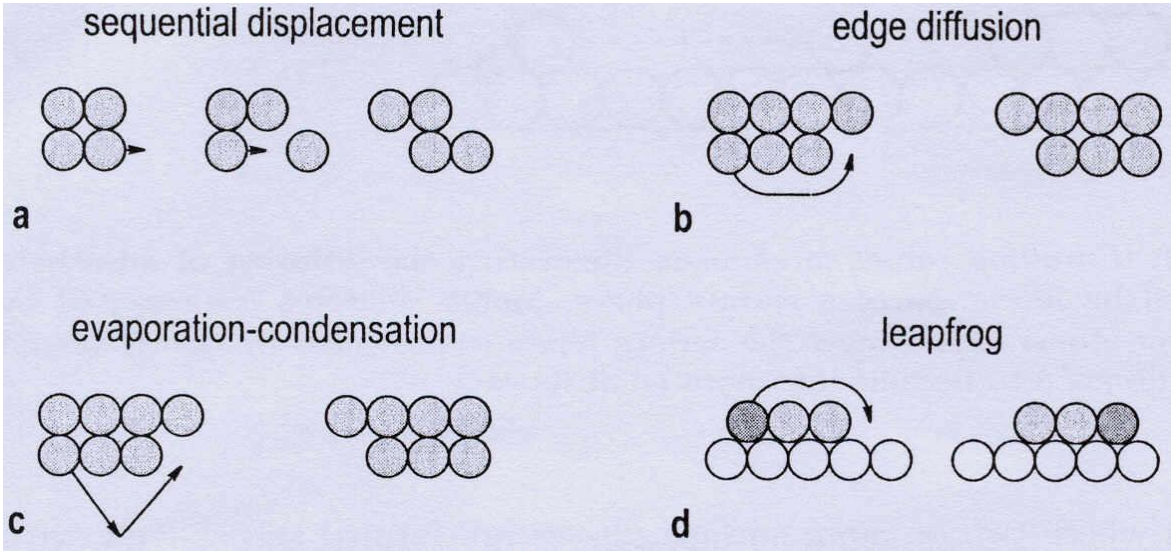
$$D = \frac{\nu_0 a^2}{4} \exp(-E_{diff} / kT)$$

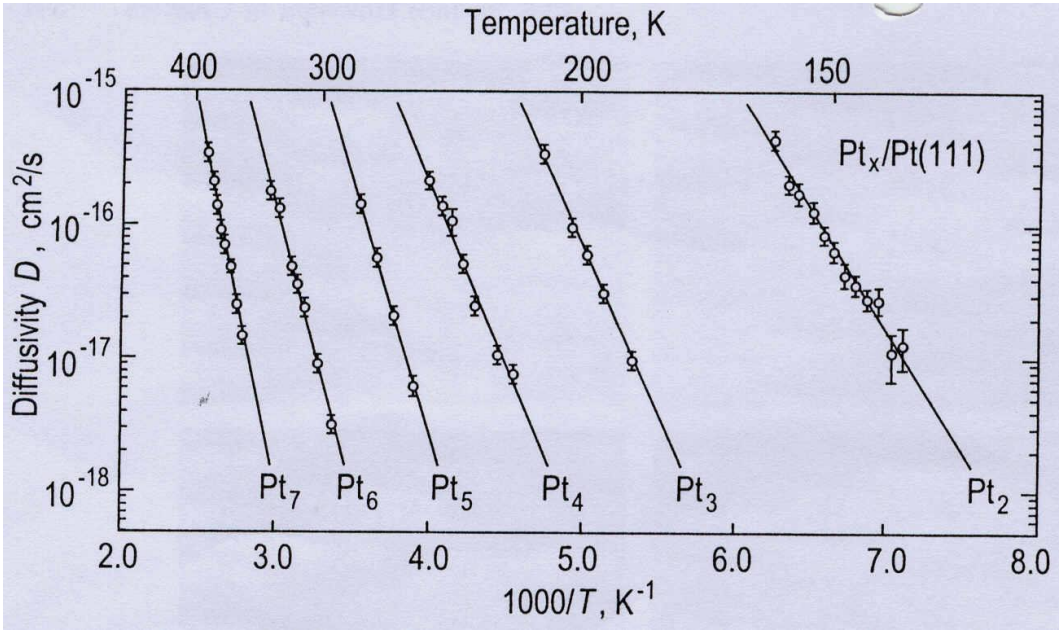


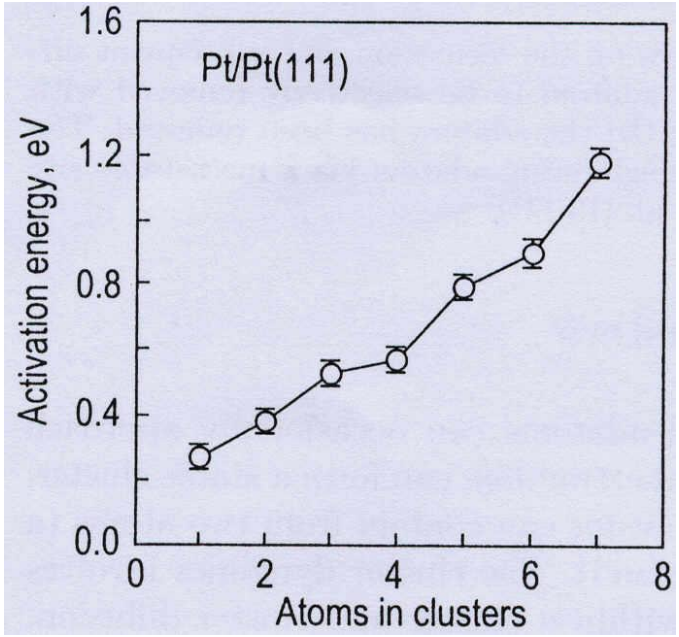
Anisotropic diffusion

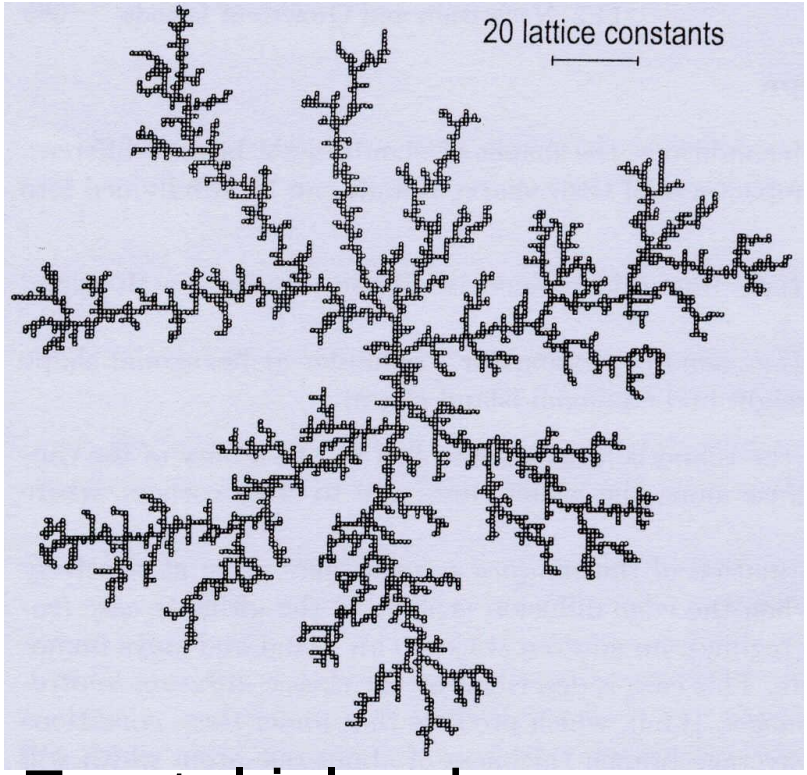
Diffusion barriers of Rh on Rh surfaces

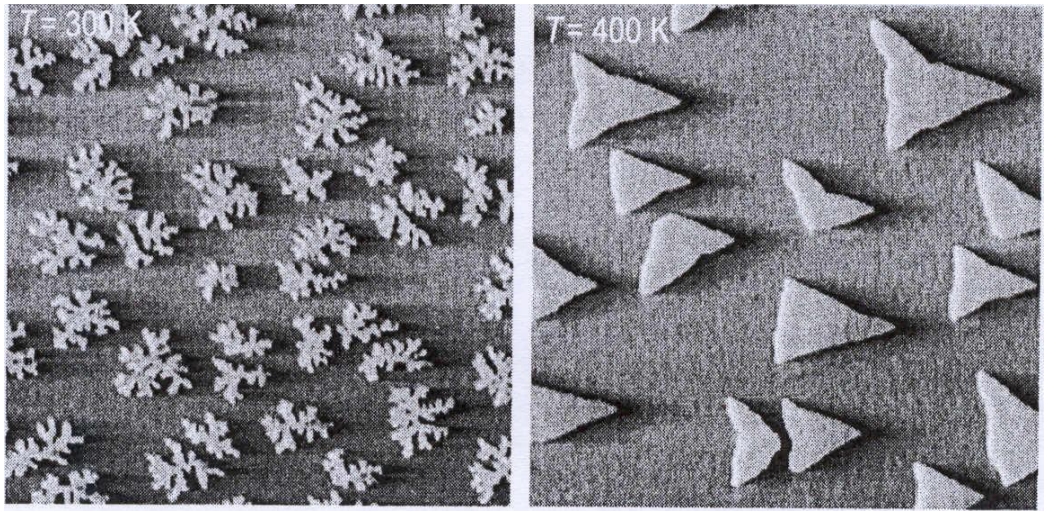
Migration of cluster on surface







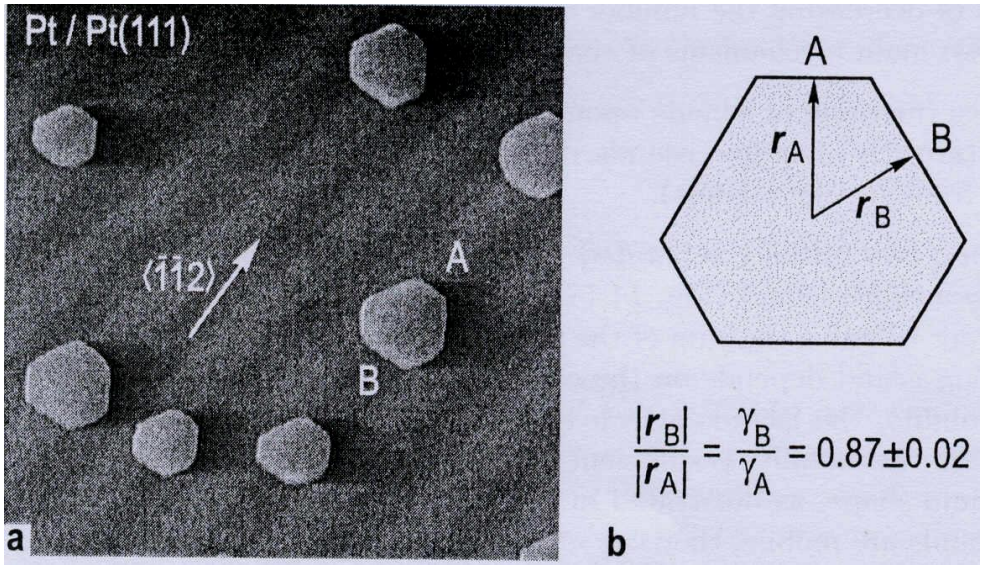




Islands grow in relatively compact shape at a raised T

Fractal islands obtained in hit-and-stick or diffusion-limited-aggregation (DLA) growth

Equilibrium island shape determined by step free energy anisotropy



Nanomateriais de dimensão 0 (zero)

$$\Delta G = -(KT/\Omega) \ln (C/C_0)$$

ΔG = variação da energia livre
K = constante de Boltzmann
T = temperatura
Ω = volume atômico
C = concentração do soluto
C_0 = concentração de equilíbrio

Nanomateriais de dimensão 0 (zero)

Crescimento

• ocorre em várias etapa e seu controle pode ser governado por **difusão**, **reações de superfície (adsorção).** Pode ainda haver processos de **incorporação irreversível**.

Nanomateriais de dimensão 0 (zero)

Difusão:

$$dr/dt = D(C\text{-}C_s)V_m/r$$

r = raio da nanopartícula
t = tempo
D = coeficiente de difusão
C = concentração do material no seio da solução
C_s= concentração do material na superfície
V_m = volume molar dos núcleos

Difusão

$$\mathrm{d}r/\mathrm{d}t = \mathrm{D}(C\text{-}C_s)V_m/r$$

$$\int r\mathrm{d}r = \int \mathrm{D}(C\text{-}C_s)V_m\mathrm{d}t$$

$$(r^2 - r_0^2)/2 = \mathrm{D}(C\text{-}C_s)V_m t,\ t_0 = 0$$

$$r^2 = 2\mathrm{D}(C\text{-}C_s)V_m t + r_0^2$$

$$2\mathrm{D}(C\text{-}C_s)V_m = K_D\ *$$

** Para isso temos que negligenciar as mudanças de concentrações no seio da solução*

Difusão

$$r^2 = K_D t + r_0^2$$

Consideremos duas partículas com diferentes raios iniciais. A medida que o tempo passa, a diferença entre os raios iniciais diminui, ou seja, começa haver o crescimento da partícula. Logo podemos escrever que:

$$\Delta r = \Delta r_0 \, r_0 / r$$

Combinando as duas equações anteriores temos que:

$$\Delta r = \Delta r_0 \, r_0 / \left(K_D t + r_0^2\right)^{1/2}$$

Difusão

$$\Delta r = \Delta r_0 \, r_0 / \, (K_D t + r_0^2)^{1/2}$$

$$\downarrow \Delta r, \uparrow r, \uparrow t$$

- Note que a diferença entre os raios das NPs diminui a medida que o tempo de ração passa e há um crescimento de ***r***

- Em casos onde os processos de formação de NPs são governados por difusão ocorre a formação de partículas com distribuição uniforme

Processo de superfície

• Reações de crescimento de NPs podem ser governadas por **processos de superfície**, ou seja, para casos onde não existe um limite difusional e pode-se aproximar que a concentração das espécies no seio da solução é a mesma na superfície.

$$dr/dt = k_m/r^2$$

onde k_mé a constante dependente da concentração das espécies

$$r^2 dr = k_m dt$$

$$1/r = 1/r_0 + k_m t$$

$$\Delta r = \Delta r_0 \, r^2/r_0^2$$

$$\boxed{\Delta r = \Delta r_0 / (1 - k_m r_0 t)^2}$$

Processo de superfície

$$\Delta r = \Delta r_0 / (1 - k_m r_0 t)^2$$

- ***Implicações matemáticas e condição de contorno:***

$$k_m r_0 t < 0$$

logo,

$$r < \infty$$

- para tempos prologados, a diferença entre os raios aumenta
- processos de superfície não favorecem a formação de nanoestruras mono-dispersas

Processo de superfície

- ***Implicações estruturais:***

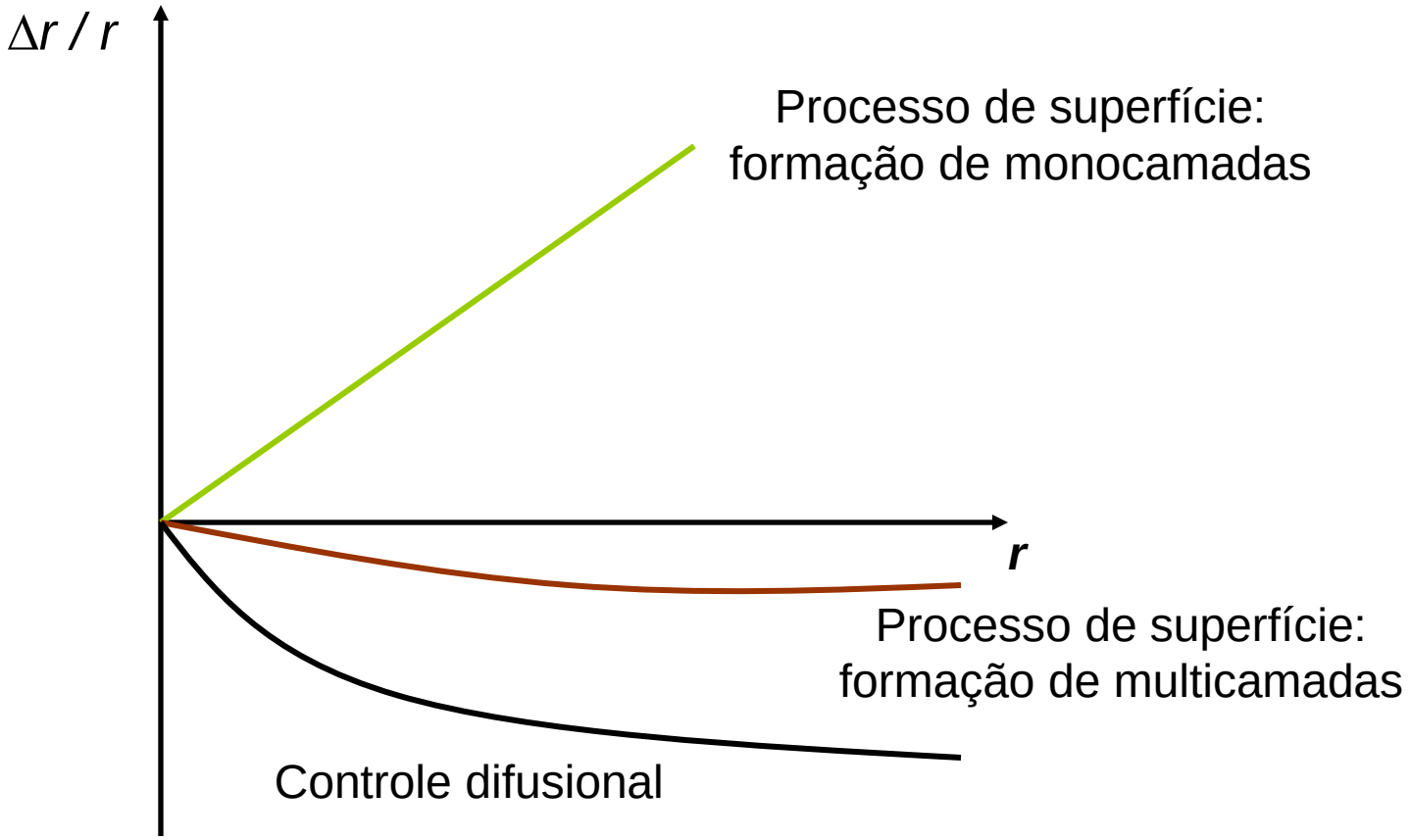
• Como as reações de superfície ocorrem com alta concentração de espécies ao redor da superfície, pode ocorrer a formação de camadas subsequentes sem que a haja a completa formação da primeira camada. Esse processo é chamado de **crescimento poli-nuclear.**

• Neste caso, a velocidade de crescimento só depende do número de choques existentes, ou seja, pode-se relacionar o crescimento em função da temperatura:

$$\mathrm{d}r/\mathrm{d}t = k_{\mathrm{p}}$$

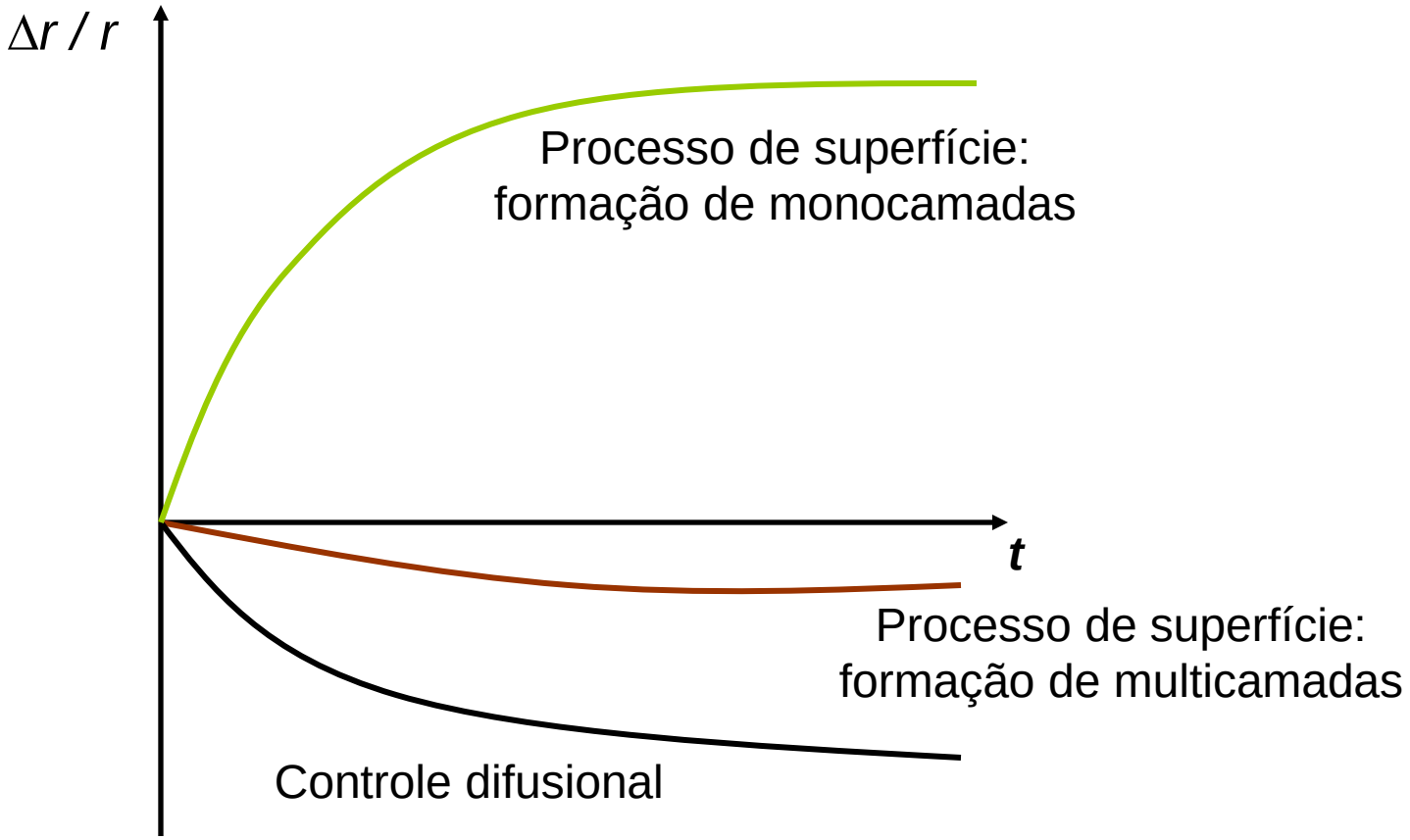
Crescimento de nanopartículas

$\Delta r / r$ *vesus* r



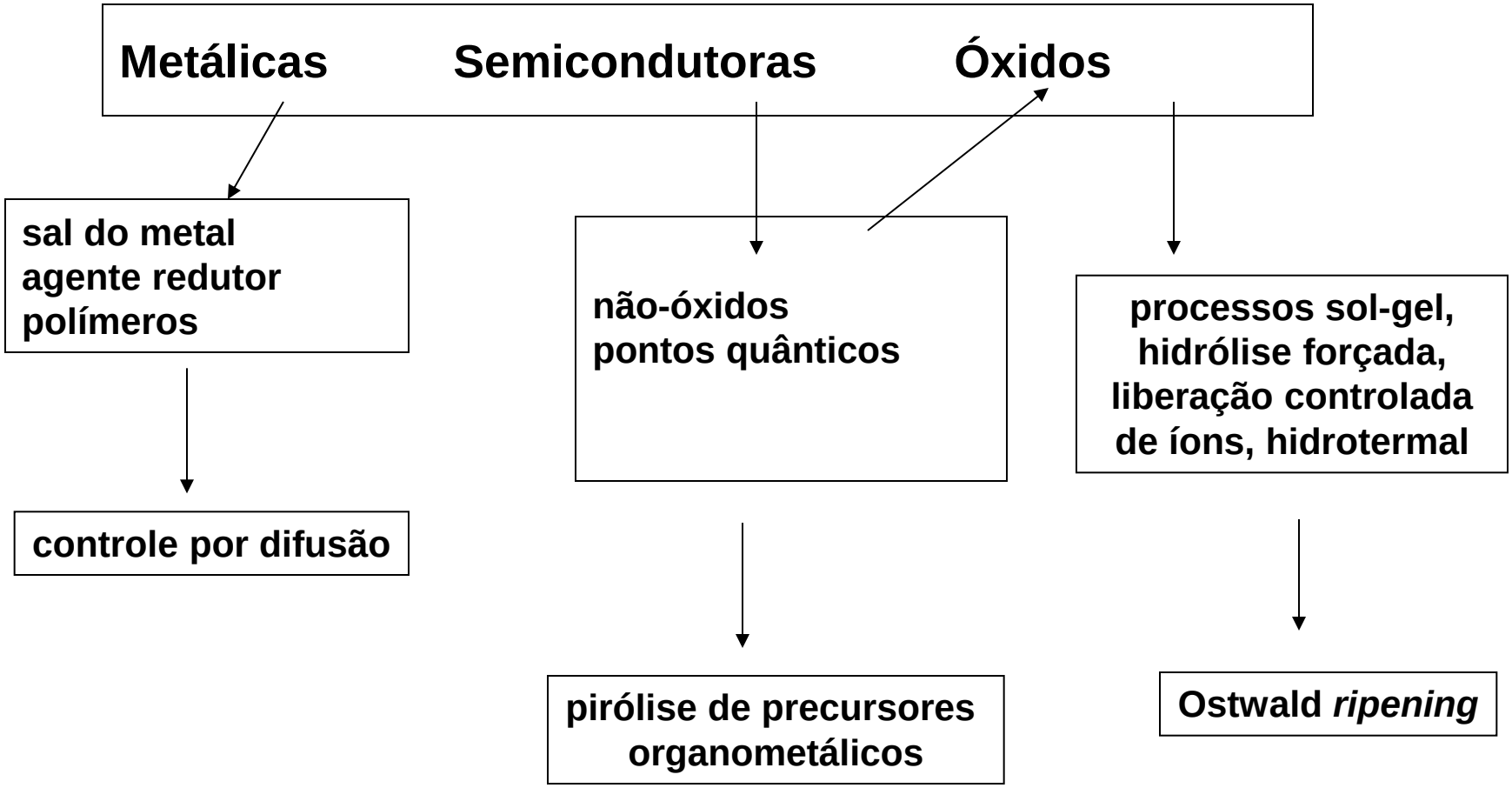
Crescimento de nanopartículas

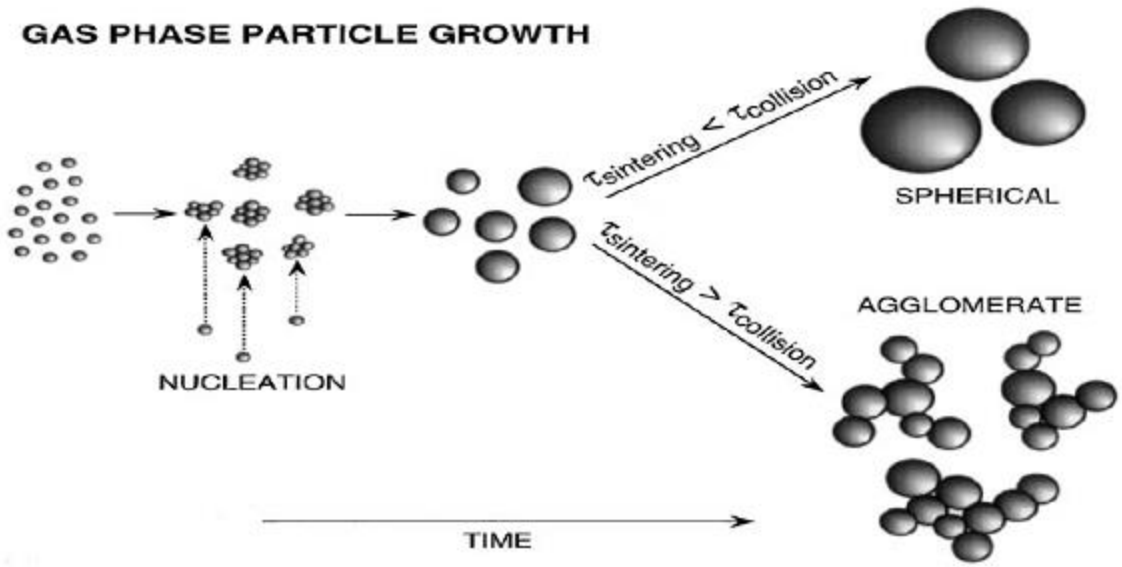
$\Delta r / r$ *vesus* t



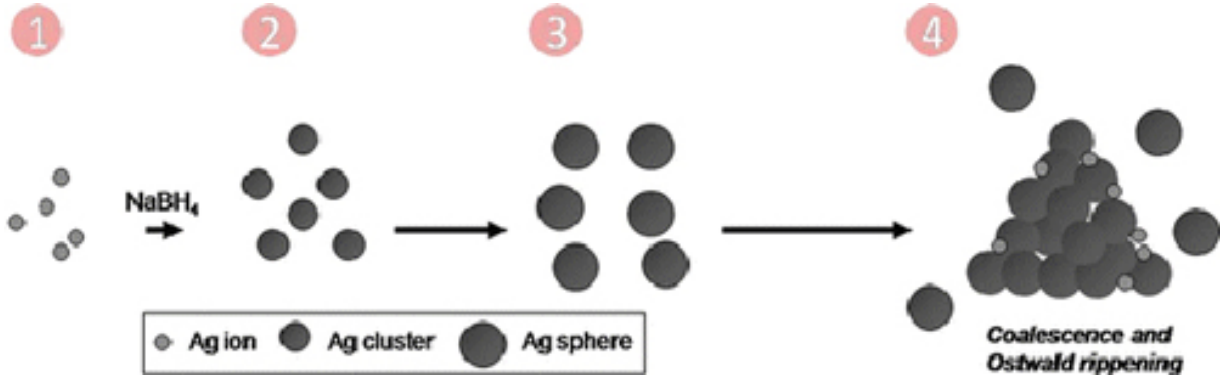
Crescimento de nanopartículas

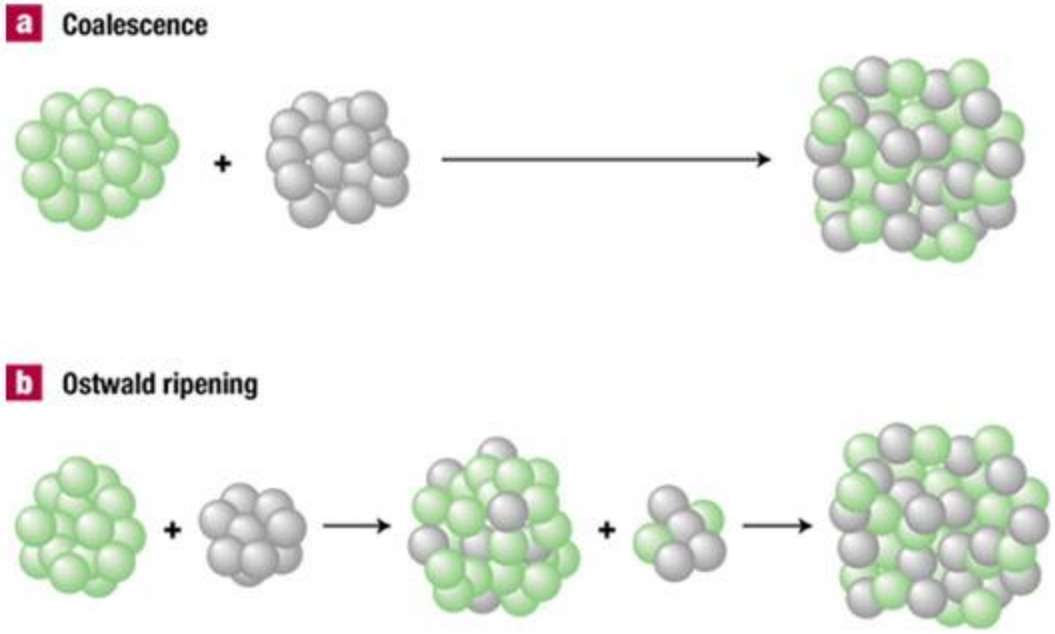
Classes de NPs





$\tau_{sintering} < \tau_{collision}$ => **Spherical particle,**
$\tau_{sintering} > \tau_{collision}$ => **Agglomerate.**


1
2
3
4
NaBH4
Ag ion
Ag cluster
Ag sphere
Coalescence and
Ostwald rippening


a Coalescence
b Ostwald ripening

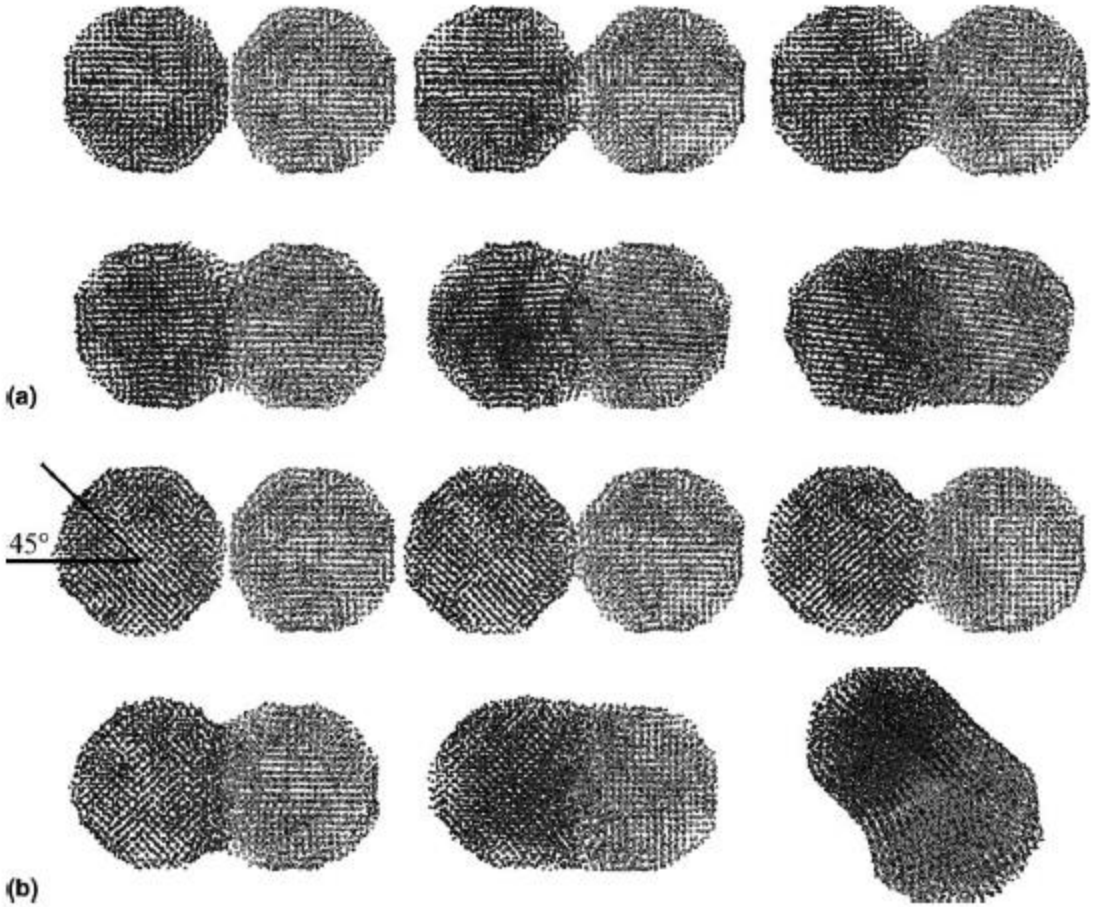
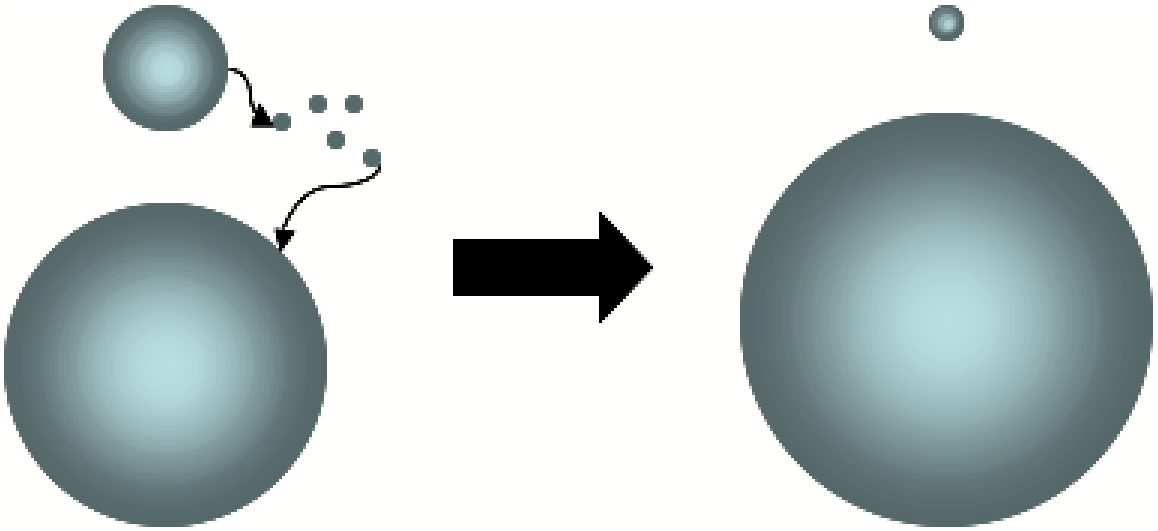
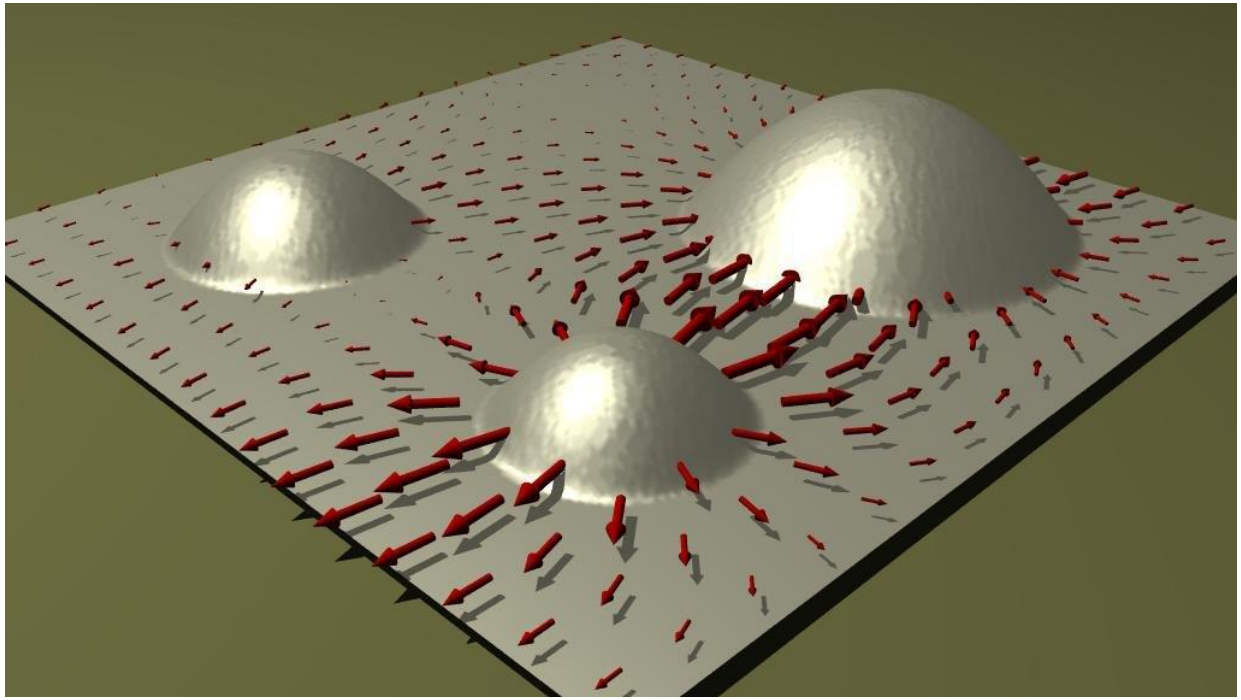


Fig. 10. Comparison of the sintering of two nanoparticles with a radius of 22.3 Å and an initial temperature of 938 K, between two different initial lattice orientations. The time distance between two frames is not constant.





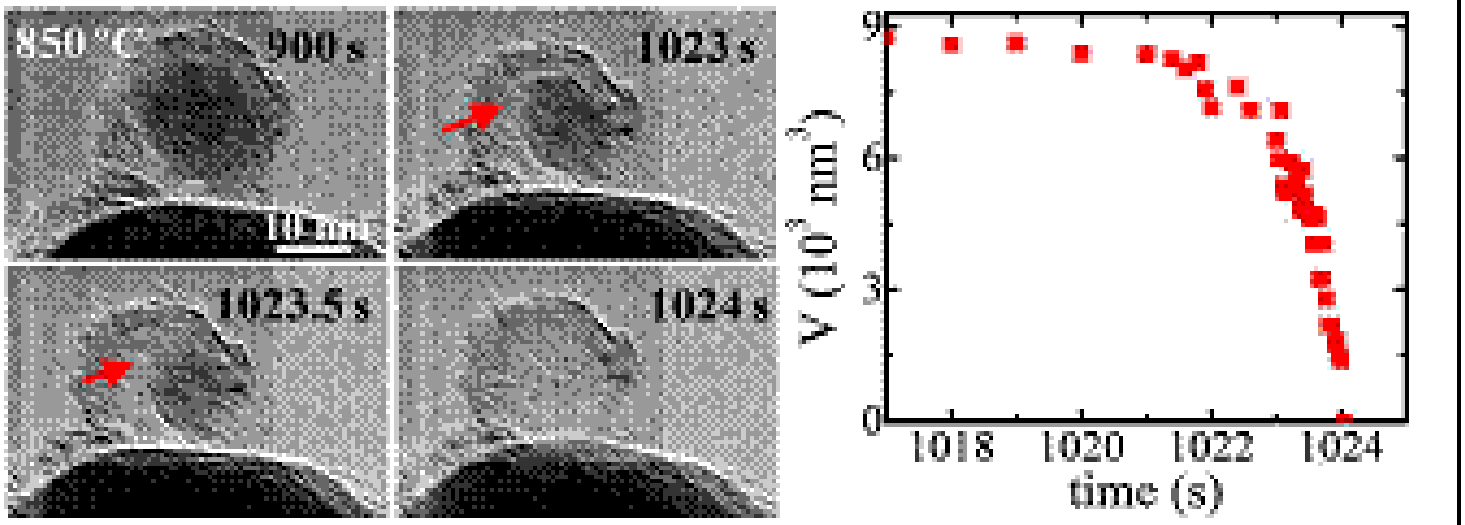
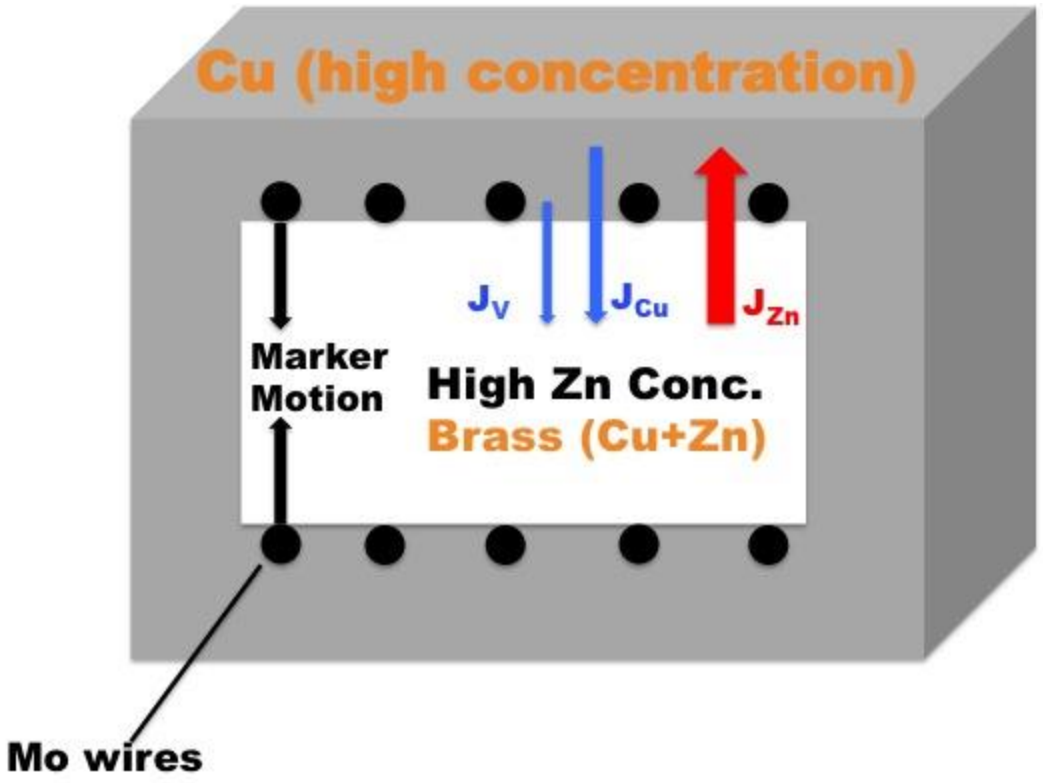


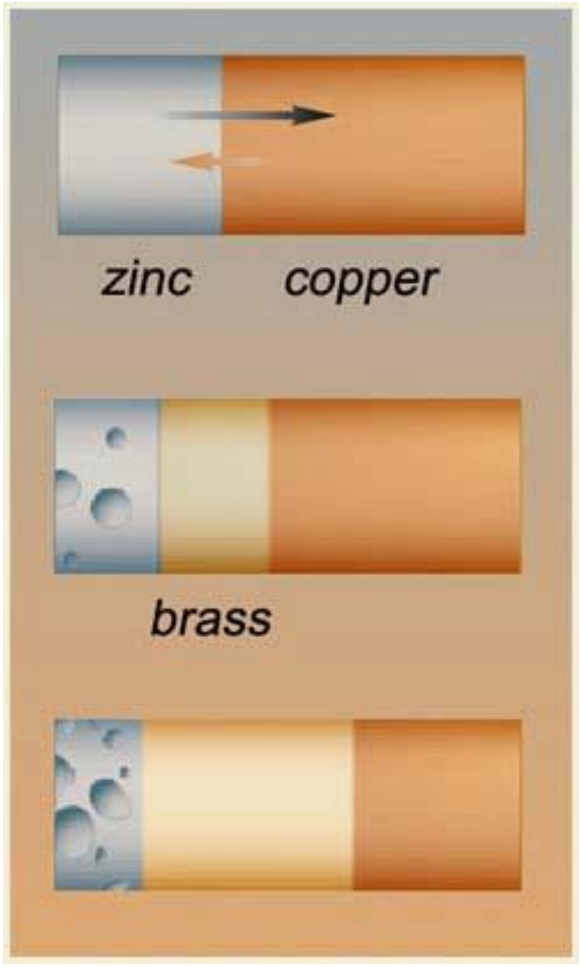
Figure 1. Ostwald ripening of TiO_2 cores within carbon shells. (Left) *In situ* TEM images acquired at 800 °C. (Right) Plot of core volume (V) vs. time.

Kirkendall effect diffusion

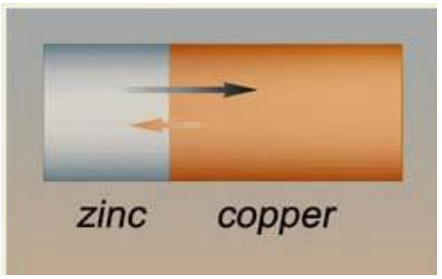


The Kirkendall effect is the motion of the boundary layer between two metals that occurs as a consequence of the difference in diffusion rates of the metal atoms. The effect can be observed for example by placing insoluble markers at the interface between a pure metal and an alloy containing that metal, and heating to a temperature where atomic diffusion is possible; the boundary will move relative to the markers.

Kirkendall effect diffusion



Kirkendall effect diffusion



$$\tilde{D} = x_A D_B^C + x_B D_A^C$$

$$= [x_A D_B + x_B D_A] \{1 + \frac{\partial \ln \gamma_A}{\partial \ln x_A}\} = [x_A D_B + x_B D_A] \{1 + \frac{d \ln \gamma_B}{d \ln x_B}\} \qquad (2)$$

This is referred to as ***Darken's equation***.

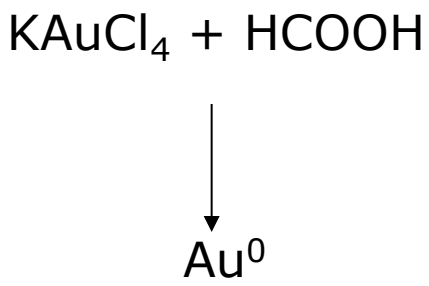
With Darken's equation, the diffusion coefficient of A and B are correlated together, reflecting the 'cooperative' diffusion in substitutional alloys, for example as illustrated above in Kirkendall experiment performed on the zinc-copper alloy diffusion. The interdiffusion coefficient $\tilde{D}$ is determined by both the diffusion coefficient of A and B, whereas in the case of interstitial diffusion as discussed in the last a few lectures, the diffusion coefficient as used in the Fick's law is determined only by that of A or B.

Síntese de NPs metálicas

• **Via húmida:** Geralmente se utiliza um **sal metálico** na presença de um **agente redutor** e um **estabilizador**

• Agentes redutores são compostos que “doam elétrons” para um agente oxidante, que no caso, podem ser os metais de transição.

• Ex.: ácido fórmico na presença de sal de ouro



Síntese de NPs metálicas

• **Influência do agente redutor**

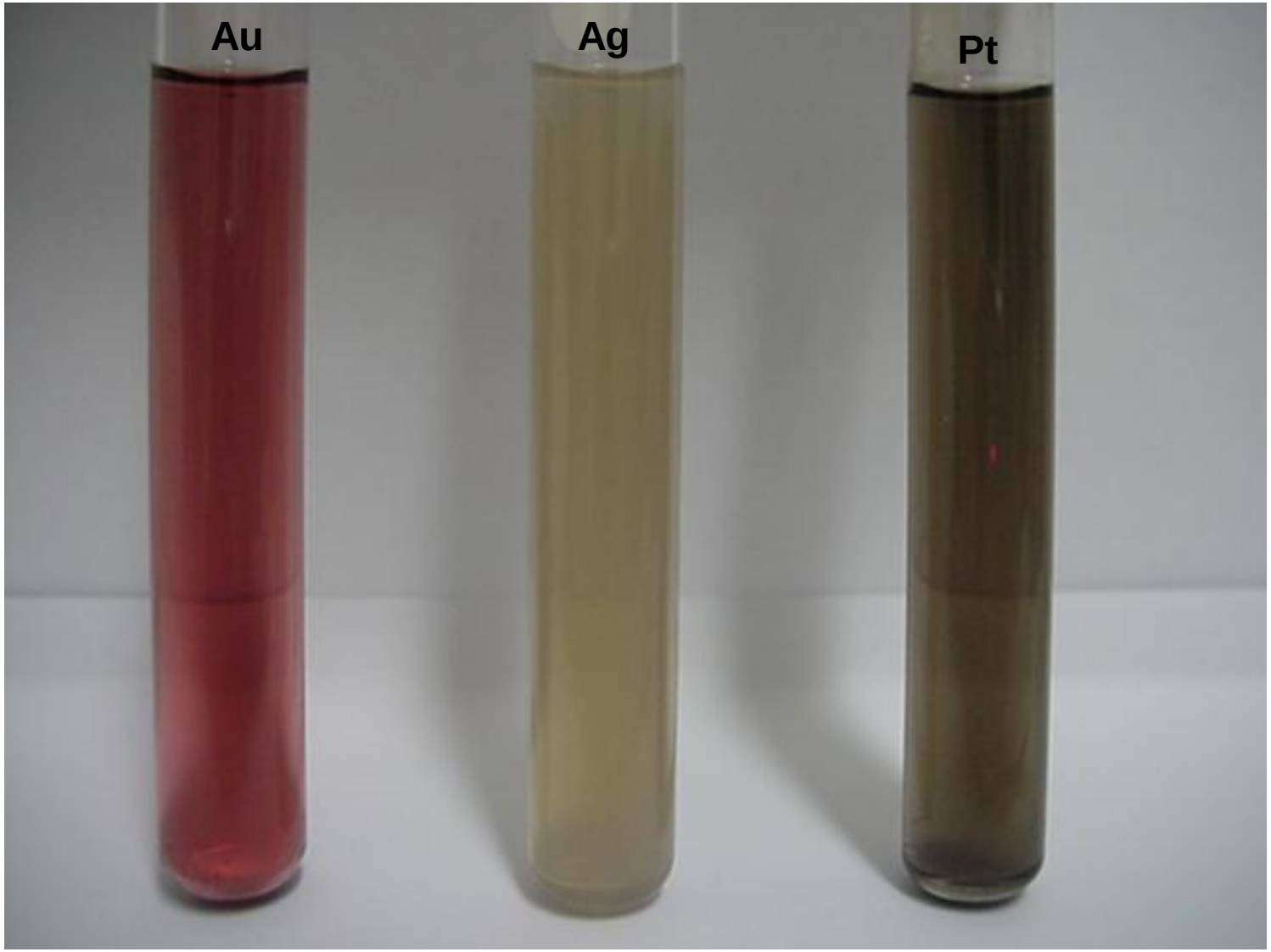
• Em geral um **agente redutor forte** promove um reação química rápida e favorece a formação de **partículas menores**.

• **Agentes redutores fracos** promovem um cinética lenta e a distribuição de tamanho pode ser **maior ou menor**. A explicação é que uma reação lenta promove a formação de núcleos secundários, formando assim, núcleos de tamanhos diferenciados. Por outro lado, se não há nucleação secundária e se a reação é limitada por difusão, estreitas distribuição de partículas podem ser obtidas.

• Exemplos de agentes redutores comummente usados na preparação de NPs metálicas: ácido fórmico, ácido acético, boroidreto de sódio, acetatos, ácido cítrico, hidrazina (N_2H_4)etc.

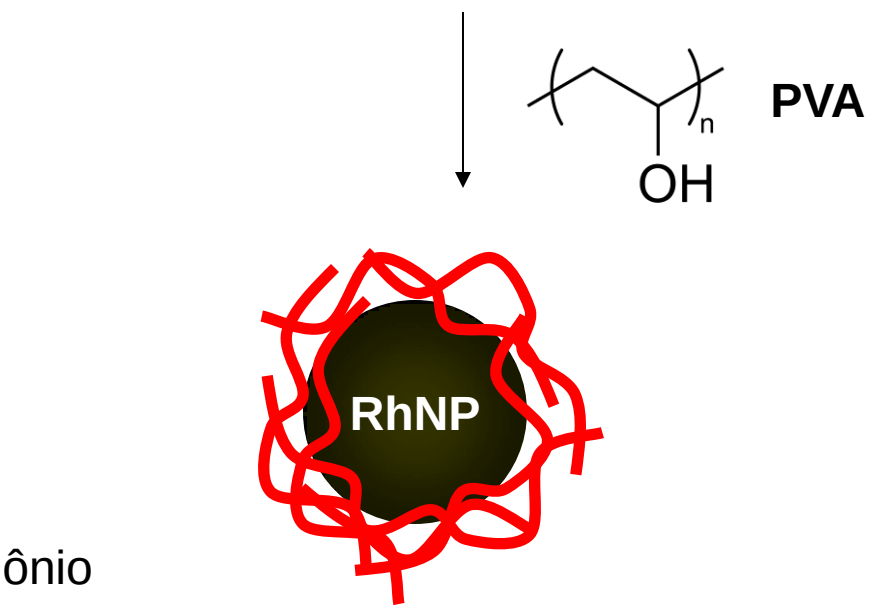
Etapas de Síntese de NPs metálicas via Botton-up

Estabilidade em Suspensão



Síntese de NPs metálicas: estabilização com polímeros

Exemplo: RhNP em solução

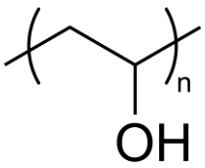


Condições:

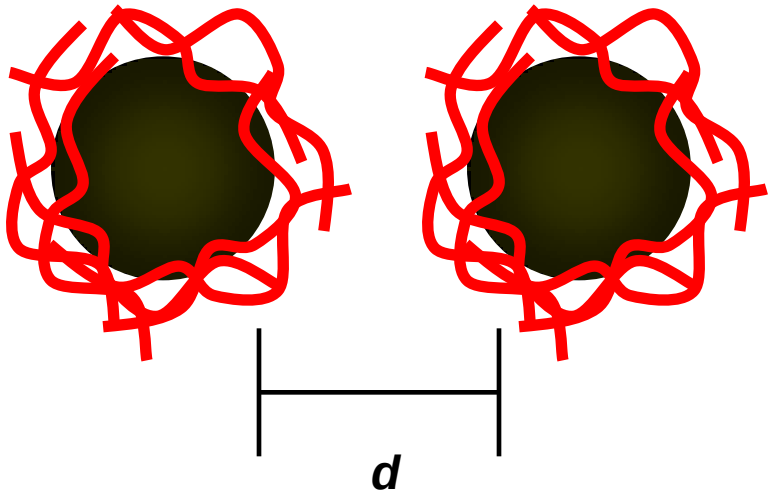
- Refluxo
- Atmosfera de argônio
- 16h

Síntese de NPs metálicas: estabilização com polímeros

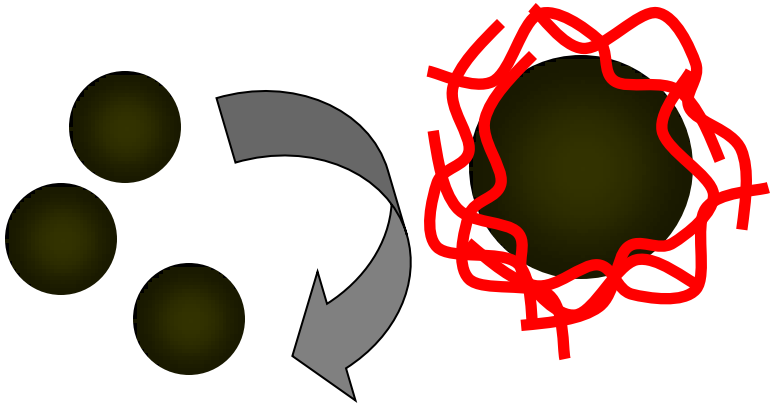
Função do PVA



Aglomeração

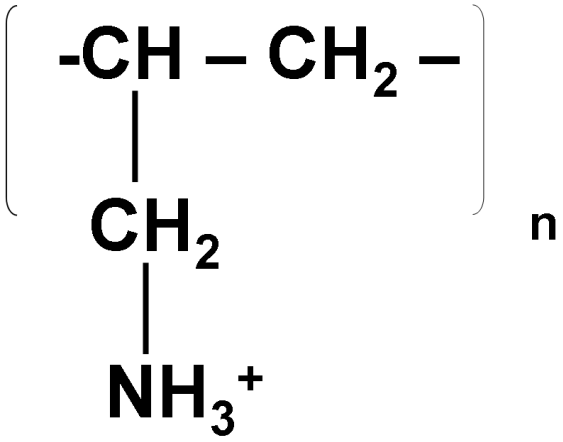


Barreira

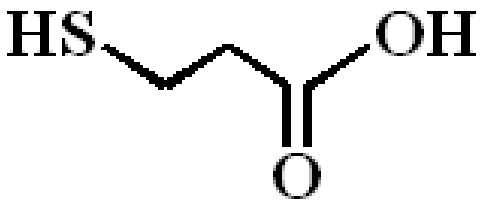


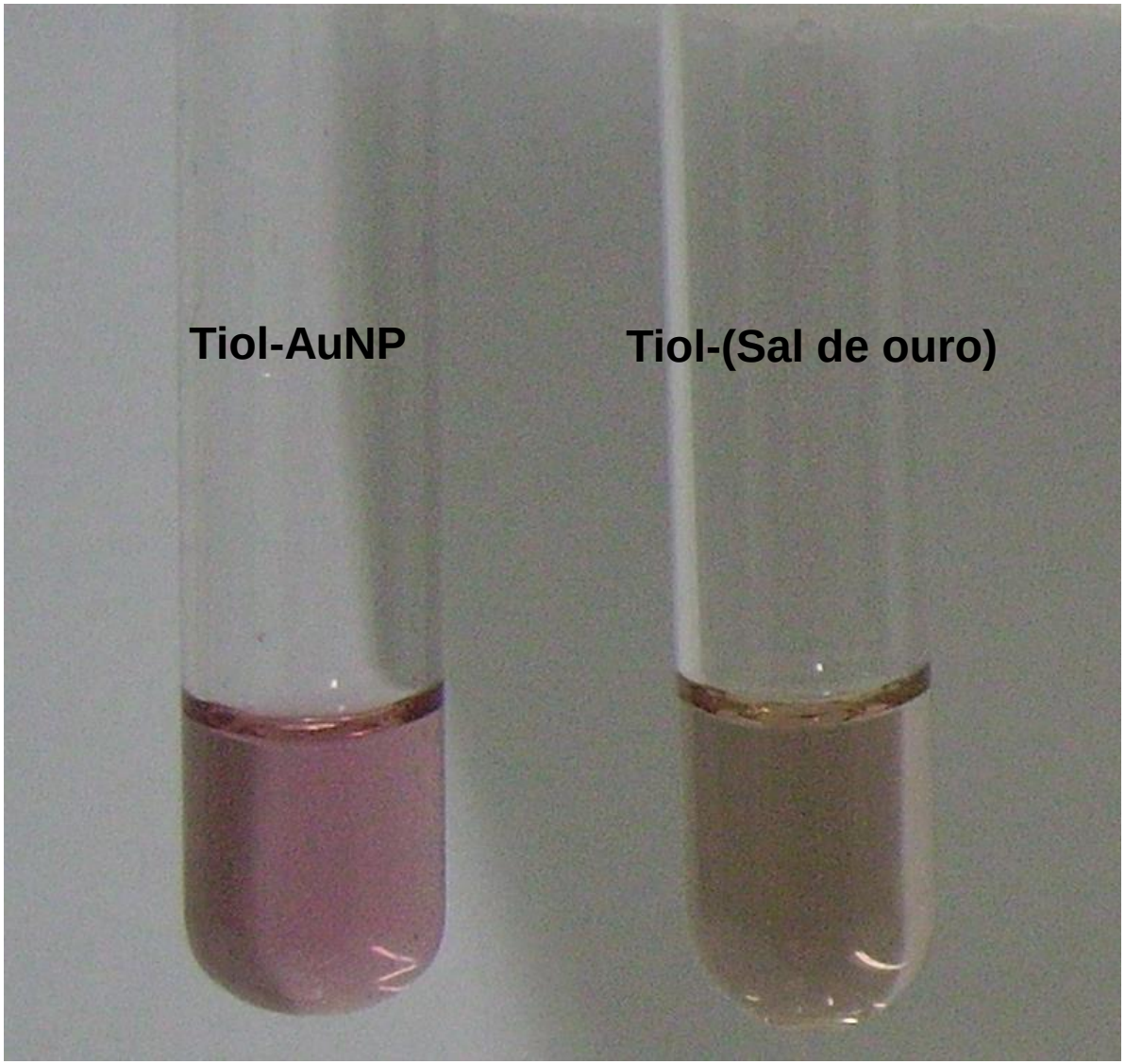
Estabilizadores

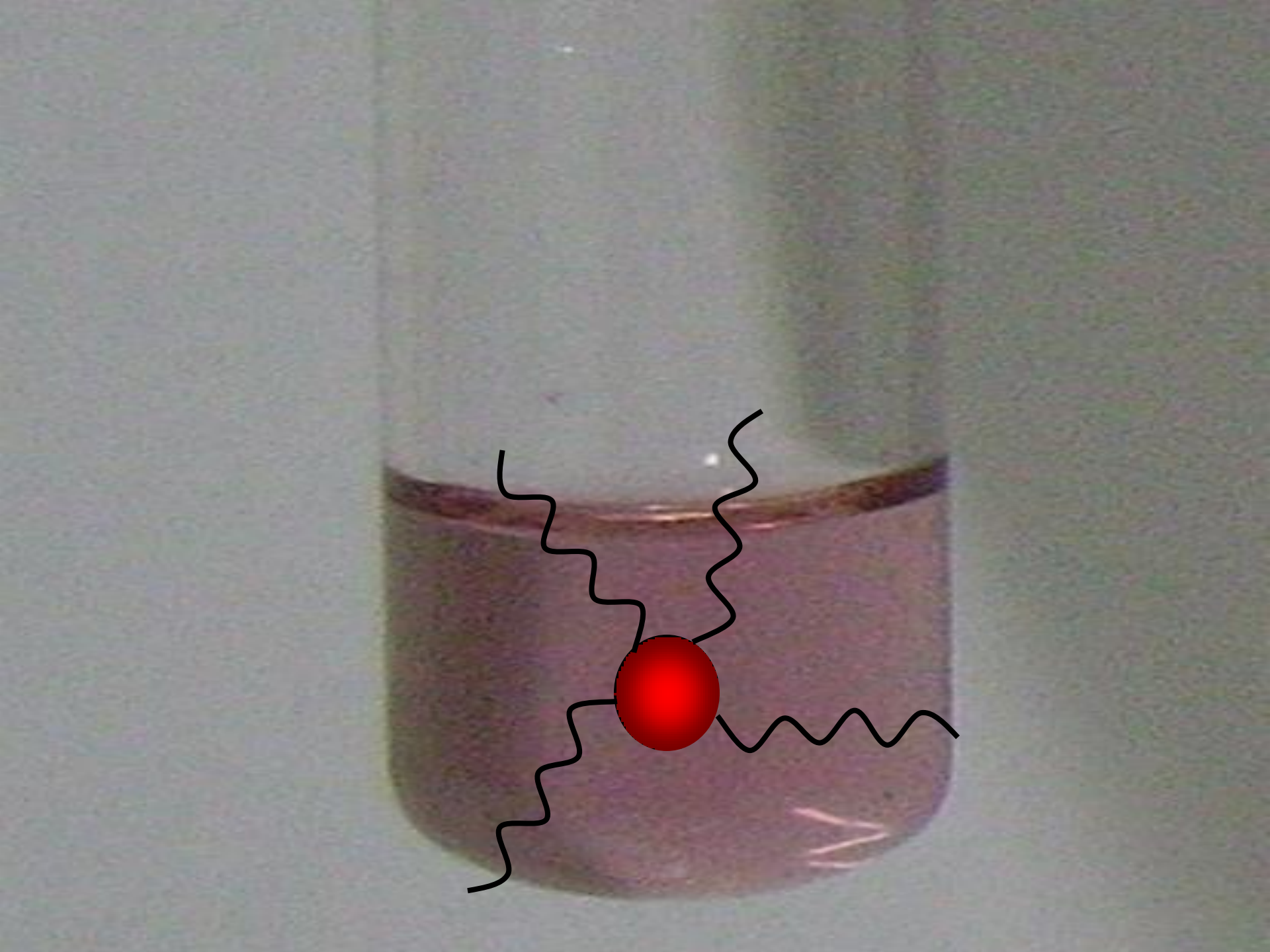
poly(allylamine hydrochloride)
(PAH)



3-mercaptopropionic acid
(3-AMP)

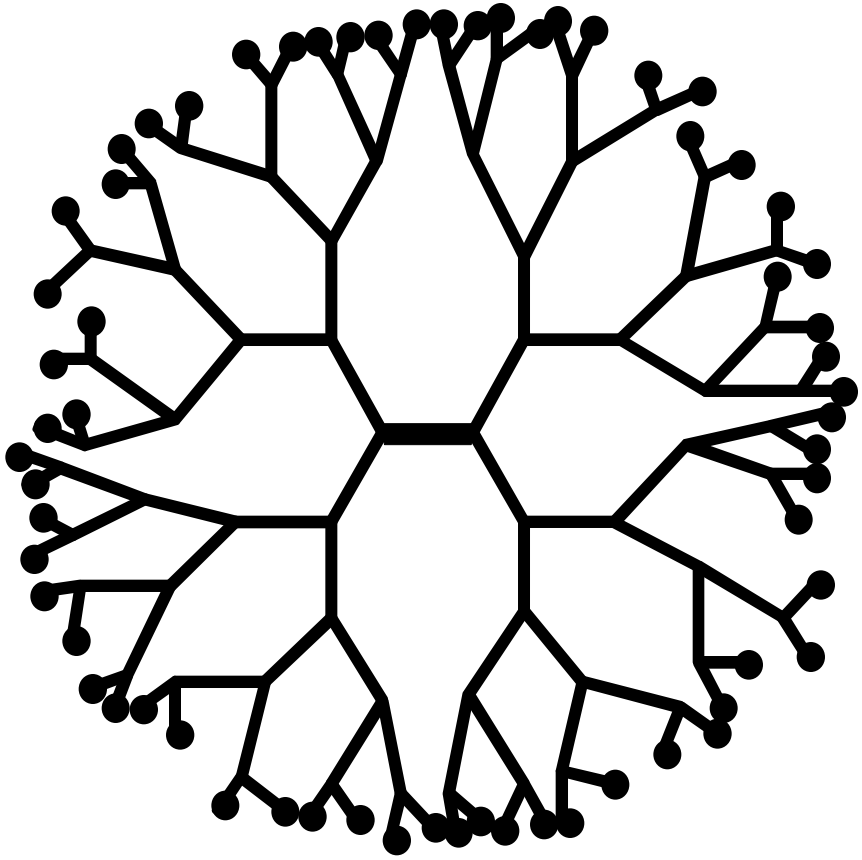



Tiol-AuNP
Tiol-(Sal de ouro)



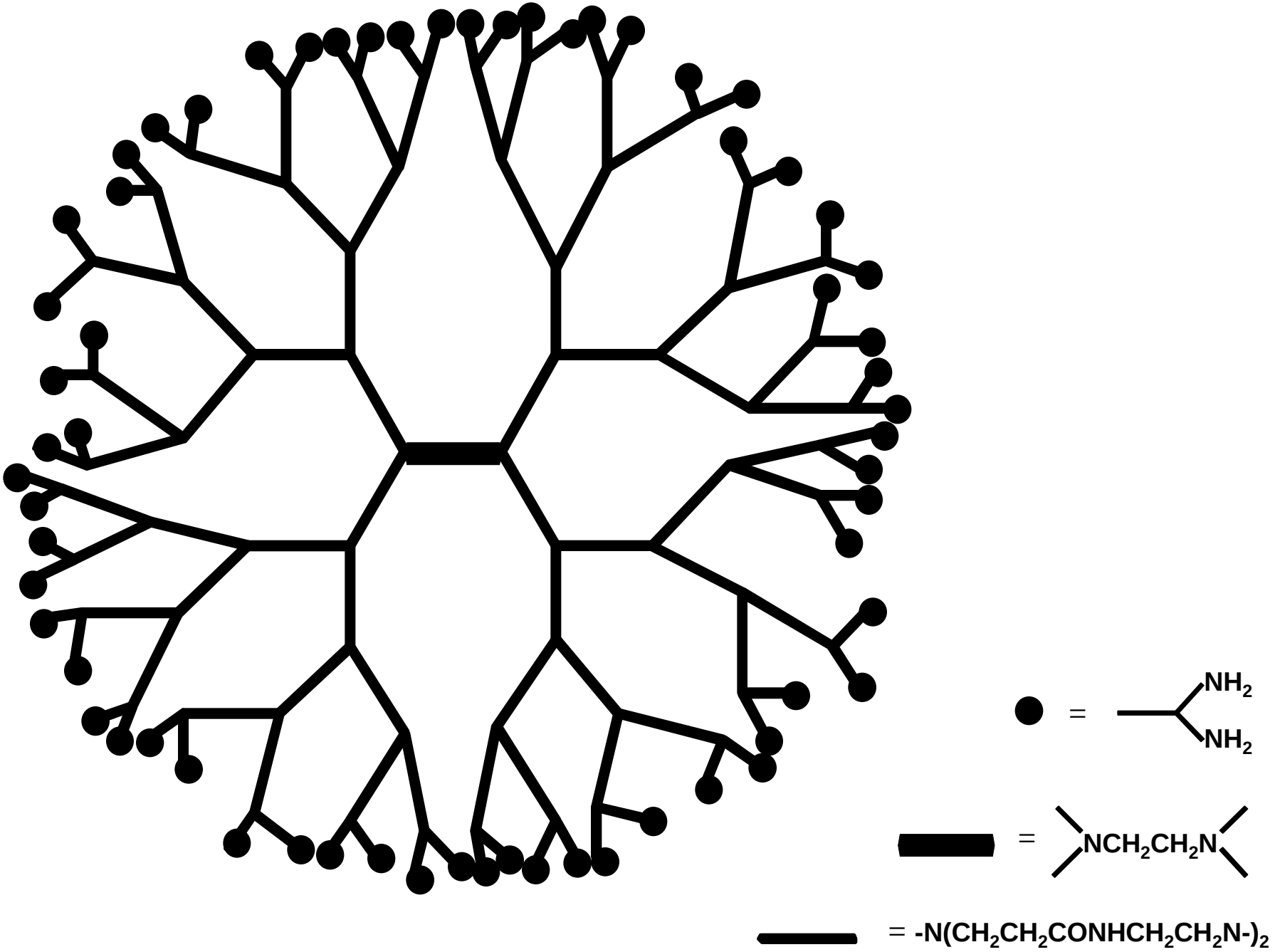
Nanopartículas encapsuladas em dendrímero

Poliamidoamina (PAMAM)



- Cavidades servem como nano-reatores

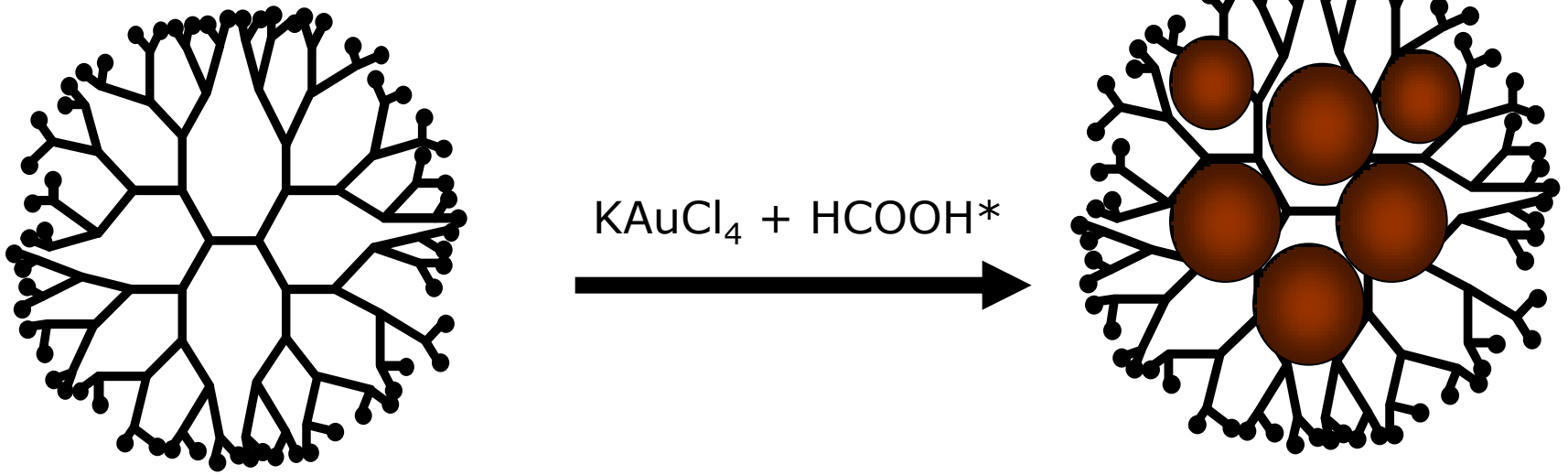
- A molécula possui grupos periféricos que conferem alta estabilidade e solubilidade


= NH2 NH2
= NCH2CH2N
= -N(CH2CH2CONHCH2CH2N-)2

PAMAM-Np

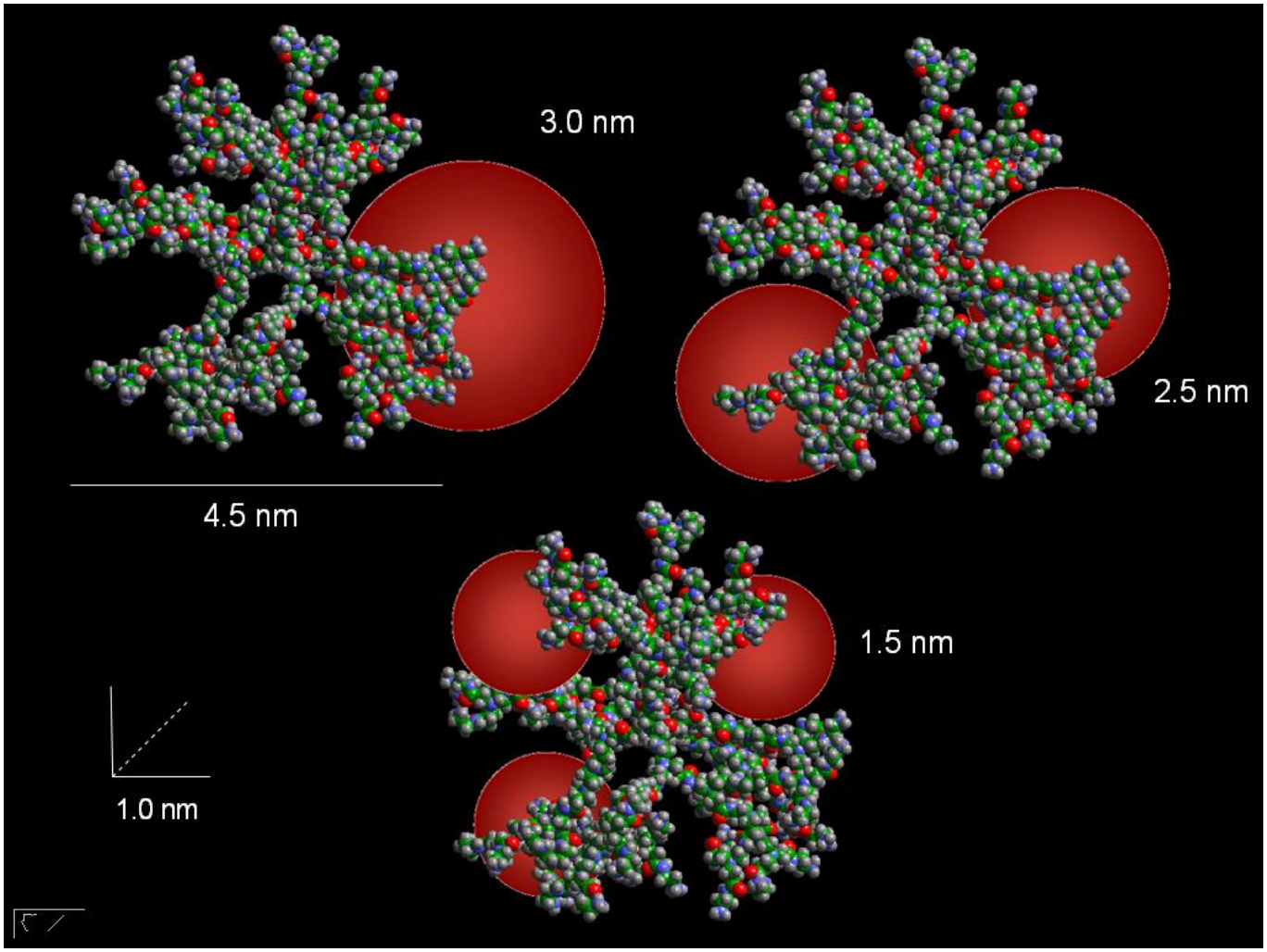
- **Nanopartículas encapsuladas em dendrímero†**

Síntese

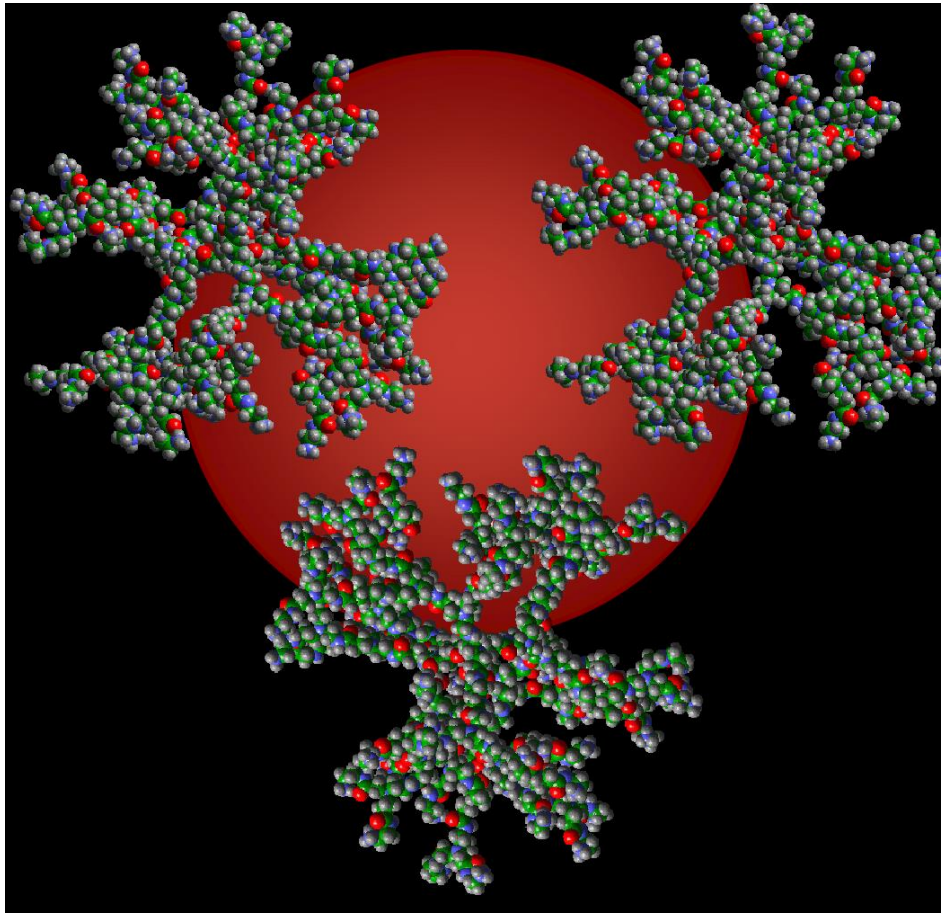


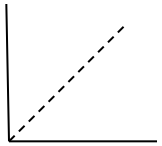
*Crespilho, F. N et. al *Electrochem. Commun.* 2006, 8, 348.

† Crooks, R. M, et. al *Accounts of Chemical Research* 34, 181.


3.0 nm
2.5 nm
4.5 nm
1.5 nm
1.0 nm

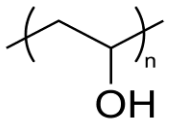
6.0 nm



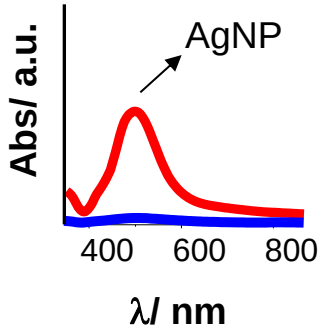


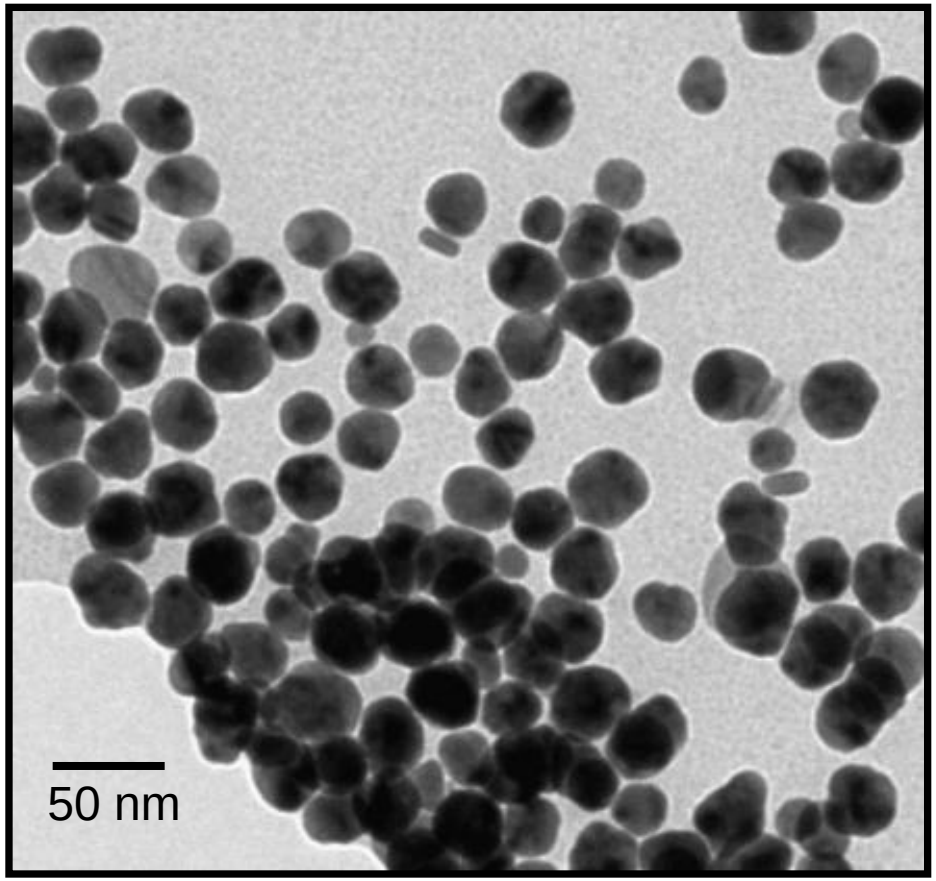
1.0 nm

PVA-AgNP

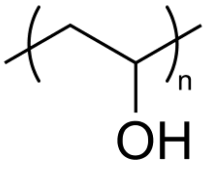


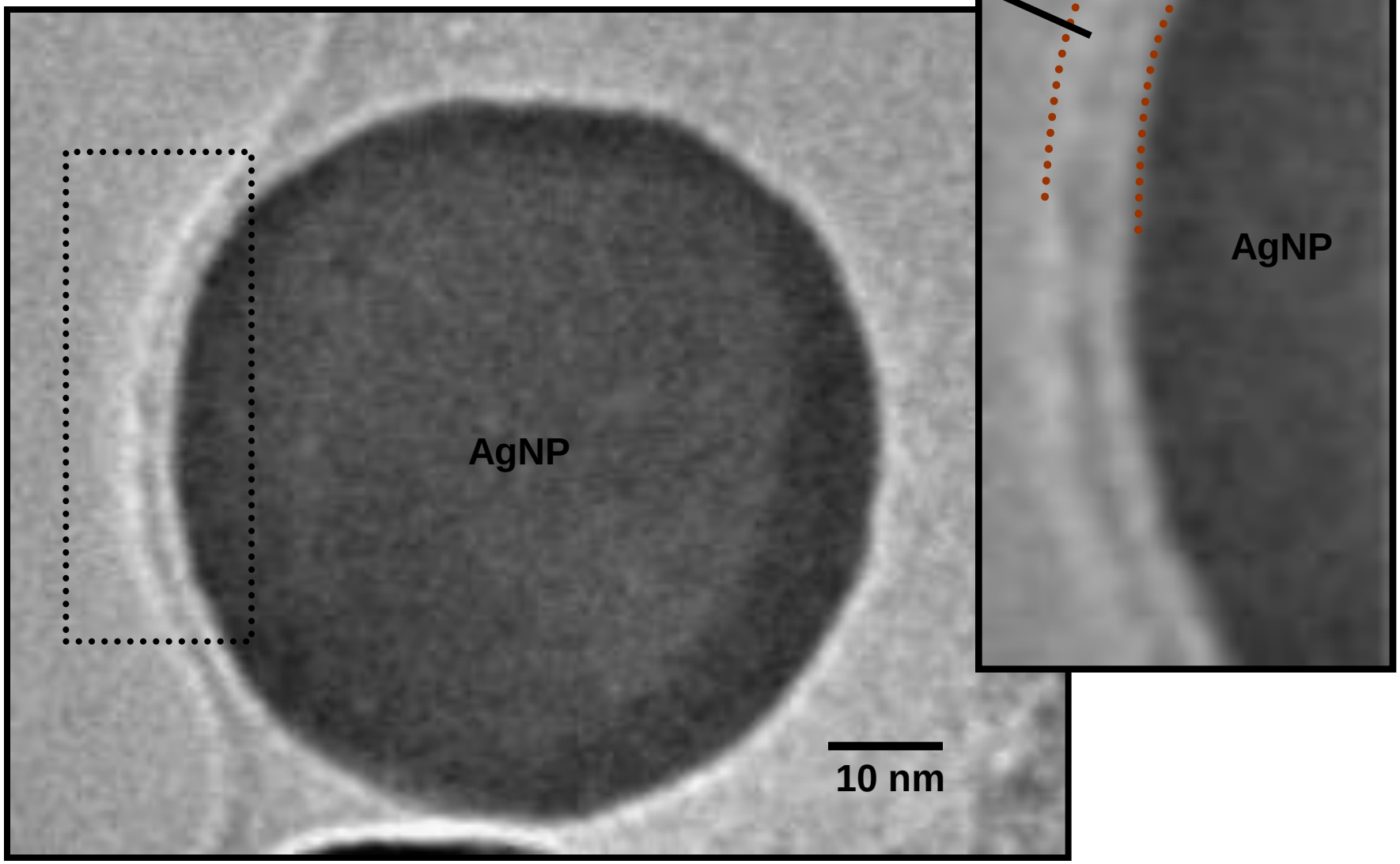
+ Ag^+ + HCOOH



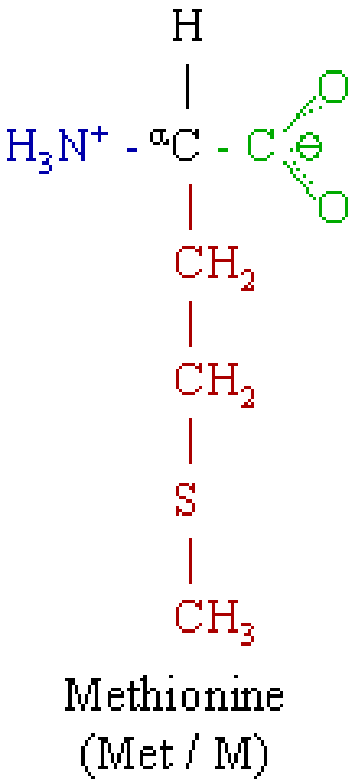


PVA-AgNP





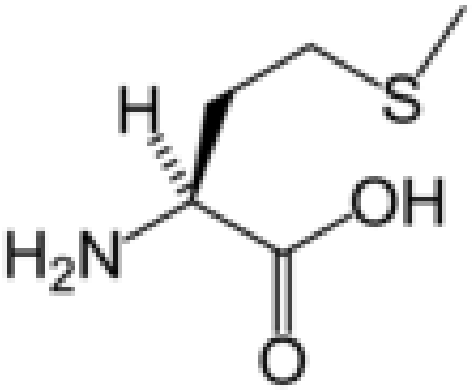
Sistemas Híbridos Bio-nano

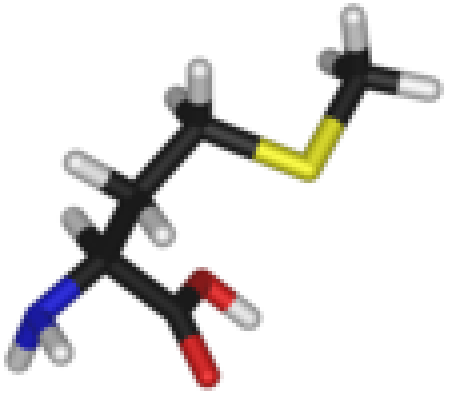


Methionine
(Met / M)

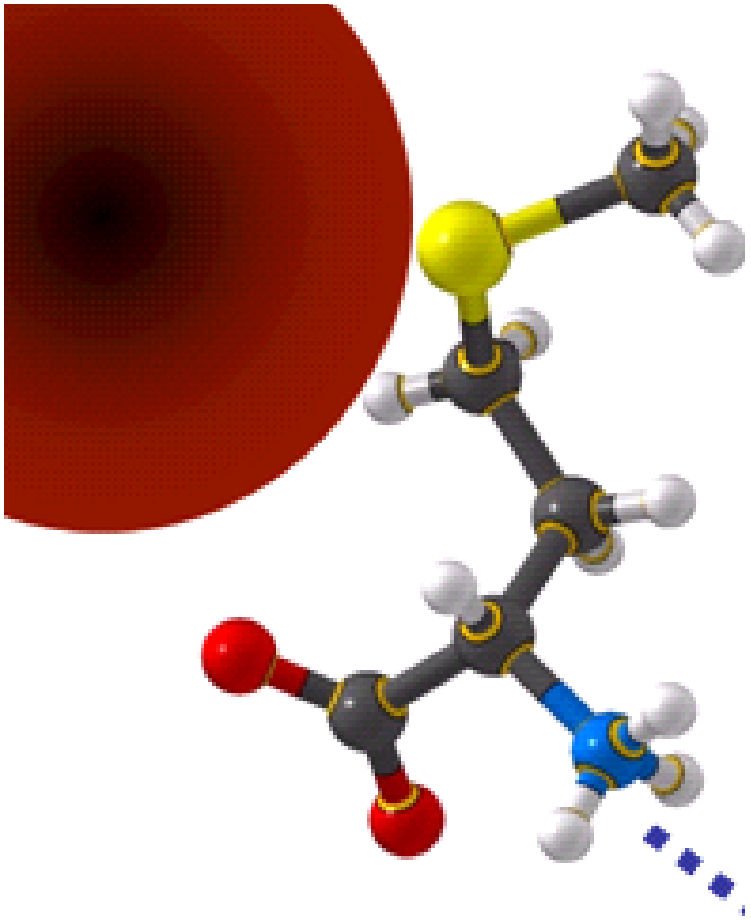
Moléculas de metionina é o bio-estabilizante para síntese de NPs

Exemplo: Met-AuNP

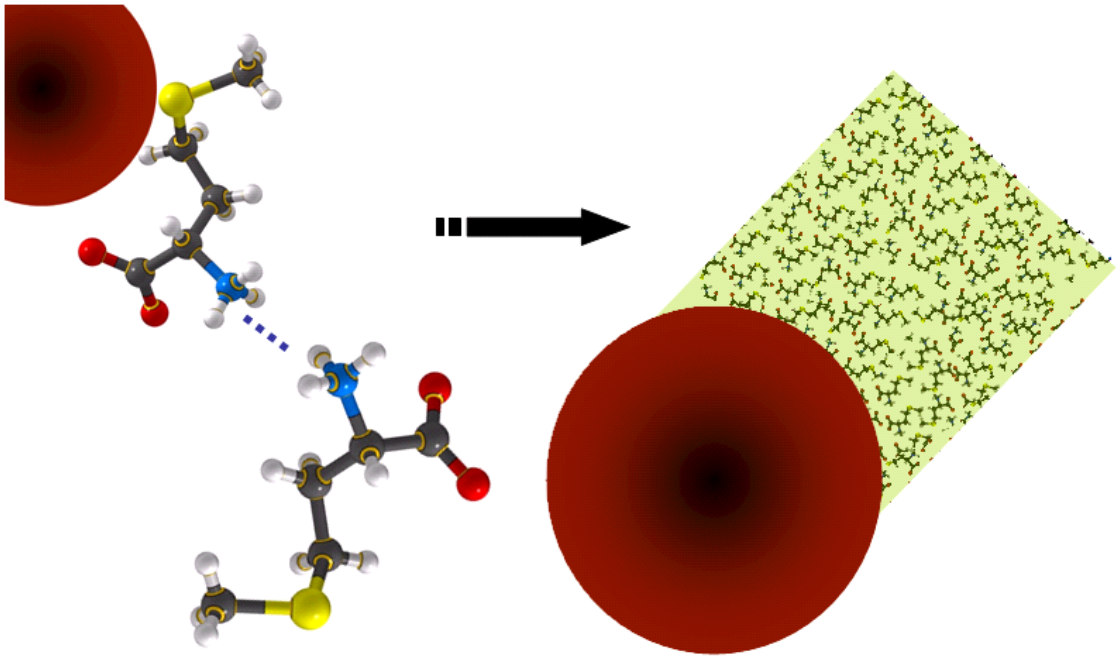




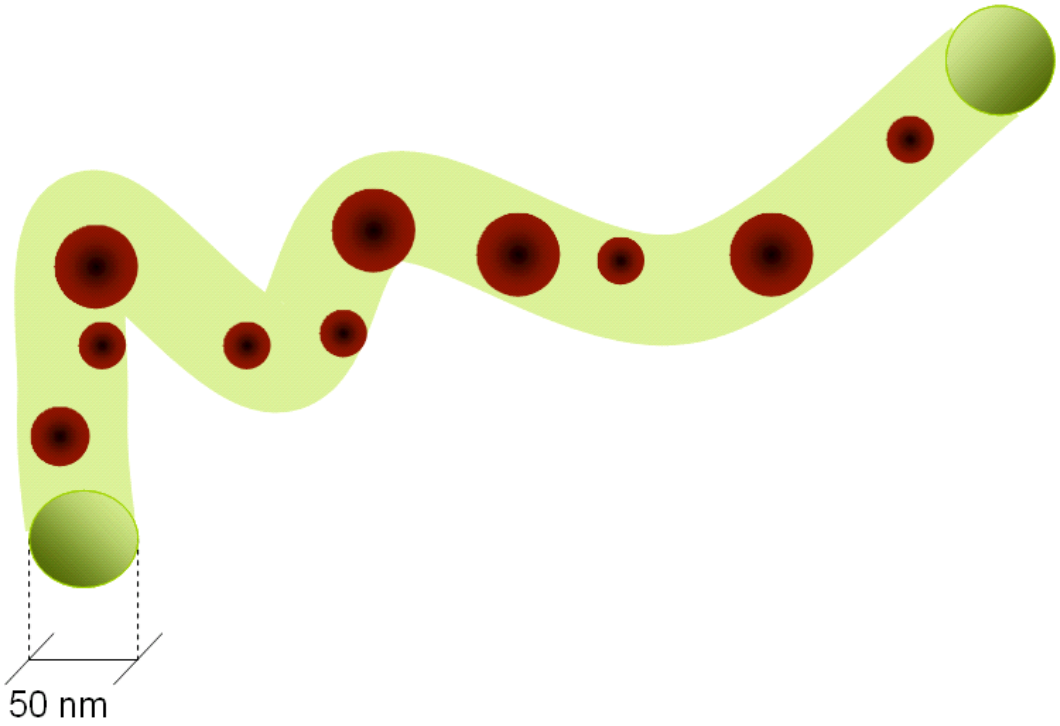
Sistemas Híbridos Bio-nano



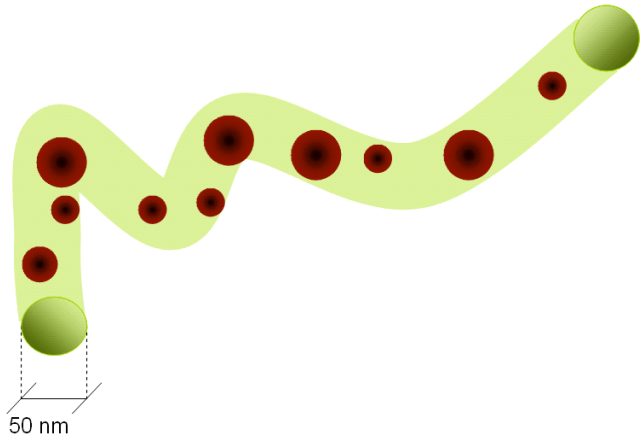
Sistemas Híbridos Bio-Nano

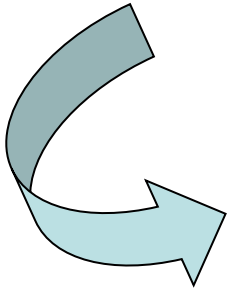


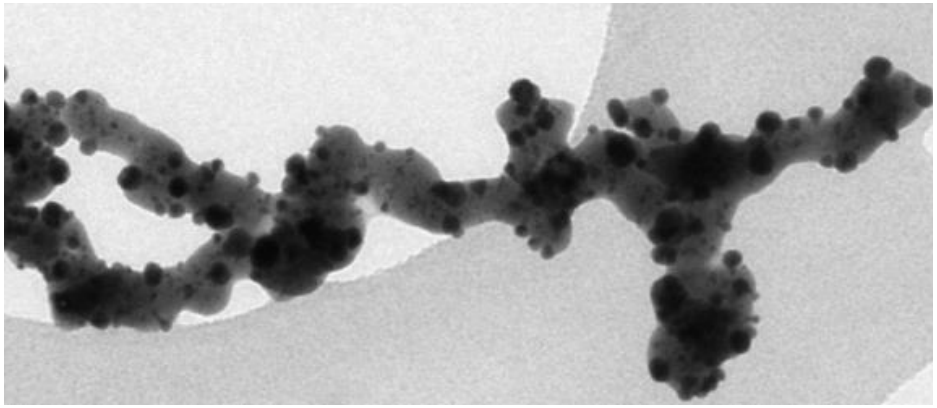
Sistemas Híbridos Bio-nano

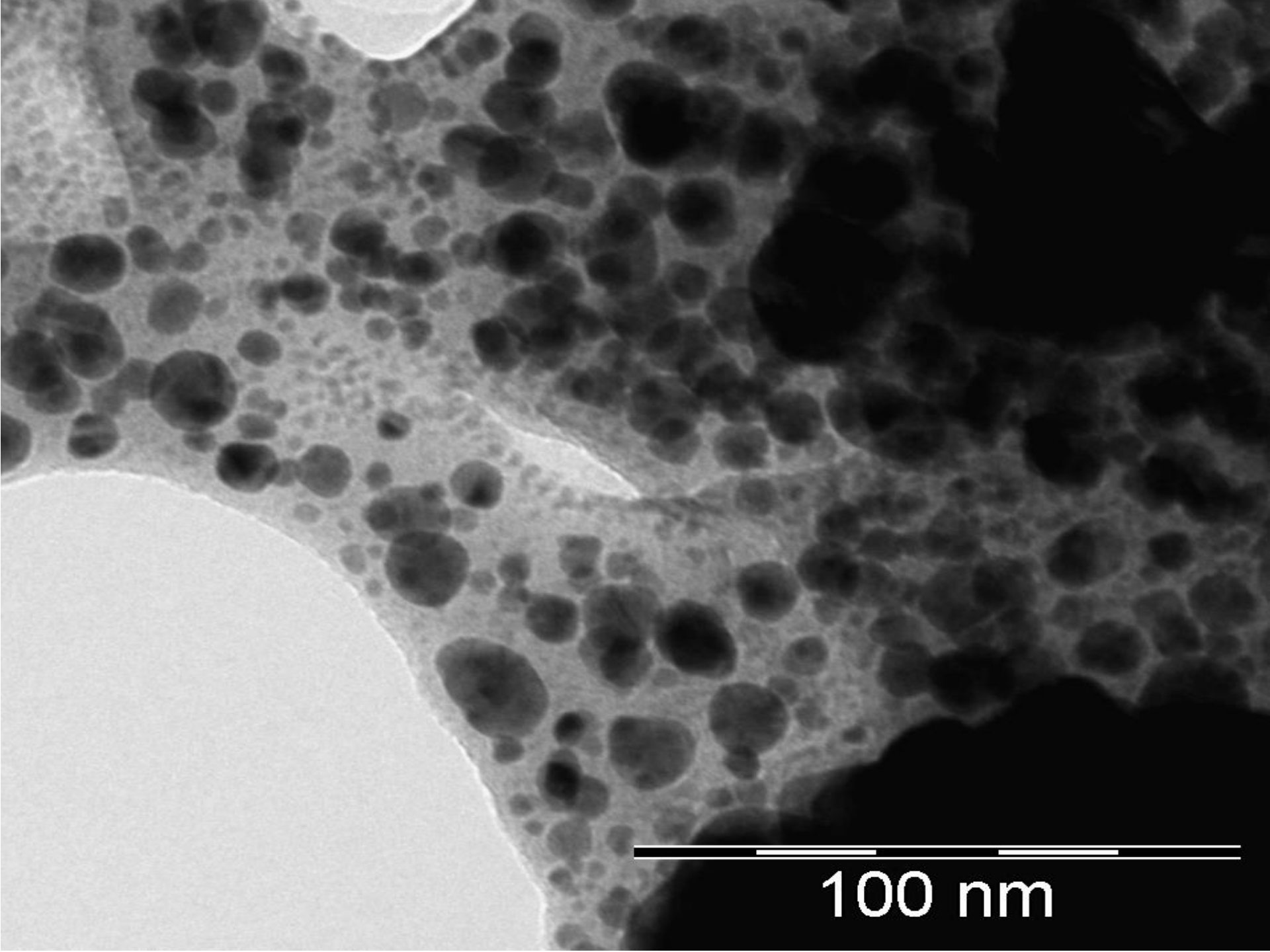


Sistemas Híbridos Bio-nano








100 nm

Síntese de NPs metálicas

Principais fatores que alteram as propriedades morfologias e estruturais das NPs:

- **Solvente**
- **Concentração de agente redutor, estabilizador e percursor metálico**
- **Estrutura molecular do estabilizador**
- **pH**
- **Temperatura**
- **Pressão**
- **Tempo de reação**

Síntese de NPs metálicas: Efeito da Temperatura

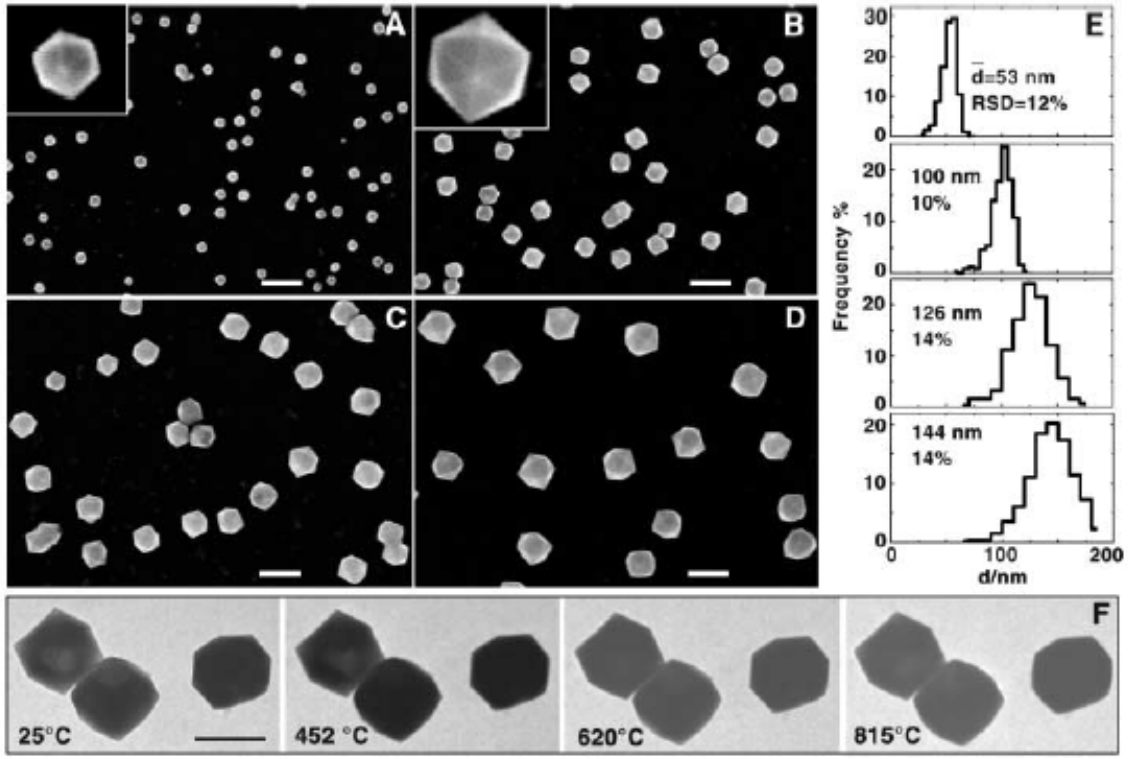
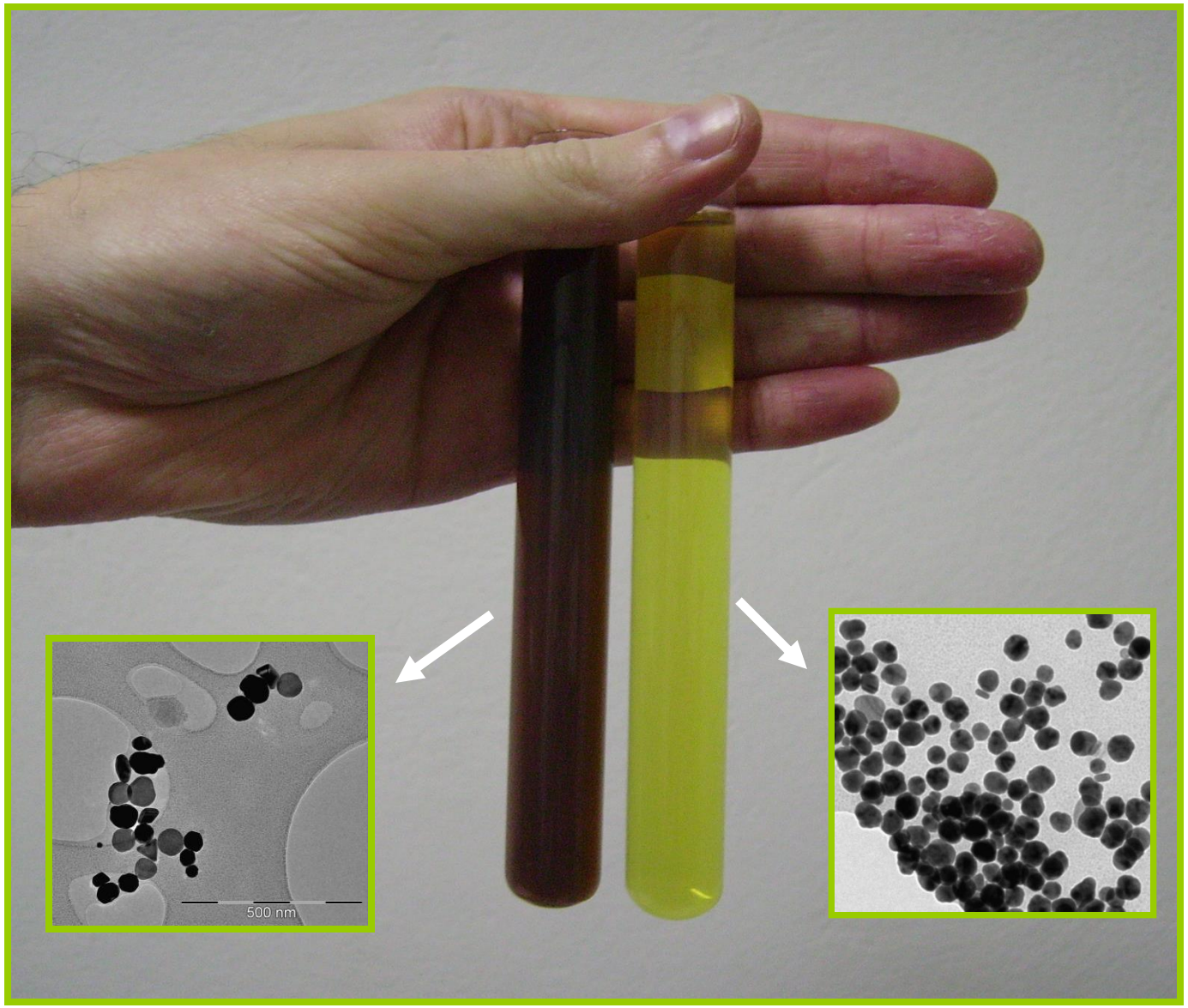


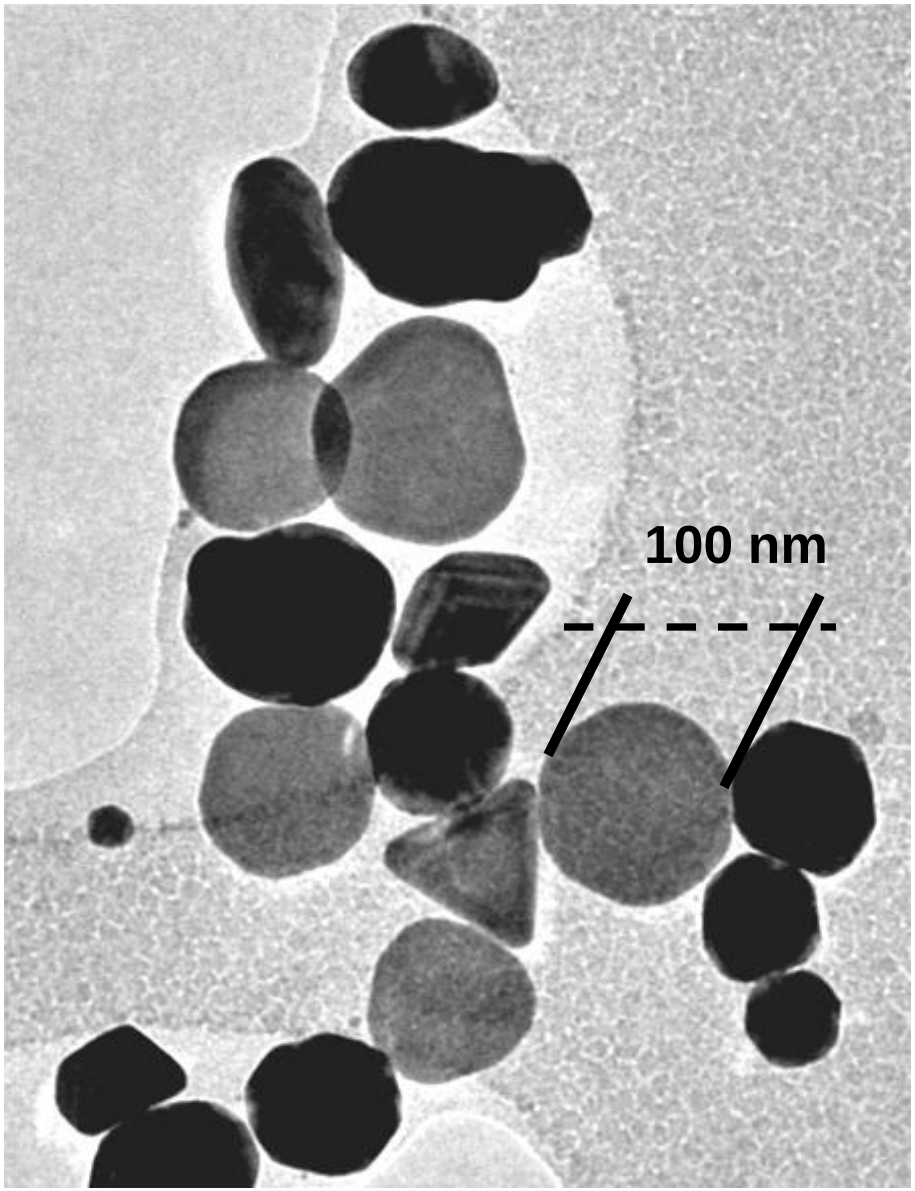
Fig. 3. Size control of THH Pt NCs and their thermal stability. SEM images of THH Pt NCs grown at (**A**) 10, (**B**) 30, (**C**) 40, and (**D**) 50 min. The insets in (A) and (B) are the high-magnification SEM images that confirm the shape of THH. Scale bars, 200 nm. (**E**) Size distributions of THH Pt NCs in (A), B), (C), and (D), respectively, after counting more than 500 particles for each sample. (**F**) In situ TEM observation on the thermal stability of THH Pt NCs. The images were recorded at various temperatures in TEM at a heating rate of 7°C/min. The NC preserves its shape to ~815°C and even higher with a slight truncation at the corners and apexes, as seen in the TEM image.

Na Tian, et al. Science 2007

Efeito da Temperatura



Efeito da Temperatura



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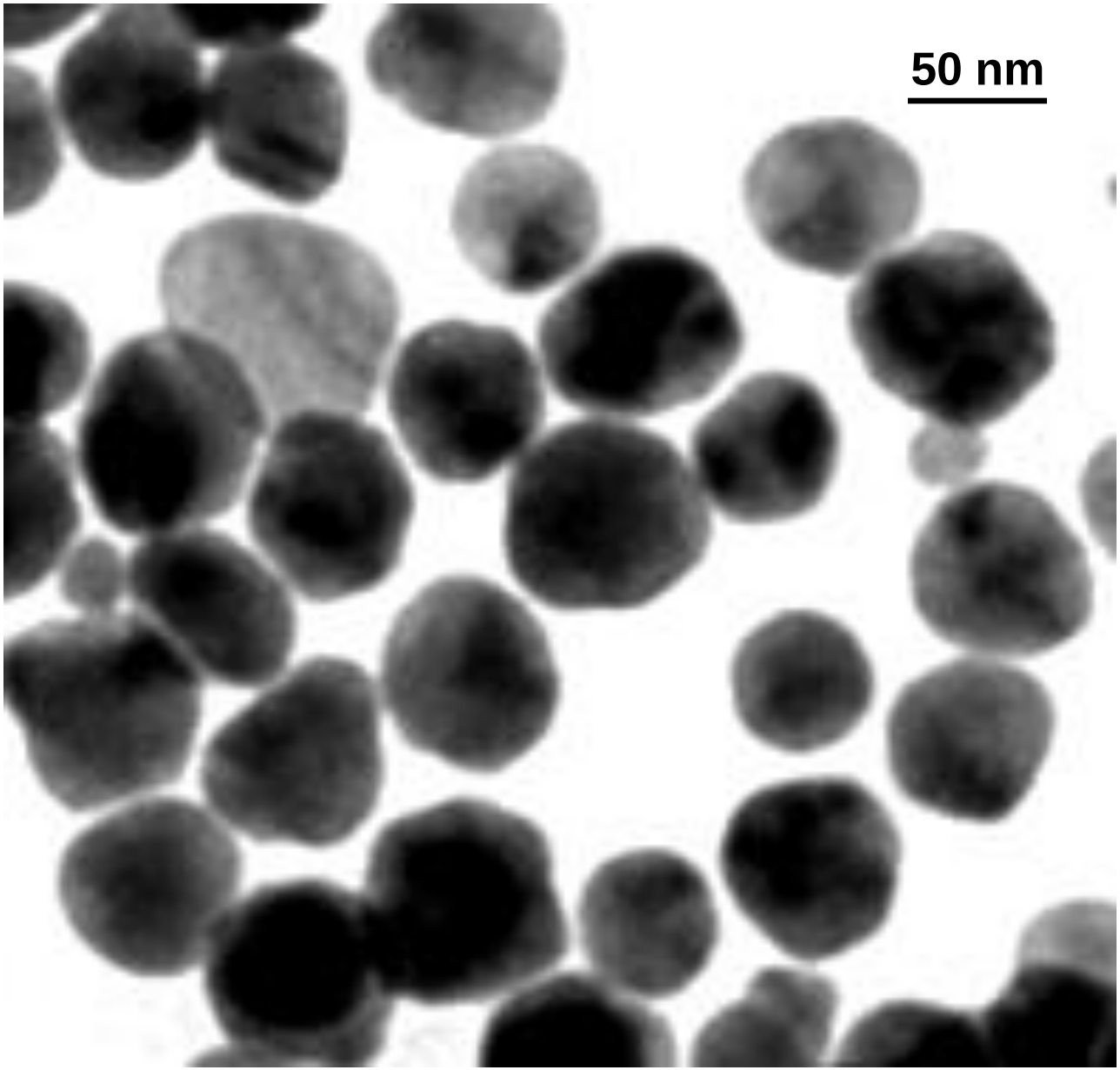
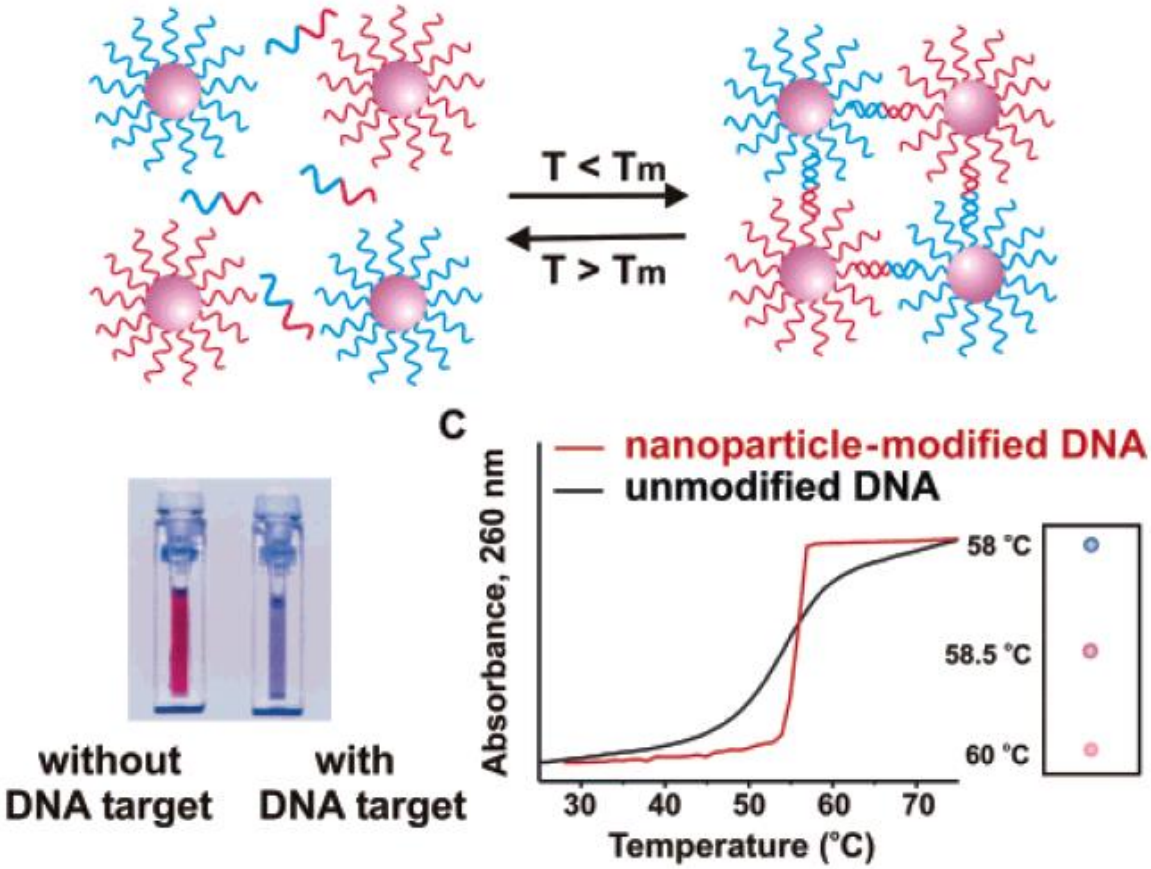
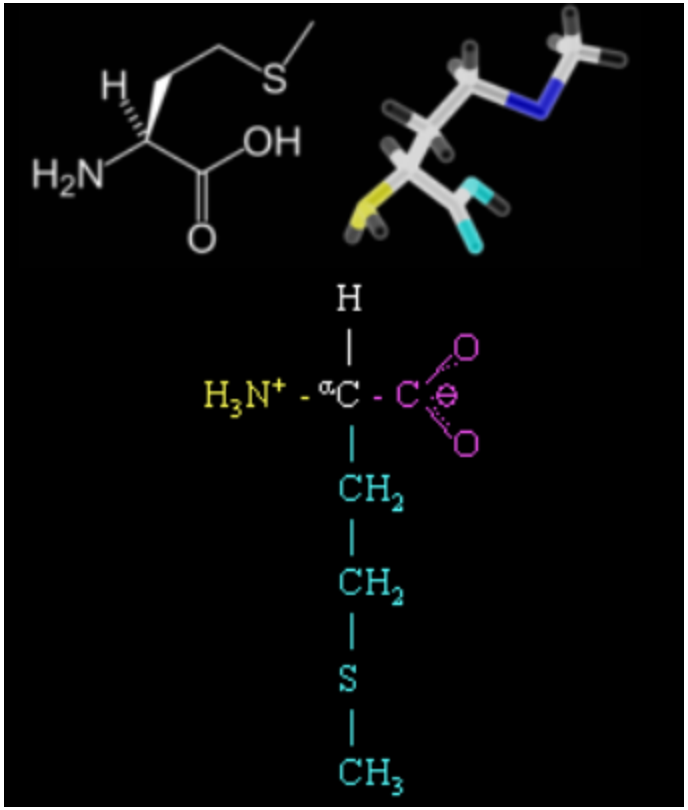


Efeito da Temperatura



Elghanian, R. *et al.* ***Science,*** 1997, *277*, 1078.

Síntese de NPs metálicas: Efeito do pH



Ponto isoelétrico: 5,62

pKa_1 = 2,16

pKa_1 = 9,08

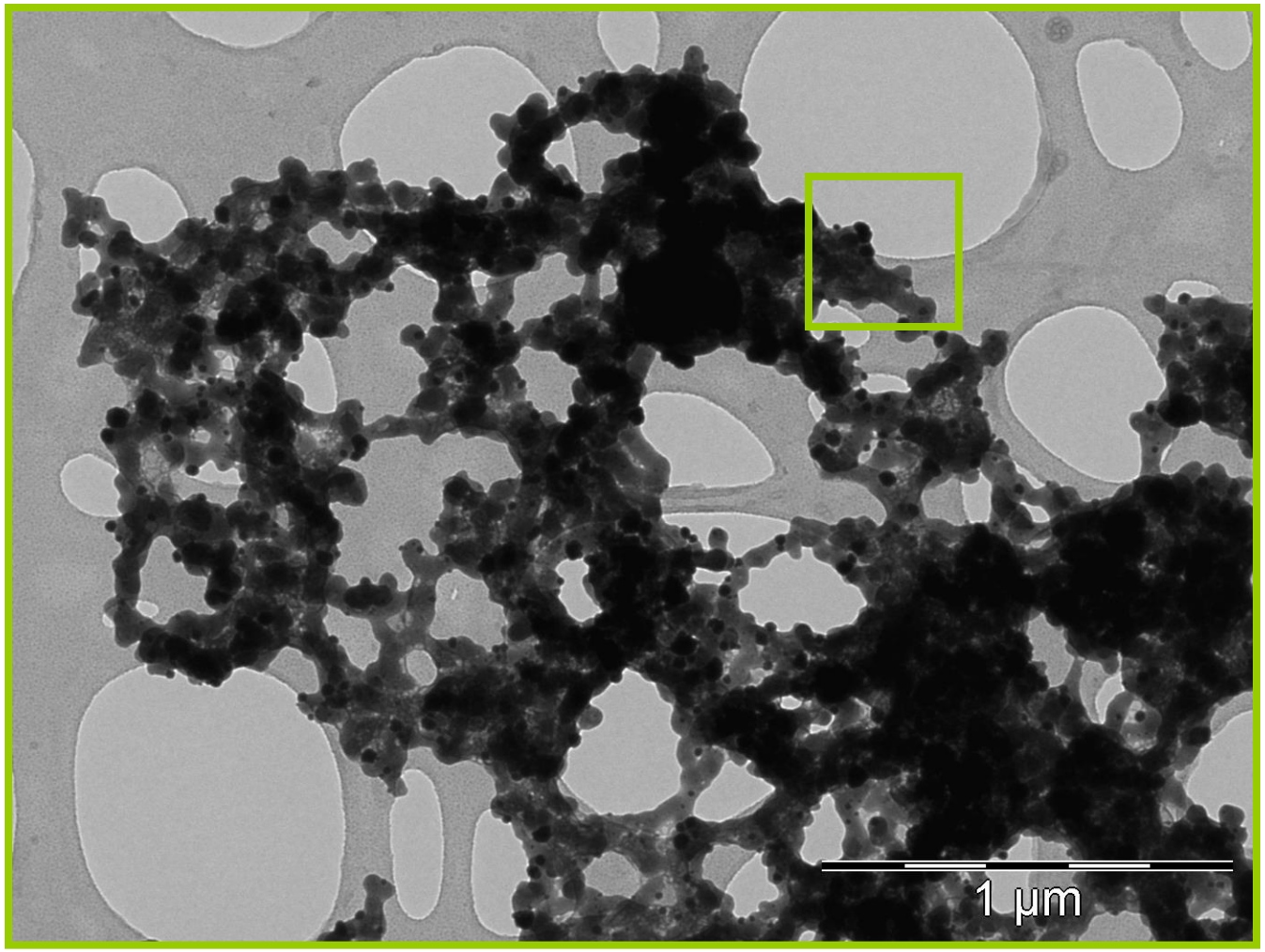
$$pI = \frac{pK_1 + pK_2}{2}$$

$KAuCl_4$ + HCOOH

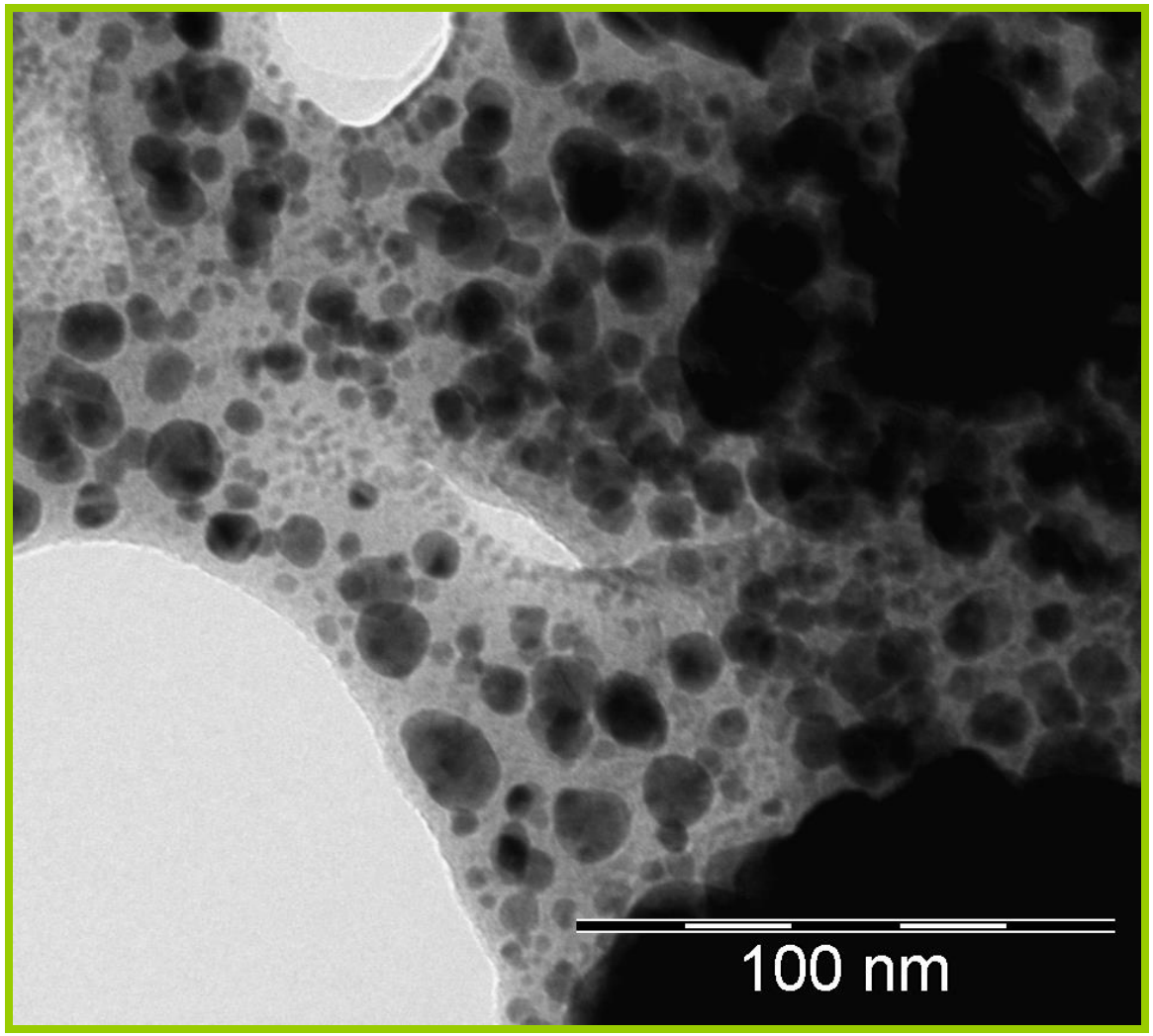
↓

Au^0

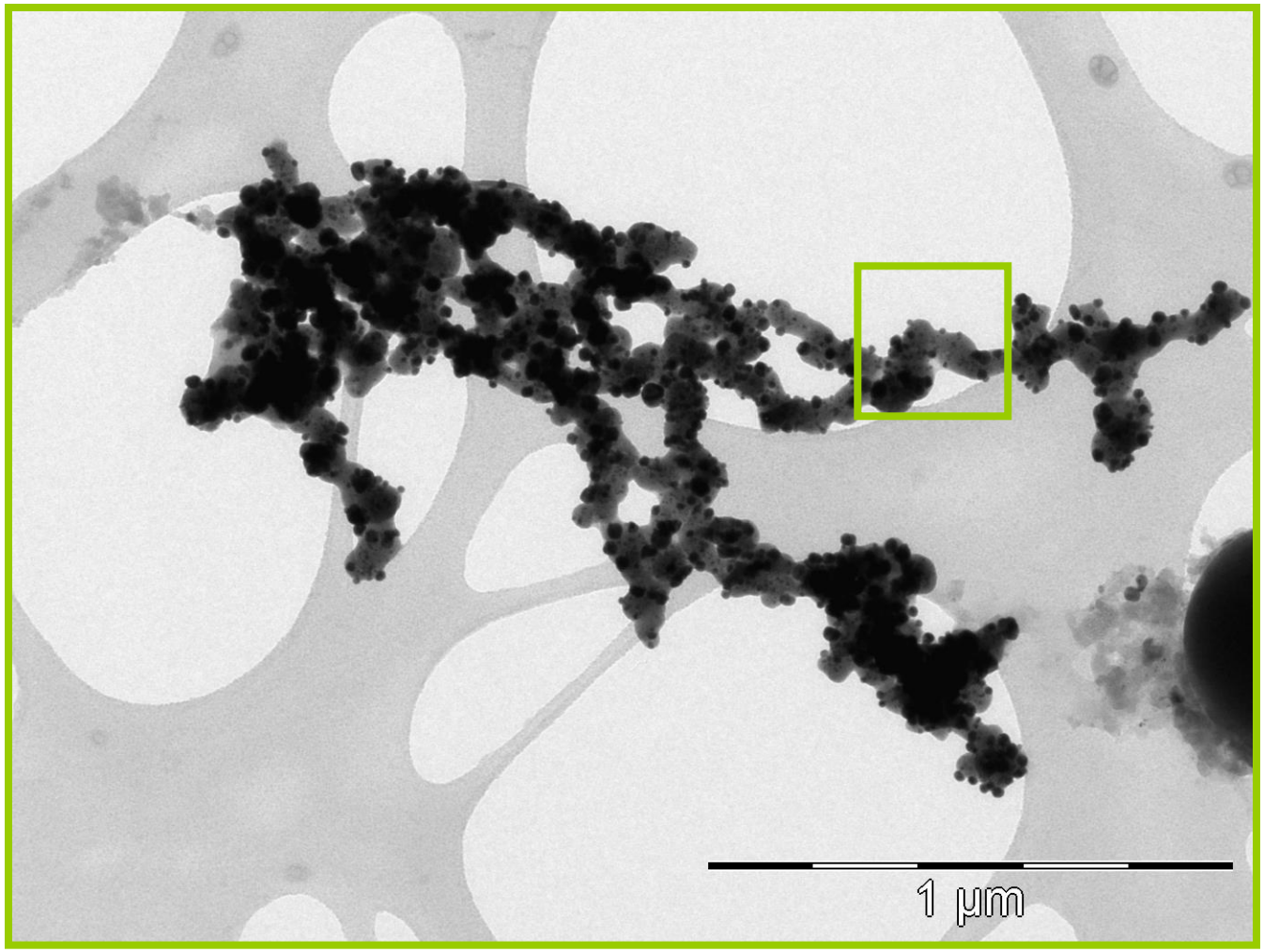
pH = 7.0



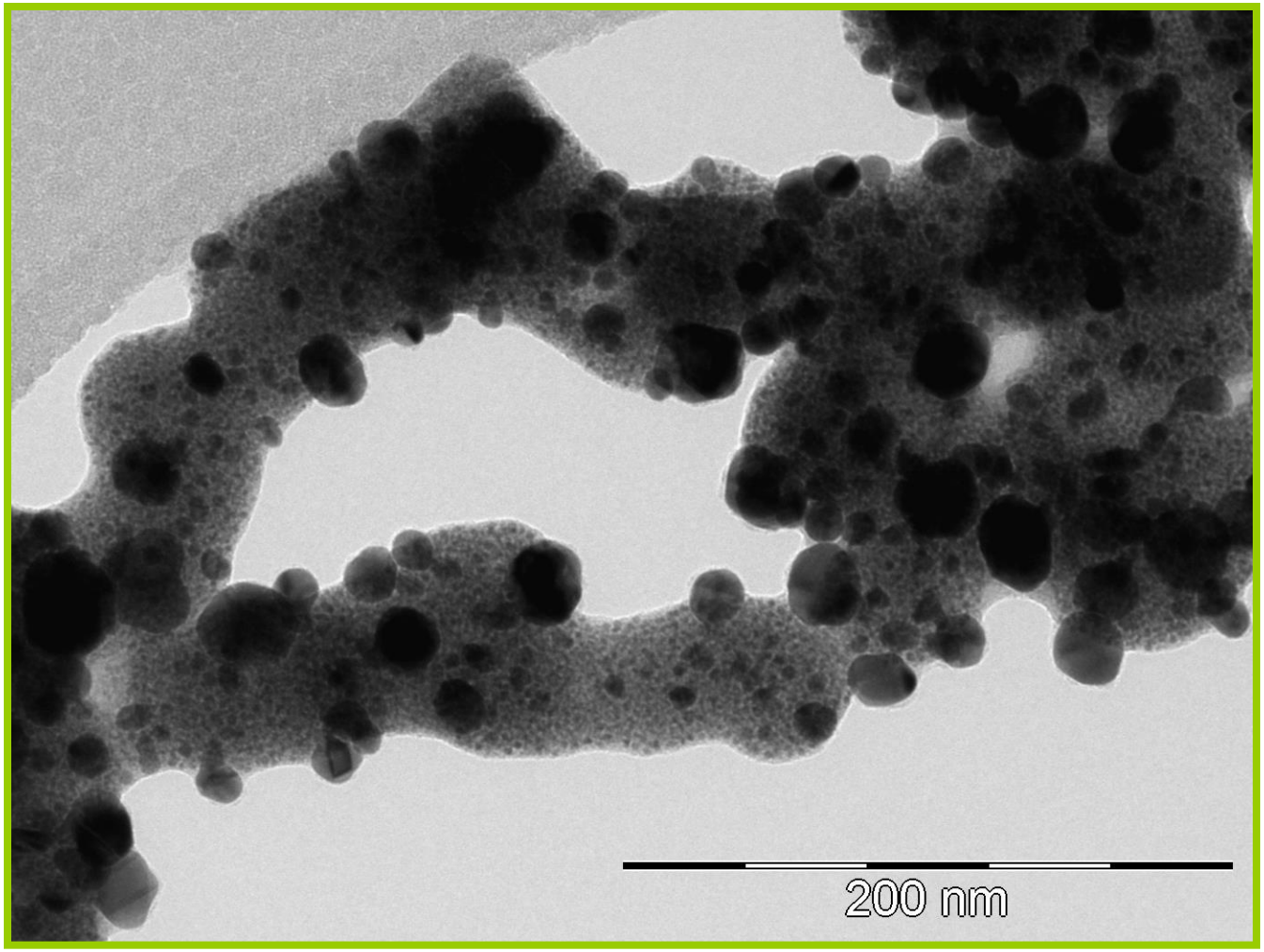
pH = 7.0

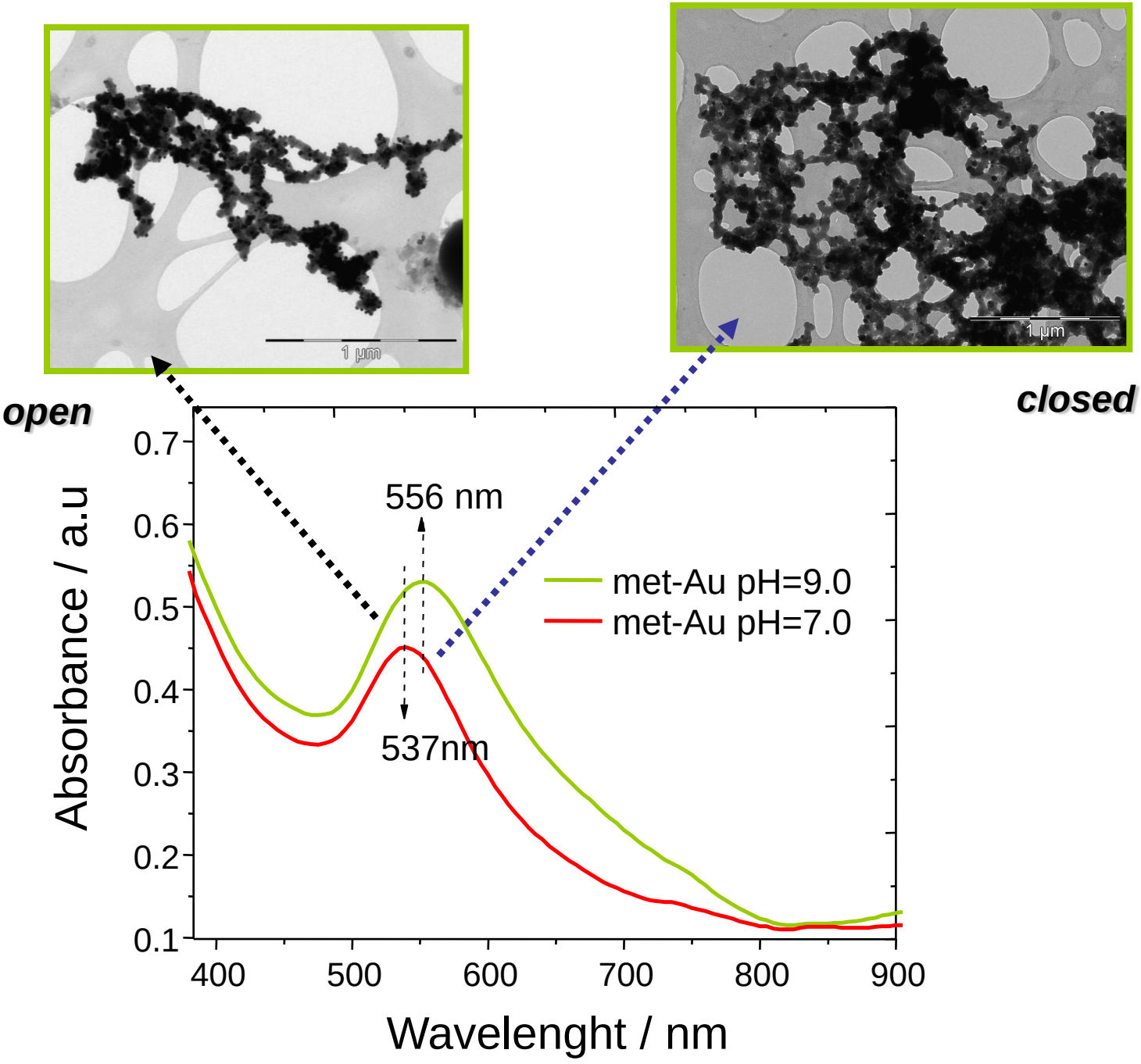


pH = 9.0



pH = 9.0




1 µm
1 µm
open
closed
556 nm
537nm
met-Au pH=9.0
met-Au pH=7.0
Absorbance / a.u
Wavelenght / nm
0.7
0.6
0.5
0.4
0.3
0.2
0.1
400
500
600
700
800
900

Sumário

- Parâmetros termodinâmicos regem a formação inicial da NPs,
com $\Delta G = -(KT/\Omega) \ln (C/C_0)$

- Parâmetros cinéticos rege o **crescimento** das NPs metálicas, onde ocorrem várias etapas e seu controle pode ser governado por **difusão**, **reações de superfície (adsorção).** Pode ainda haver processos de **incorporação irreversível**.

- Principais fatores que alteram a morfologia e distribuição de NPs metálicas: solvente, concentração de agente redutor, estabilizante e percursor metálico, pH, temperatura, pressão, tempo de reação e maturação.