

Chapter 3

Inorganic nanostructures in telecommunications

3.1 transparent conducting oxide electrodes (TCO)

3.2 electrochromy

3.3 electroluminescence (OLED, nano-based LED)

3.4 planar waveguides and NIR amplifiers in photonic circuits



3.1 transparent conducting oxides TCOs

Introduction

Figure of merit $\sim T/R$

$$t R = \rho = 1 / e N \mu$$

R: lateral resistivity

ρ : resistivity

N: free carrier concentration

μ : carrier mobility

t: thickness

e: elementary charge

T: optical transmission

Desired parameters:

T (400-1200 nm) > 80%

$E_g > 3 \text{ eV}$

$N \sim 10^{20} - 10^{21} \text{ cm}^{-3}$

$\mu > 100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

t $\sim 500 \text{ nm} - 1 \mu\text{m}$

$\rho < 10^{-4} \Omega \text{ cm}$

$R < 2 \Omega \text{ sq.}^{-1}$ (t = 500 nm)

Application domaines:

Photovoltaics (CdTe, Si, CIGS)

Telecommunication

(LCD, OLED, electrochromy)

Smart windows

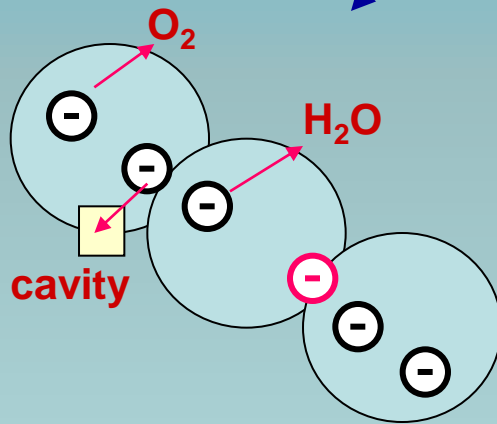
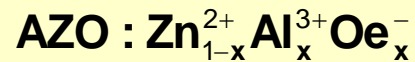
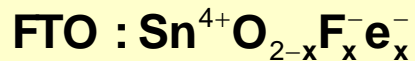
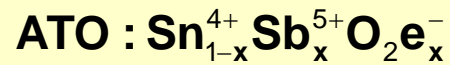
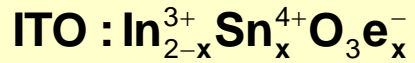


Transparent conductors as solar energy materials: A panoramic review

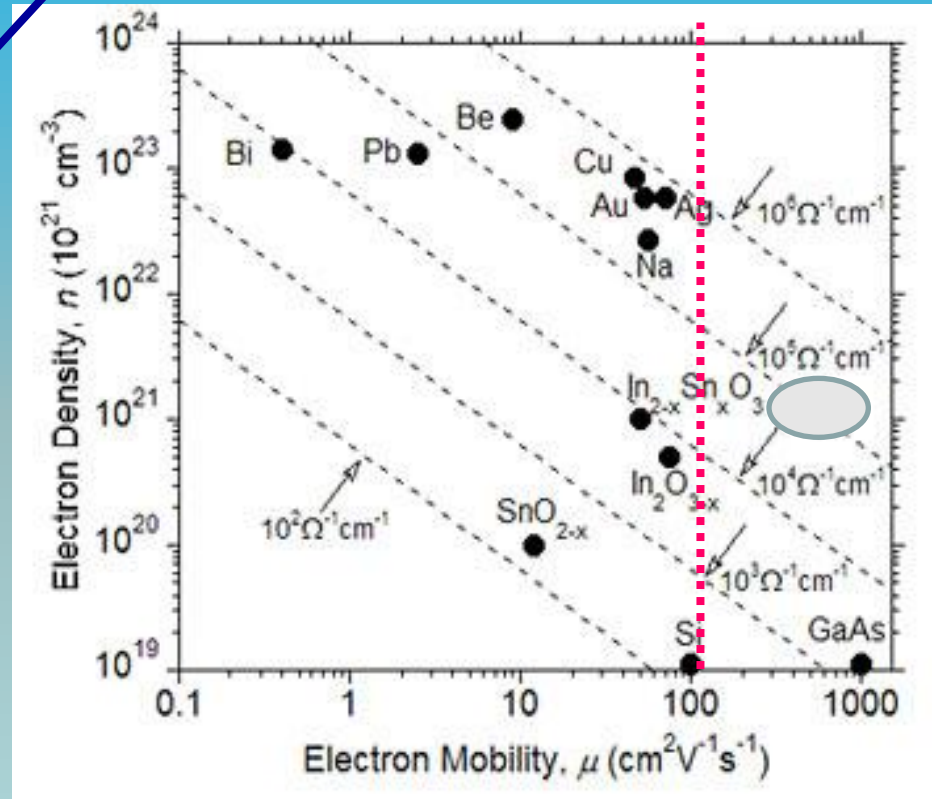
Claes G. Granqvist*

Solar Energy Materials & Solar Cells 91 (2007) 1529–1598

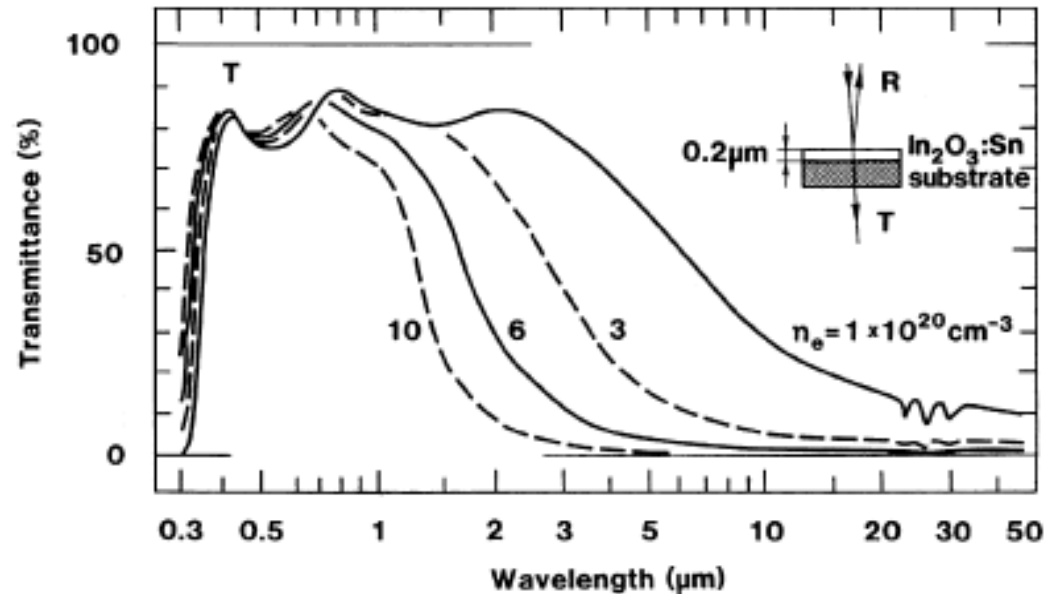
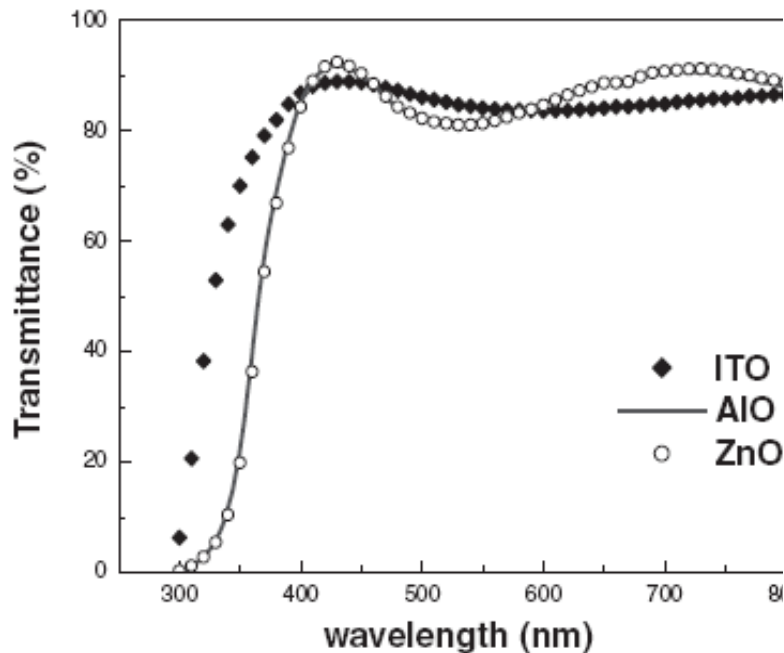
TCO n-doped



1. Control of N : doping!
2. Control of μ : morphology!
3. Optical gap : oxides!

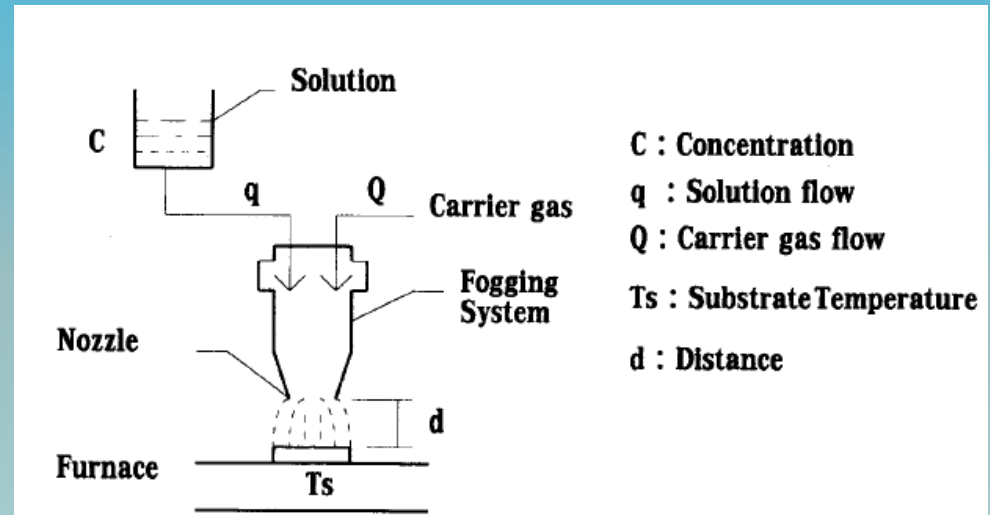
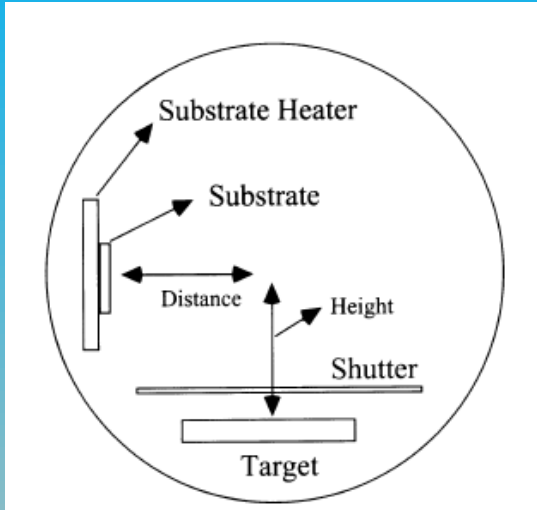


Profile spectrale de transmission optique

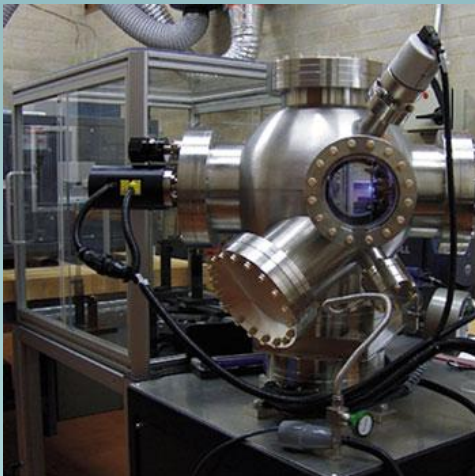


Elaboration of thin film electrodes

Pulsed Laser Deposition
Rf-magnetron sputtering



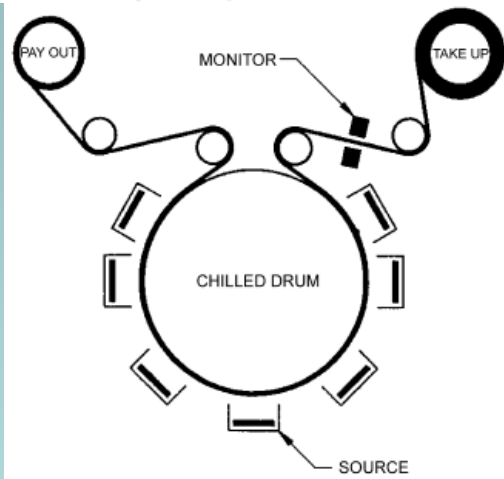
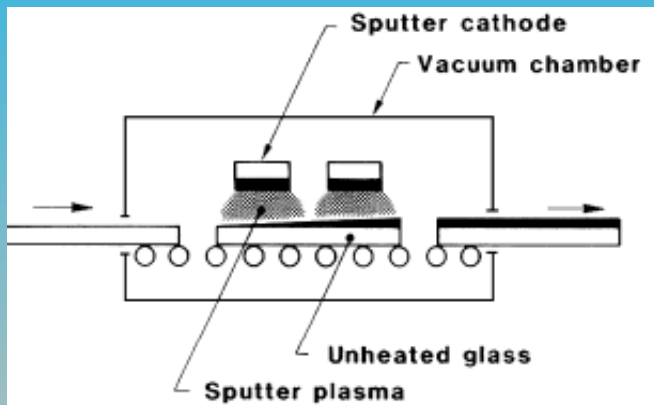
Chemical spray



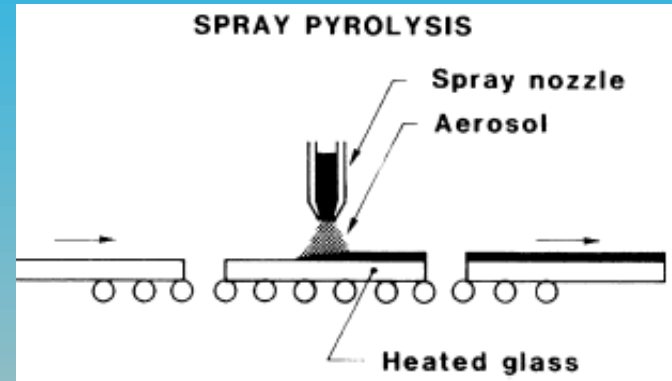
Contineous Elaboration of TCO

Pulsed Laser Deposition

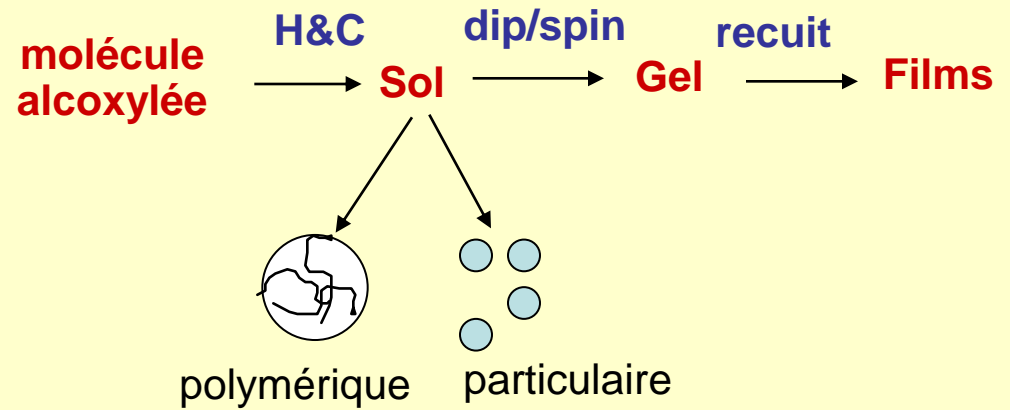
Sputtering

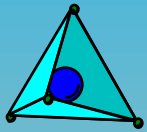
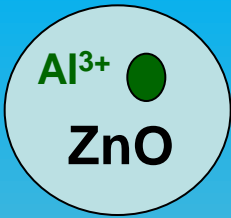


Spray pyrolysis



Chimie douce



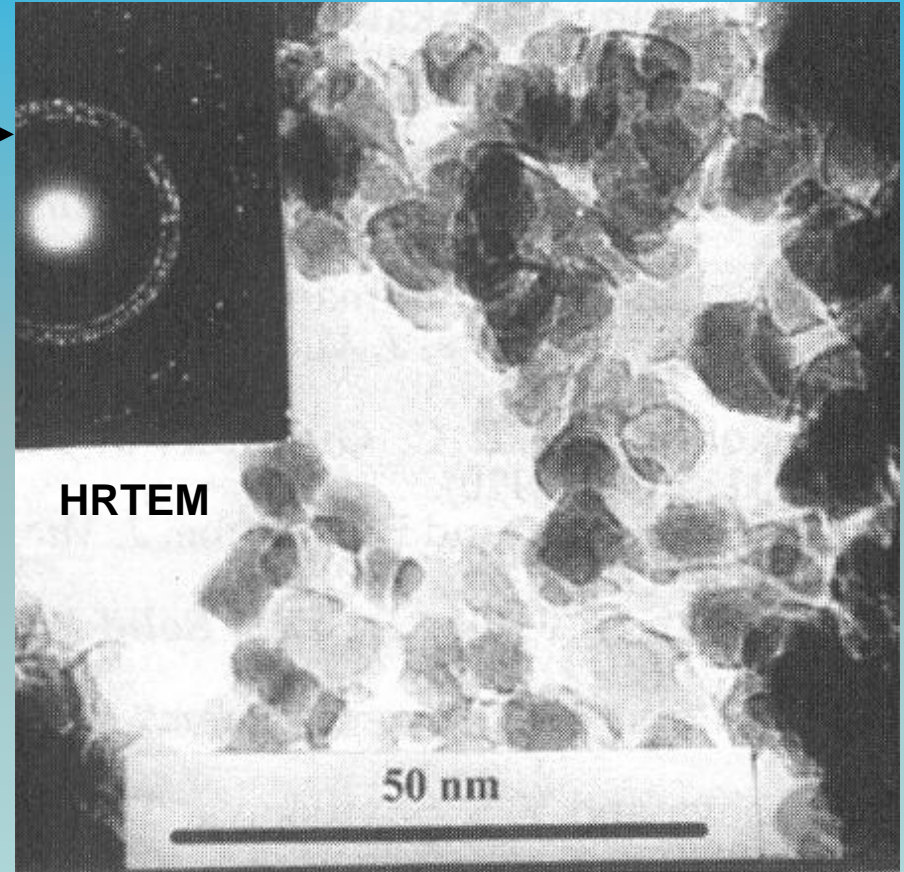
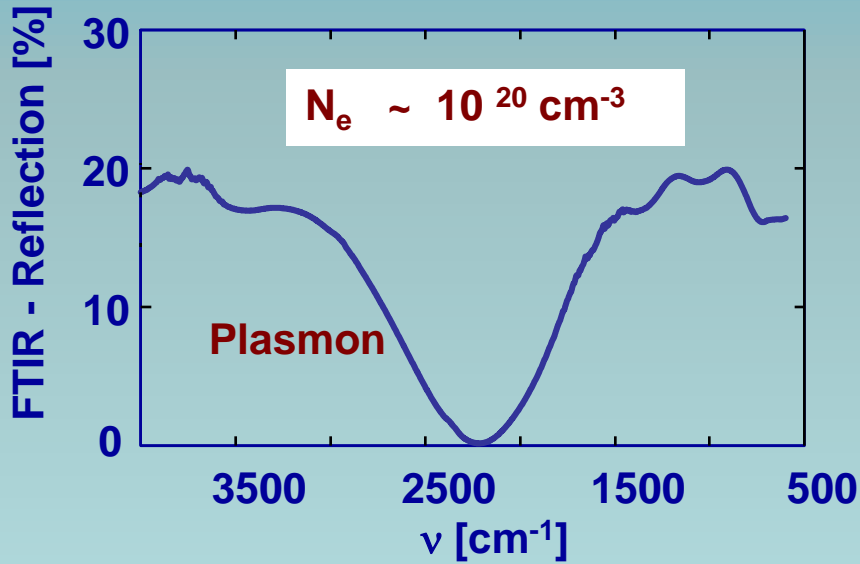


TMA-OH
90°C



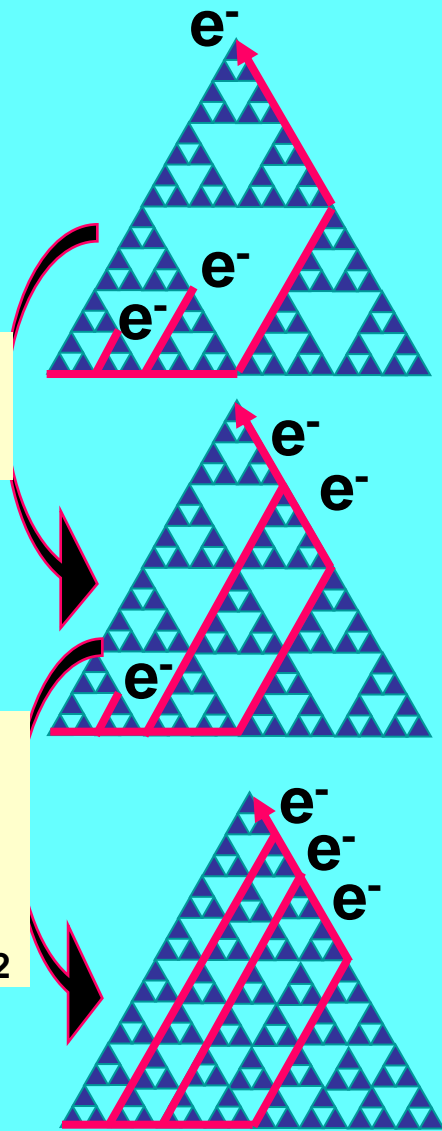
Dip coating
 N_2/H_2 - sintering

$\mu_e < 10^{-3} \text{ cm}^2/\text{V s}$



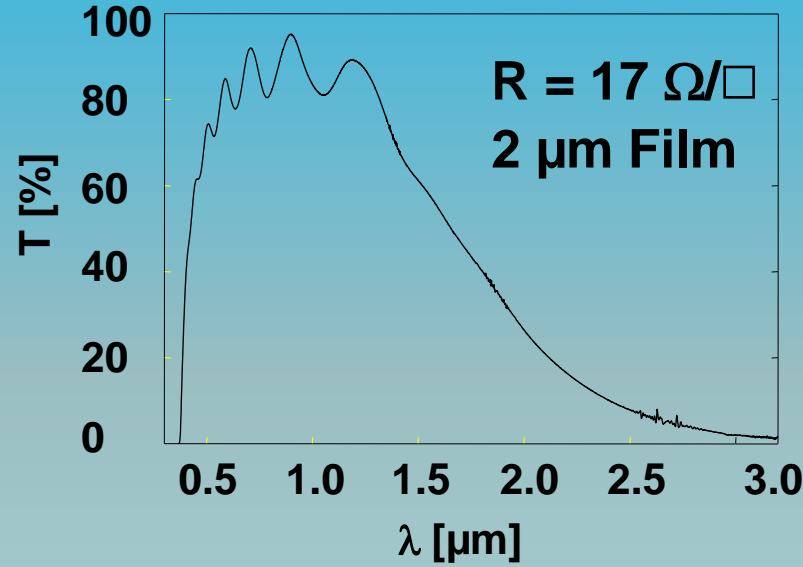
condensation
dans mesopores

Infiltration
des mesopores
&
recuit sous N_2/H_2



$$n_D \sim 1.7$$

$$\mu_e = 0.001 \text{ cm}^2/\text{Vs}$$



$$n_D \sim 2.1$$

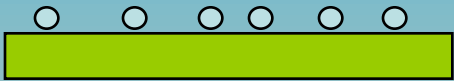
$$\mu_e = 9 \text{ cm}^2/\text{Vs}$$

ISAM = "ionic self-assembled monolayer", Chem. Phys. Lett. 1998, 298, 315

HAuCl₄/NaBH₄/H₂O/PDDA

**Sol: Au:PDDA
size: 3-6 nm**

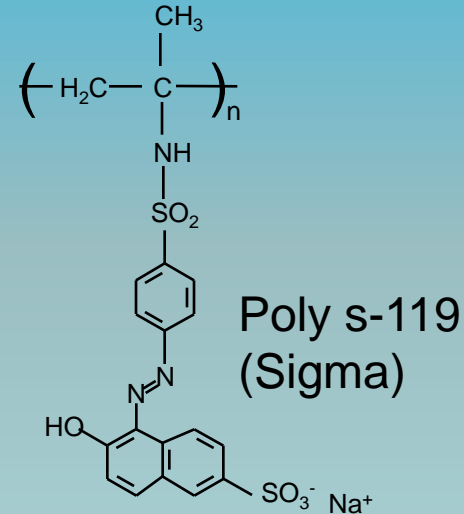
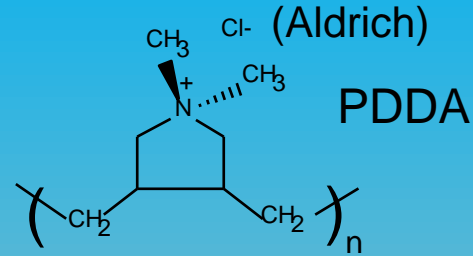
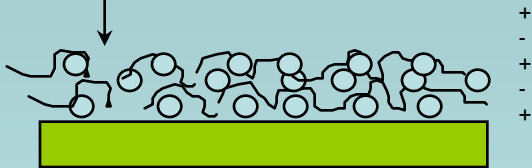
Spin-on



**washing &
deposition of Poly s-119**



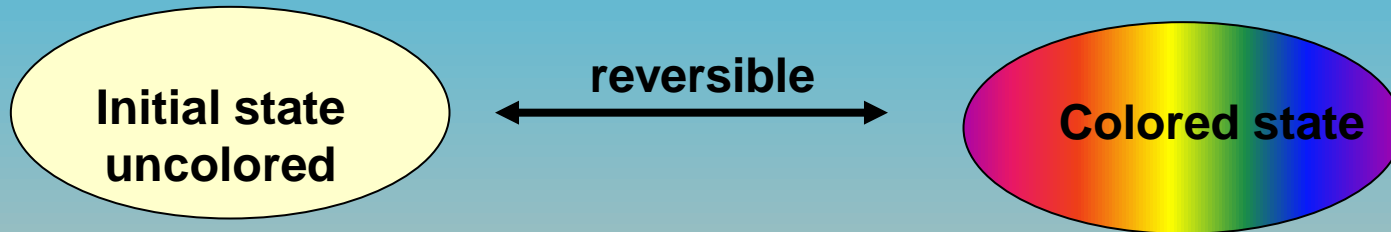
12 times repeated coatings



**thickness : 50 nm
R = 10⁻⁶ Ω cm**

3.2 Chromatic materials

Principle of chromaticism

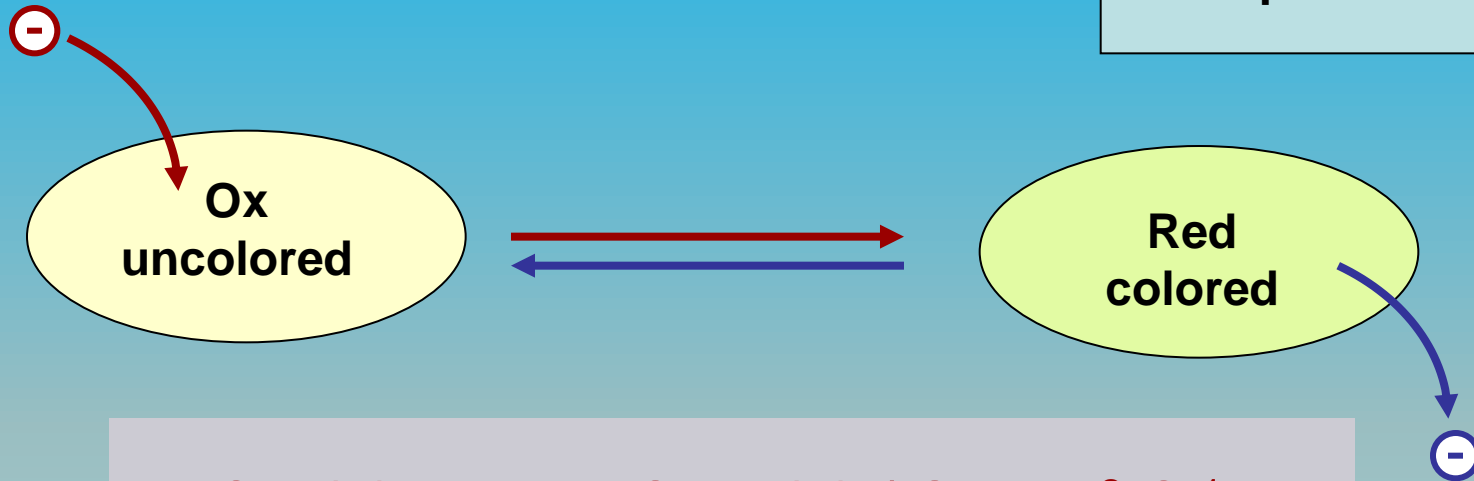


ΔT : thermochromy
 \vec{E} : electrochromy
 $h\nu$: photochromy
 H_2/O_2 : gasochromy

Electrochromy

Basic principle

Coloration in reversible redox process



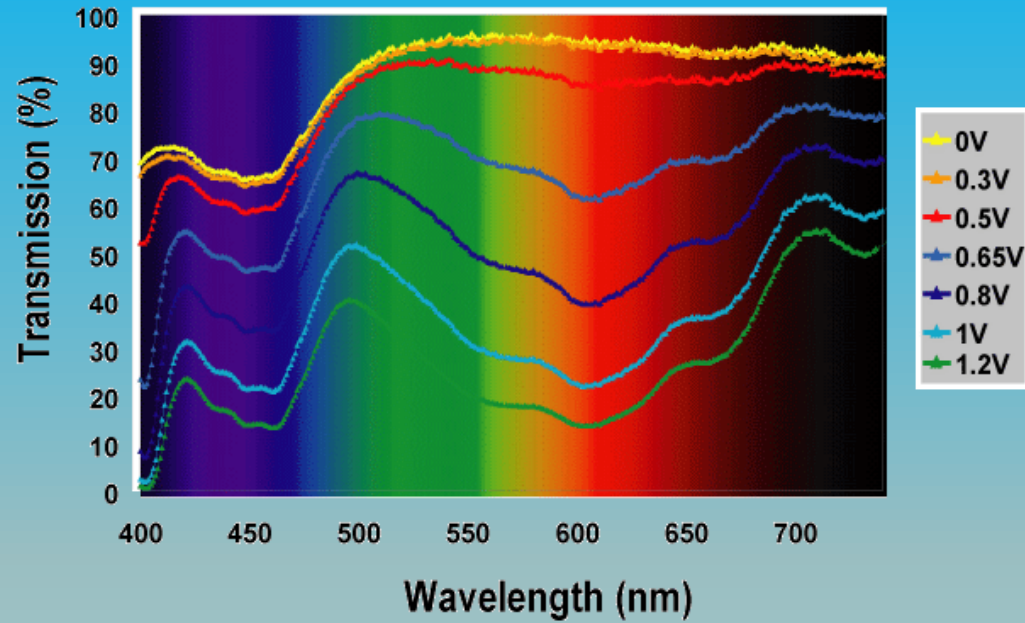
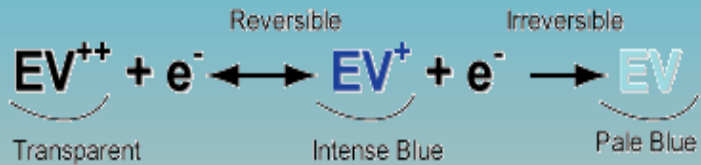
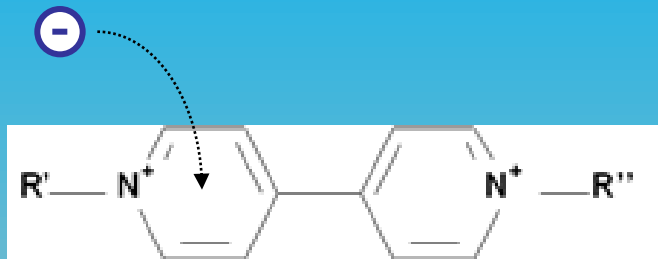
$$CE(\lambda) = \eta = \Delta O.D.(\lambda) / Q \text{ [cm}^2 \text{ C}^{-1}\text{]}$$

CE = coloration efficiency

O.D. = optical density

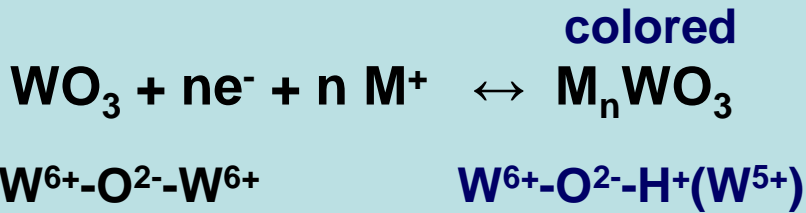
Q = charge transferred per cm²

Alkyl-viologenes (methyl-, ethyl-)



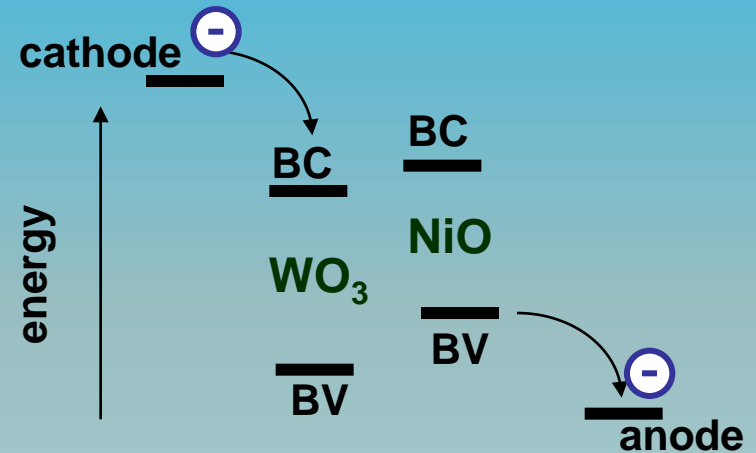
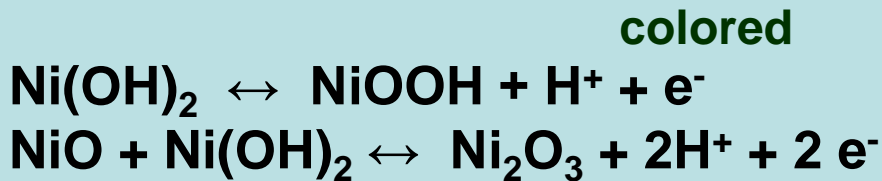
Catodic Coloration:

WO_3 , MoO_3 , V_2O_5 , Nb_2O_5 , TiO_2 , Cu_2O



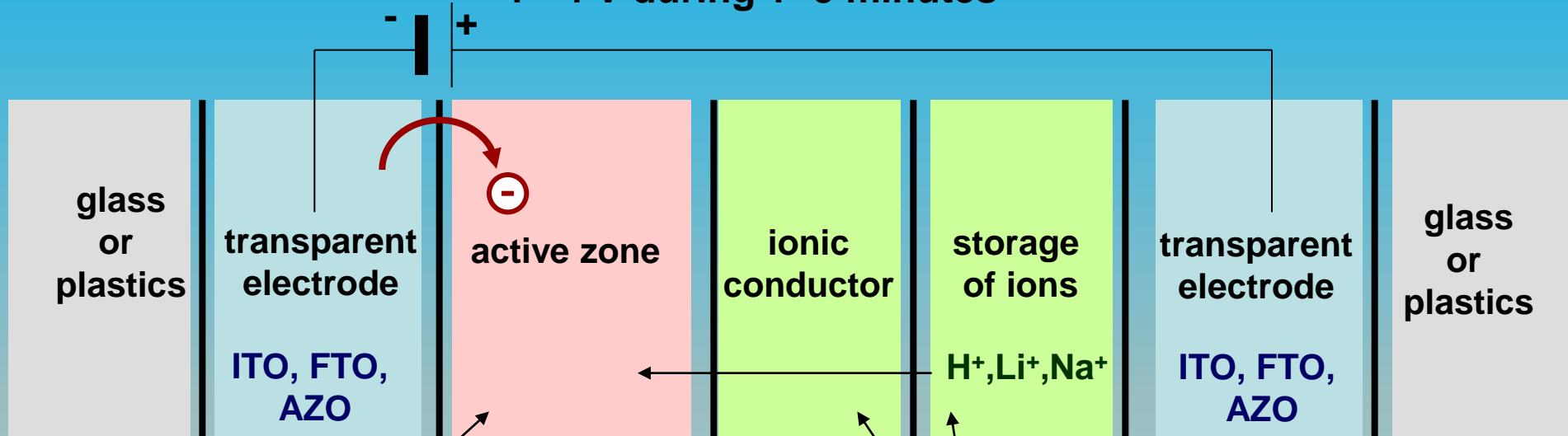
Anodic Coloration:

NiO , CoO , Cu_2O , IrO_2



Electrochromic cells

1 - 4 V during 1- 5 minutes

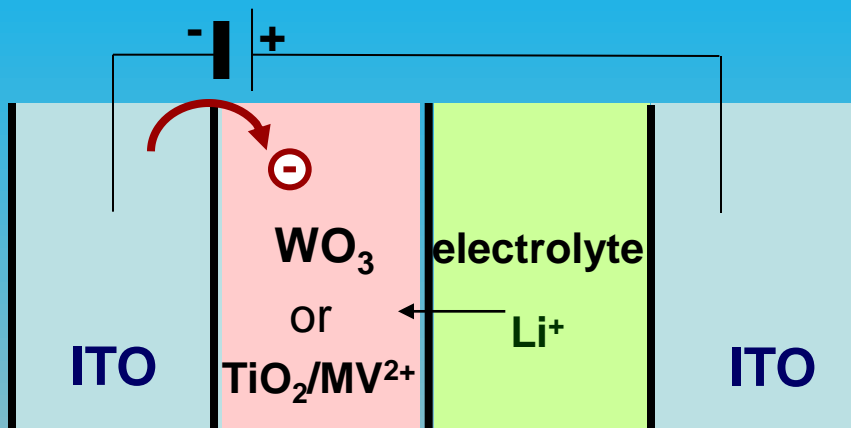


molecules
nanoparticles
org. polymers

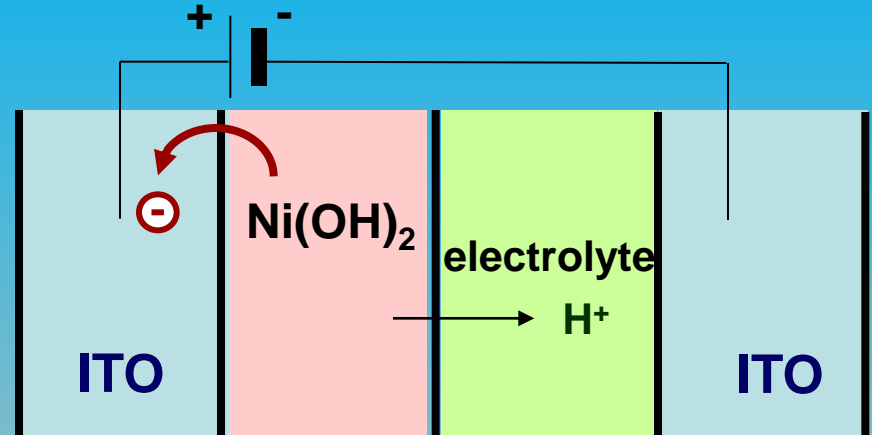
**Good conductor
(ionic/electronic!)
Life time: 10.000 - 100.000 cycles
(5-20 years)**

Ionic conductors
Gels, membranes:
- ZrO_2 , Ta_2O_5
- organosiloxanes
- org. polymers: PEO, PVA

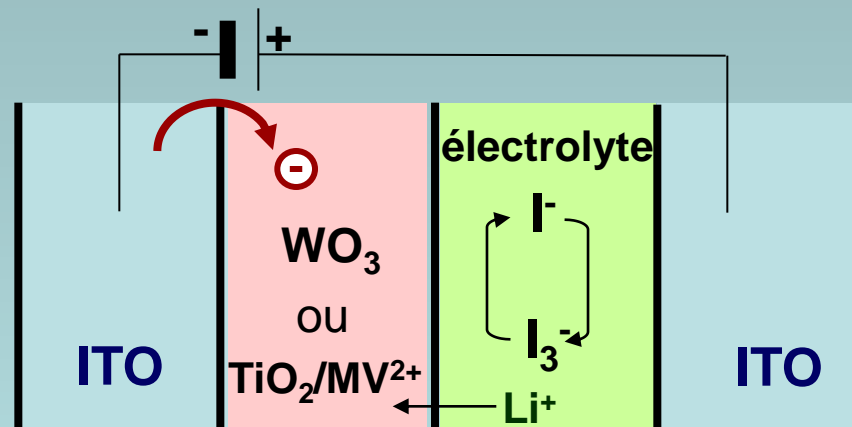
Catodic Coloration



Anodic Coloration



Catodic Coloration with propulsion



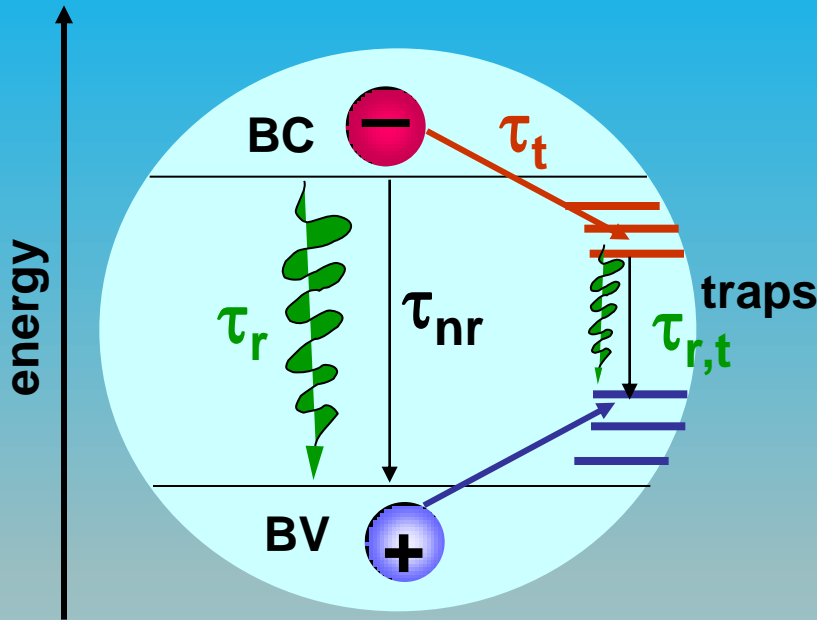
Pilkington, St Gobain,
Daimler Chrysler



3.3 Photo- and electroluminescence of semiconductor nanoparticles

Application domains:

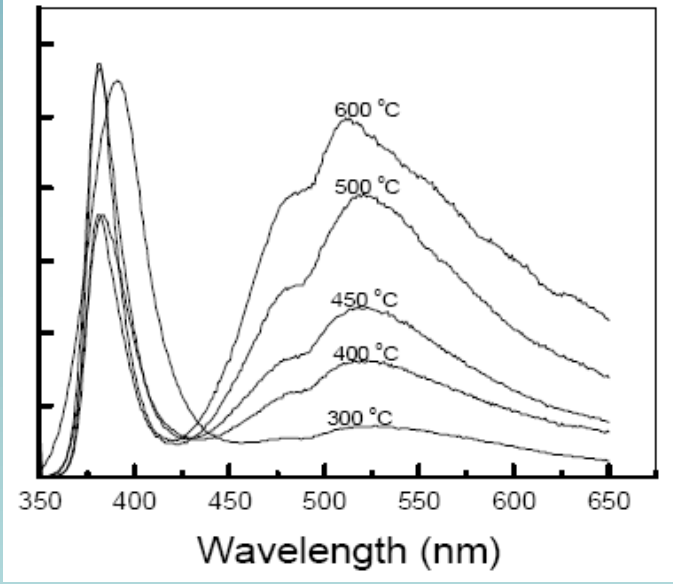
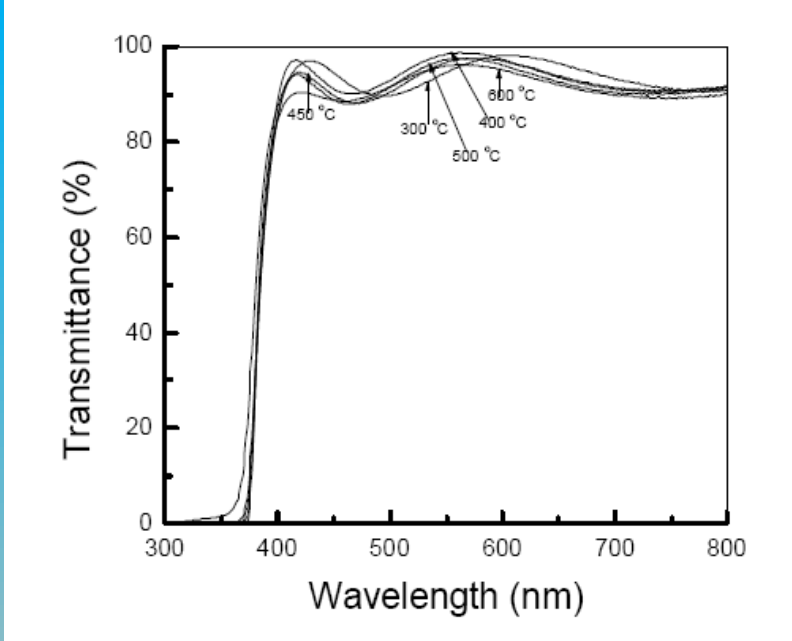
1. Bio-imaging systems
2. Electroluminescence (displays)
3. Photonic circuits: amplifiers (LASER)



$$\tau_t \sim \tau_D \sim \tau_{nr}$$

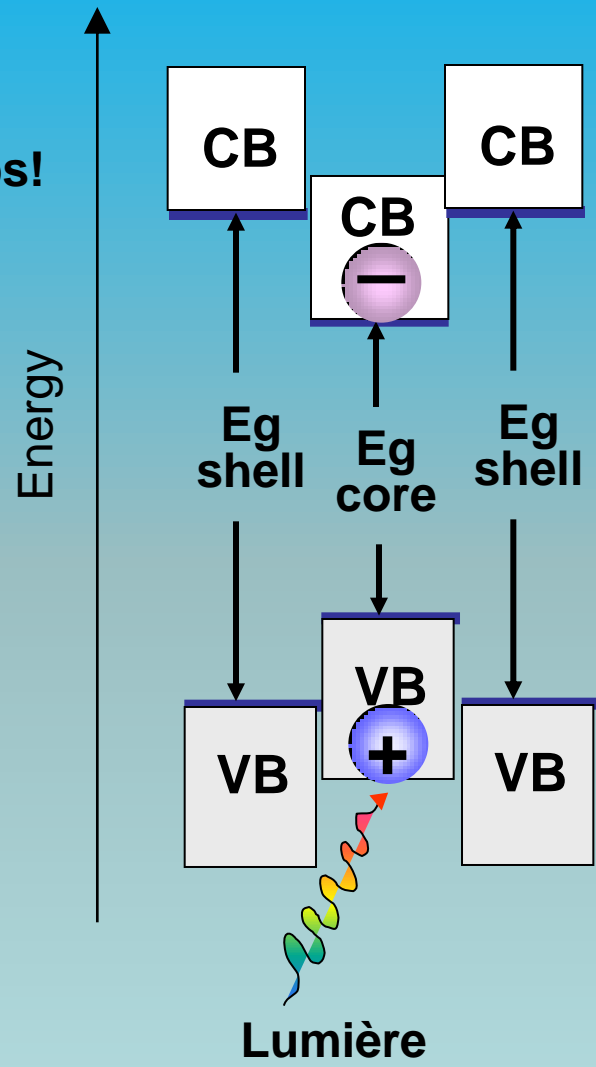
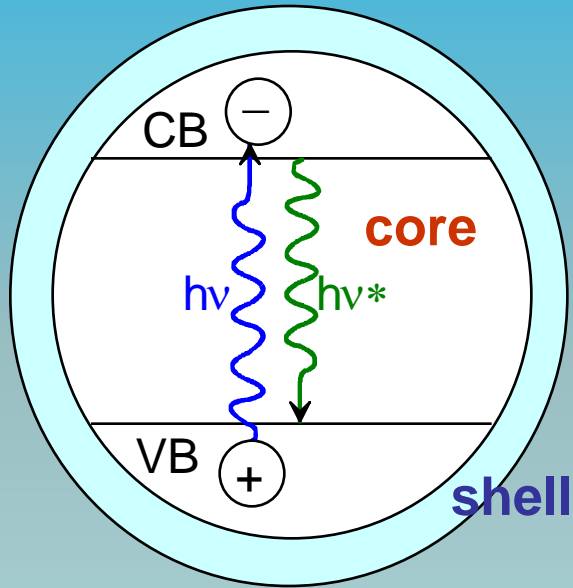
$$\tau_{r,t} > \tau_r > \tau_{nr}$$

$$\Phi < 0,1\%$$

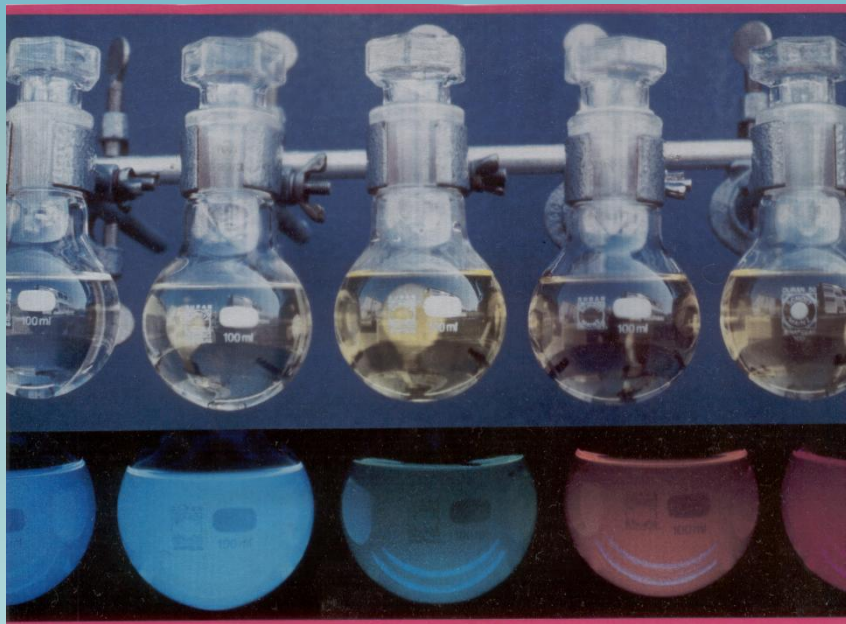
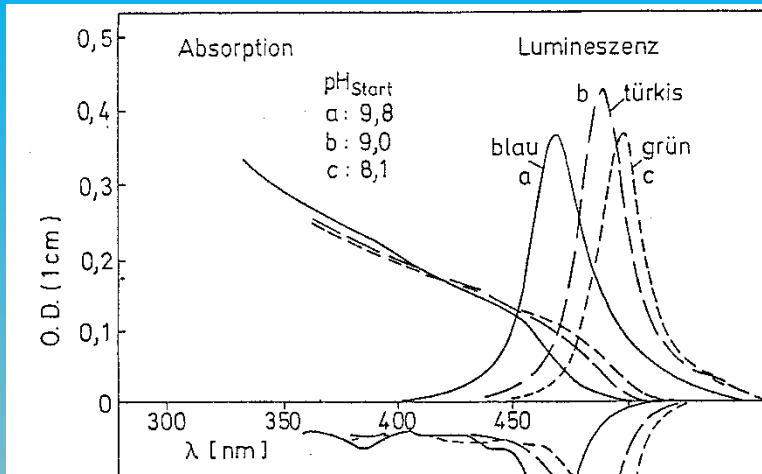


"core/shell" nanostructures

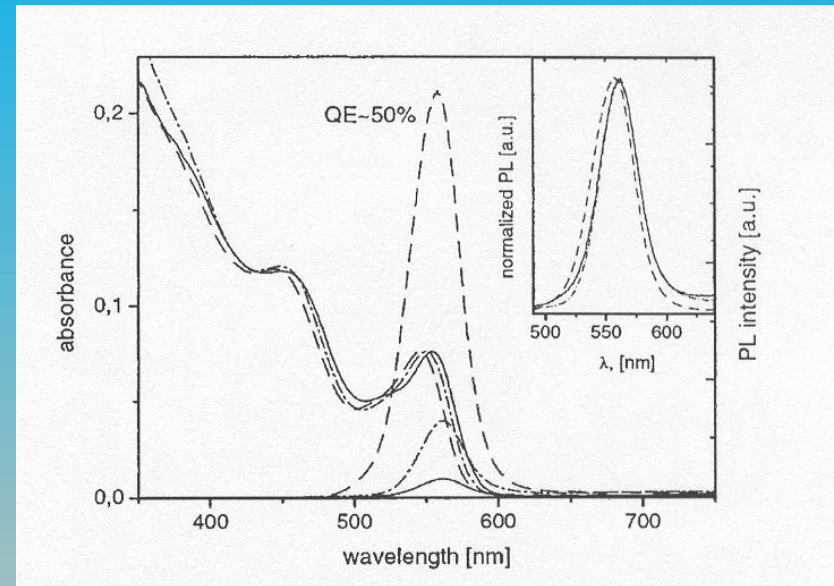
Surface passivation, elimination of traps!



CdS-Cd(OH)₂



CdSe-ZnS



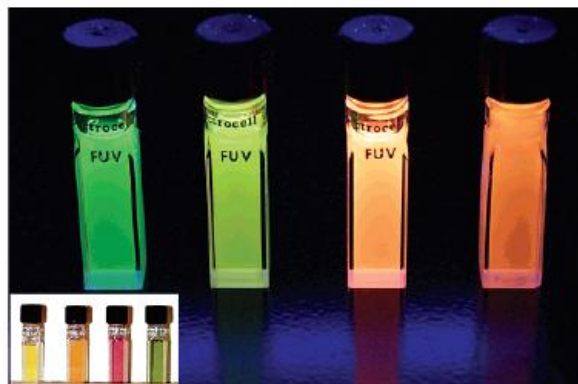
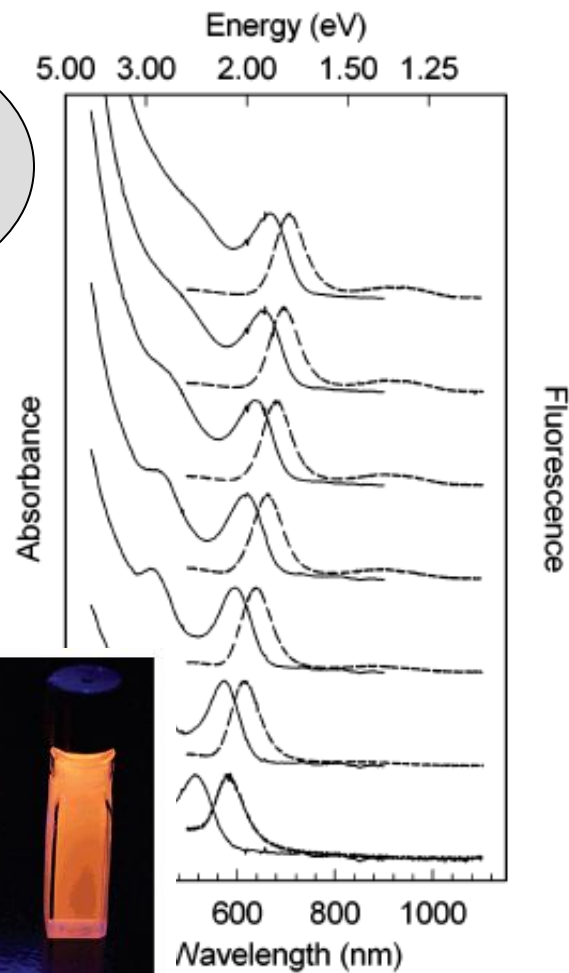
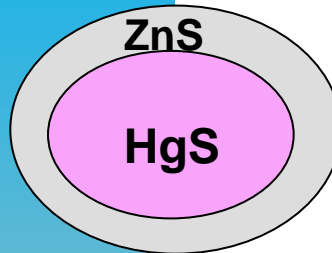
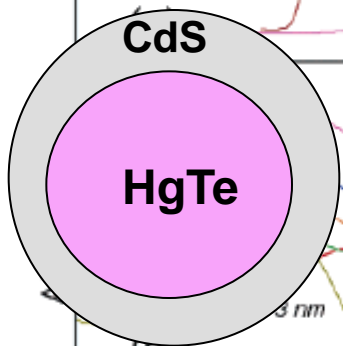
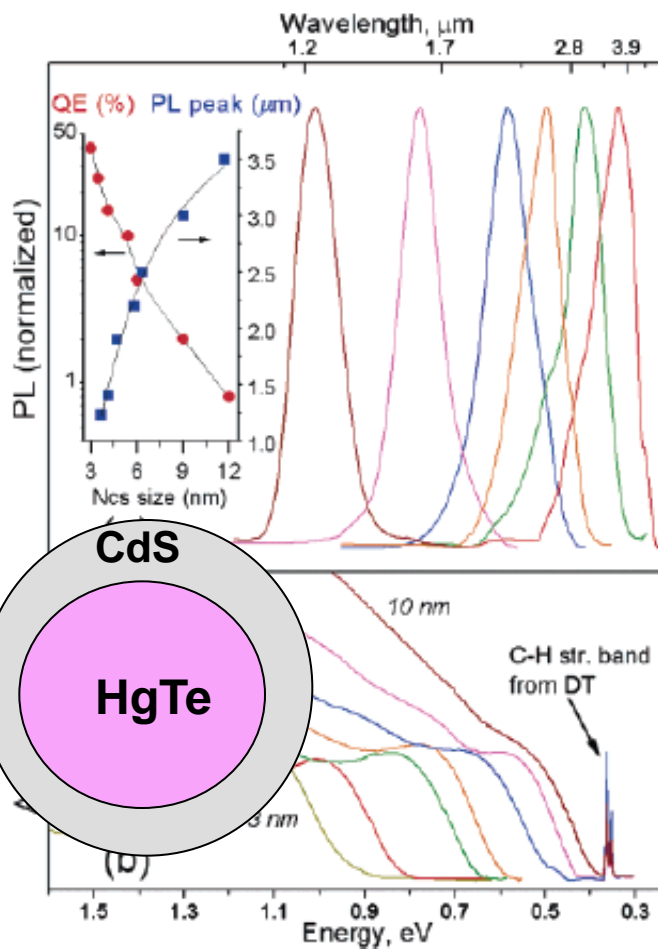
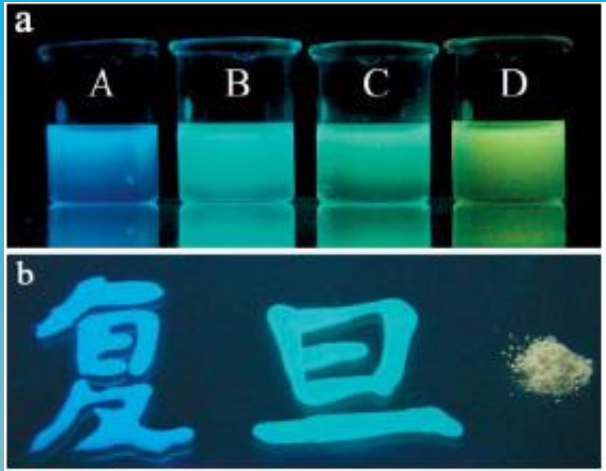


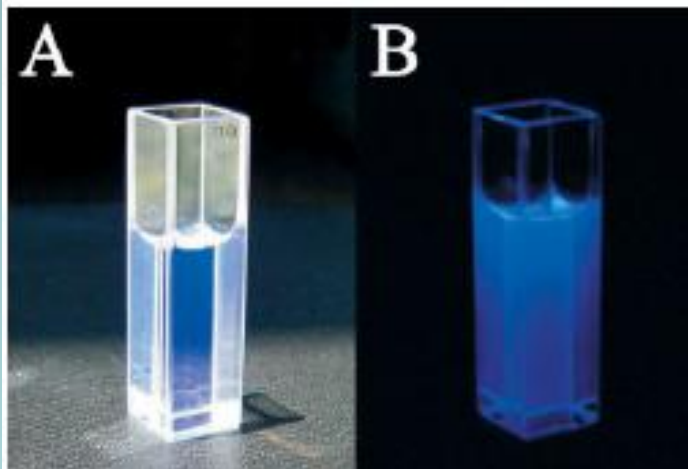
Figure 1. Representative room temperature PL (a) and absorption spectra of DT-capped HgTe NCs in CCl_4 . The insets show the dependence of the PL peaks with the corresponding quantum efficiency (a) and illustrate the phase transfer completeness for MEA used as stabilizer (b).

PEG-ZnO nanocomposites



H.M. Xiong et al
Adv. Funct. Mater. 2005
Adv. Mater. 2006

PMMA-ZnO „core-shell“



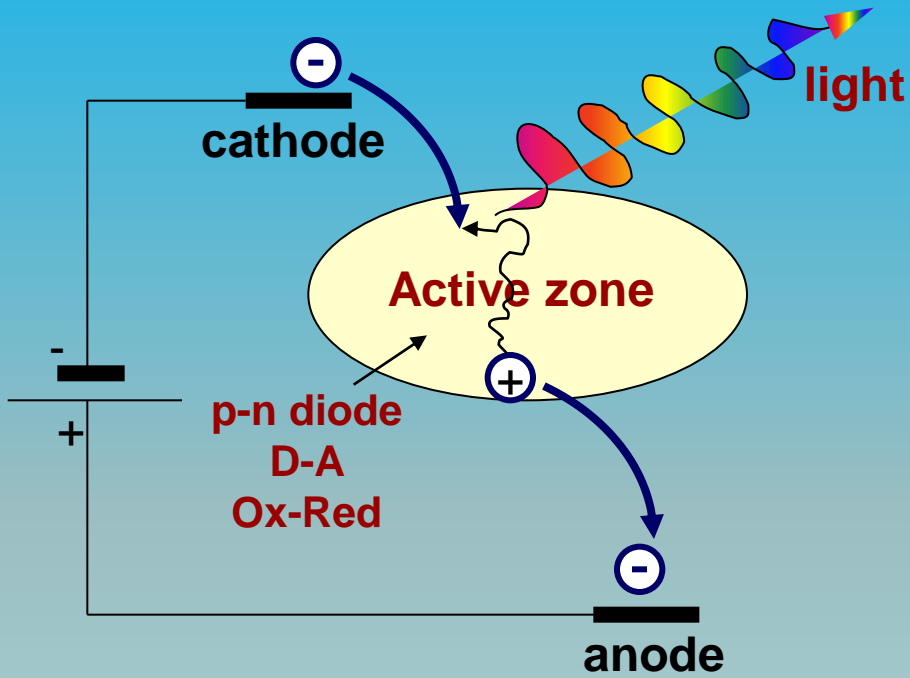
Li-ZnO-SiO₂ „core-shell“



X. Yu et al. J. Lumin. 2006

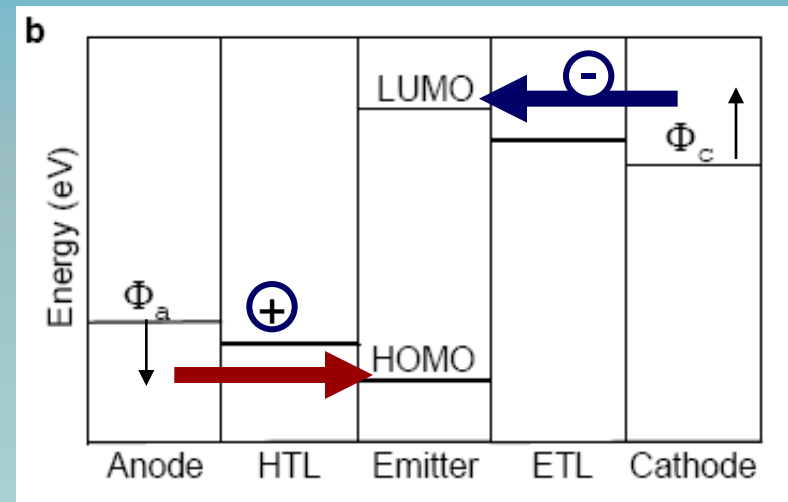
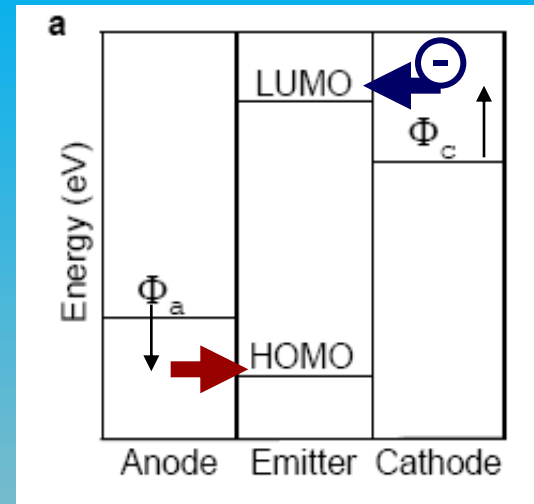
Electroluminescence

(inverse photovoltaic effect)



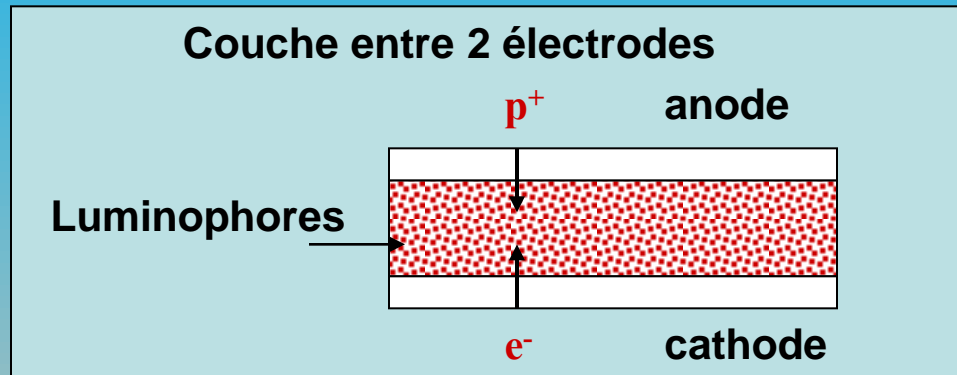
$$ELE = \eta = P_{\text{light,out}} / P_{\text{el,in}}$$

ELE = electroluminescence efficiency

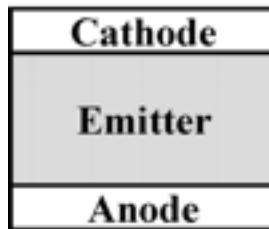


Cellule électrochimique d'écran électroluminescente

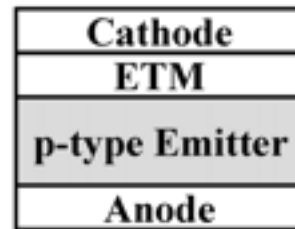
Principe de fonctionnement



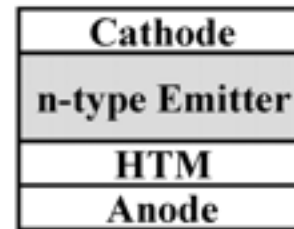
Systèmes à plusieurs couches



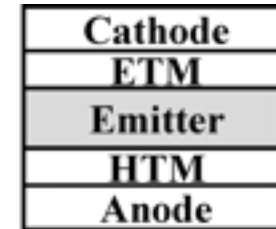
a



b.

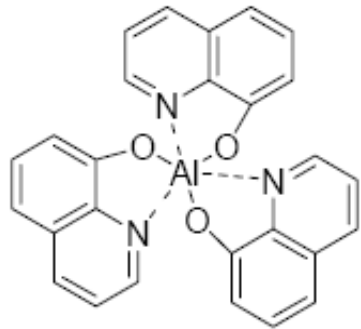


c

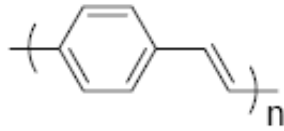


d

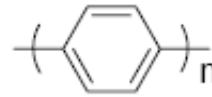
Molécules actives d'OLED



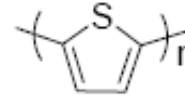
1



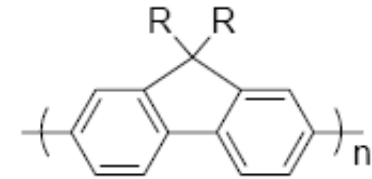
2



3



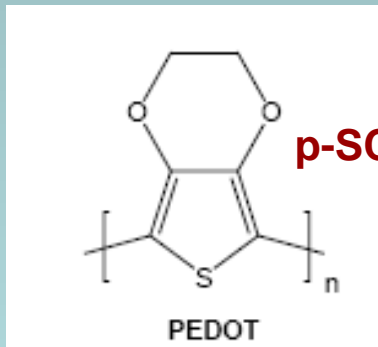
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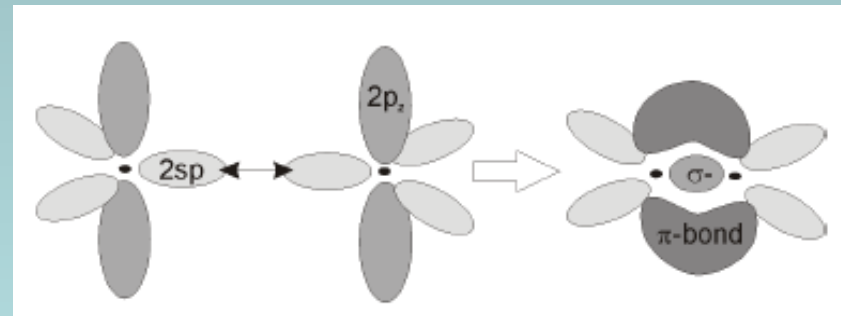
5

1. Alq₃ = aluminium tris(8-hydroxyquinoline)
2. PPV = poly(p-phenylene-vinylene)
3. PPP = poly(1,4-phenylene)
4. PTh = polythiophenes
5. PF = polyfluorenes

PEDOT



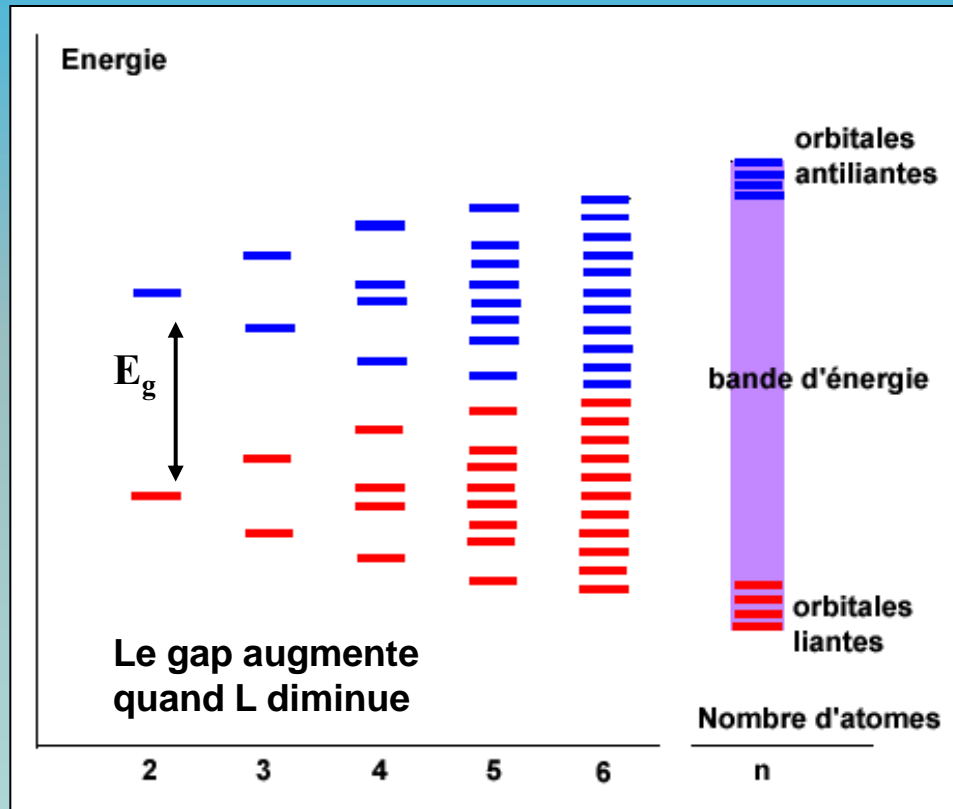
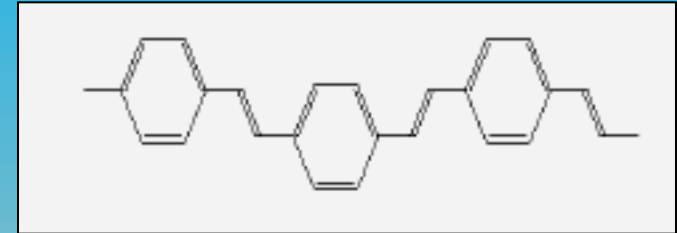
PEDOT



Poly-(3,4-ethylenedioxythiophene)

Les systèmes polymériques à doubles liaisons conjuguées

PPV = poly(phénylène-vinylène) $E_g = 2,5$ eV
émission jaune-vert



Dopage des semi-conducteurs organiques

chimique ou électrochimique

⇒ **Oxydation** → trous positifs → semi-conducteur 'p'



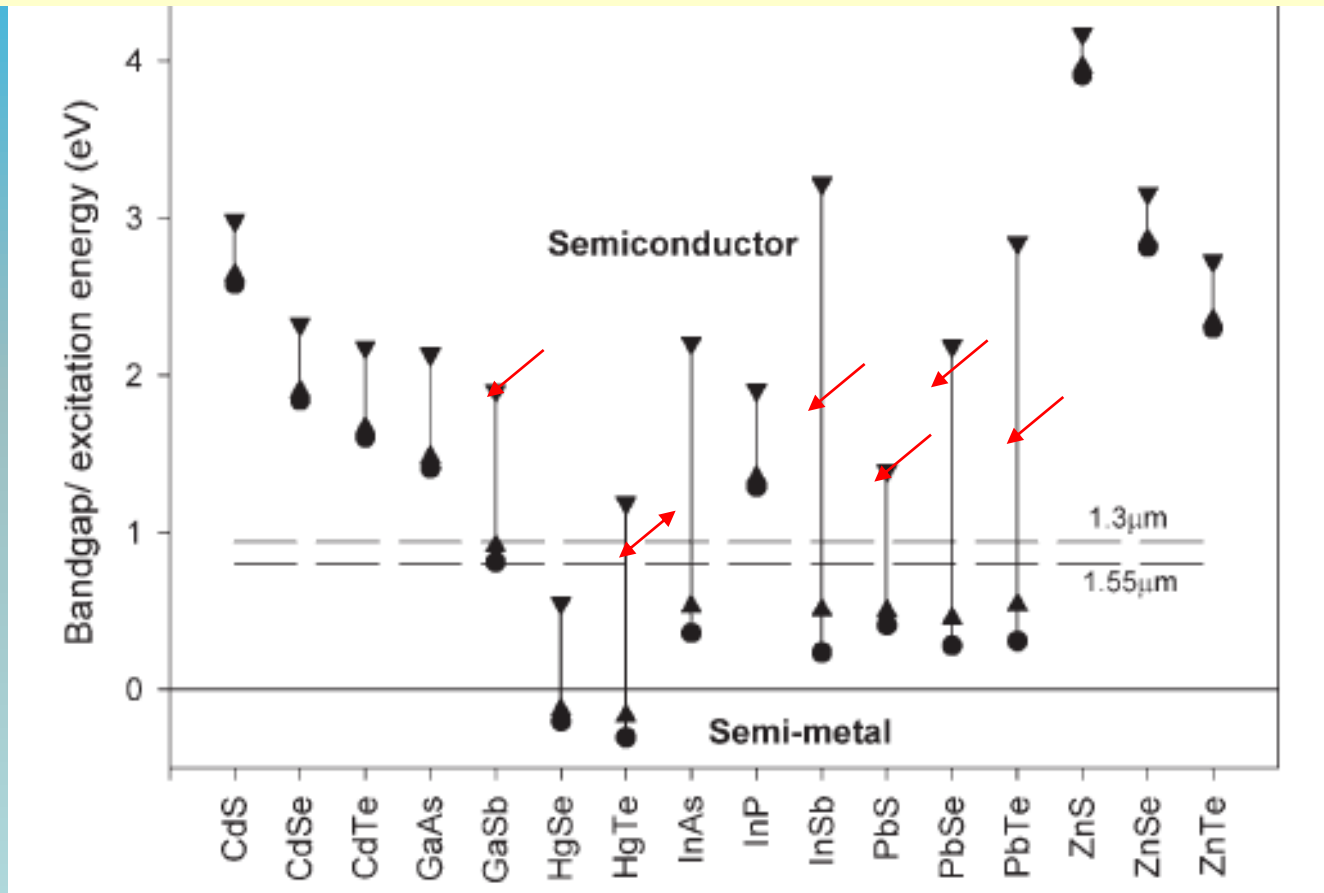
⇒ **Réduction** → électrons → semi-conducteur 'n'

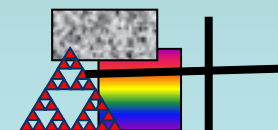
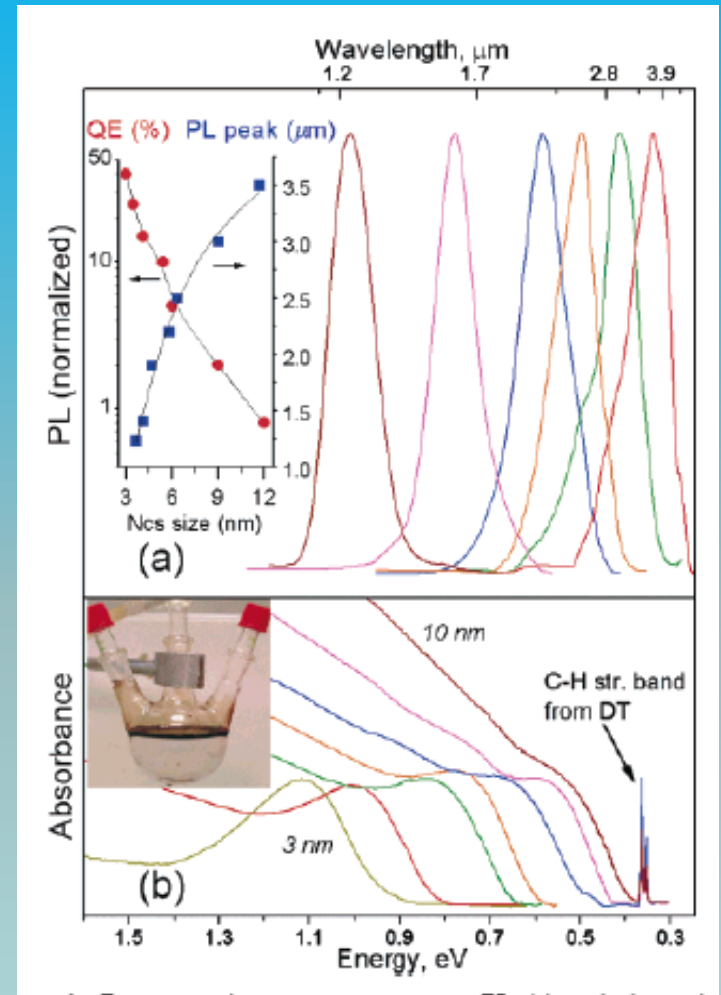
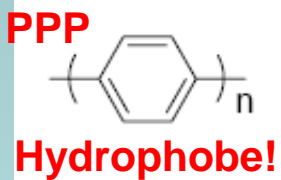
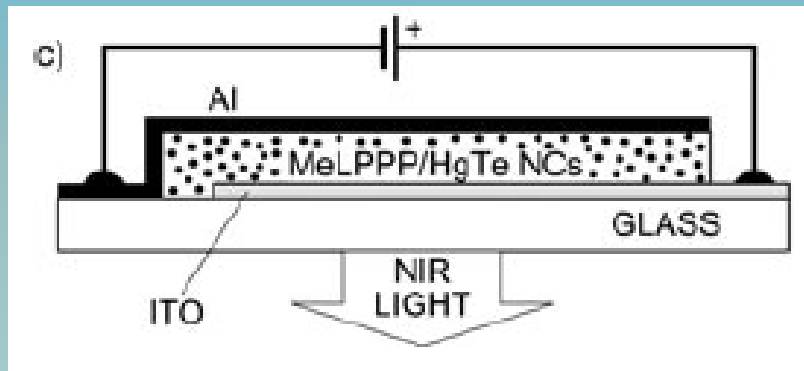
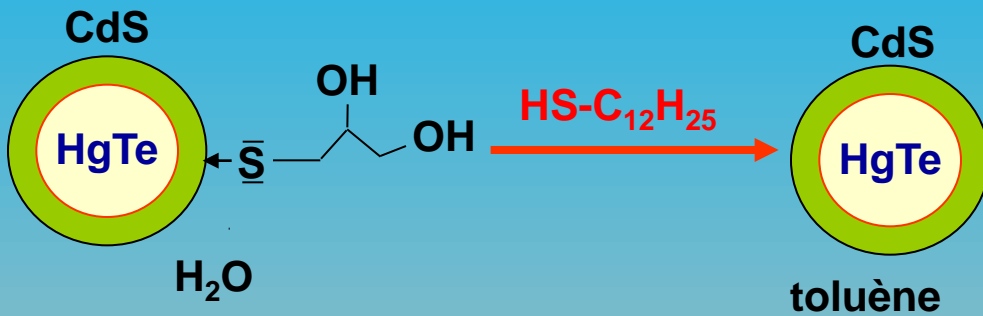


La conductivité passe de 10^{-5} à 10^3 S/cm

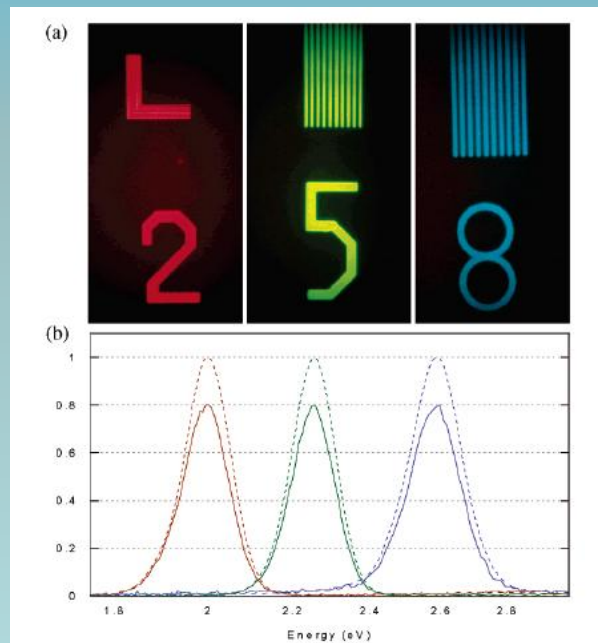
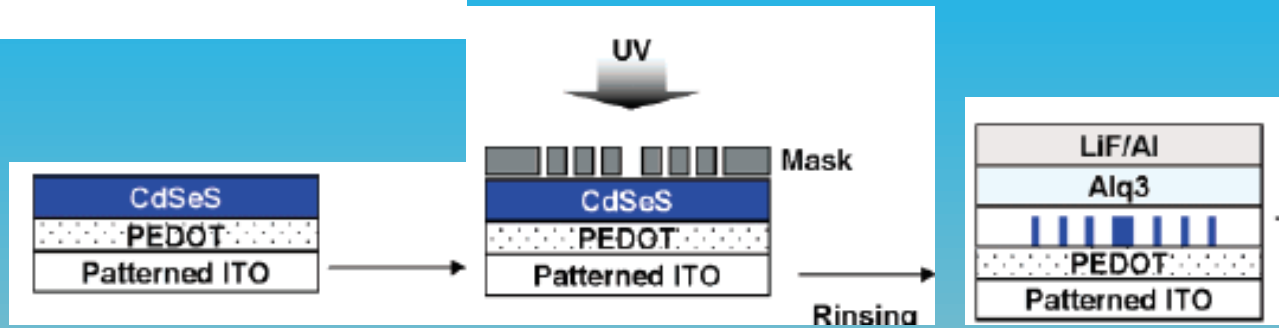
Électroluminescence avec nanostructures semi-conductrices

« *Band gap engineering* » avec nanocristaux quantiques
Taille moyenne: 3 nm – 10 nm

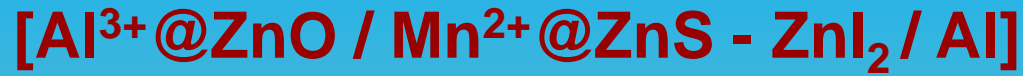




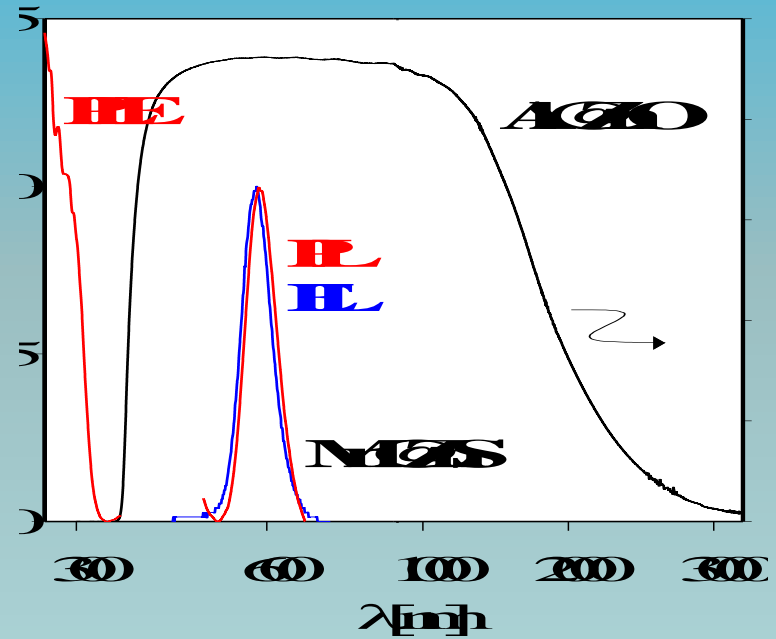
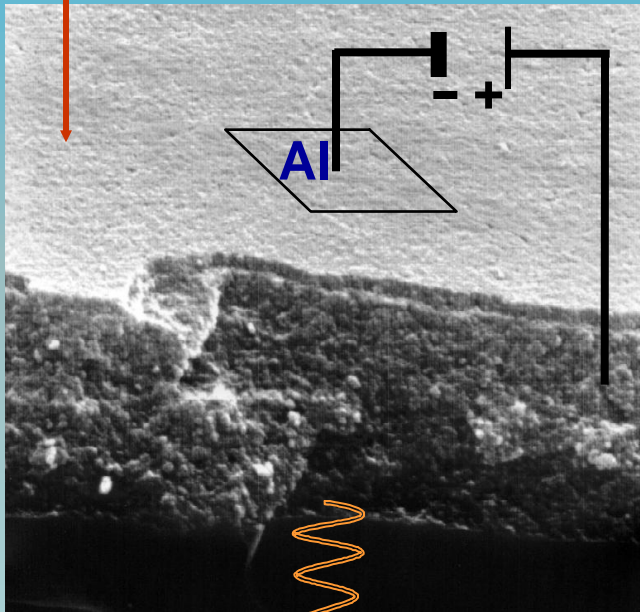
Langmuir 2006, 22, 2407–2410



Electroluminescence in nanocrystalline bilayers

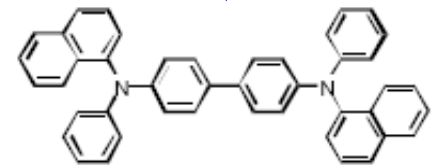
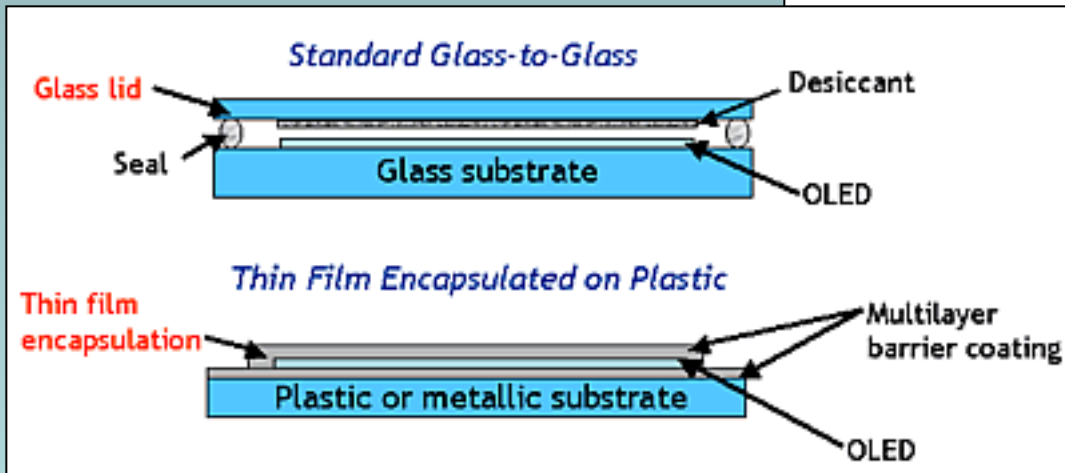
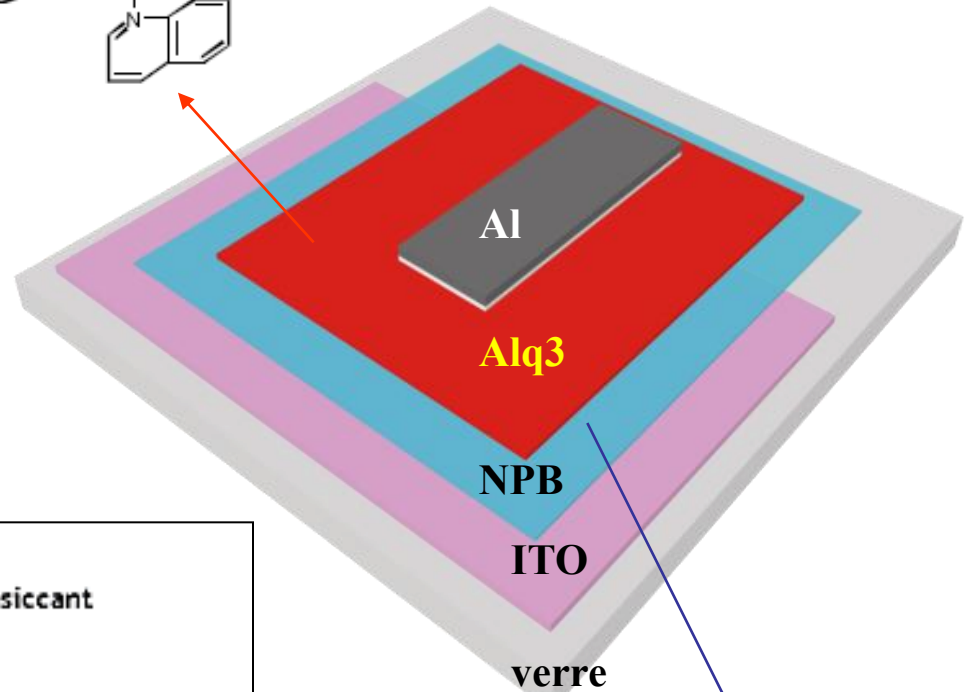
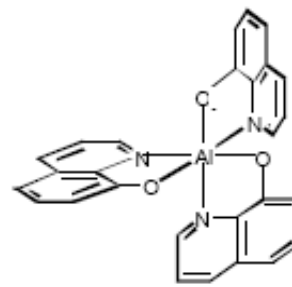
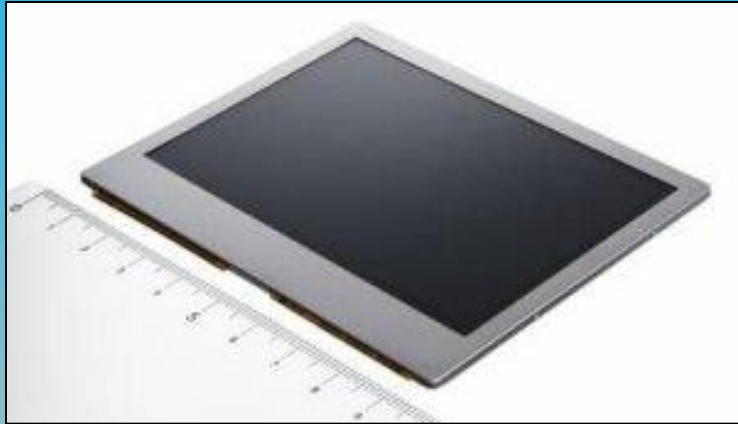


$ZnI_2(TBP)_2$ – infiltré



J. Phys. Chem. B 1998

Flat panels



NBP





émission des deux côtés



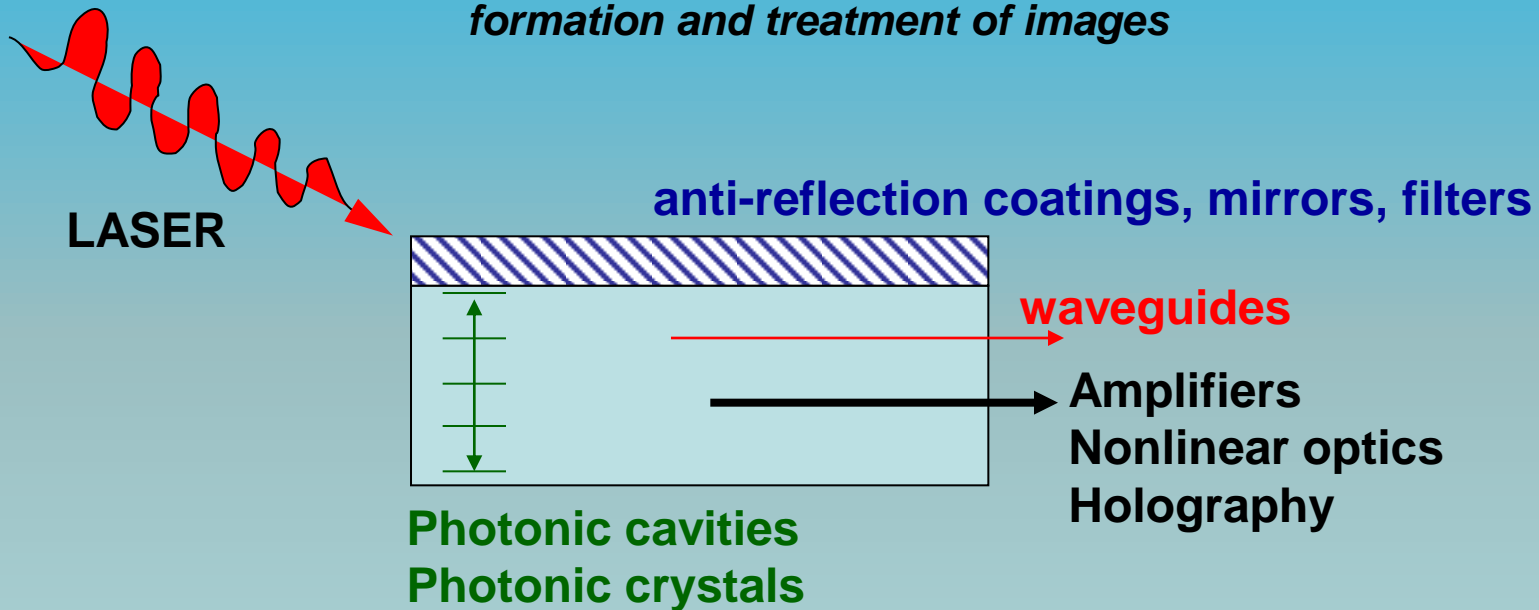


**Miniaturized plastic TV
(180000 pixel, at present 500000pixel)**

3.4 Photonic nanomaterials

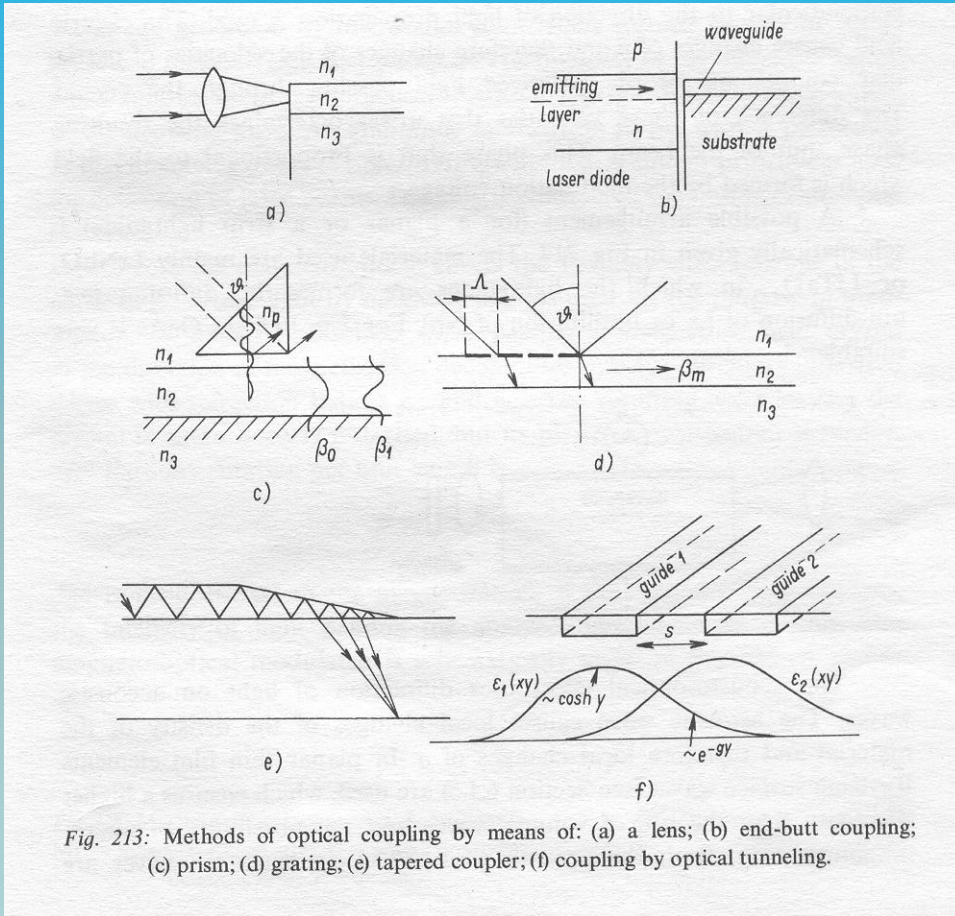
Photonics = Science of light

*production, guiding and manipulation of light
formation and treatment of images*



Waveguides (passive, active)

Coupling methods:



Descartes rules:

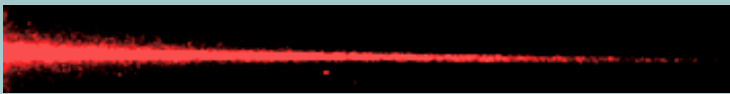
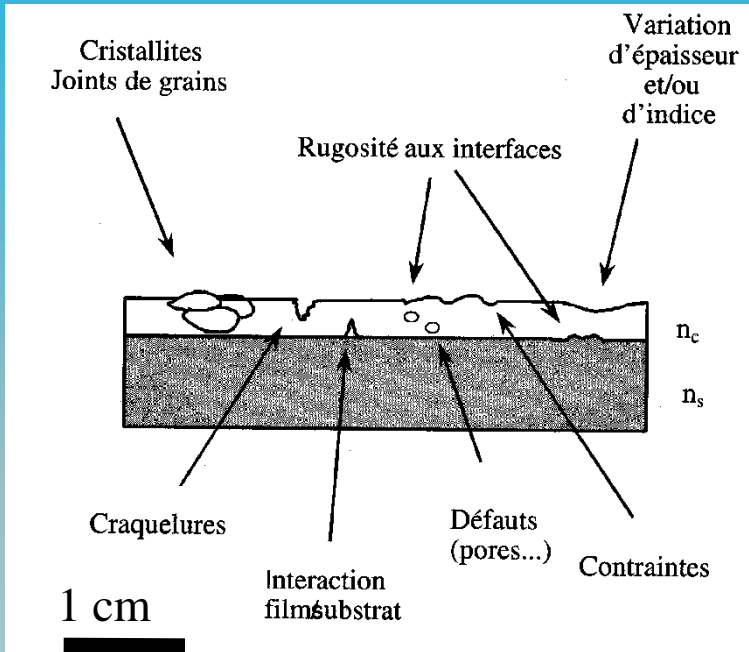
1. Total reflection

$$n_{\text{film}} > n_{\text{substrat}}, n_{\text{air}}$$

2. Number of guided modes - m

$$m \propto \frac{e}{\lambda} \cdot n_{\text{film}}$$

Propagation losses



Damping coefficient : k_A [dB cm⁻¹]

$$k_A [\text{dB} \cdot \text{cm}^{-1}] = \frac{10}{x} OD = \frac{10}{x} \log \frac{I_0}{I}$$

Optical Absorption :

$$\alpha [\text{cm}^{-1}] = \frac{\ln 10}{10} \cdot k_A [\text{dB} \cdot \text{cm}^{-1}]$$

Light scattering in composites:

$$D.O. = 0,325 \cdot \Phi_p \cdot x \cdot R_p^3 \cdot \frac{1}{\lambda^4} \left(\frac{n_{\text{particule}}}{n_{\text{matrix}}} - 1 \right)$$

Desired quality:

1 dB km⁻¹ (longe distances)

0,1 dB cm⁻¹ (short distances)

sol-gel derived materials:

1. organosiloxanes:

$k_A \sim 0,1 \text{ dB cm}^{-1}$

2. Metal oxides

TiO₂ (2,7) ; ZrO₂ (2,2) ; ZnO (2)

$k_A \sim 0,5 - 2 \text{ dB cm}^{-1}$

3. Polymers

PMMA

$k_A \sim 10 \text{ dB cm}^{-1}$

Origin of opt. absorptions:

TELECOM domain 1 - 2 μm:

vibrations of OH's, CH's

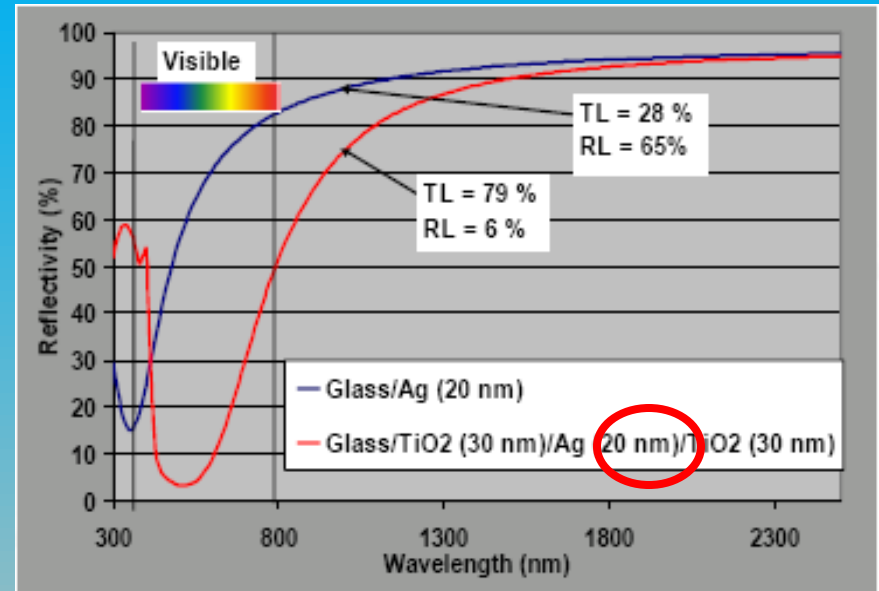
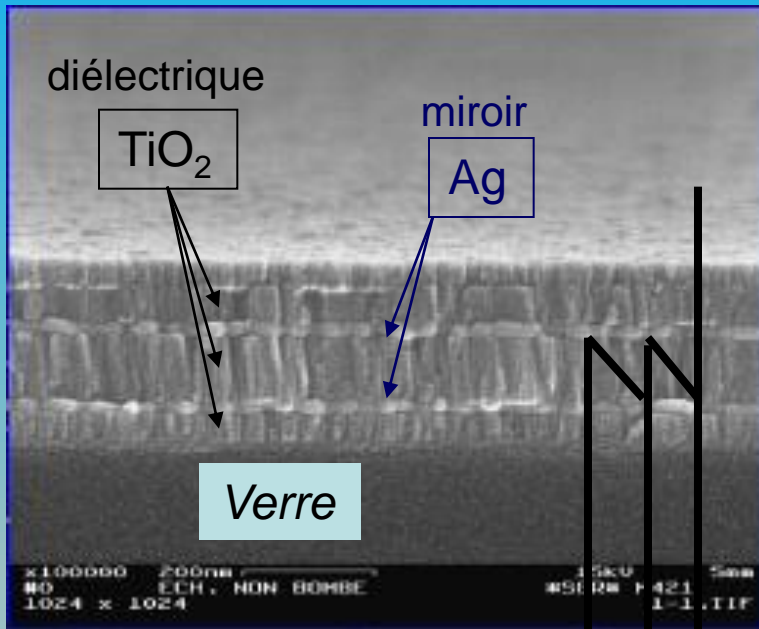
Electronic transitions of foreign atoms

Silica: < 250 nm

Polysiloxanes: 300 - 400 nm

Polyphosphazenes: < 220 nm

Fabry-Pérot coatings



Dépôt des couches minces
via "sputtering"

UV-vis

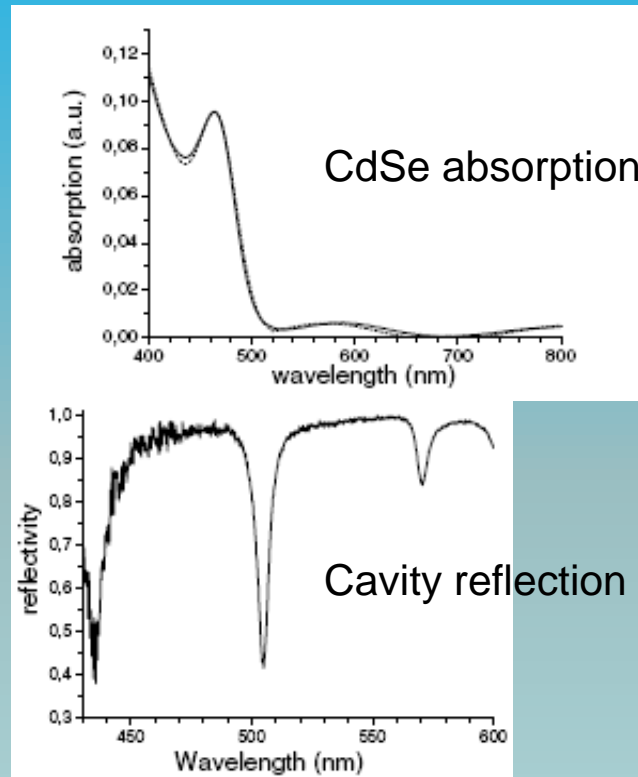
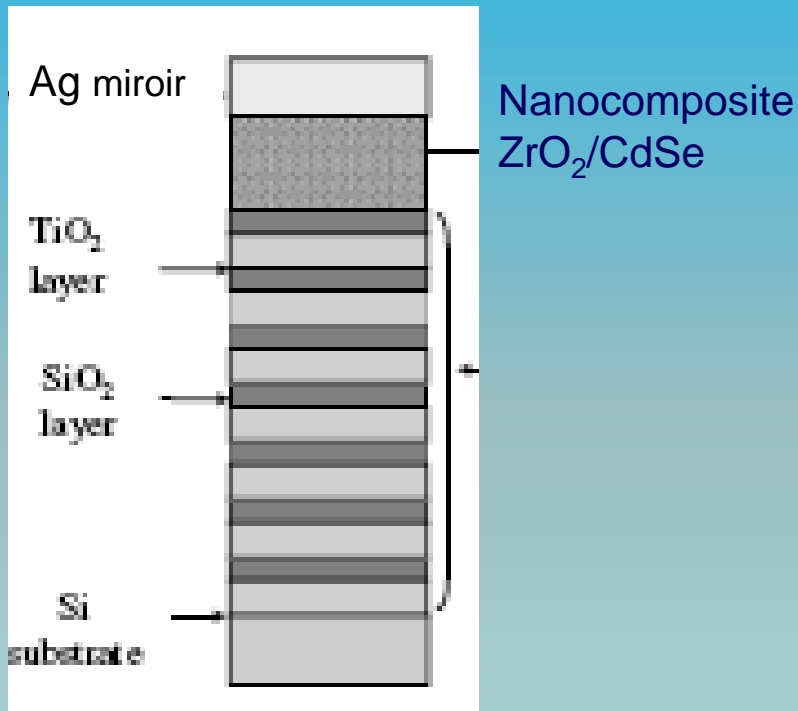


Source: St. Gobain
Herve Arribart

Sol-gel derived nanomaterials:

Bragg reflection produced in alternate SiO_2 , TiO_2 multilayers

Microcavity composed of nanocrystalline ZrO_2 with 10% CdSe

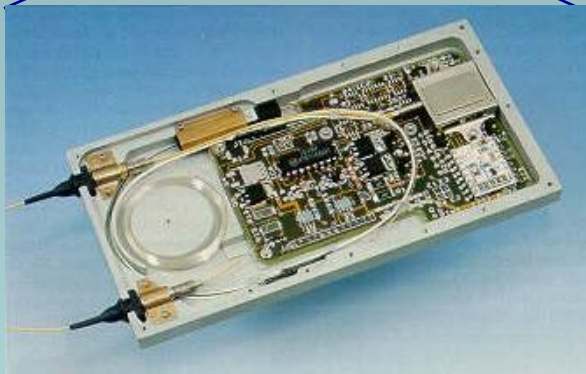
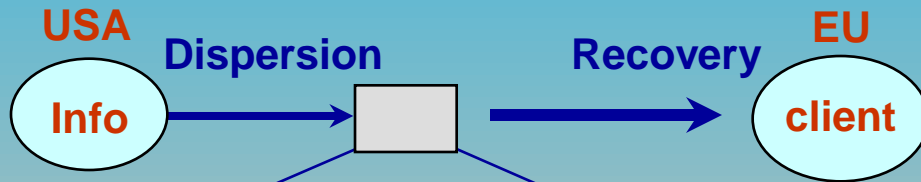


Microcavity strongly doped with CdSe nanocrystals

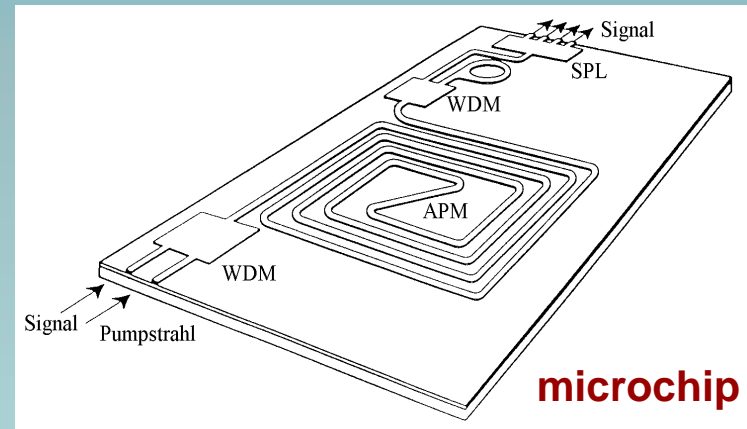
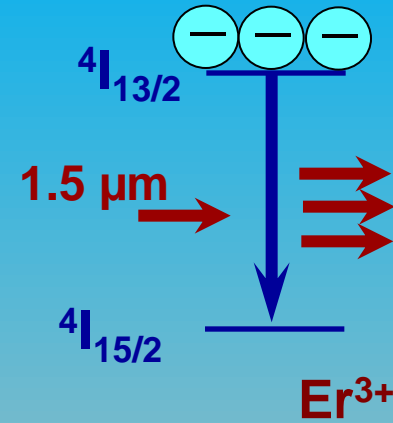
S. Rabaste¹, J. Bellessa^{1,a}, C. Bonnard¹, J.C. Plenet¹, and L. Spanhel²

¹ Laboratoire de Physique de la Matière Condensée et des Nanostructures, Université Claude Bernard Lyon 1, CNRS-UMR 5586, 43 boulevard du 11 Novembre, 69622 Villeurbanne Cedex, France

Light amplifiers in the NIR regime based on Er³⁺-doped matrix



today



tomorrow

microchip

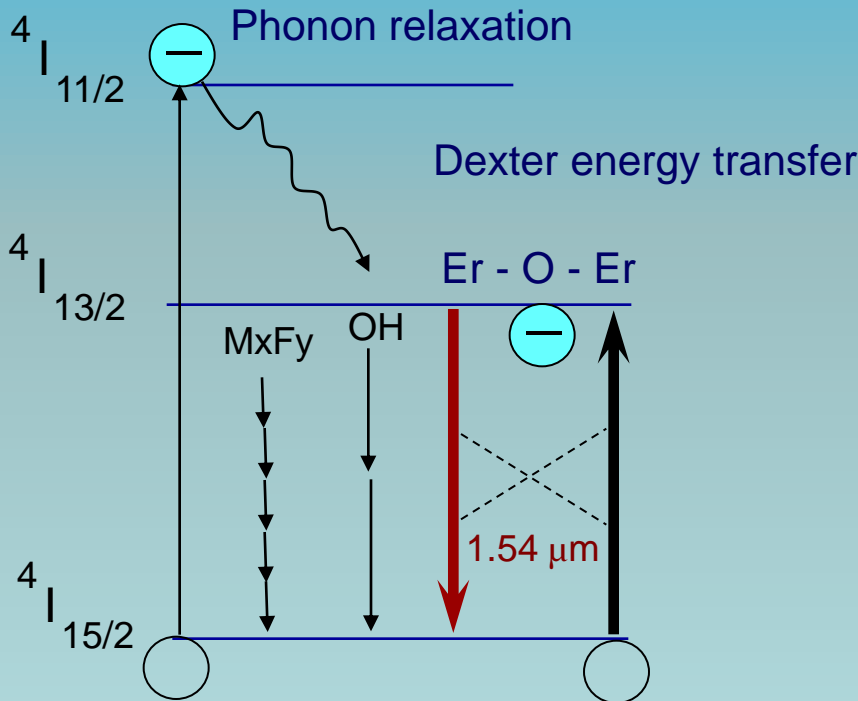
Critical parameters:

1. $N = 10^{20} - 10^{21} \text{ Er}^{3+}/\text{cm}^3$
2. Mean life time of fluorescence (ms !)

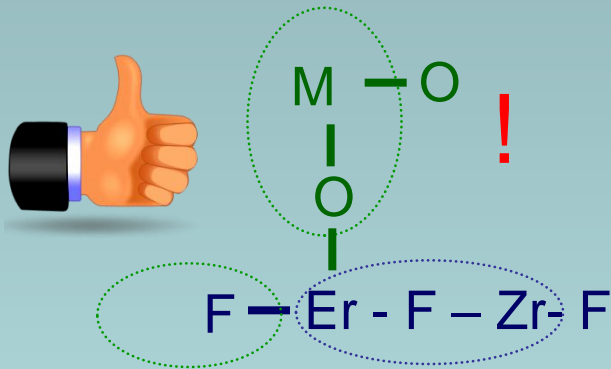
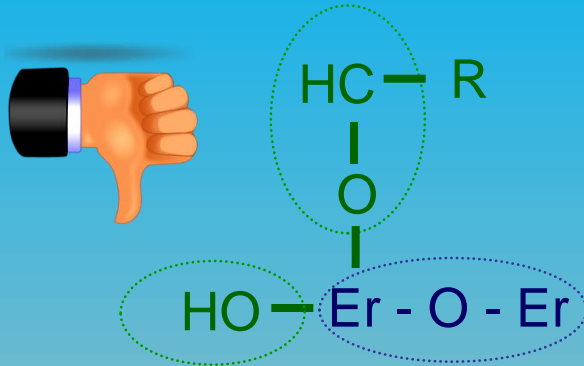
Quantum yield of fluorescence

$$\eta = \frac{W_r}{W_r + W_{nr}} = \frac{W_r}{W_r + A e^{-Bp}}$$

$p = \text{phonon} = \text{lattice vibration}$
 $p = \Delta E / \hbar \omega = 6537 \text{ cm}^{-1} / \hbar \omega$

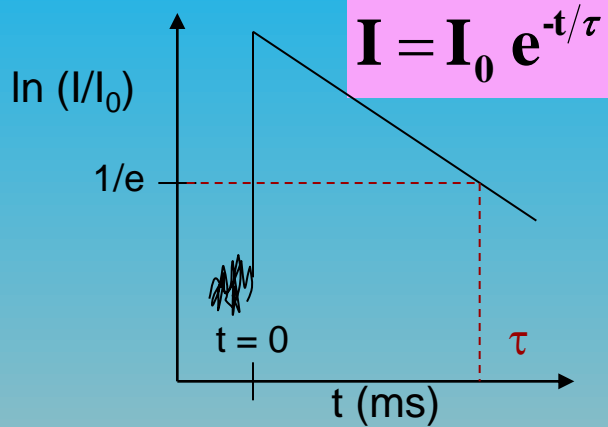


$$p = \Delta E / \hbar \omega = 6537 \text{ cm}^{-1} / \hbar \omega$$

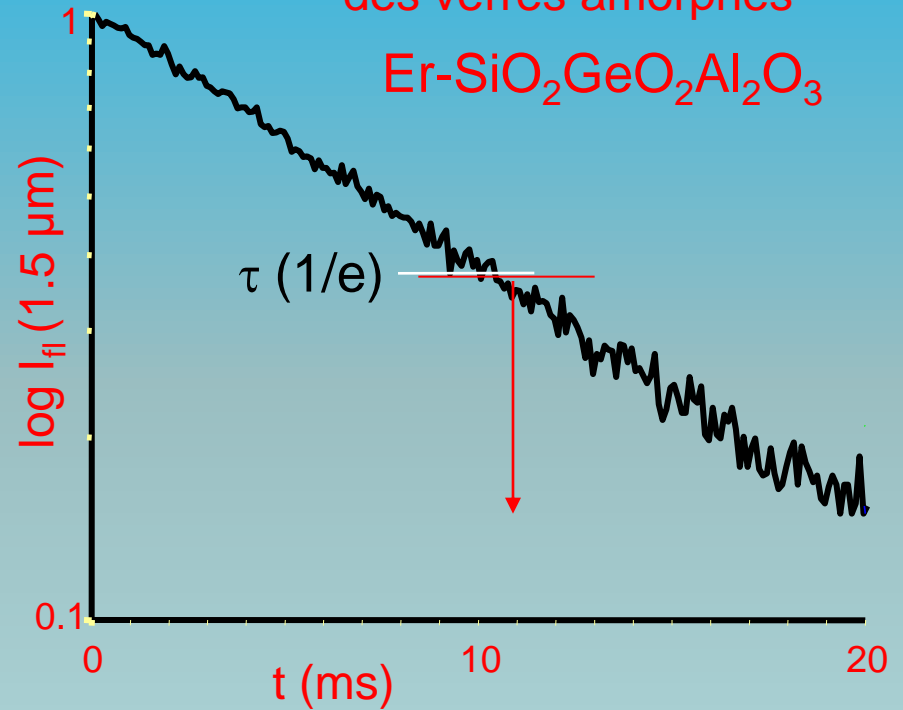


Vibration	$\hbar\omega$ (cm ⁻¹)	p - phonons
O-H	3000-3500	2
C-H	2800	2-3
P-O-P	1300	5
Si-O-Si	1000	6
M _x O _y M _x Chalc _y	300-800	8-20
fluorures des métaux	200-400	15-30

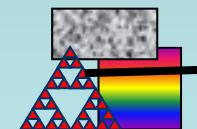
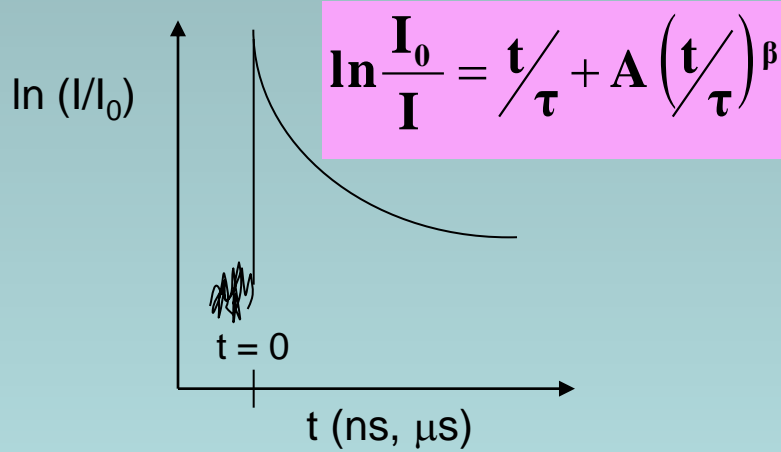
Er³⁺ non-agrégé
Absence des vibrations OH,CH



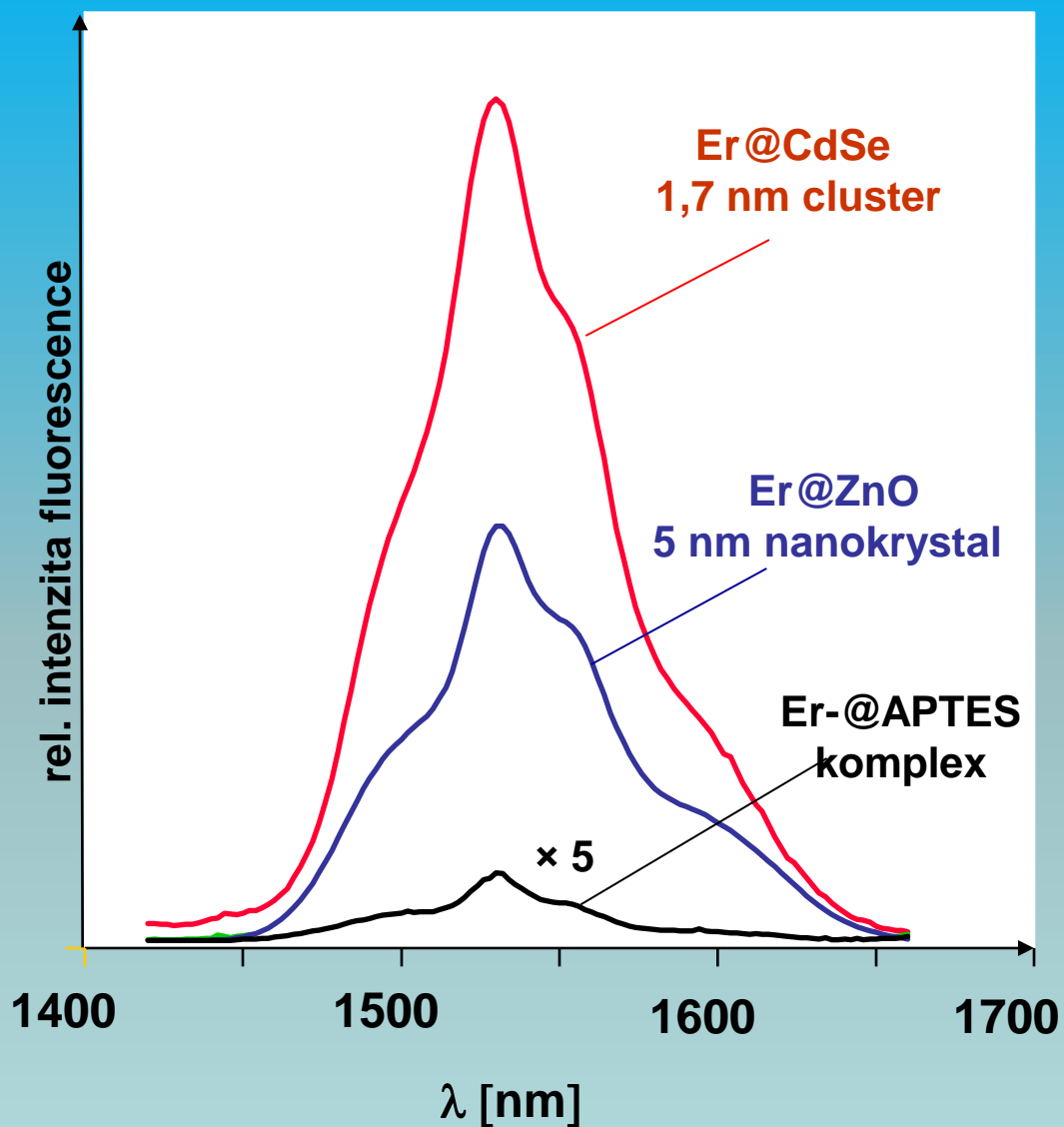
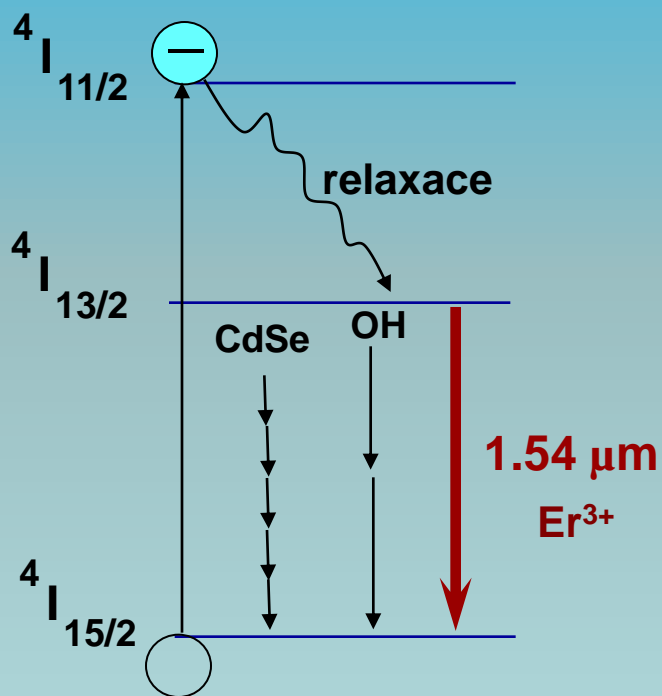
Préformes industrielles
des verres amorphes



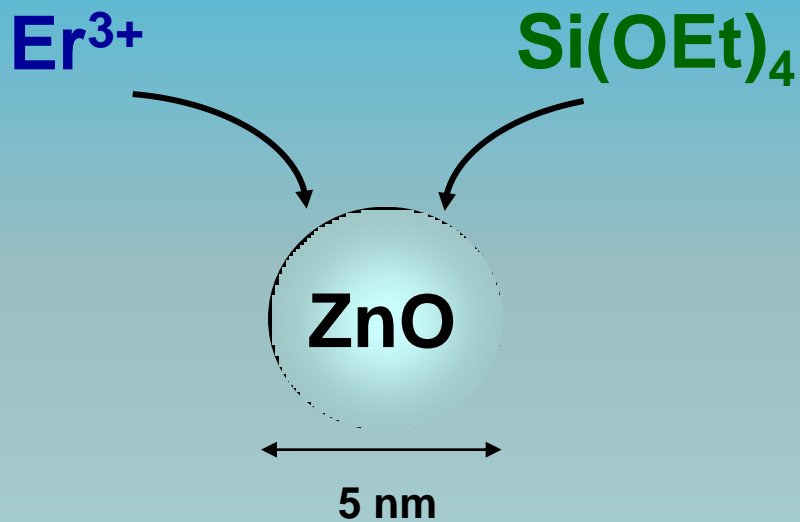
Er³⁺ agrégé
présence des vibrations OH,CH



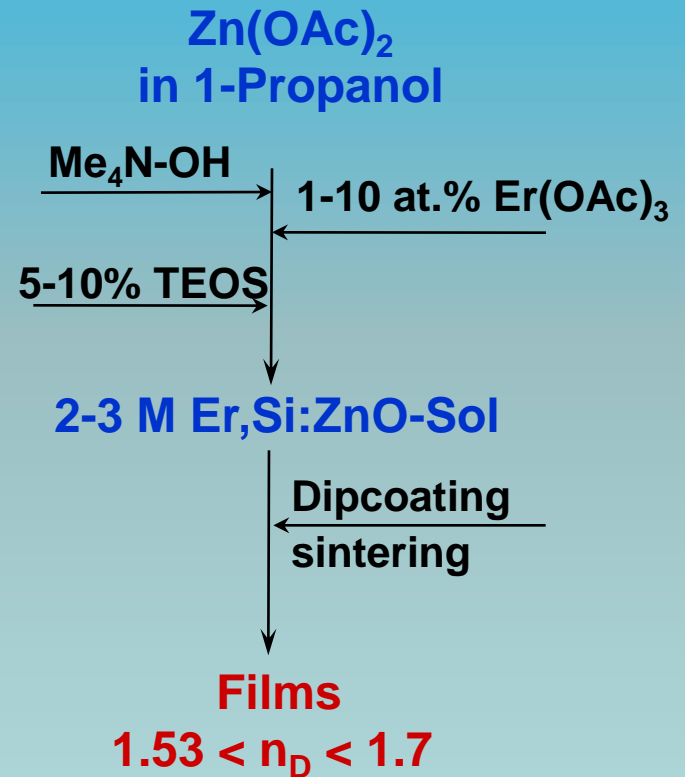
Multifononová relaxace ve fotoexcitovaných etanolických nanokoloidech



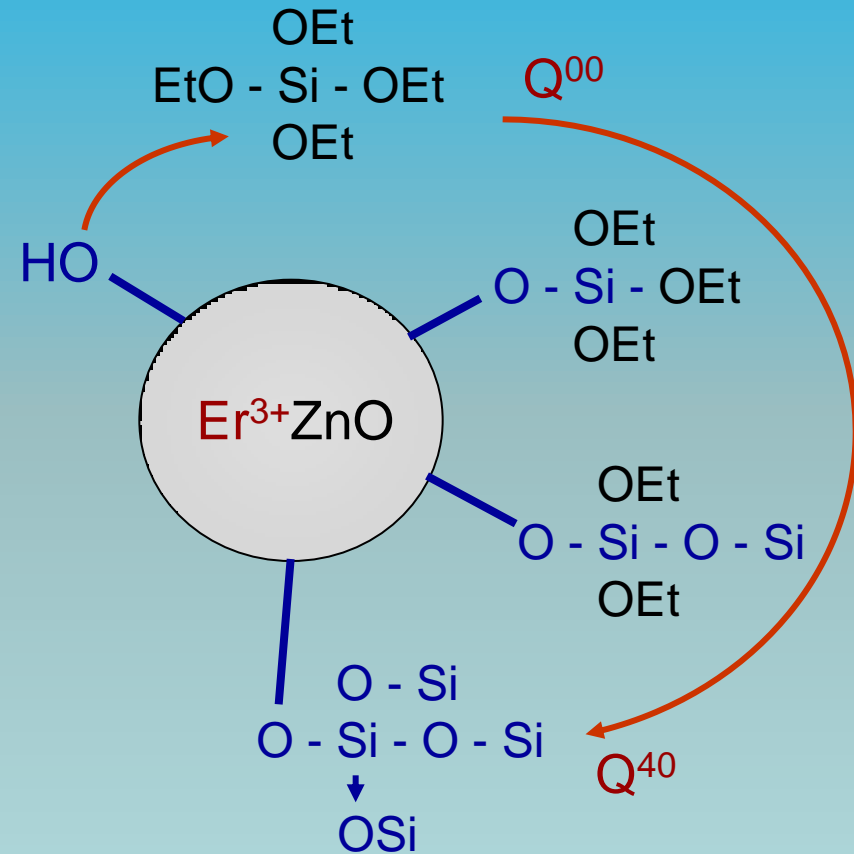
„co-dopování“ nanočástic ve 2M etanolickém solu ZnO



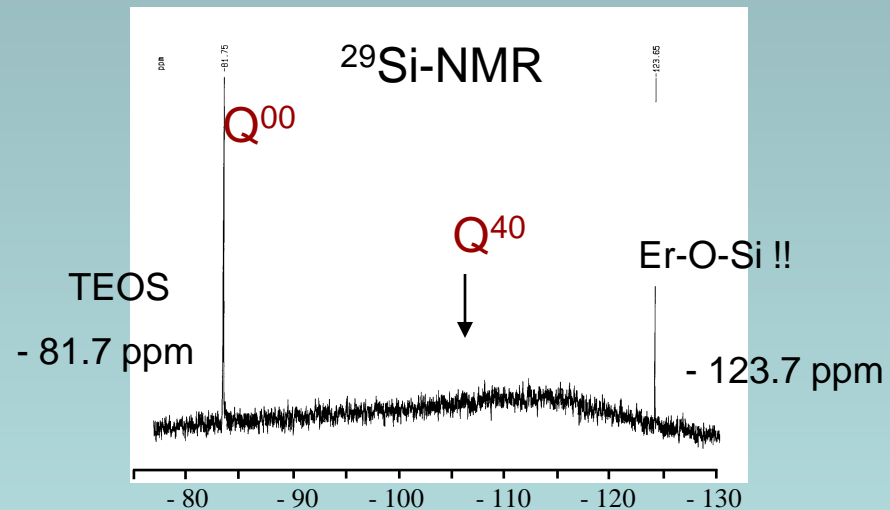
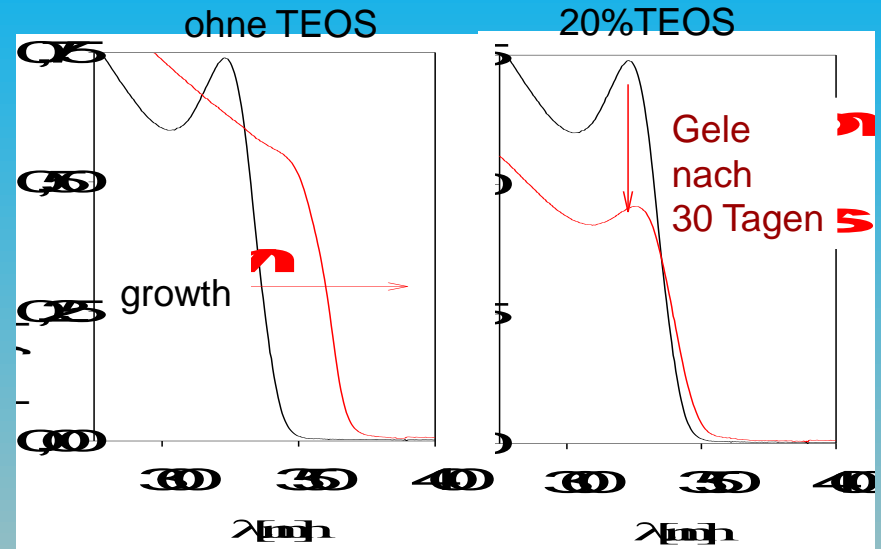
Er:ZnO synthesis



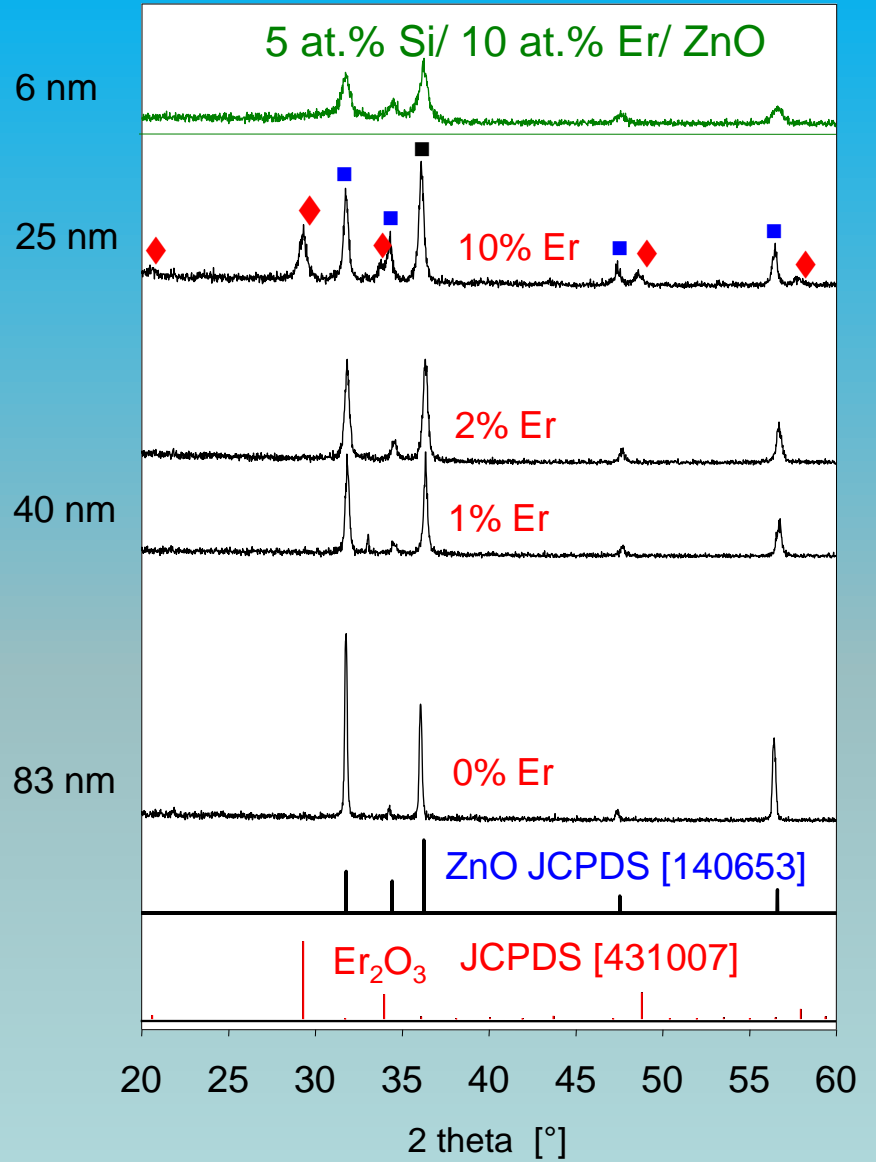
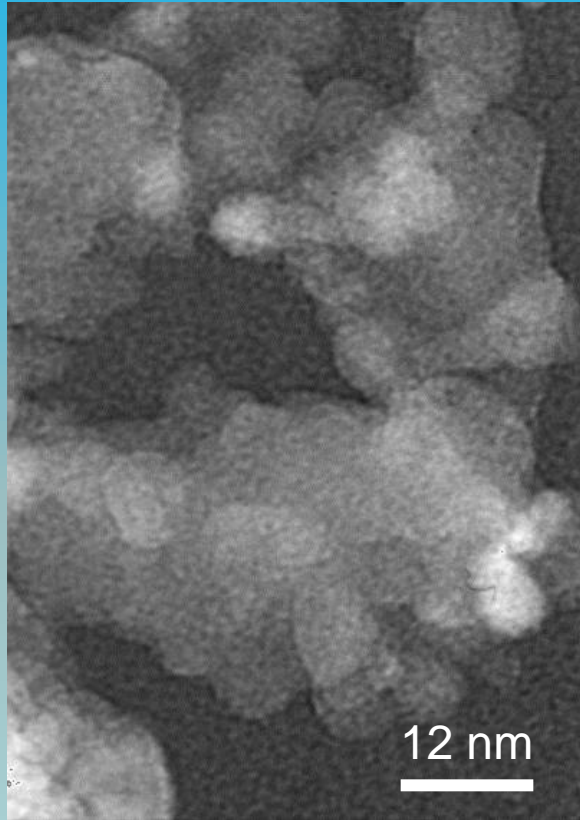
TEOS Kondensation in Er@ZnO Nanokolloiden



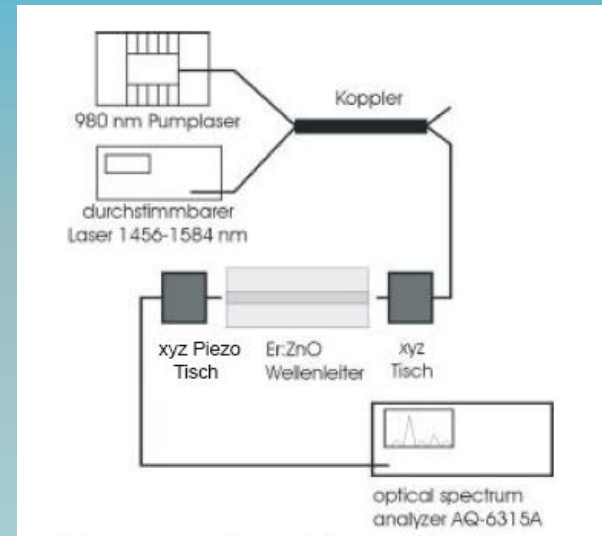
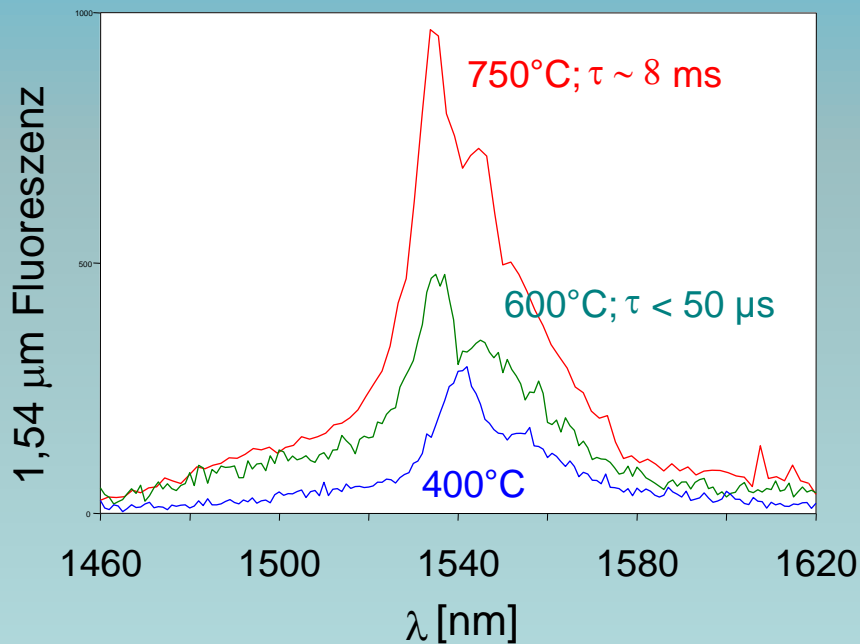
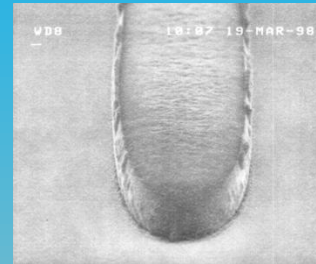
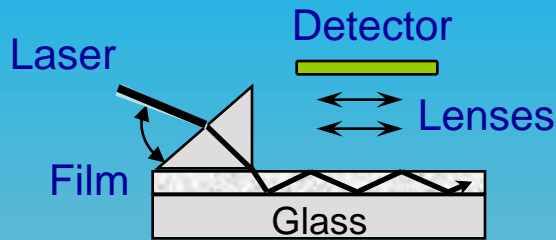
UV-vis



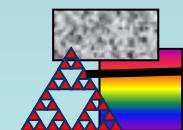
Filmsintern bei 750°C



Er³⁺, Si⁴⁺ @ ZnO wave guide

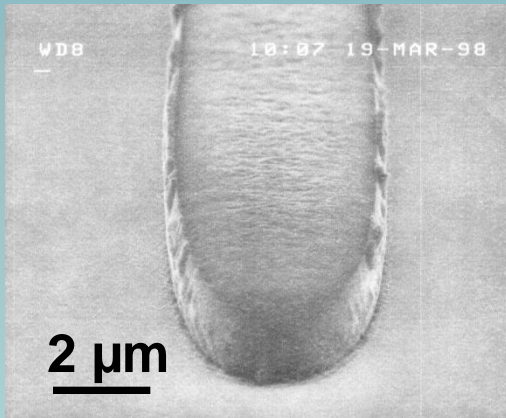


Optischer Netto Gewinn
1.5 μm : 3 dB/cm

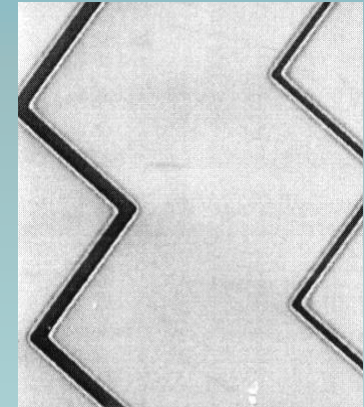
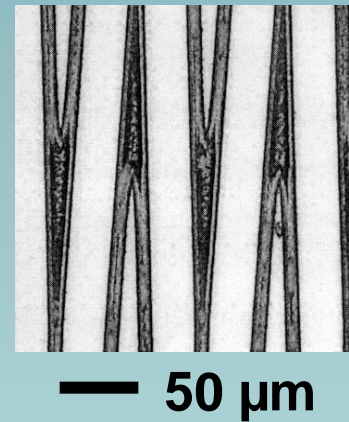


Er³⁺, Si⁴⁺ @ ZnO vlnovody a multiplexy

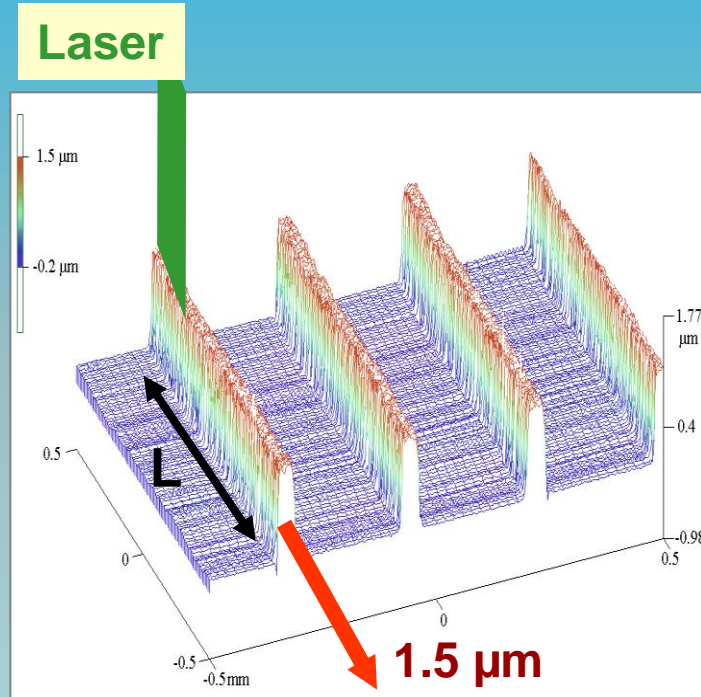
Fotolitografie



Laserová ablace



Optické zesílení ve vlnovodivých mikrostrukturách $\text{Er}^{3+}, \text{Si}^{4+} @ \text{ZnO}$



$$I(L) = \frac{I_{\text{spon.}}}{gL} [e^{gL} - 1]$$

g = koeficient zesílení

L = délka excitace

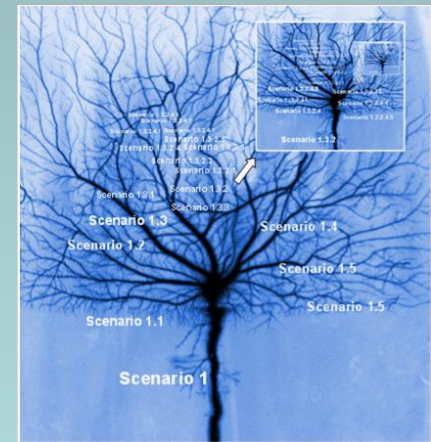
$g = 80 - 100 \text{ cm}^{-1}/500 \mu\text{m}$

Výkon Laseru $< 70 \text{ mW}$

Interní zesílení $I/I_0 \sim 50$

Chapter 4

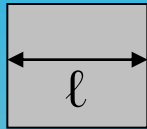
Fractal approach to physical chemistry and materials science



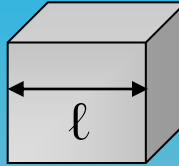
Chap. 4.1 Dimension d'un objet - D



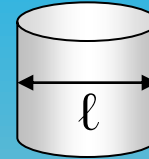
$$L_0 = \ell^1$$



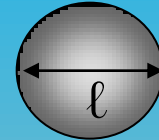
$$A_0 = \ell^2$$



$$V_0 = \ell^3$$



$$= (\pi/4)\ell^3$$



$$= (\pi/6)\ell^3$$

On se propose d'occuper l'espace de dimension 1, 2 ou 3 de la longueur latérale - L avec un nombre N des initiateurs (molécules) ayant longueur (de liaison chimique) ℓ

$$\left. \begin{aligned} N(L) &= m L^1 \\ N(L) &= n L^2 \\ N(L) &= p L^3 \end{aligned} \right\}$$

$$N(L) \sim C L^D$$

$$\log N(L) = \log C + D \log L$$

$$D = \frac{\log N}{\log L}$$

Relation générale pour les objets de n'importe quelle dimension $0 < D < 3!$

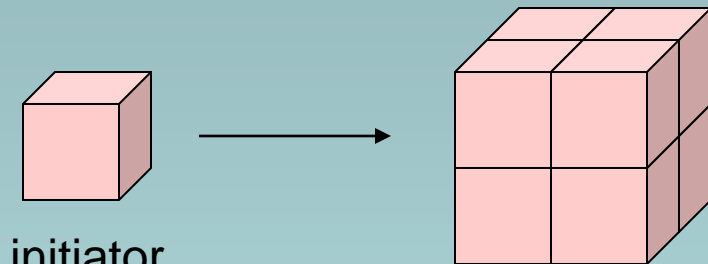
Concept of dimension - D in regular systems

$$D = \lim_{L \rightarrow \infty} \frac{\log N}{\log L}$$

D = dimension of an object

N = generator (collection of initiators)

L = linear size of the object



generator

N = 2 (line)

N = 4 (square)

N = 8 (cube)

Regular objects are characterised by an integer dimension (D = 1, 2 or 3); Their density does not change

$$D(\text{line}) = \lim_{L \rightarrow \infty} \frac{\log 2}{\log 2} = 1$$

$$D(\text{square}) = \lim_{L \rightarrow \infty} \frac{\log 4}{\log 2} = 2$$

$$D(\text{cube}) = \lim_{L \rightarrow \infty} \frac{\log 8}{\log 2} = 3$$



L. Spanhel

La dimension fractale

(Introduit par Benoît Mandelbrot)

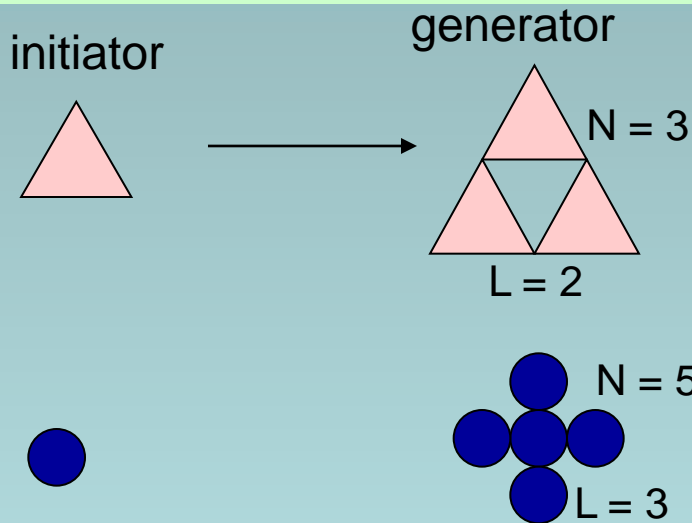
$$D = \lim_{L \rightarrow \infty} \frac{\log N}{\log L}$$

D = dimension of an object

N = generator (collection of initiators)

L = linear size of the object

Fractal objects are characterised by a non-integer dimension ($1 < D < 3$);
Their density drops with increasing size



$$D(\text{triangle}) = \lim_{L \rightarrow \infty} \frac{\log 3}{\log 2} = 1,584$$

$$D(\text{carré}) = \lim_{L \rightarrow \infty} \frac{\log 5}{\log 3} = 1,465$$

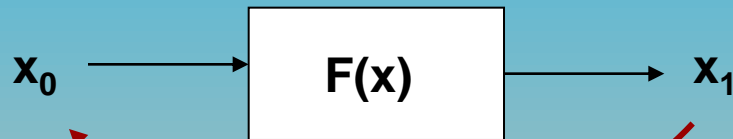


Fractal objects are self-similar

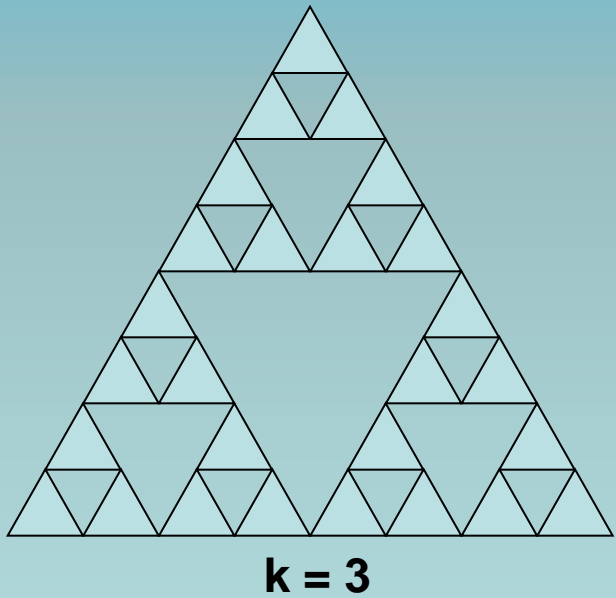
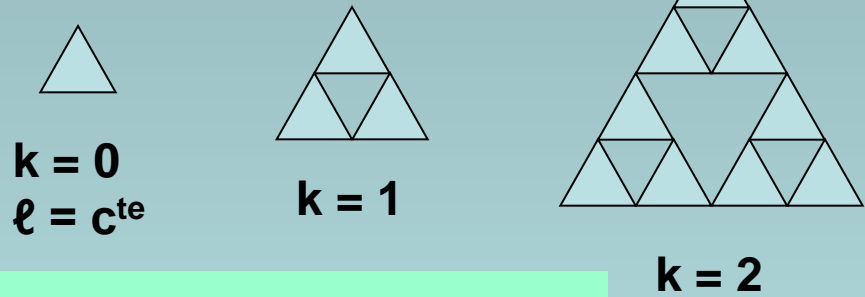
Constructions répétitives
("iteration based construction")

$$D = \lim_{L \rightarrow \infty} \frac{\log N^k}{\log L^k} = \frac{\log 3^k}{\log 2^k}$$

Analogie mathématique

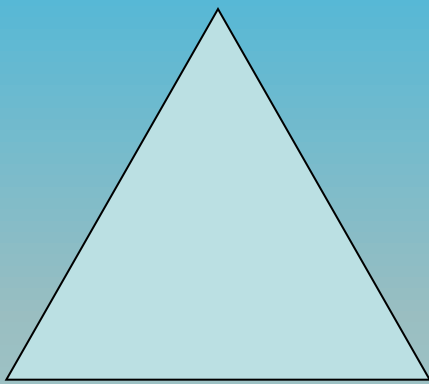


$$N = 3^k, L = 2^k$$



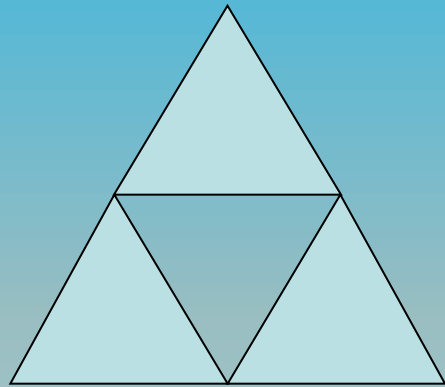
extension shift operation

$$D = \lim_{\ell \rightarrow 0} \frac{\log N^k}{\log (1/\ell)^k} = \frac{\log 3^k}{\log (1/2)^k}$$

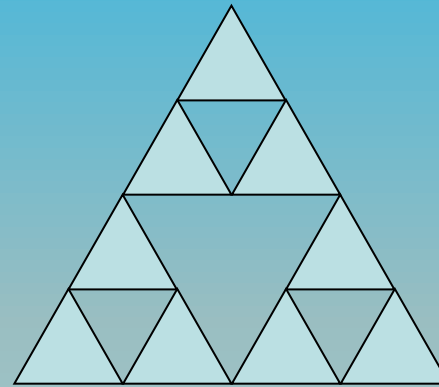


k = 0

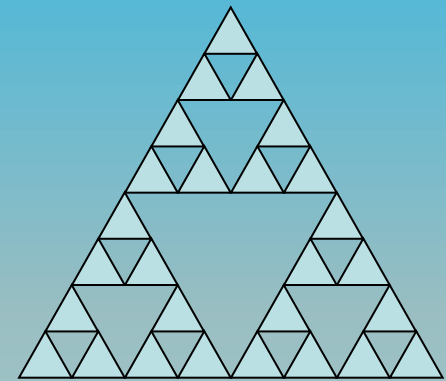
L = c^{te}



k = 1



k = 2

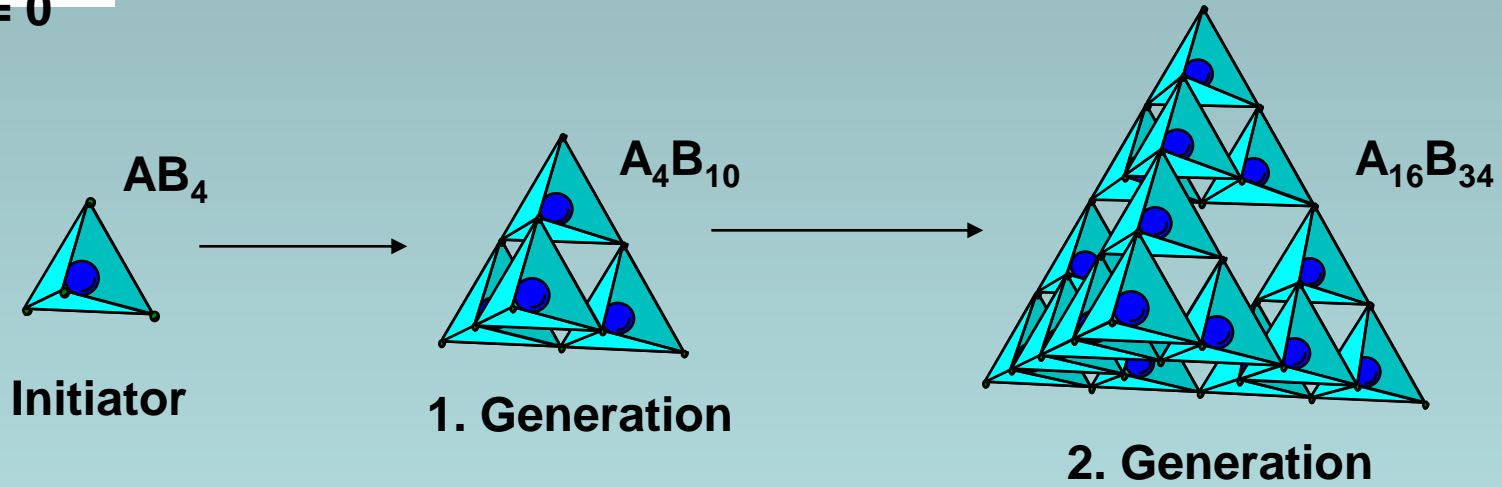
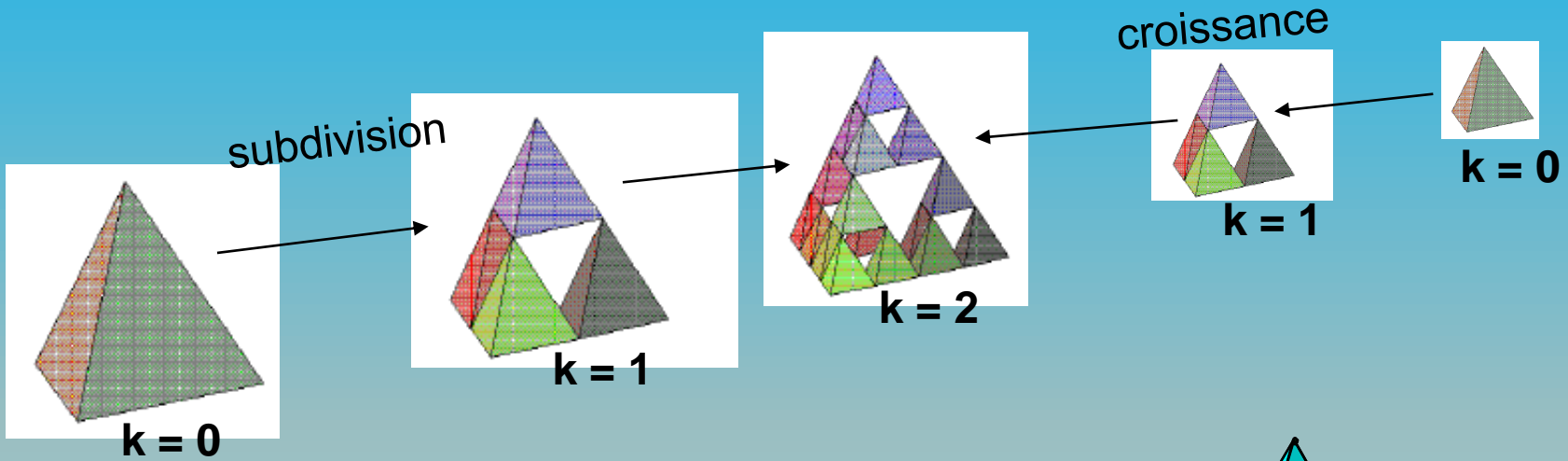


k = 3

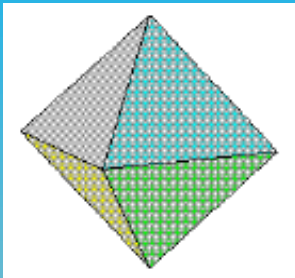
contraction shift operation

Fractal Tetrahedron

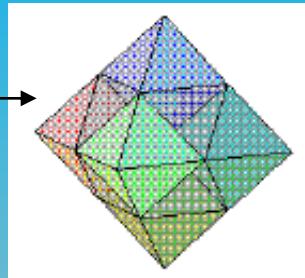
$$D = \frac{\log 4}{\log 2} = 2 \quad N = 4^k, L = 2^k$$



Fractal Octahedron



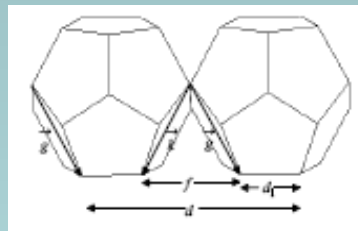
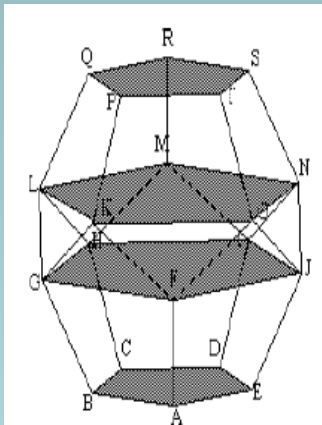
$k = 0$



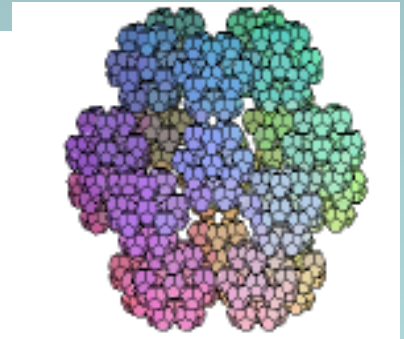
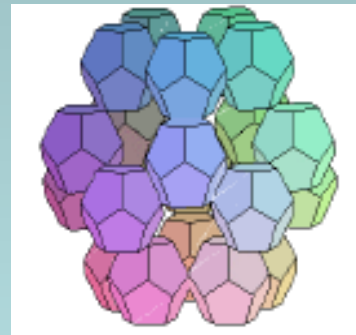
$k = 1$

$$D = \frac{\log 6}{\log 2} = 2,585 \quad N = 6^k, L = 2^k$$

Fractal Dodecahedron

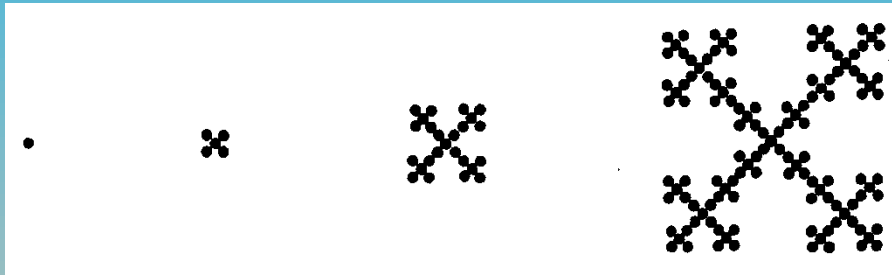


$$D = \frac{\log 20}{\log d/d_1} = 2,329$$

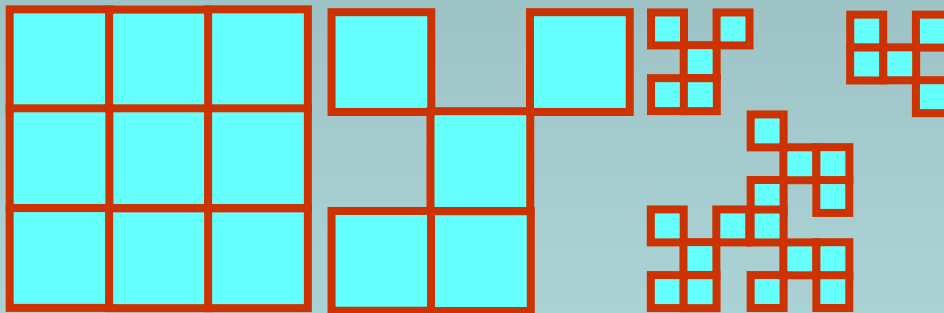


Il y a deux structures différentes et pourtant ayant la même dimension fractale

Structures fractales selon Vicsek: $D_f = \log 5 / \log 3 \sim 1.465$



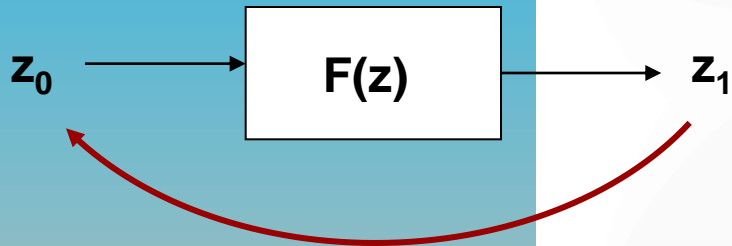
Croissance
déterministe



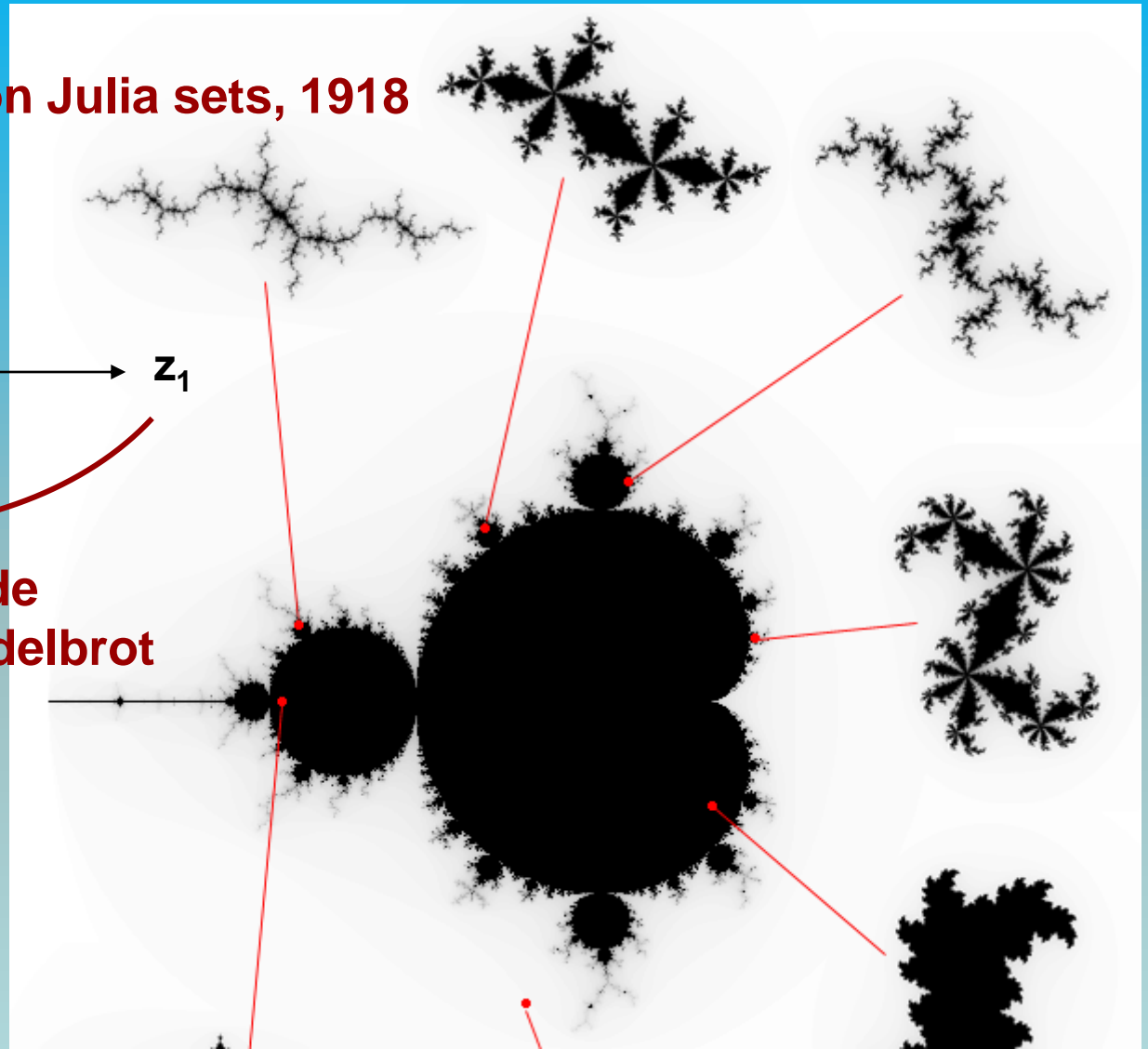
Gravure à l'acide
(ou corrosion)
stochastique

Gaston Julia sets, 1918

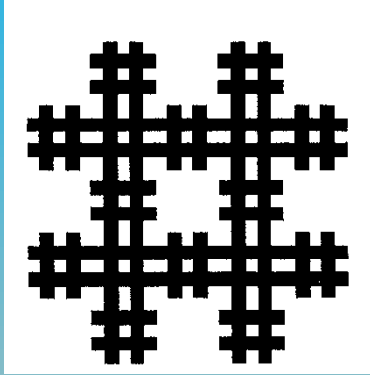
$$F(z) = z^2 - \mu$$
$$z = i c_1 + c_2$$



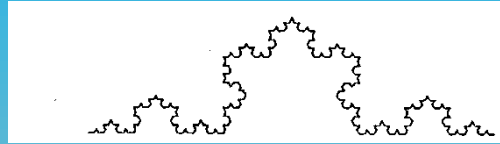
La pomme de
Benoît Mandelbrot



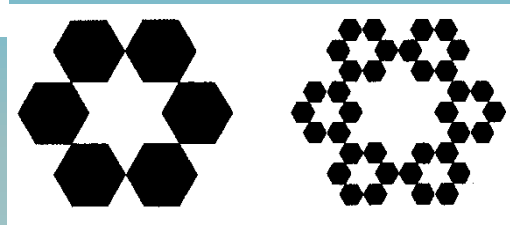
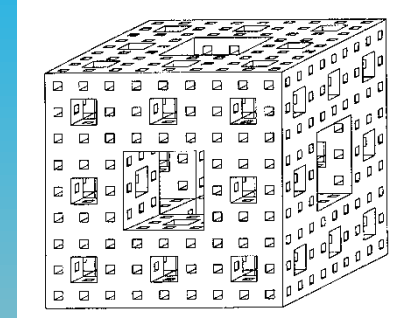
Sierpinski carpet



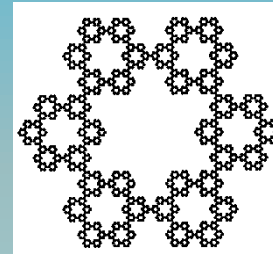
Koch curve



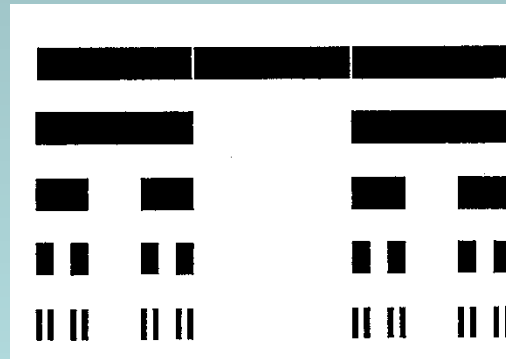
Menger sponge



David fractal



Cantor set



Classification of fractals and summary of fractal rules

1. Formation par voie itération

soit l'extension soit subdivision

2. Autosimilarité

l'observation du même image sous n'importe quelle résolution

3. Types des fractales (en longueur, en surface et en volume)

aérosols et poussières fractales : $0 < D < 1$

périmètres d'un grain ou d'une île,
surfaces planes (mosaïques) : $1 < D < 2$

surfaces rocheuses, rugueuses $D > 2$
agrégats colloïdaux, éponges : $2 < D < 3$

4. Masse volumique n'est pas constant dans l'espace fractale!

conséquence: distributions multimodales de pores/particules souvent observées

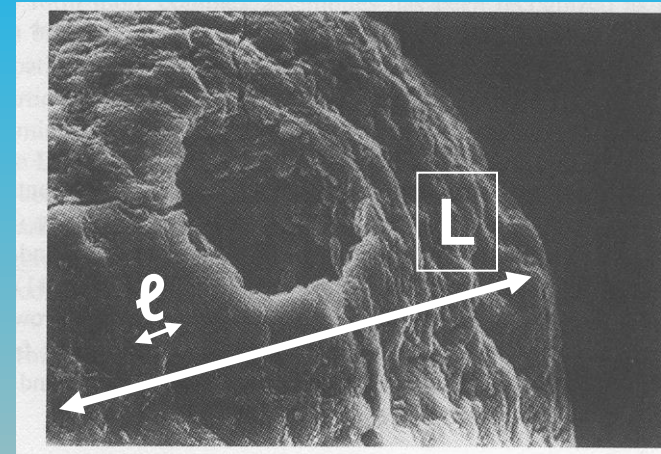
5. Dimension fractale reflète le mécanisme de croissance

structures déterministes (régulières) et stochastiques (irrégulières)
on trouve structures différentes ayant la même dimension fractale!

Chap. 4.2 Mesures expérimentales de D_f

$$D = \lim_{\ell \rightarrow 0} \frac{\log N^k}{\log (1/\ell)^k} \rightarrow N(\ell) \sim \ell^{-D}$$

$\varepsilon = \ell/L$
"yardstick"



Nombre des pixels carrés
billes
molécules

$$N(\varepsilon) \sim \varepsilon^{-D}$$

le but:
 $\varepsilon \ll 1$

Nombre des détails \sim (résolution d'une mesure) $^{-D}$

Stratégie principale:

On cherche à compter le nombre de détails en fonction de la taille du segment ε choisi pour le recouvrement d'une structure complexe

“Standard tiling relations”

$$\text{Longueur } L \text{ (périmètre)} = N(\varepsilon) \varepsilon \sim \varepsilon^{-D} \varepsilon \sim \varepsilon^{1-D}$$

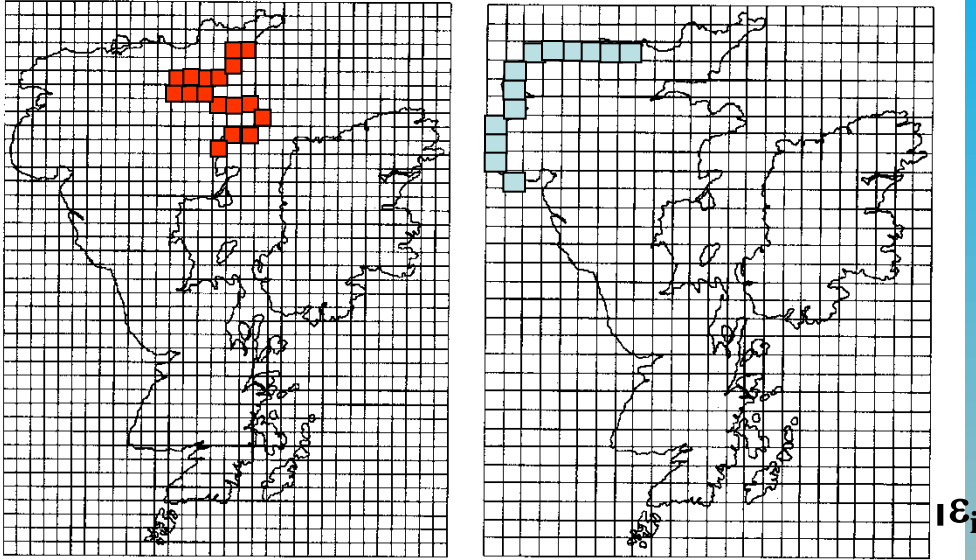
$$\text{Surface } A \text{ (couche)} = N(\varepsilon) \varepsilon^2 \sim \varepsilon^{-D} \varepsilon^2 \sim \varepsilon^{2-D}$$

$$\text{Volume } V \text{ (agrégat)} = N(\varepsilon) \varepsilon^3 \sim \varepsilon^{-D} \varepsilon^3 \sim \varepsilon^{3-D}$$

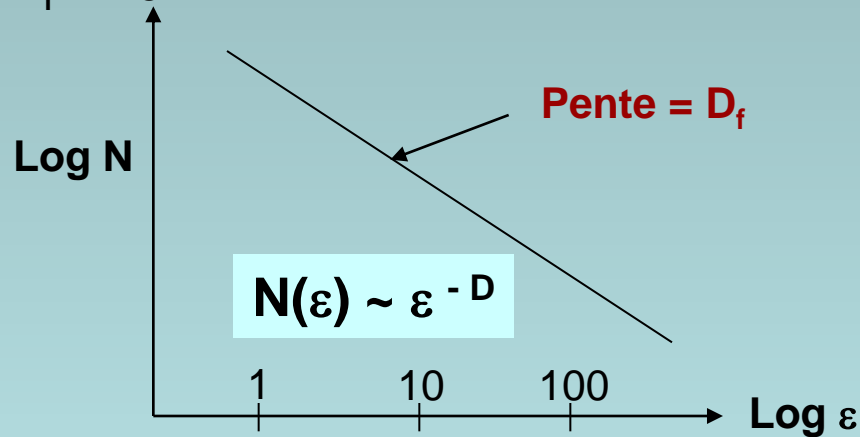
grandeur \sim (résolution d'une mesure) $\beta(D, \dots)$

Power law!

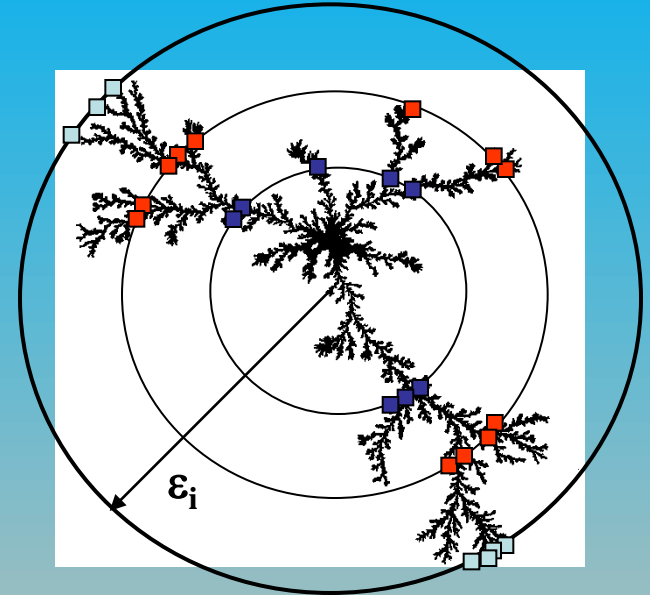
“box counting method”



Dimension fractale de la côte littorale de Grande Bretagne $D_f = 1.31$



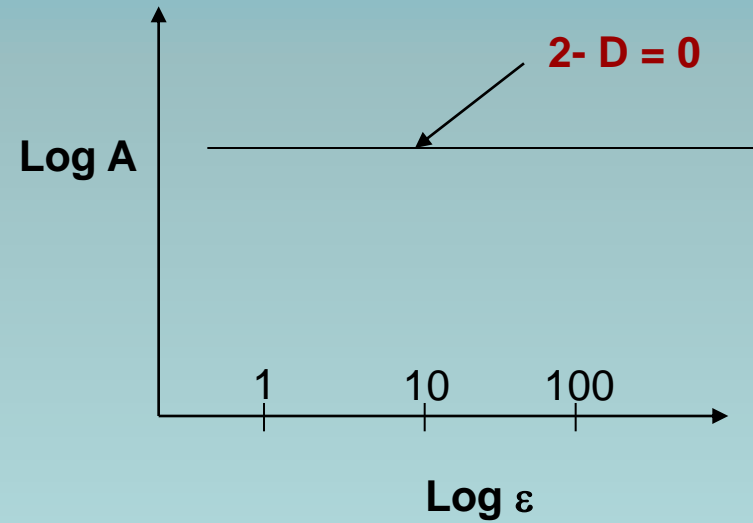
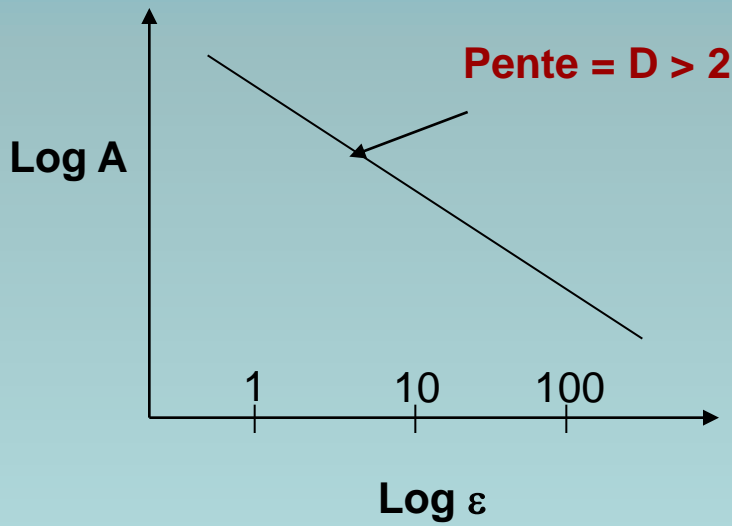
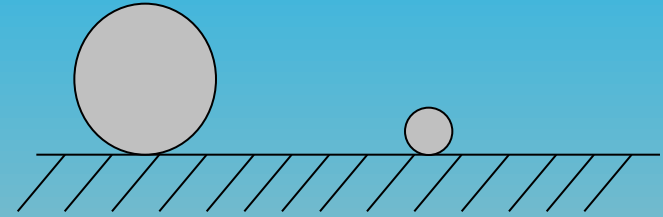
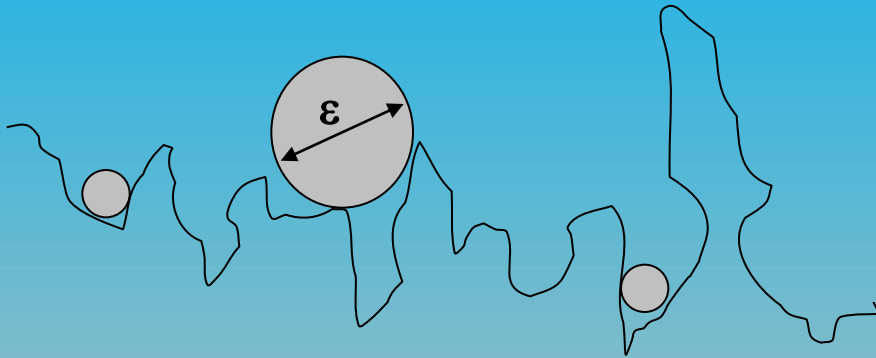
“sandbox method”



Cluster dendritique de zinc formé en électrolyse, $D_f \sim 1.7$

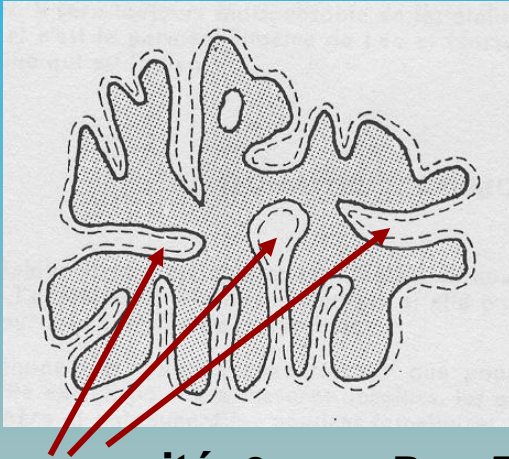
Physisorption des molécules

$$\text{Surface } A = N(\varepsilon) \varepsilon^2 \sim \varepsilon^{2-D}$$



Physisorption de N₂ (BET)

Rappel:



Mésoporosité, $2 \text{ nm} < R_p < 50 \text{ nm}$

$$R_p = - 2 \gamma V_m / RT \ln (p/p^\circ)$$

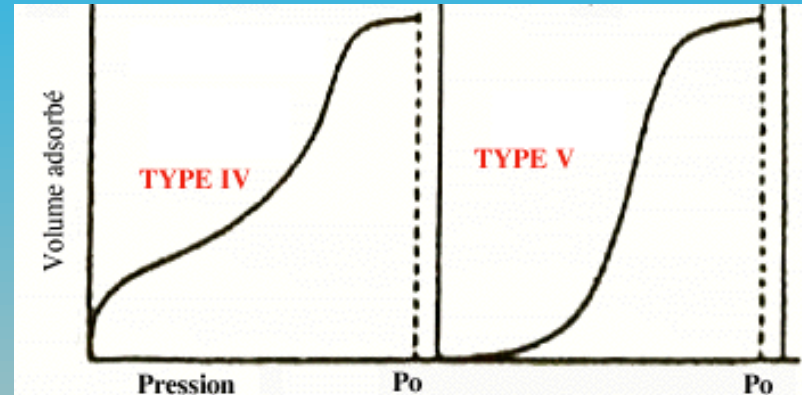
$$R_p \sim 1 / \ln (p/p^\circ)$$

$$V = N(\varepsilon) \varepsilon^3 \sim \varepsilon^{3-D}$$

$$\left. \begin{array}{l} R_p \sim 1 / \ln (p/p^\circ) \\ V = N(\varepsilon) \varepsilon^3 \sim \varepsilon^{3-D} \end{array} \right\} \varepsilon = R_p \rightarrow V \sim R_p^{3-D} \sim [\ln (p/p^\circ)]^{D-3}$$

Autre option: variation de la taille des molécules (ε) appliquées en physisorption

condensation capillaire



Mesures SAXS, SANS, LALLS

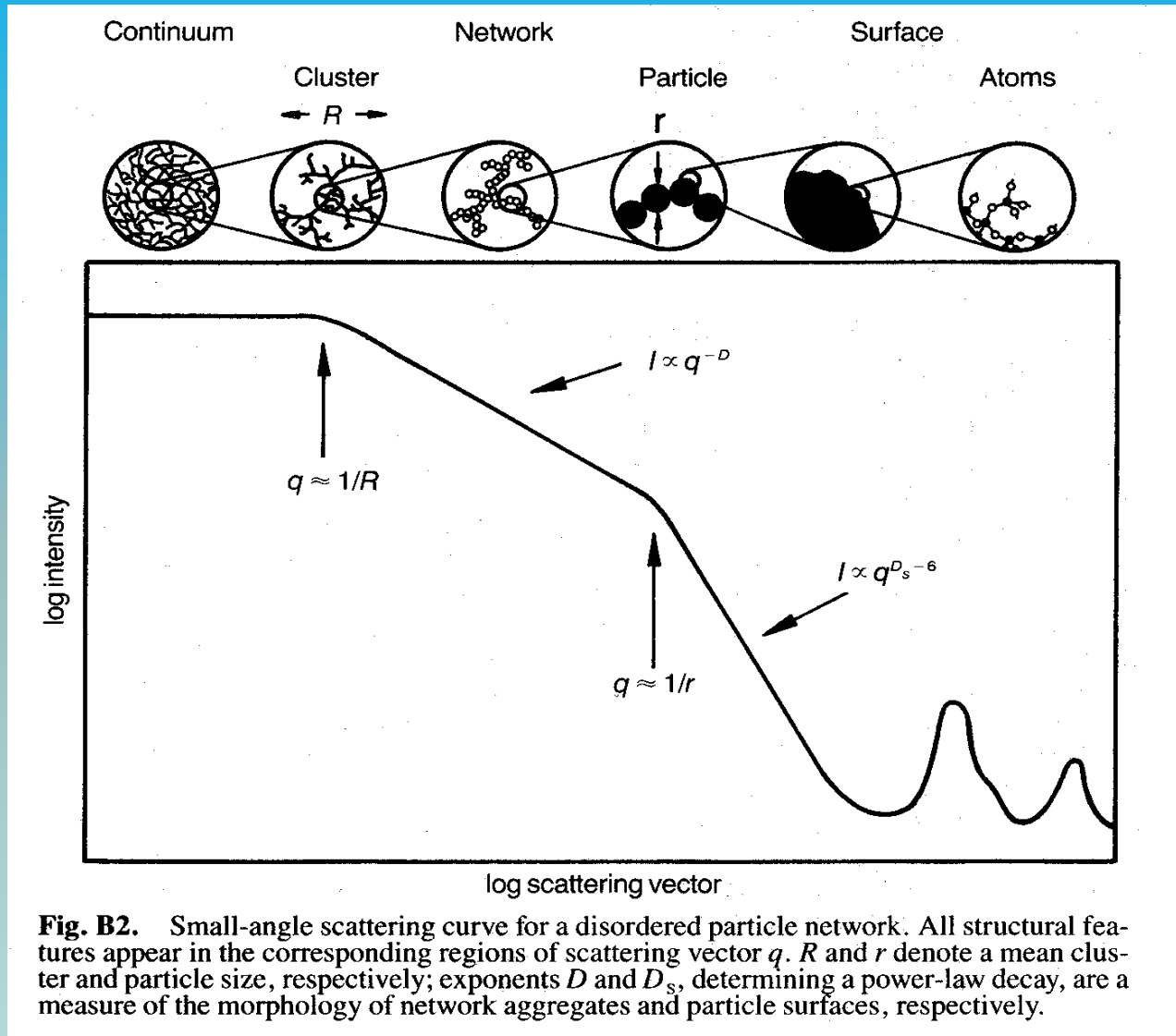
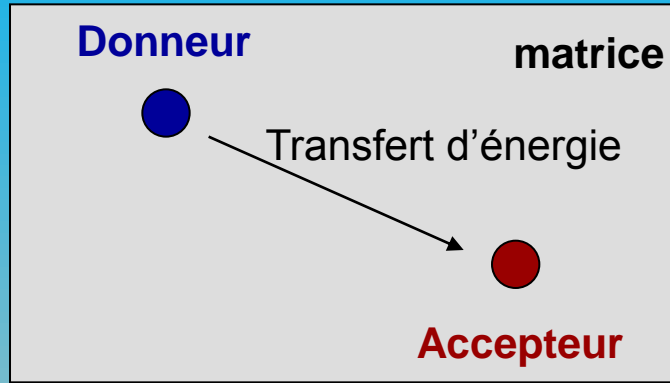


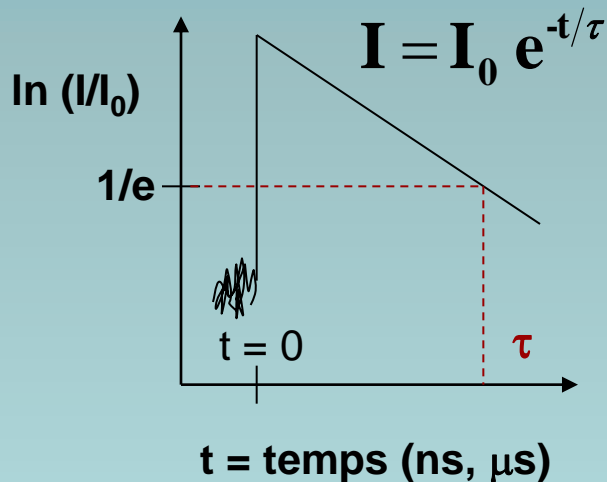
Fig. B2. Small-angle scattering curve for a disordered particle network. All structural features appear in the corresponding regions of scattering vector q . R and r denote a mean cluster and particle size, respectively; exponents D and D_s , determining a power-law decay, are a measure of the morphology of network aggregates and particle surfaces, respectively.

D_f à partir des mesures de fluorescence

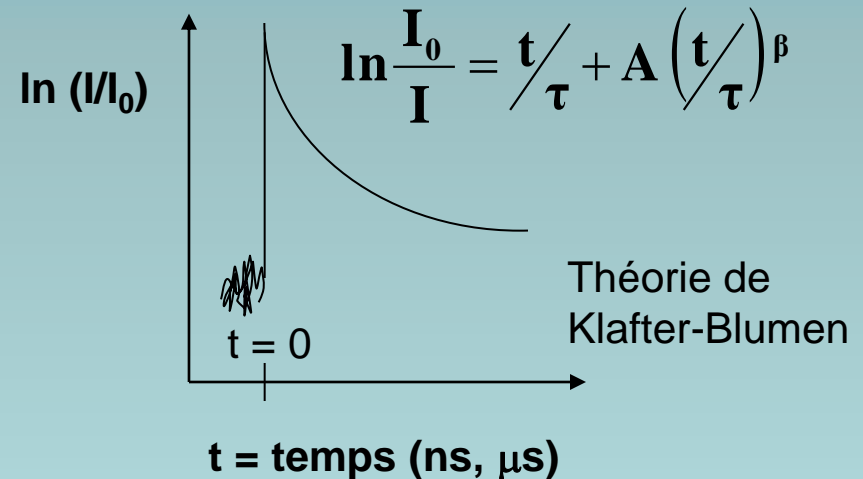


soit molécules organiques
soit lanthanides

Donneur singulière



Pair Donneur - Accepteur



$\beta = D/s = 0,5$ pour le réseau non-fractal avec $s = 6$
 $S = 6$ implique l'interactions dipôle - dipôle



L. Spanhel

FIN

