Jaro 2021
C9906

Spektroskopické metody charakterizace nanomateriálů

1. Spektroskopie multifunkčních koloidálních nanostruktur
- *reprezentativní strategie kondenzace polymérních a nanočásticových solů*
- *příklady spektroskopického pozorování fyzikálních a strukturálních vlastností*

2. Polovodičové nanočástice v elektrotechnickém sektoru (ZnO, „CdZnSSe“)
- *Transparentní planární elektrody*
- *Elektrochromie*
- *Elektro/fotoluminescenčí systémy*

3. TiO_2 v solárním nanosektoru
- *Úvod do solární technologie*
- *Nanofotokatalytické systémy*
- *Nanofotovoltaika*

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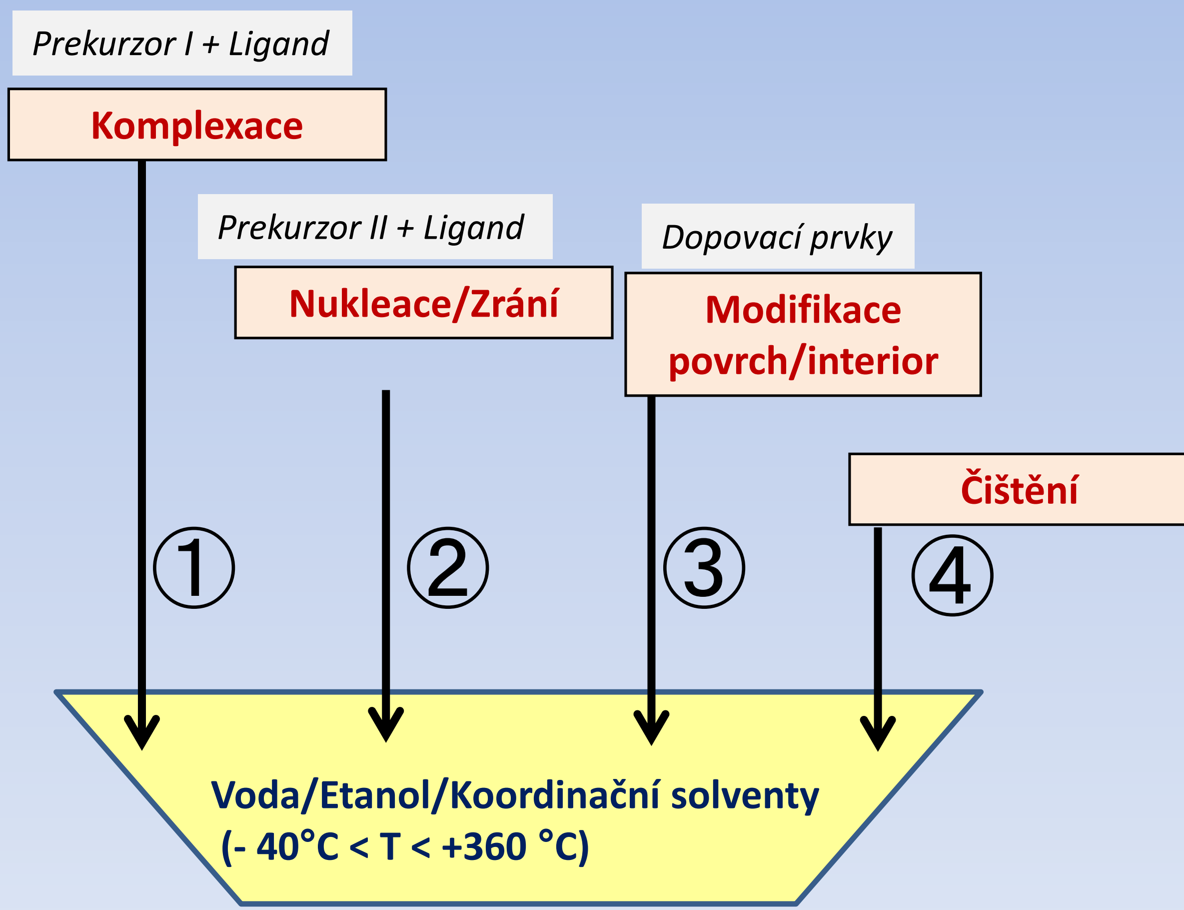
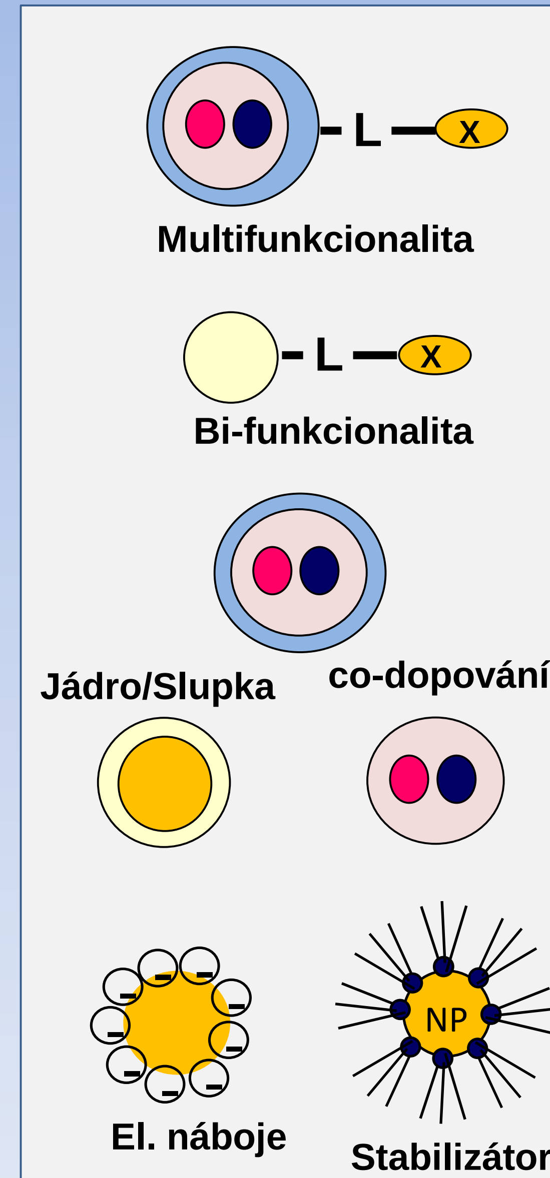
Chemické inženýrství anorganických nanokoloidů

Multiparametrální syntézy:

Cíl: Monodisperzita, stabilita, bez toxicity, jednoduchou cestou





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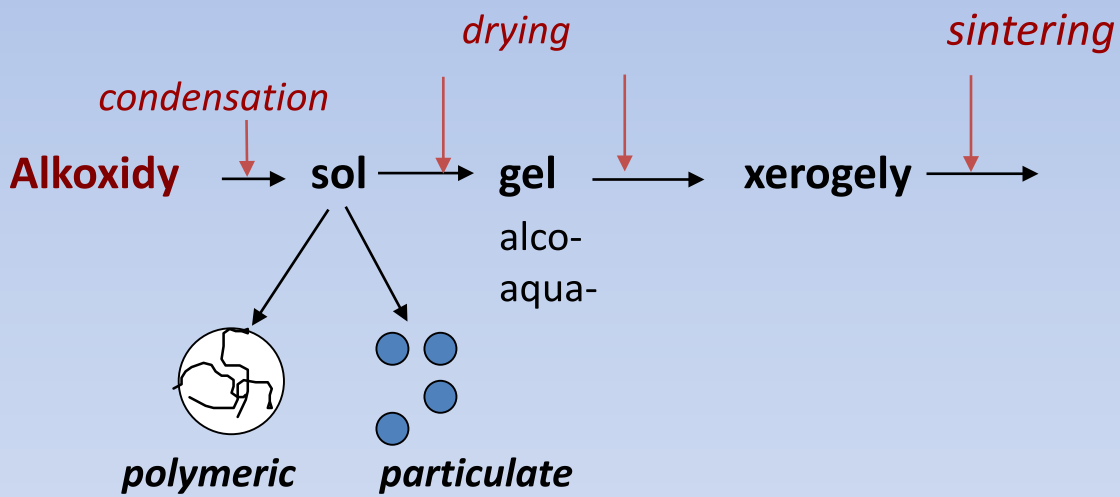
Sol-gelová Nanochemie

1. Molecular bottom-up approach
2. High homogeneity of multi-atomic compositions
3. Macroscopic property tuning on the molecular scale



Products:
fibers,
layers,
membranes,
monolithes,
nanocomposites,
powders

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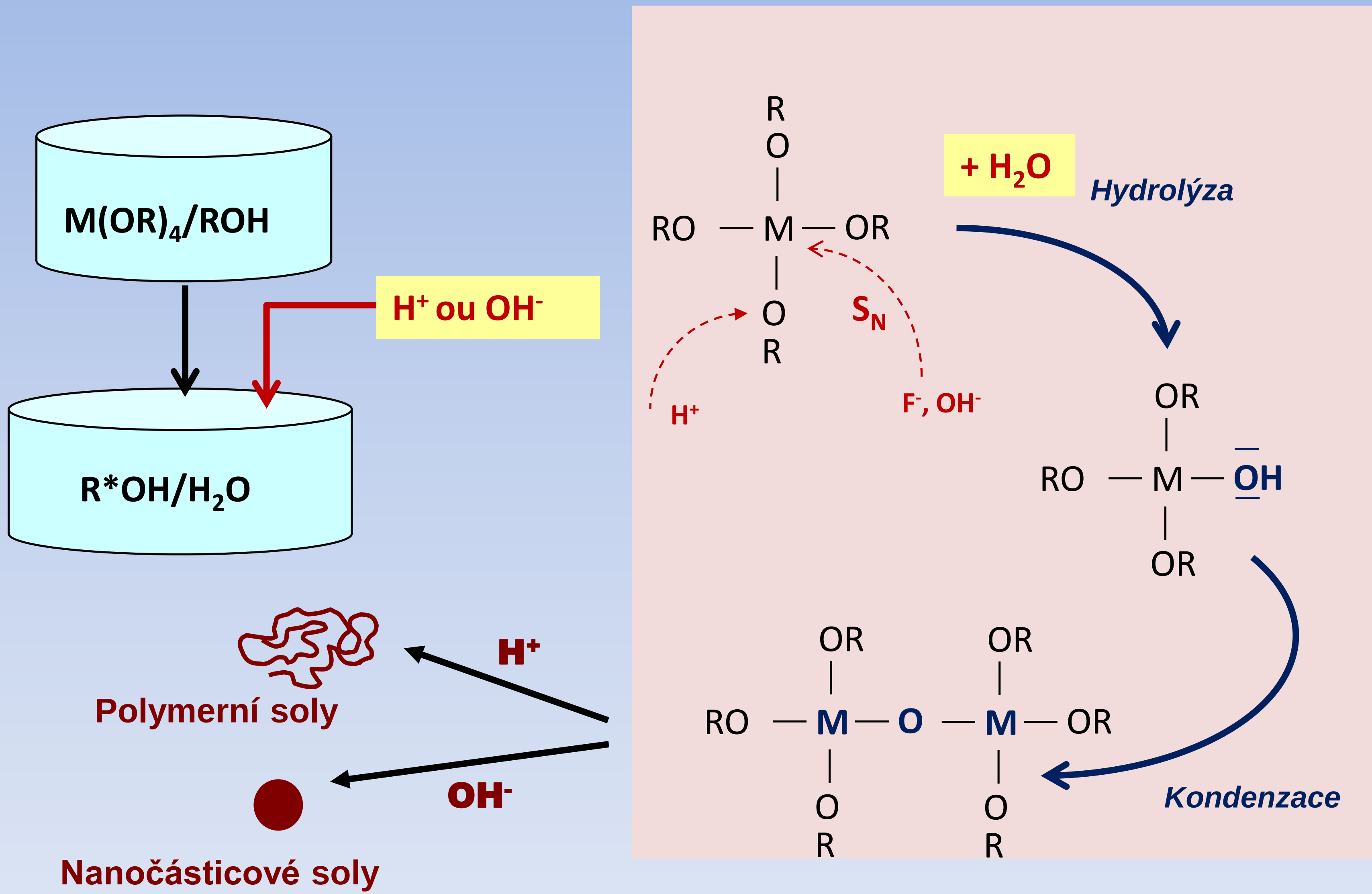
Oxidy kovů v alkoholu

Kov = V, W, Sn, Ti, Zr, Ce, Al, Y, Zn,…



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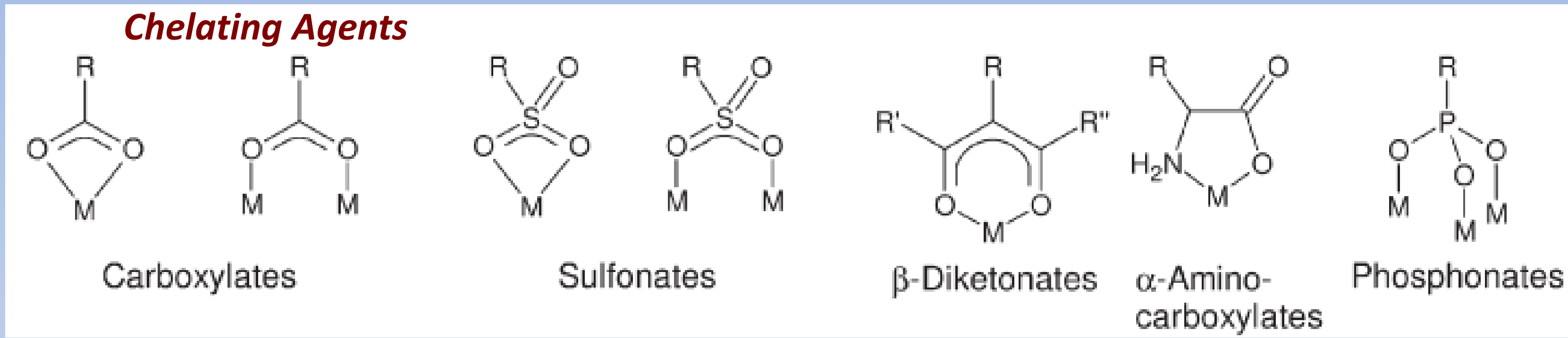
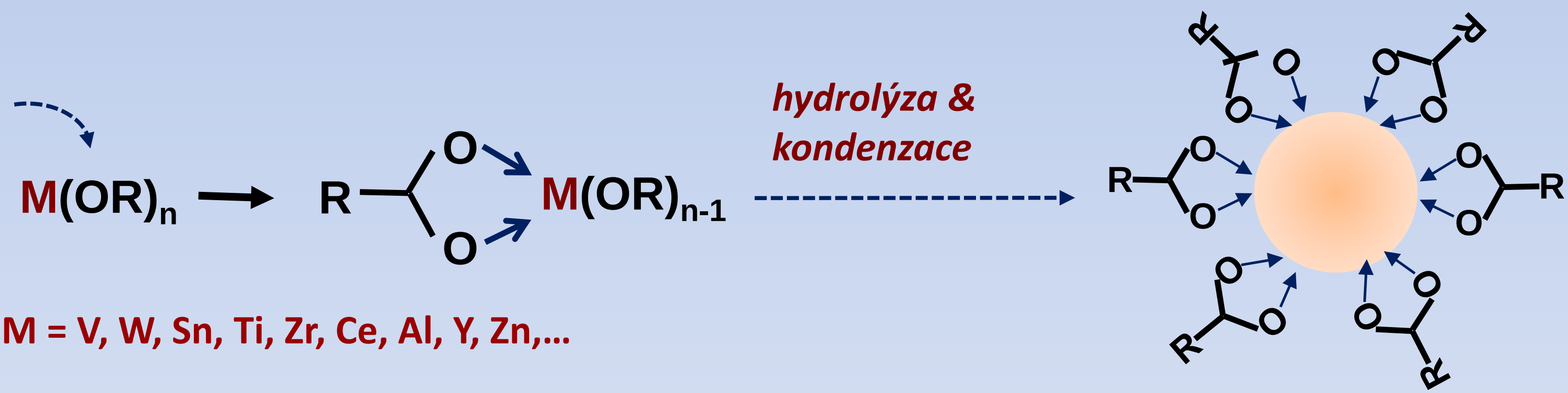
Komplexace alkoxidů

Snížení reaktivity a protekce vůči srážení





M = V, W, Sn, Ti, Zr, Ce, Al, Y, Zn,…

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Strategie organizace nanočástic na substrátech

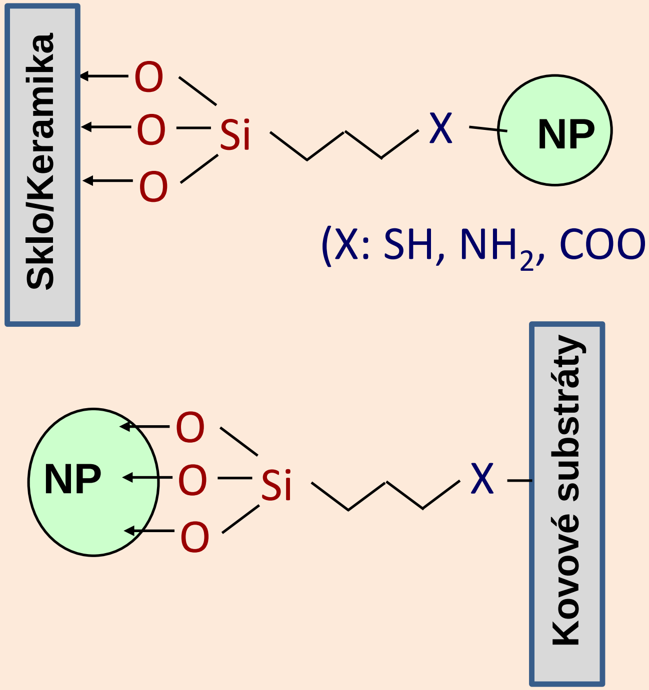
Tvorba tenkých vrstev

- dip-coating
- spin-coating
- spray
- Doctor Blade

Adhéze !

Kovalentní vazby

Elektrostatické spojení



(X: SH, NH_2, COO)

Sol → **vrstva** → **Spékání**
Fotolitografie

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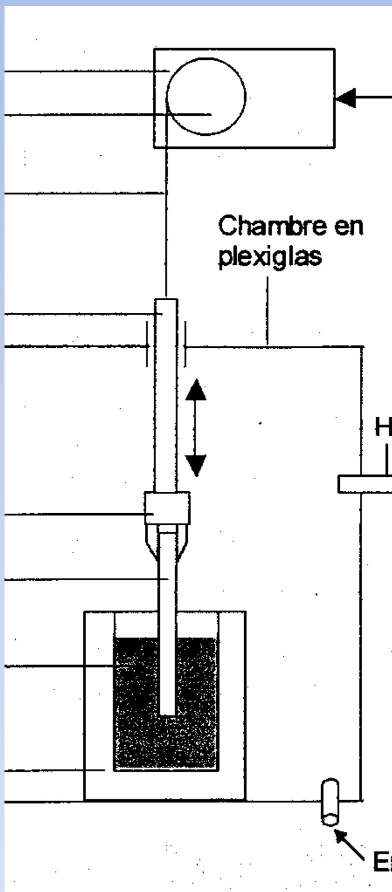
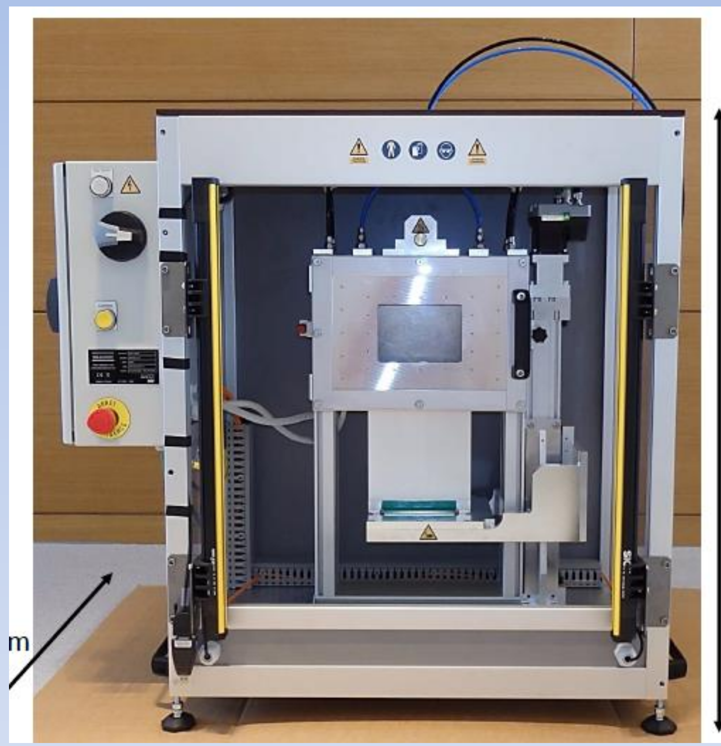
Kontrolované ponořování/tažení substrátu
(angl. dip coating)





Solgelway Paris

Landau- Levichova teorie:

$$e[\mu m] = \frac{0{,}94(\eta \cdot v_t)^{2/3}}{(\gamma_{gl})^{1/6} \cdot (\rho \cdot g)^{1/2}}$$

- e tloušťka vrstvy
- η dyn. viskozita
- γ_{gl} napětí fázového rozhraní
- ρ hustota roztoku
- g gr. zrychlení (9,806 m/s^2)
- v_t rychlost ponoru

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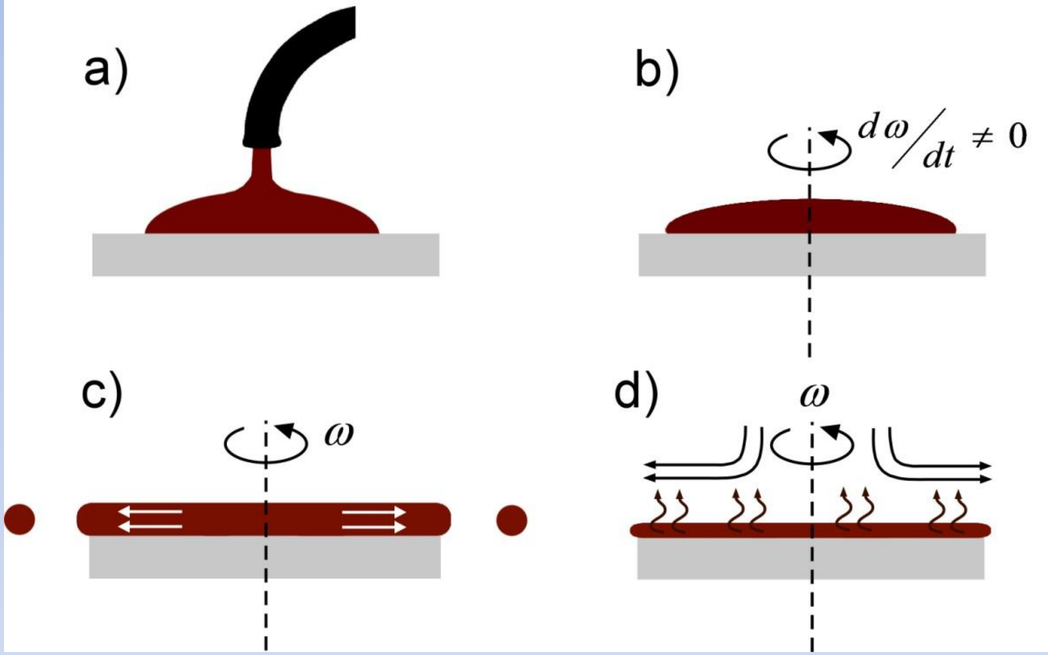
Centrifugální pokrytí :

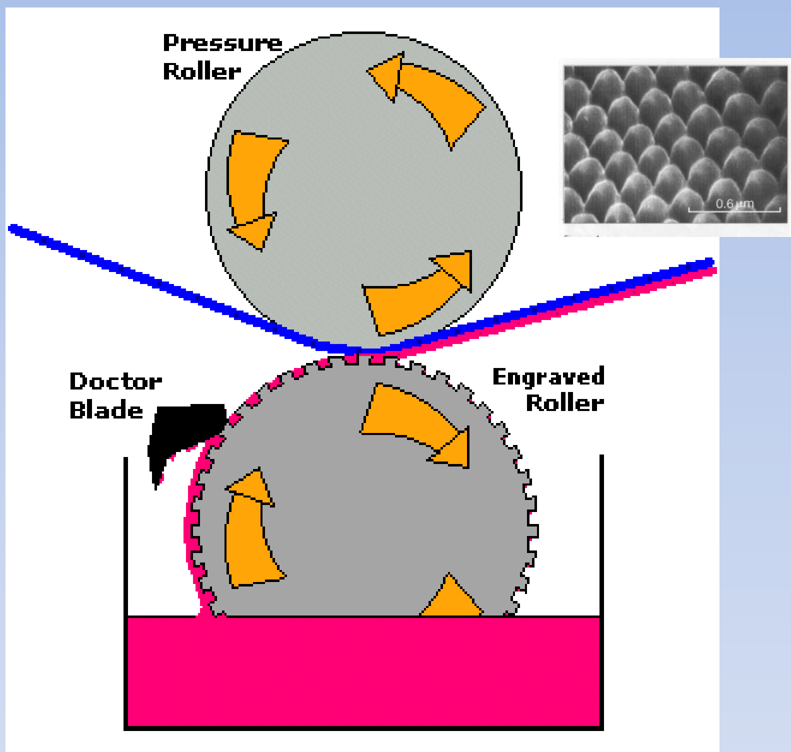
Roztok na rotujících substrátech, angl. Spin-on coating



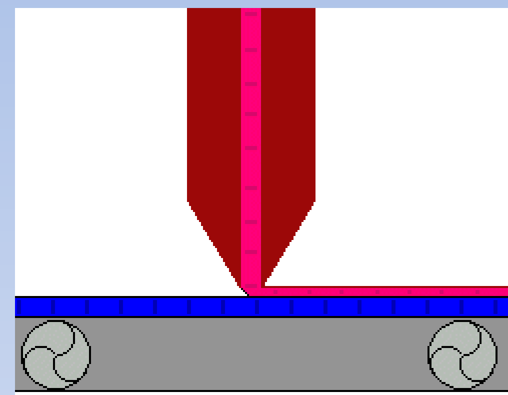
$$e[\mu m] = \frac{e_0}{\sqrt{1 + \frac{4 \cdot \rho \cdot \omega^2 \cdot e_0^2 \cdot t}{3 \cdot \eta}}}$$

- e tloušťka filmu
- e_0 počátková tloušťka
- η dyn. viskozita
- ω rotační rychlost substrátu
- ρ hustota roztoku
- t doba rotace

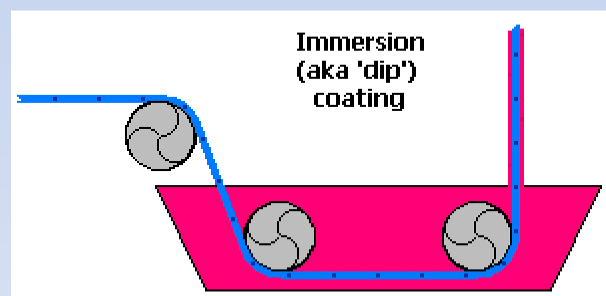
Doctor Blade, spray



Flexible substrates (textiles, plastics)



Steady substrates



mobile substrates

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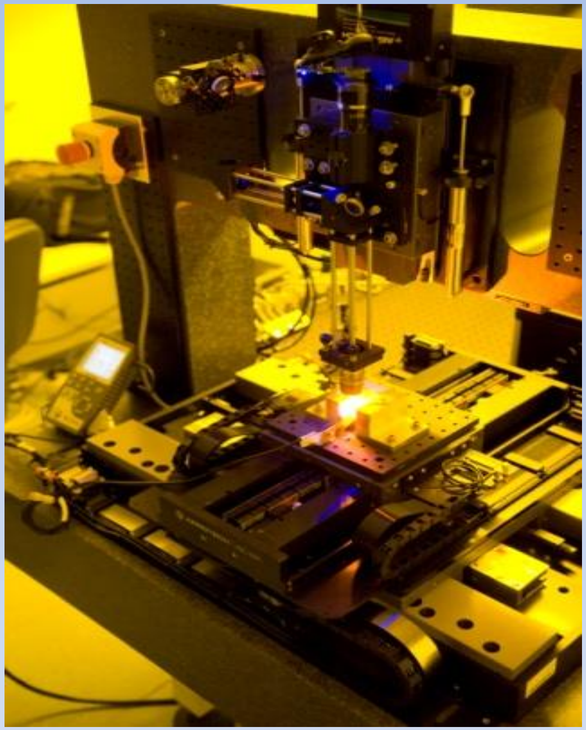
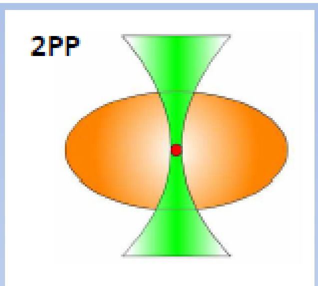
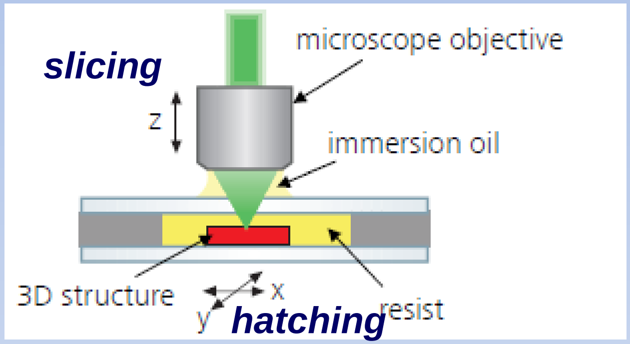
fs-Laser Printed Freeform 3D Structures



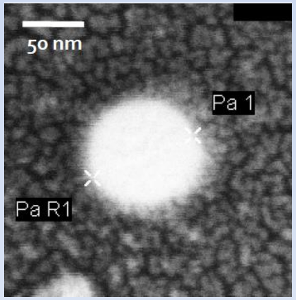
Laser source: 100-400 fs, MHz-kHz

SHG $\omega \rightarrow 2\omega$ initiates 2PP (340 nm – 540 nm)





Sub-100 nm voxel



Low NA focus →

auditory ossicles human middle ear

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FhG, ISC, Würzburg, Germany

Fraunhofer ISC

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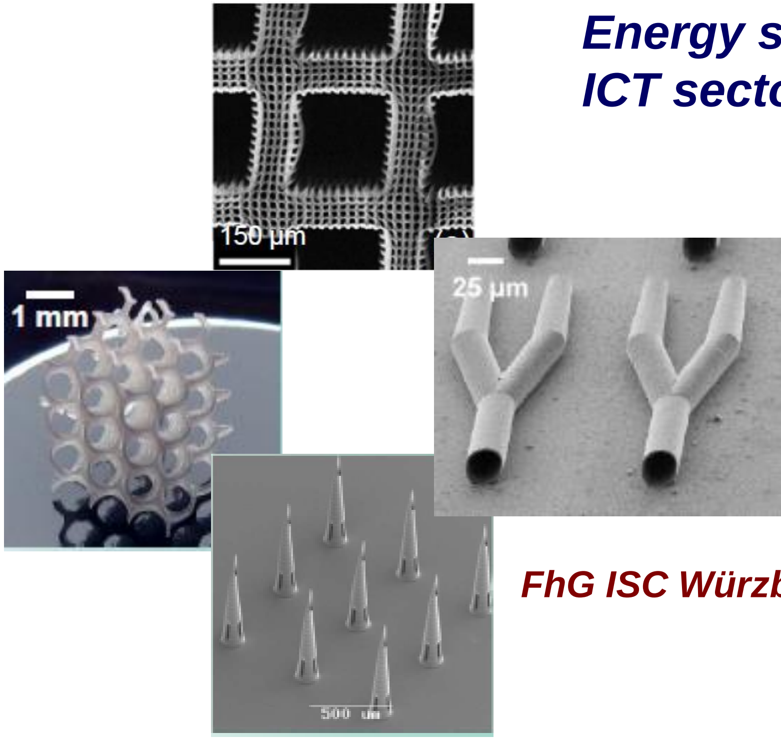
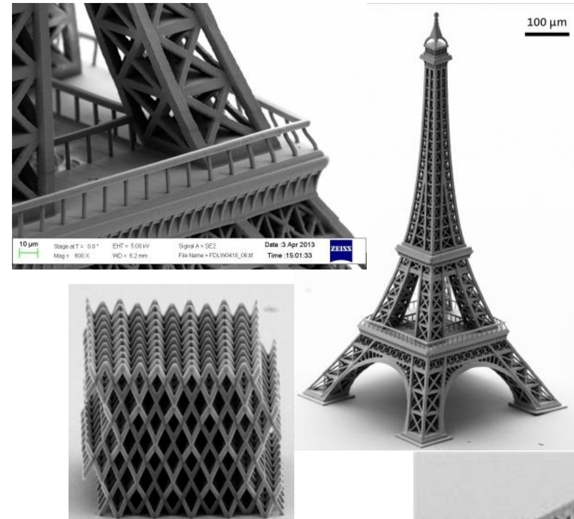
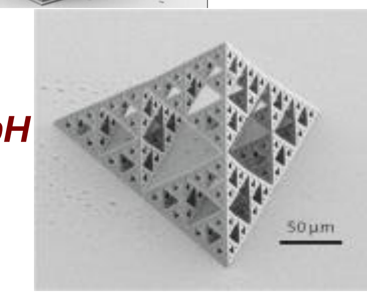
Targets:

Life sciences
Energy sector
ICT sector

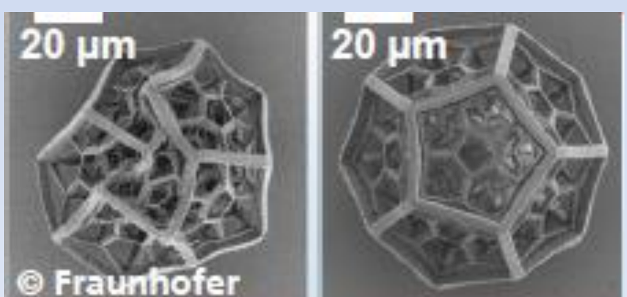


FhG ISC Würzburg





Nanoscribe GmbH
Karlsruhe



New generation of nanoinks to come…

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Analytic methods employed to study structural evolution in the sol-gel process

NMR, FTIR, Raman, SAXS

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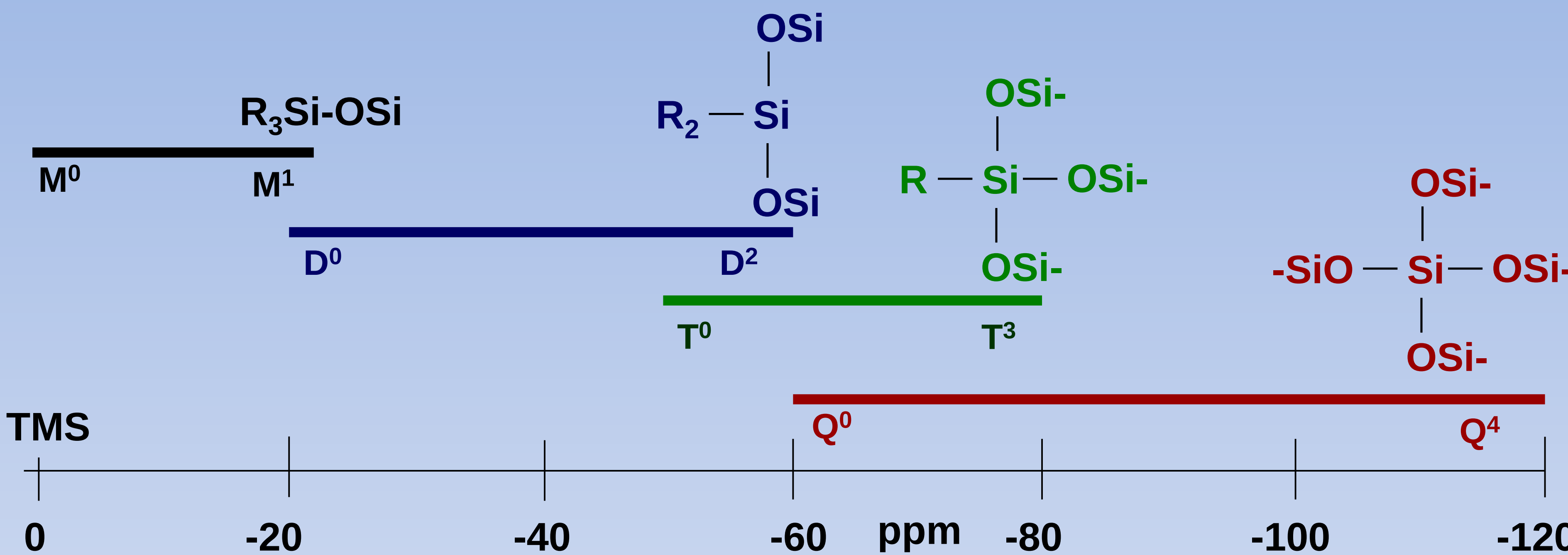
Nomenclature and chemical shift in ^{29}Si- and ^{31}P-NMR



Control questions:
2. Structural formula of the Si-Q^2 state?
3. Structural formulas of X^0 states (X: M,D,T,Q)?

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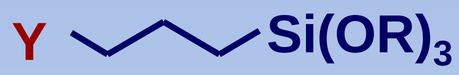
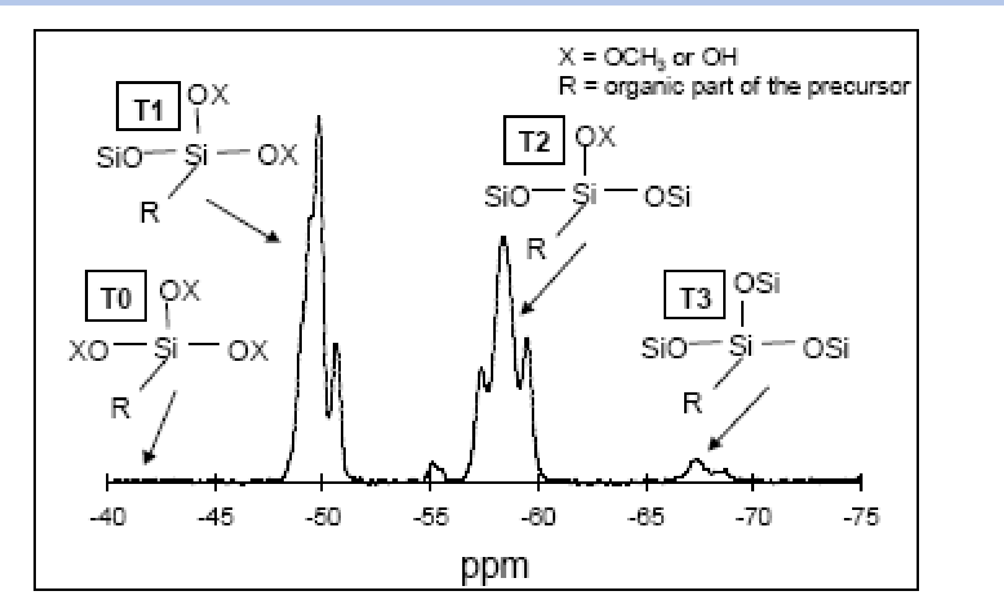
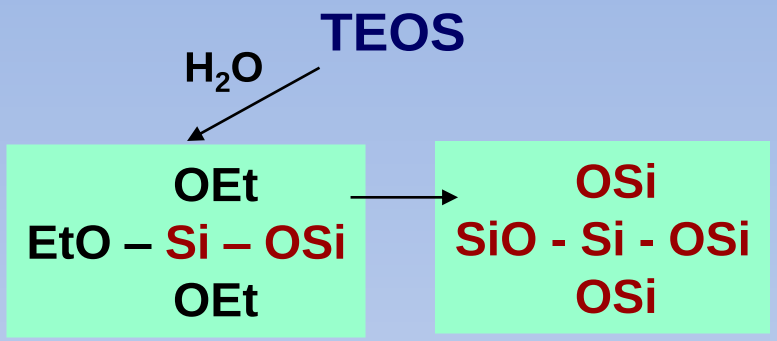
Application of ^{29}Si - NMR

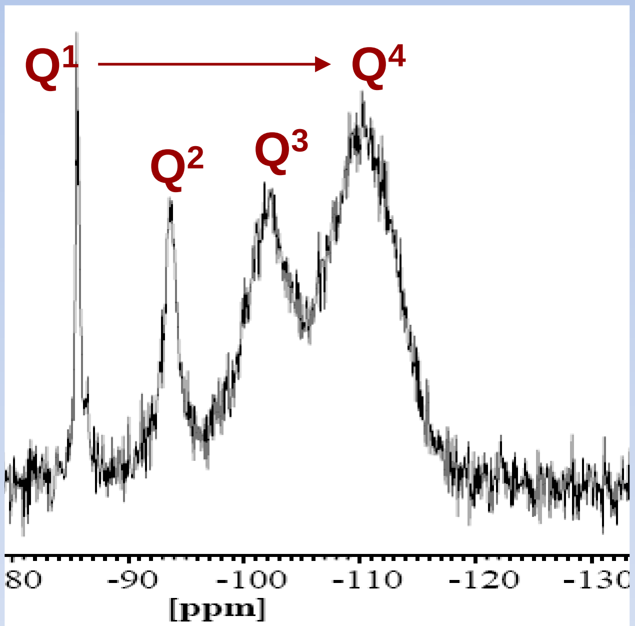


$T^1 \longrightarrow T^3$



Condensation degree →





Condensation degree →

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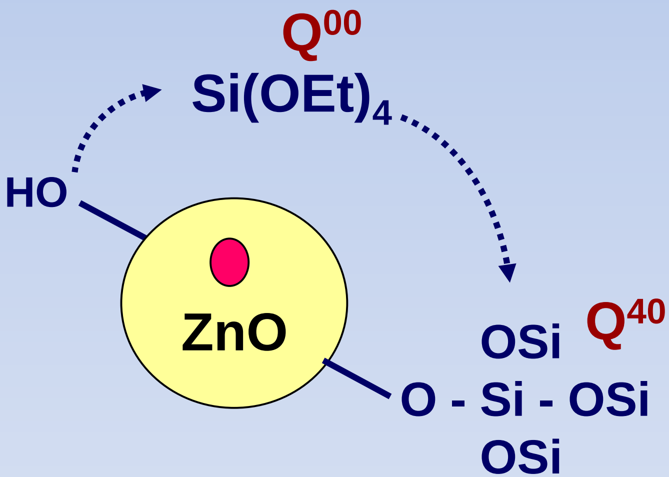
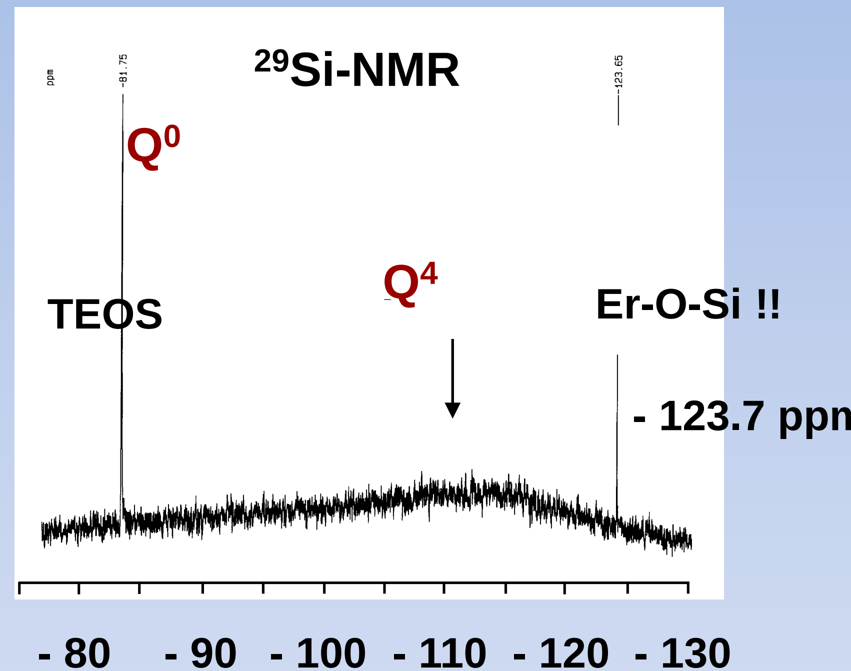
NMR-Spectroscopy of ZnO co-doping

$\longrightarrow$ $ErAc_3$

$\longrightarrow$ TEOS





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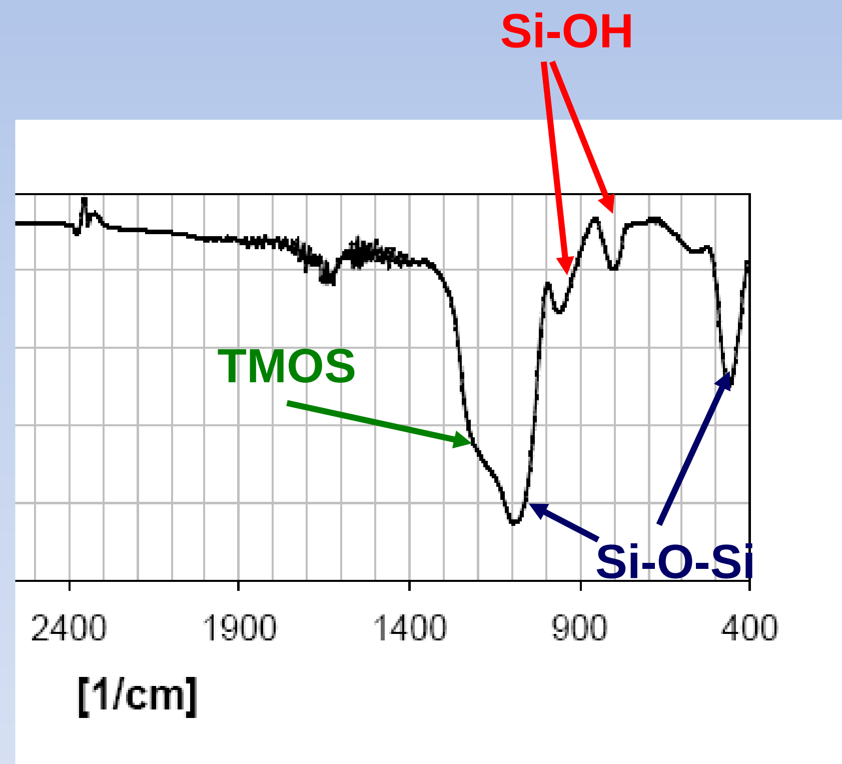
FTIR characterizations

HO - Si – O - Si
I
$(OCH_3)_2$

Group	λ (cm^{-1})	Observations
Si-OH	3700-3300	streching Si-O-H
	955-835	streching Si-O
	982-950	bending Si-O-H
Si-O-Si	1090-1020	streching Si-O-Si
	800-780	bending Si-O-Si
Si-O-CH_3	~ 2860	streching –CH_3
	~ 1190	CH_3 rocking
	~ 1100	streching Si-O-C
	850-800	streching Si-O-C
H_2O	3600-3100	
	1640-1615	
CO_2	2349	

TMOS/EtOH/H_2O, pH 4,9



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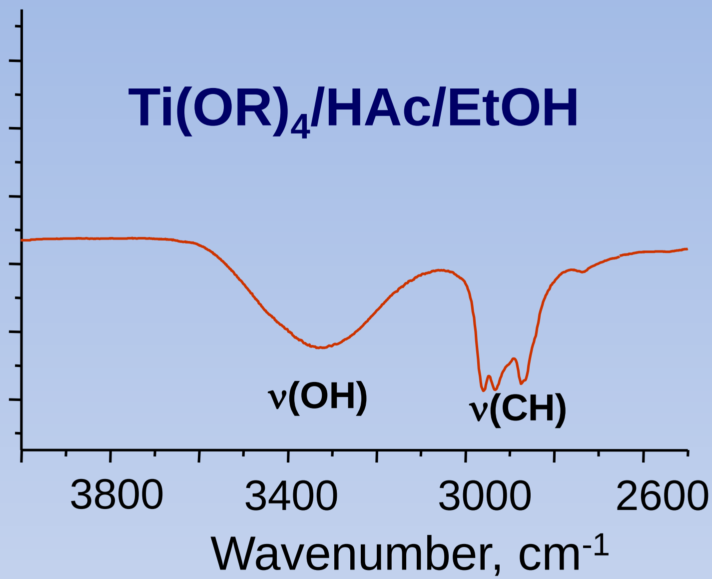
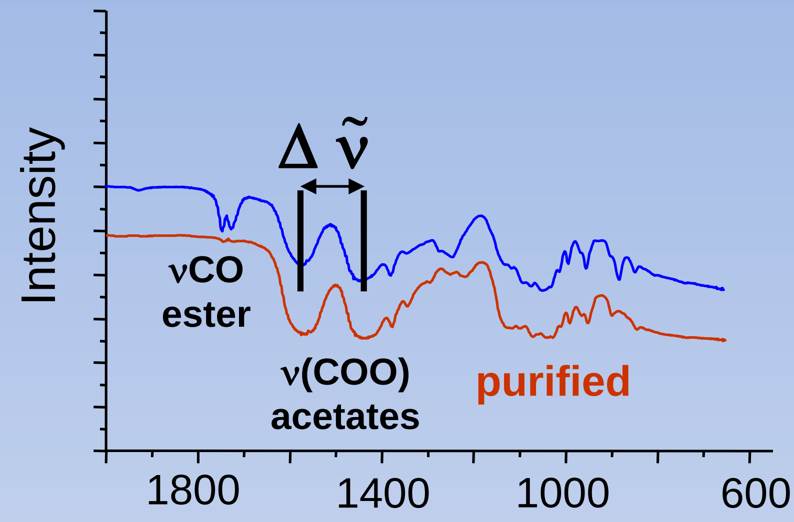
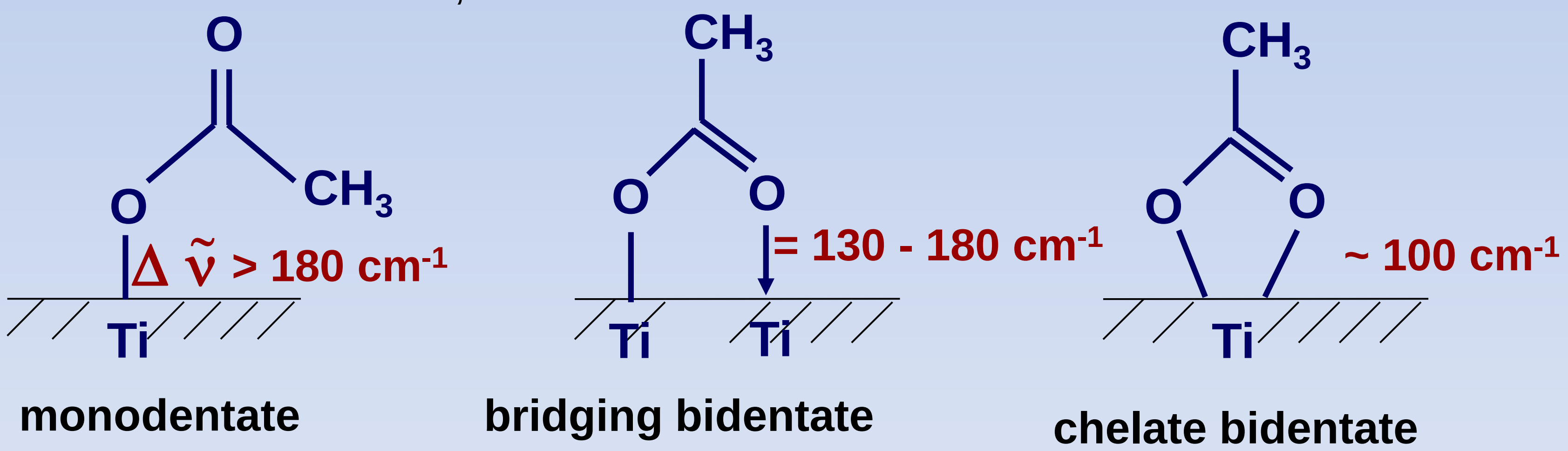
Interfacial chemistry of TiO_2 xerogel formed in ethanol







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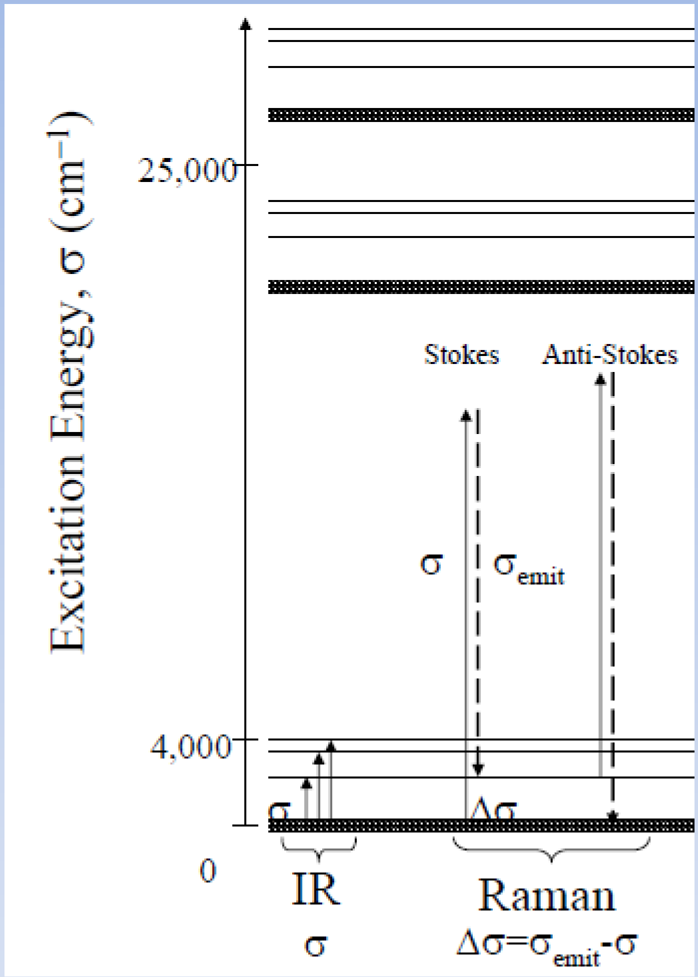
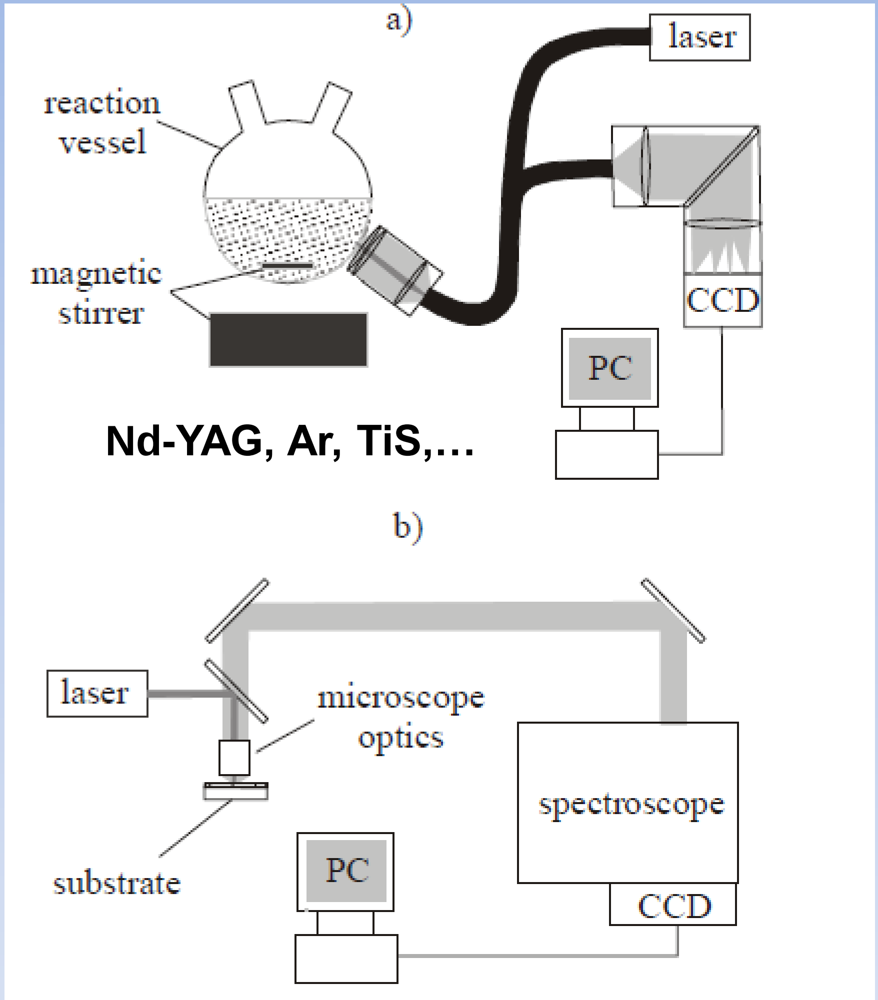
Raman spectroscopy in sol-gel process





Nd-YAG, Ar, TiS,…

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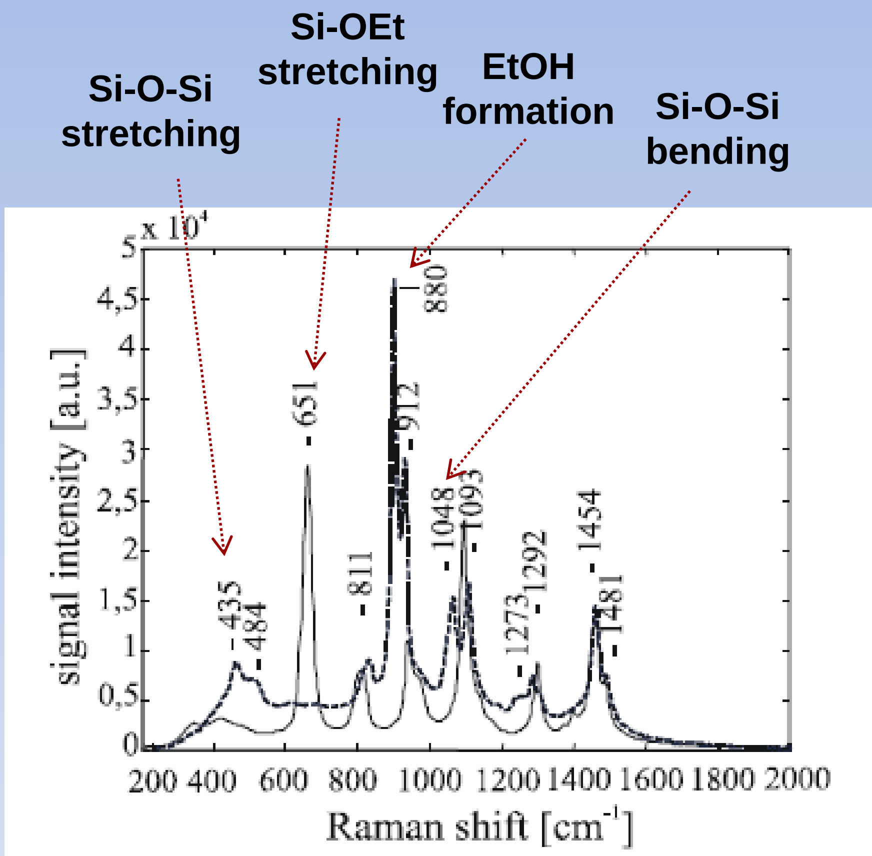
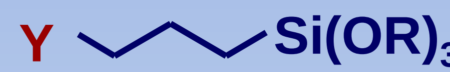
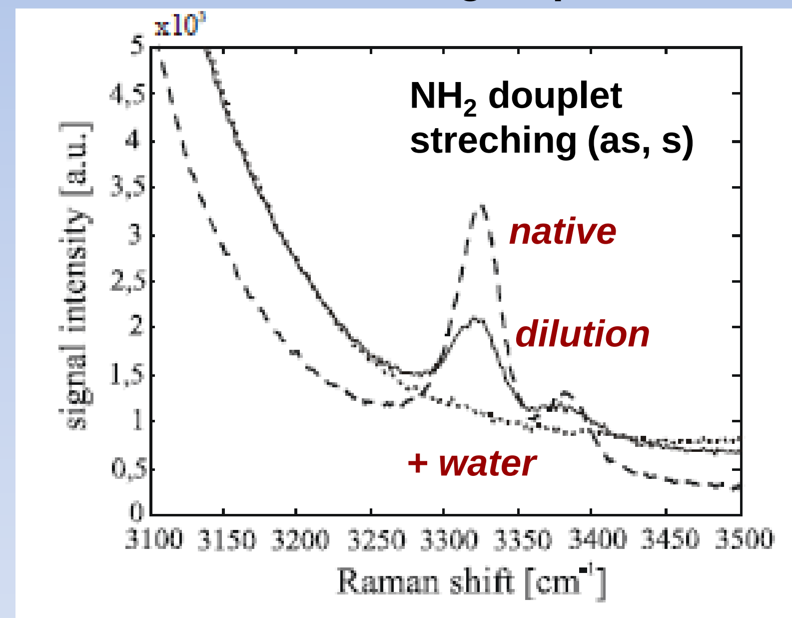
TEOS/THF/water/HCl



GPTES/APTES/water



Y: Epoxy group
Amine group



What happened?

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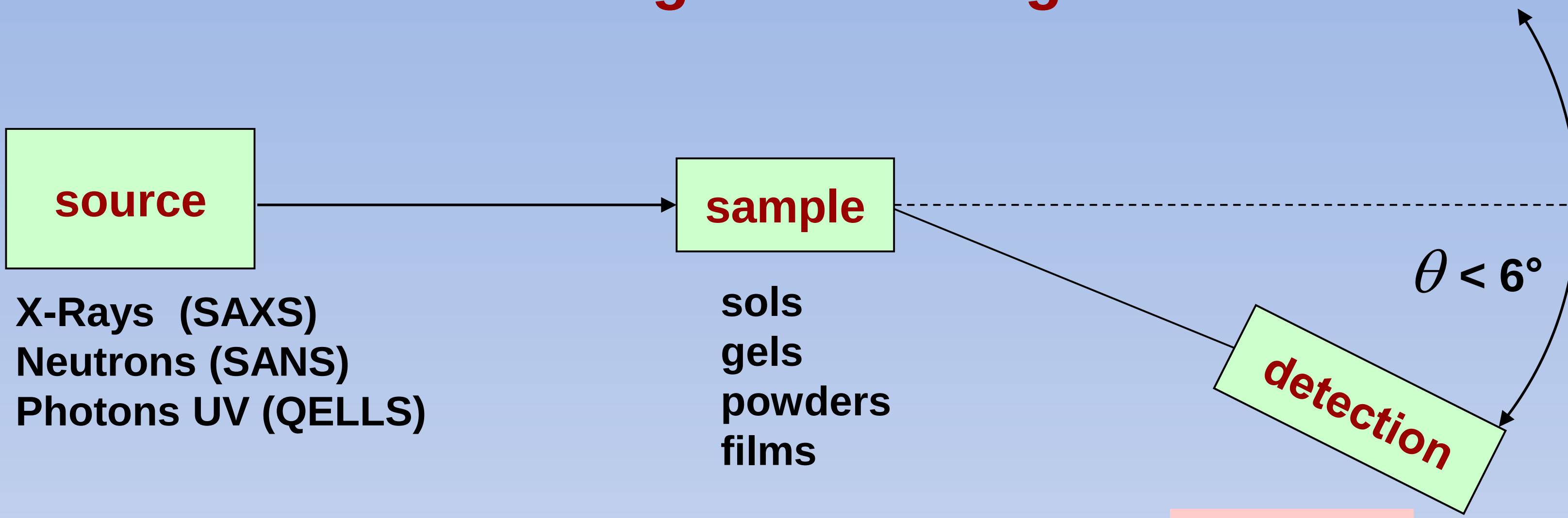
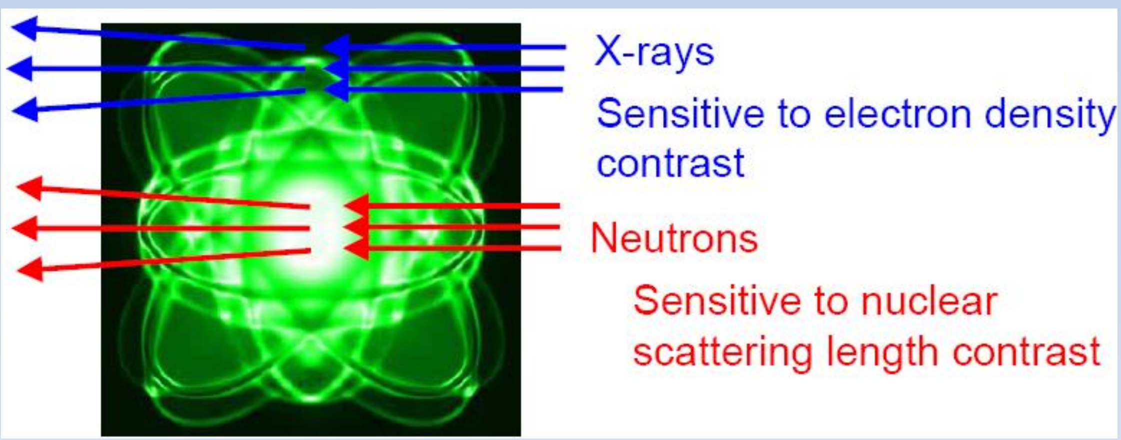
Small Angle Scattering





$$I_q \sim q^{-D}$$

I =scattered intensity

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$$

q = scattering vector
D = dimension of the structure

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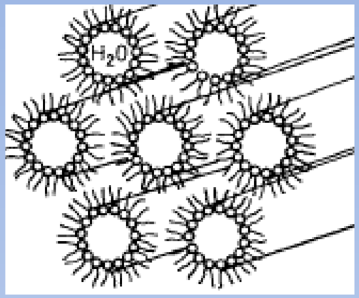
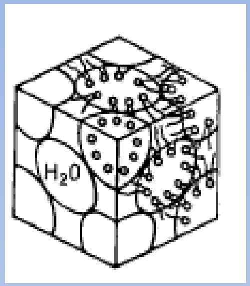
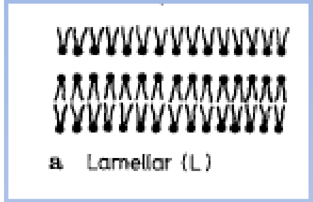
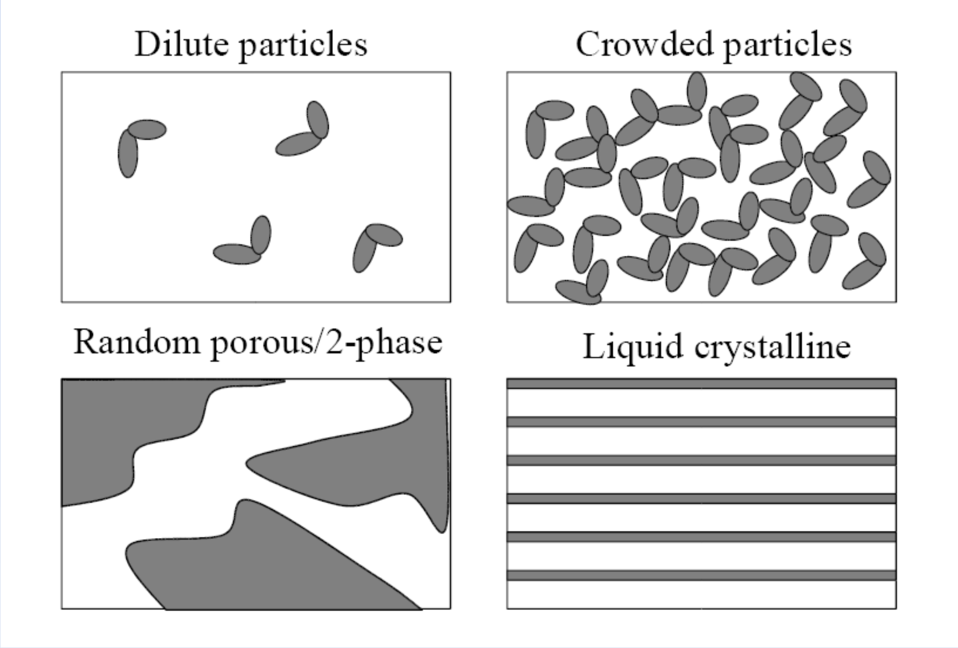
R_g – gyration radius
(primary particles and aggregates)
V_p – pore and particle volume
m_p – particle mass
A – specific surface area
D_f – fractal dimension
Shape of primary particles and aggregates

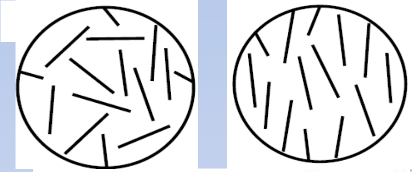






Orientation and self-organisation






Hydrated DNA

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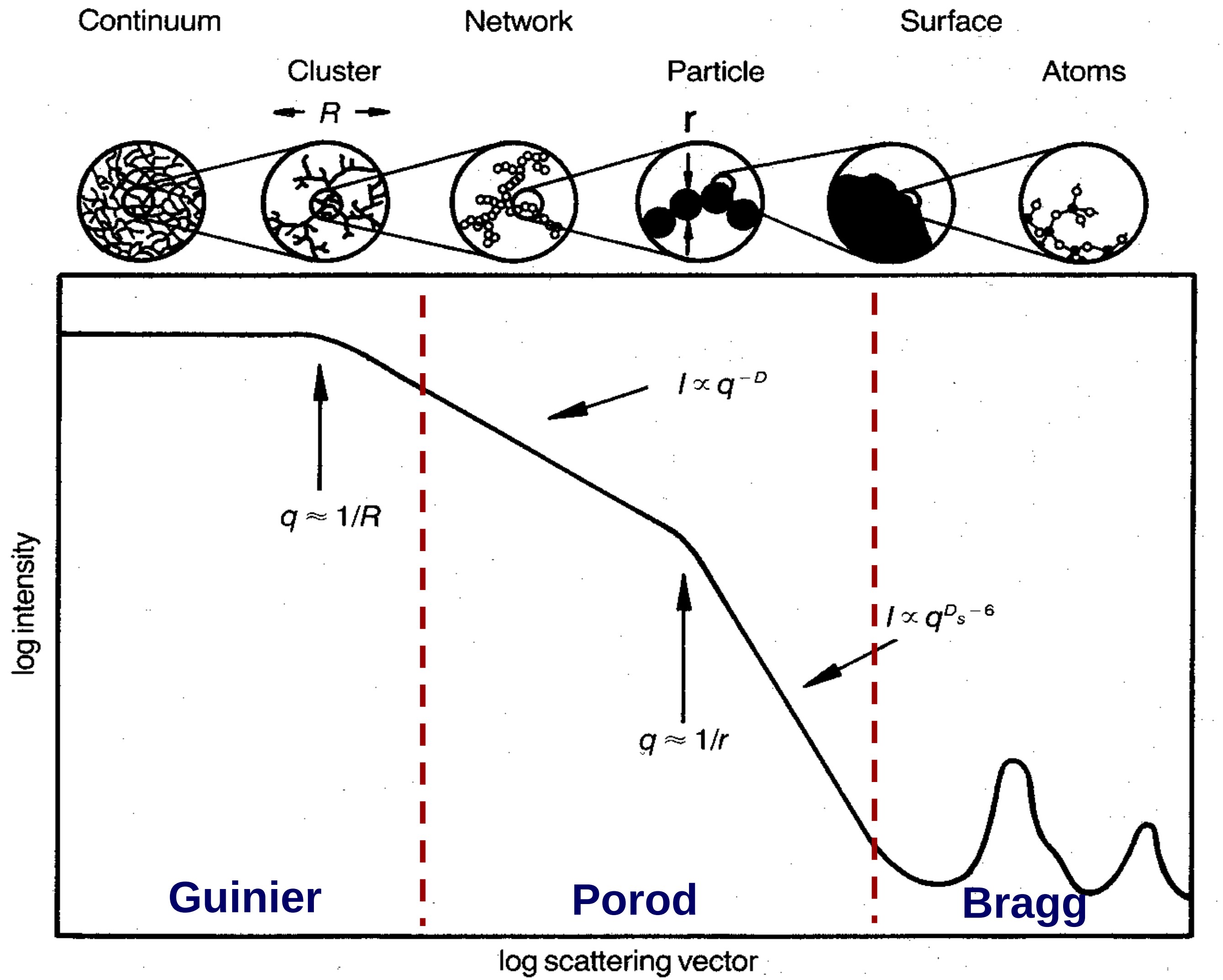
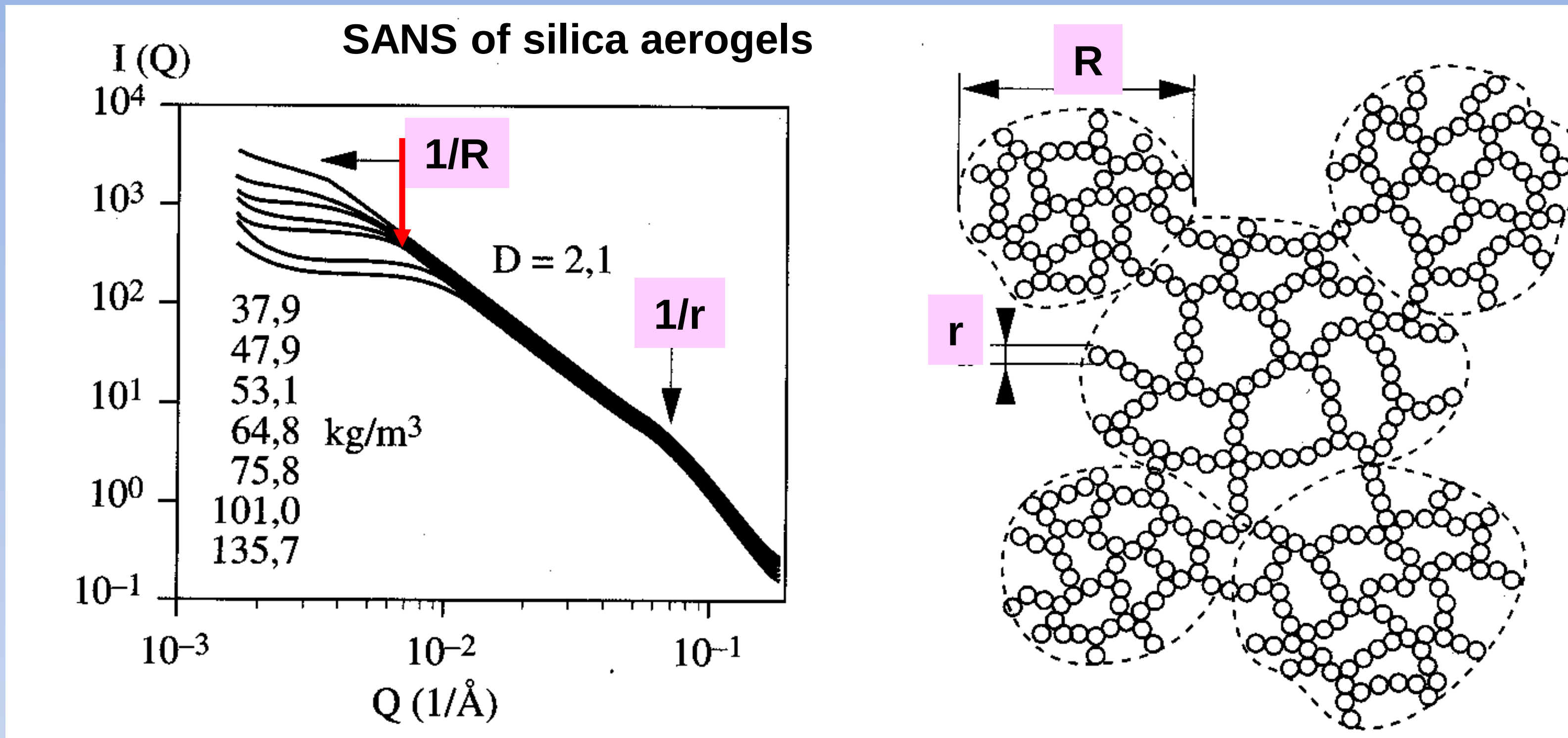


Fig. B2. Small-angle scattering curve for a disordered particle network. All structural features appear in the corresponding regions of scattering vector q. R and r denote a mean cluster and particle size, respectively; exponents D and D_S, determining a power-law decay, are a measure of the morphology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



Note:

masse ~ R^D

Euclidien objects
D = 3

Mass fractal objects
$1 < D_f < 3$

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1 Chapter, revision

1. What are the principal molecular precursors of the sol-gel process used to elaborate glasses, ceramics and hybrid composites;
2. To transform $Ti(OC_3H_7)_4$ into polymeric heterosol containing "Zn-O-Ti" moieties, Zn- acetate dehydrate is used. Hereby, an isopropanolic reactants mixture is refluxed during several hours;

   Give the principal chemical reactions taking place in the reaction mixture;
3. Using FTIR, various surface states of carboxylates can be identified; explain how?
4. Interpret the previous Raman data of the GPTES/APTES/water reaction mixture
5. How the Si^{29} NMR spectrum would look like in the case of a complete TEOS condensation?
6. Explain the usefulness of the Porod region in the experimental SAXS and SANS data? (see the log I – log Q plot)

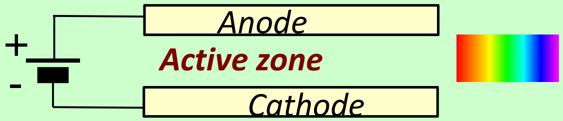
Chapitre 2

Nanocomposites in telecommunication

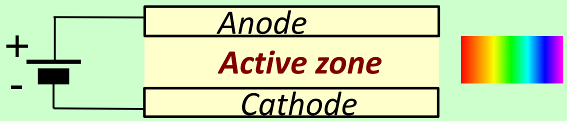
① Transparent electrodes

TCO = transparent conducting oxides

② Electrochromy



③ Electroluminescence



④ Photoluminescing nanoparticles

- *Spectral profile and quantum yield of photoluminescence*
- *Chemical activation strategies (« core-shell », lanthanide doping, FRET)*

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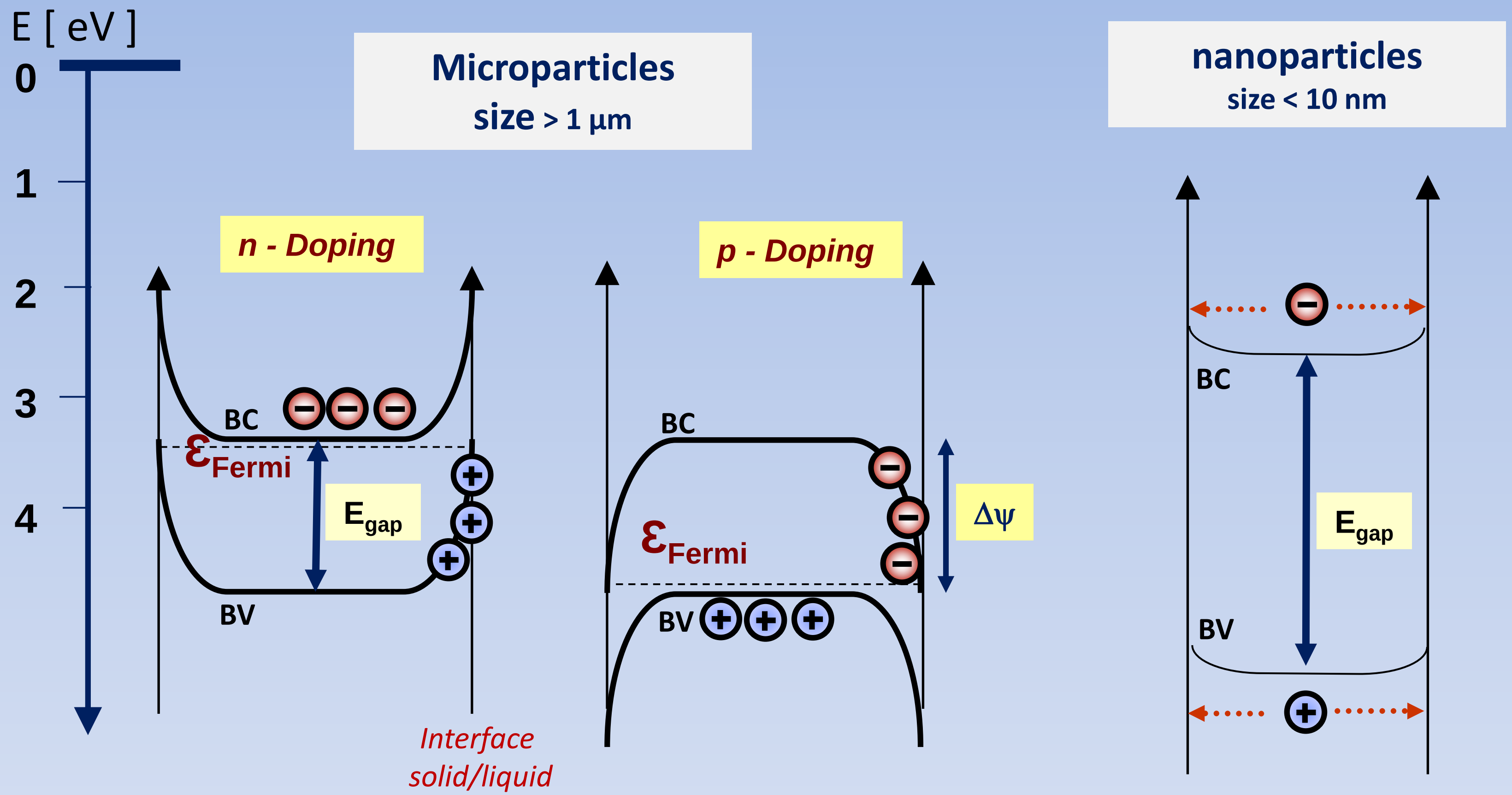
Energy diagram macro versus nano



Note:

$\Delta\psi$ = energy barrier at the interface (> 100 nm)

E_{gap} = gap energy varies with size

ε_{Fermi} = Fermi level (eV)

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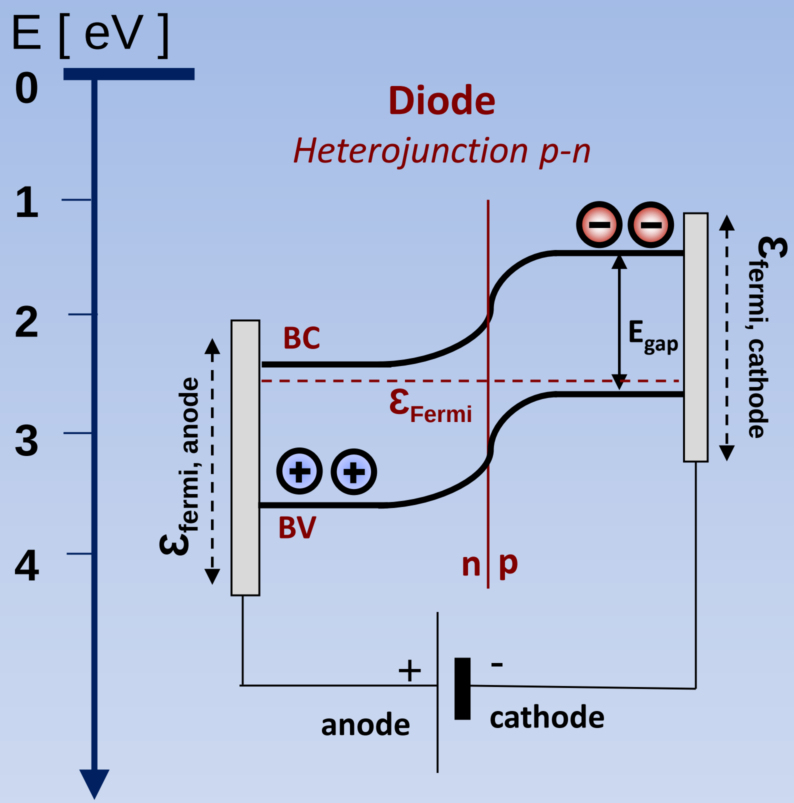
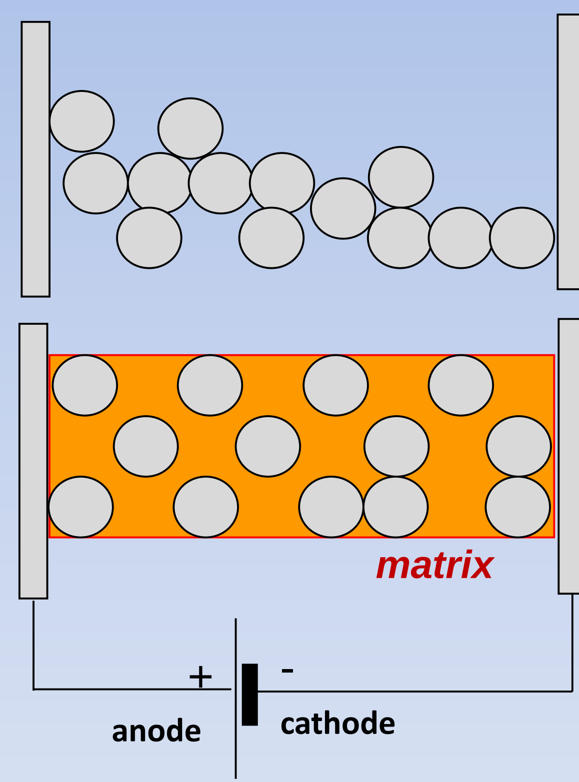
Diode

Heterojunction p-n



Nanoparticulate agregates



Note:
Surface chemistry, nanoporosity
And size are the key parameters !

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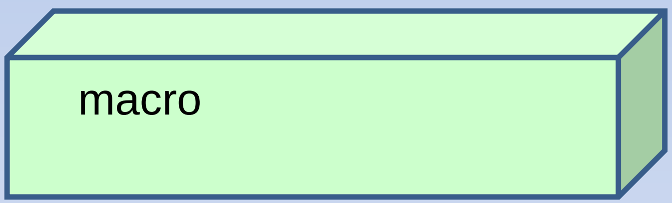
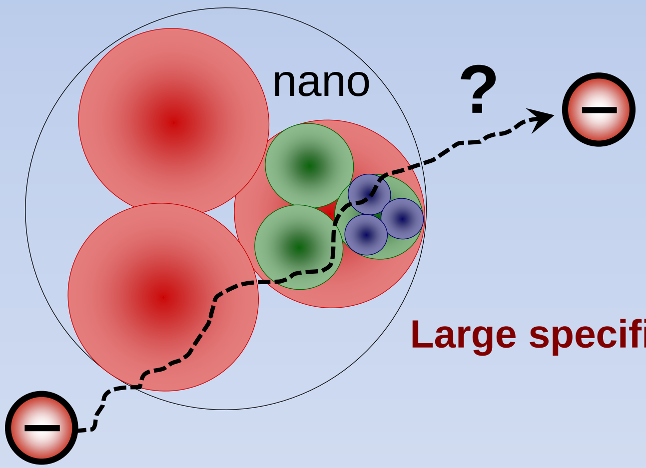
Transparent Conducting Oxides TCO's

Figure of merit ~ T / R_s

T = optical transmission (UV : 400-900 nm)
R_s = surface (sheet) resistance (< 20 Ω)





Large specific surface area!!

T and R_s are controled by :
Morphology (porosity, degree of crystallinity)
Surface chemistry (traps, oxidizing agents)
Defects – intrinsic and extrinsic
Doping ionic/cationic

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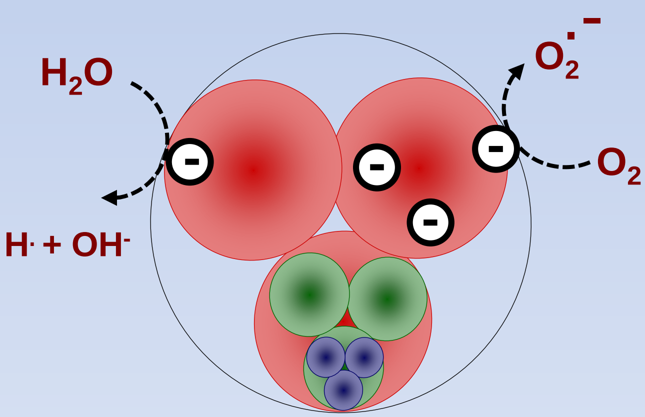
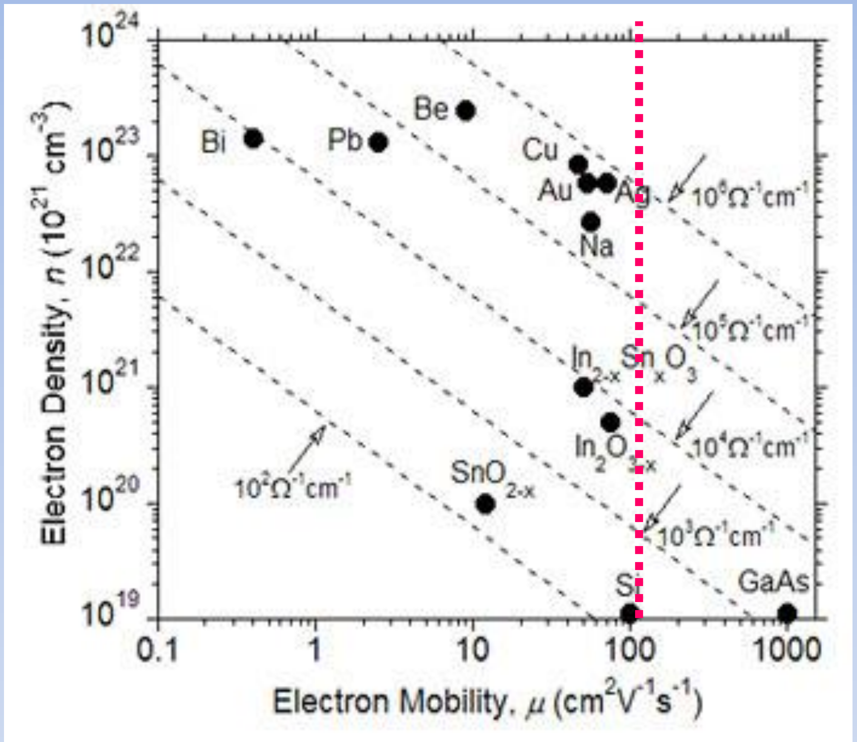
$R_s = \rho / e = 1 / q\, n_e\, \mu\, t$

R_s: sheet resistance (Ω/□)
ρ: electyric resistivity (Ω cm)
t: film thickness (< 2 μm)
n_e: number of free electrons / cm^3
μ: electron mobility ($cm^2V^{-1}s^{-1}$)
q: elementary charge
N μ q = conductivity ($\Omega^{-1}\,cm^{-1}$)





↑μ via morphology
& surface chemistry

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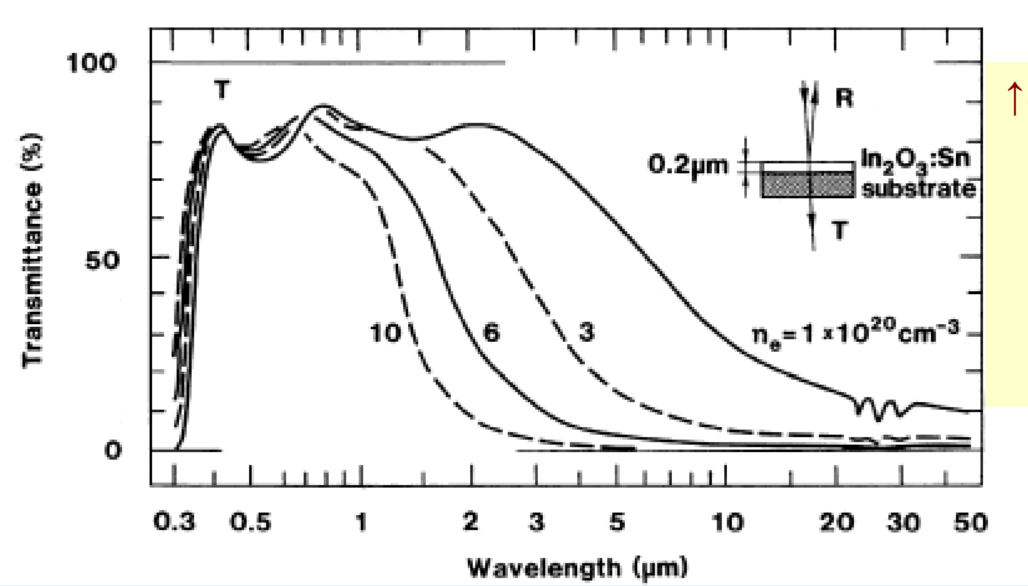
Optical Spectral Profiles of TCO's

↑T : optical transmission
400-1200 nm > 80%
E_g > 3 eV



↑n_e : n - type doping

ITO : $In^{3+}_{2-x}Sn^{4+}_{x}O_3e^{-}_{x}$

ATO : $Sn^{4+}_{1-x}Sb^{5+}_{x}O_2e^{-}_{x}$

FTO : $Sn^{4+}O_{2-x}F^{-}_{x}e^{-}_{x}$

AZO : $Zn^{2+}_{1-x}Al^{3+}_{x}Oe^{-}_{x}$

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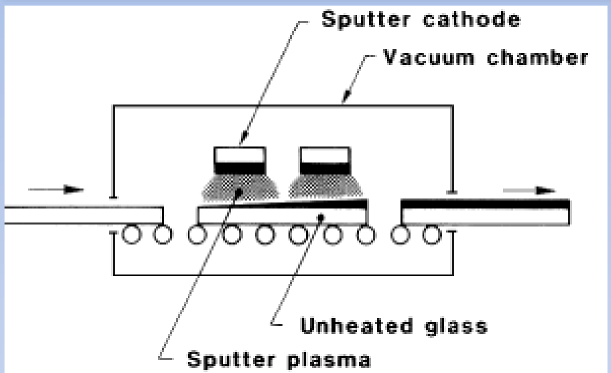
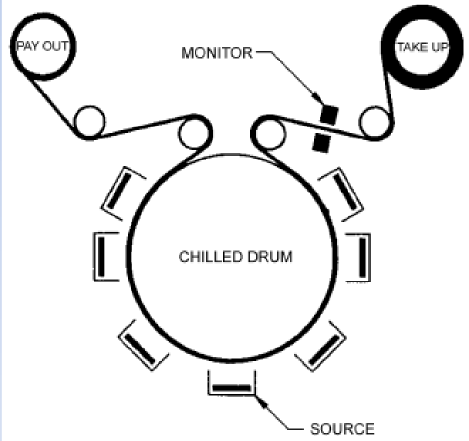
Elaboration methods

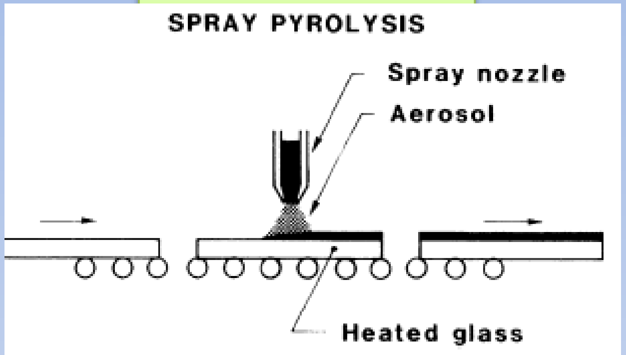
Pulsed Laser Deposition

Sputtering



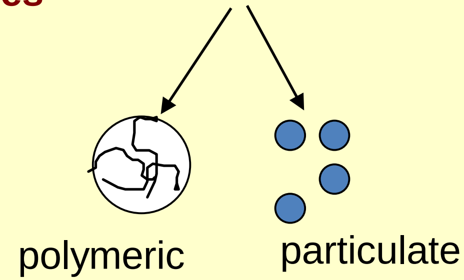


Spray pyrolysis



Soft chemistry

Metal alkoxides → *H&C* → **Sol** → *dip/spin* → **Gel** → *heat* → **Films**



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nano-ZnO

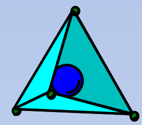
JACS 1991, 113, 2826

EtOH, 90°C

$$4\ Zn(Ac)_2 \cdot 2(H_2O) \Leftrightarrow 2\ HAc + 7\ H_2O + [Zn_4O](Ac)_6$$

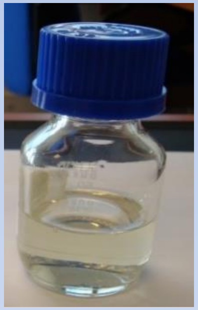
① *nanoparticulate*

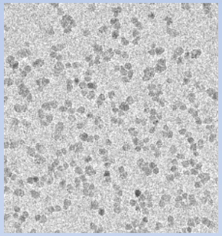
2.5 nm ≤ taille ≤ 5 nm



$[Zn_4O](Ac)_6$

$LiOH \cdot H_2O$



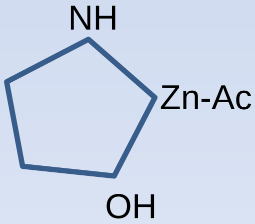


H_2O

② *polymeric*

taille ≤ 1 nm

$Zn(Ac)_2 2(H_2O)$
2-aminoethanol



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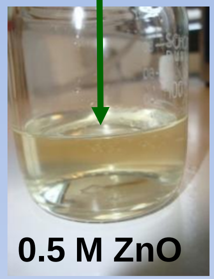
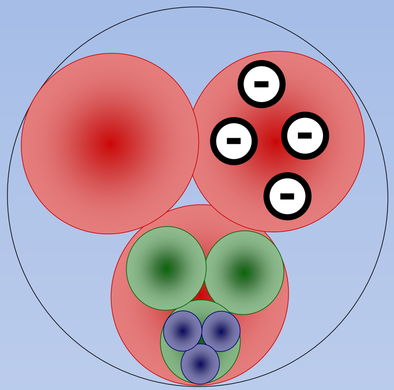
AZO electrode via sol-gel (ZnO/Al^{3+})

$Al\text{-}sec(OC_4H_9)_3$

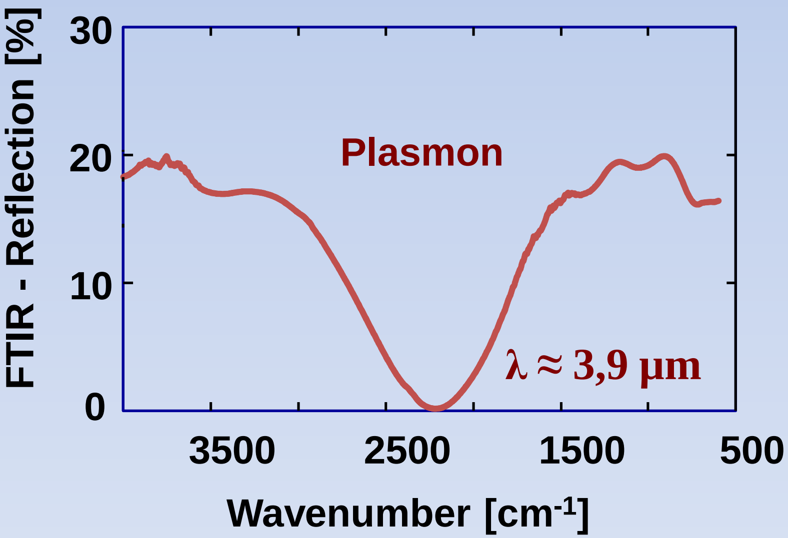
Doping



Thin layer
Sintering



$N_e \sim 2\ 10^{20}\ cm^{-3}$
$\mu_e < 10^{-3}\ cm^2/Vs$
$R_s > 1000\ \Omega/\square$



Note:
1. ***Doped oxides behave like metallic***
2. ***Nanoparticles (localized plasmons)***
3. ***Nano- and mesoporosities block the delocalization of free electrons***

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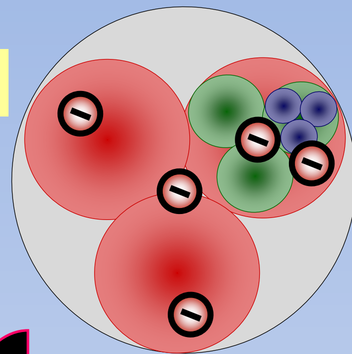
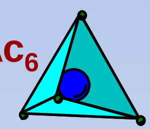
n_D ~ 1.7

μ = 0.001 cm²/Vs



(Zn₄O)Ac₆

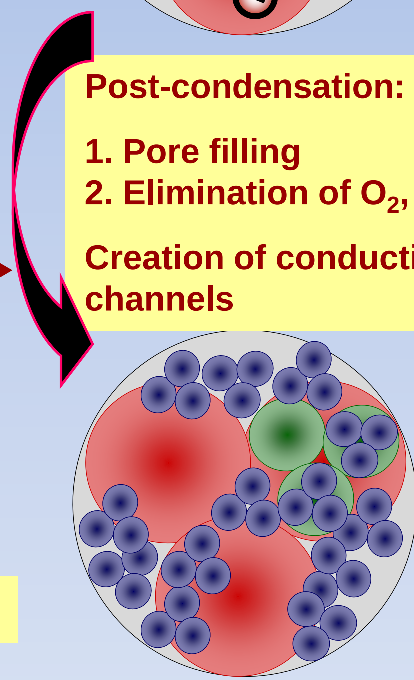


OH⁻

Post-condensation:

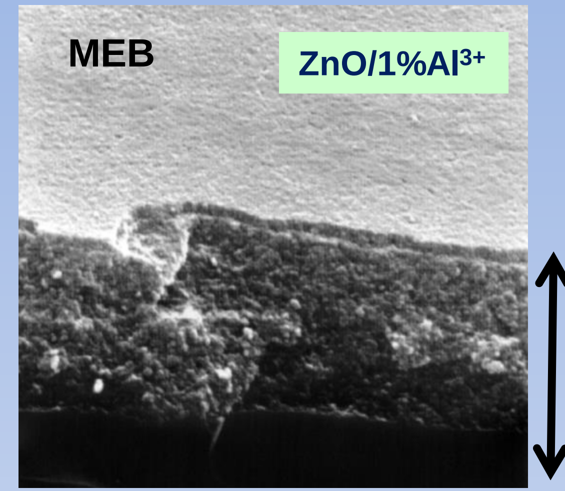
1. Pore filling
2. Elimination of O_2, H_2O

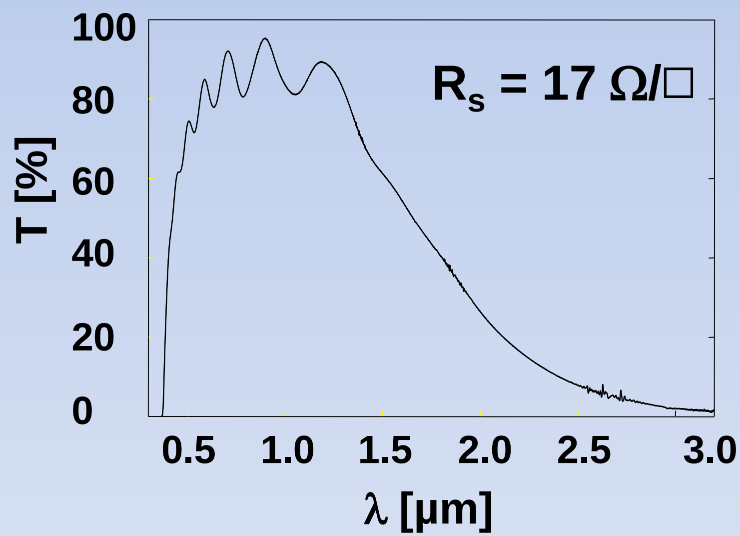
Creation of conducting channels



n_D ~ 2.1

μ = 9 cm²/Vs





n_D = refractive index (ZnO bulk: = 2.1)

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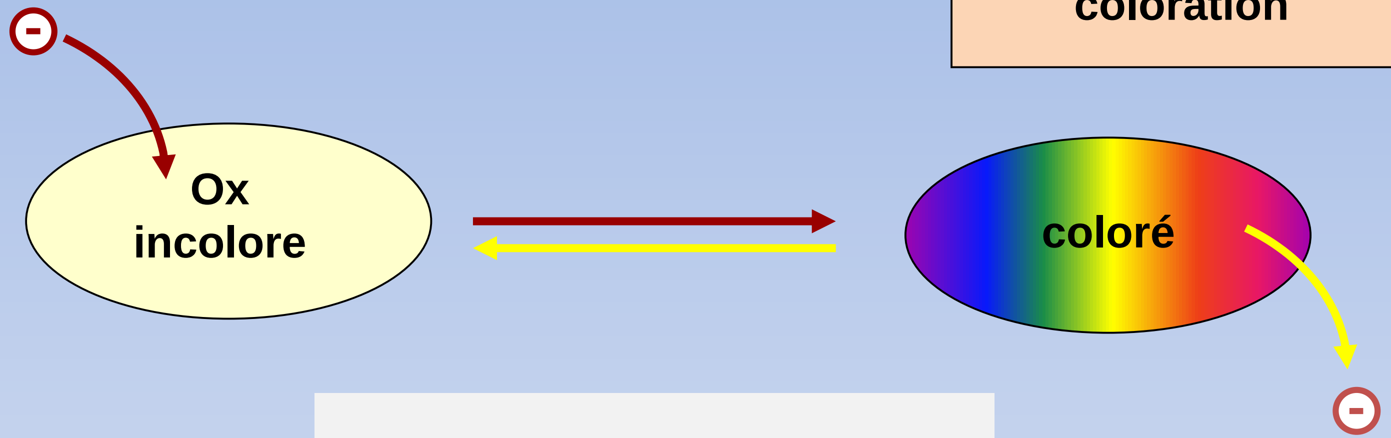
Electrochromy

reversible electrochemical coloration



$$\eta (l) = \Delta \text{ O.D. } (l) / Q$$

η CE = coloration yield (optical efficiency)
Δ O.D. = optical density change (contrast)
Q = injected charges (C/cm^2)

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Cathodic coloration :
WO_3, MoO_3, V_2O_5, Nb_2O_5, TiO_2, Cu_2O

coloré

$WO_3 + ne^- + n\,Li^+ \leftrightarrow Li_nWO_3$

W^{6+}-O^{2-}-W^{6+} W^{6+}- O^{2-}- Li^+ (W^{5+})

Yellow to blue

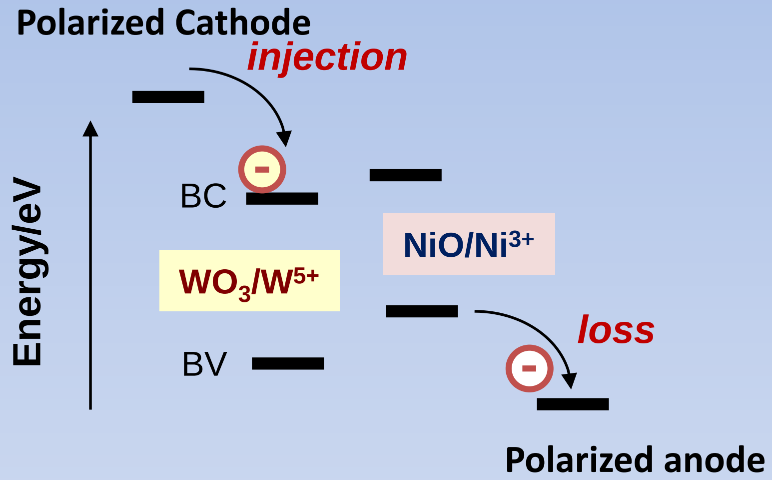
Anodic coloration :
NiO, CoO, Cu_2O, IrO_2

coloré

$Ni(OH)_2 \leftrightarrow NiOOH + H^+ + e^-$

$NiO + Ni(OH)_2 \leftrightarrow Ni_2O_3 + 2H^+ + 2\,e^-$

green to brownish



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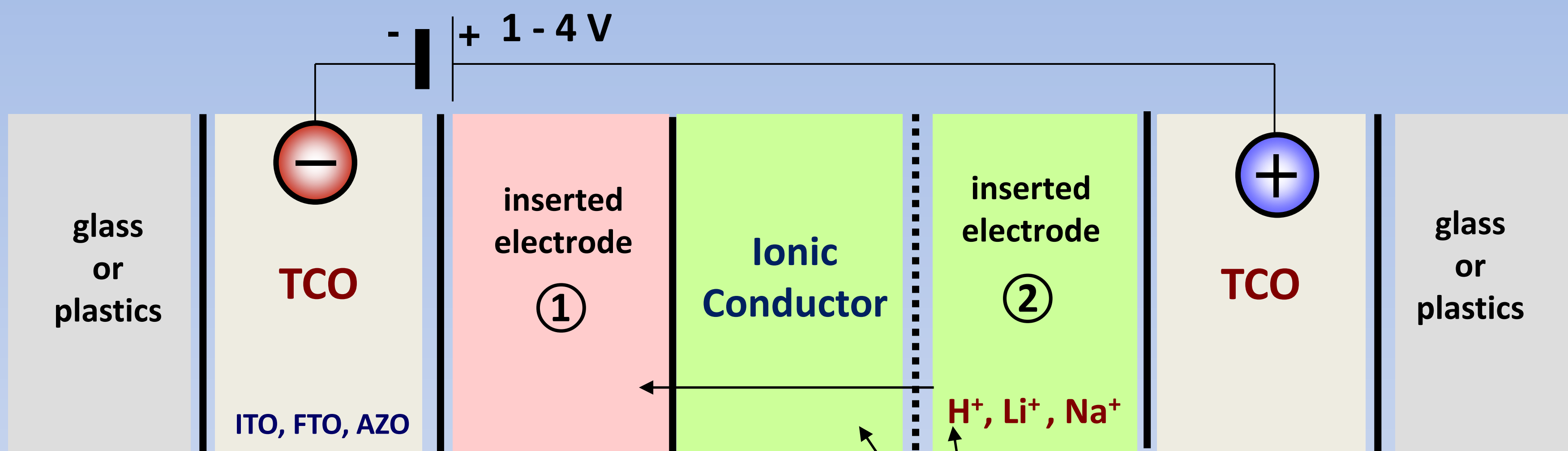
Electrochromic cells design (*global overview*)



Molecules
Nanoparticles
Org. Conjugated Polymers

Ionic Conductors :

Gels, membranes, organoceramics
- ZrO_2, Ta_2O_5
- Organic-inorganic hybrids
- polyelectrolytes: PEO, PVA

Key parameters:

Engineering of electronic and ionic transport
Life time: 10^4 – 10^5 cycles (5-20 ans)
Coloration/decoloration dynamics – ms, sec, min
Temperature : - 50°C till + 100°C
Optical transparency of multilayers

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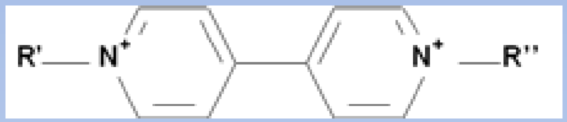
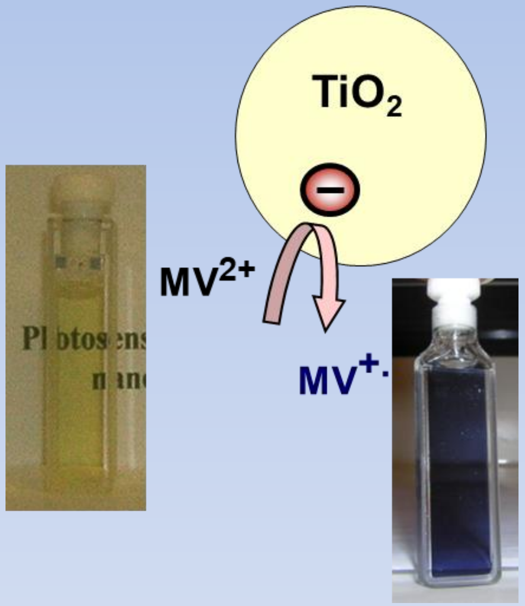
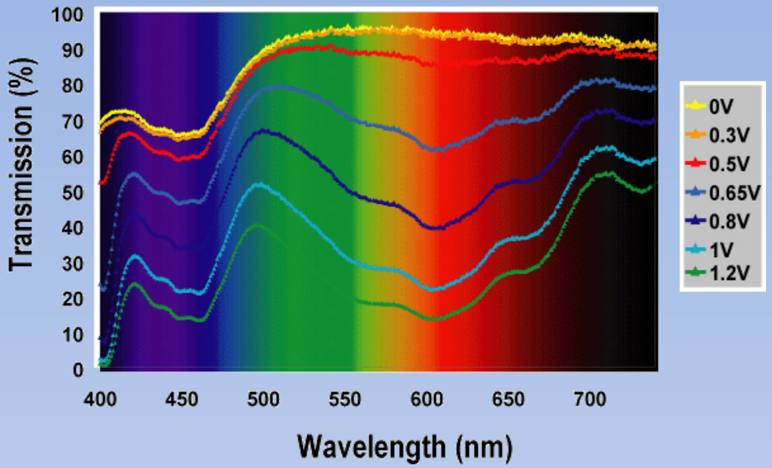
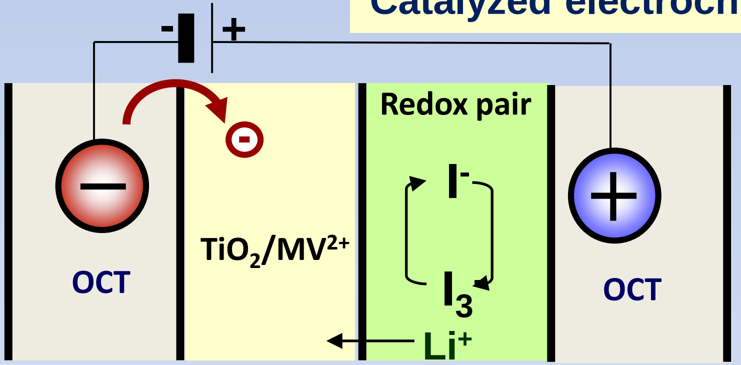
Viologenes (methyl-, ethyle-) at the TiO_2 NP's interface







Catalyzed electrochromy



$TiO_2/MV^{2+} + LiI$

bleached

$TiO_2/MV^{\cdot +} + e^- + Li^+ + I^3$

darkened

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Thin film technologies

1. *rf-sputtering*
2. *CVD (molecular precursors of W, Nb, Ti)*
3. *Sol-gel*
   - *- $WO(OEt)_4$, $WO_2(OEt)_2$*
   - *- $W/H_2O_2/(COO)_2$*
   - *- $Nb(OR)_5$*
   - *- $Ti(OR)_4$*
   - *- $Ni(Ac)_2\ 4H_2O$/MeOH/dimethylaminoethanol*

Pilkington, St Gobain, Daimler Chrysler, Renault, Toyota, Skoda etc…




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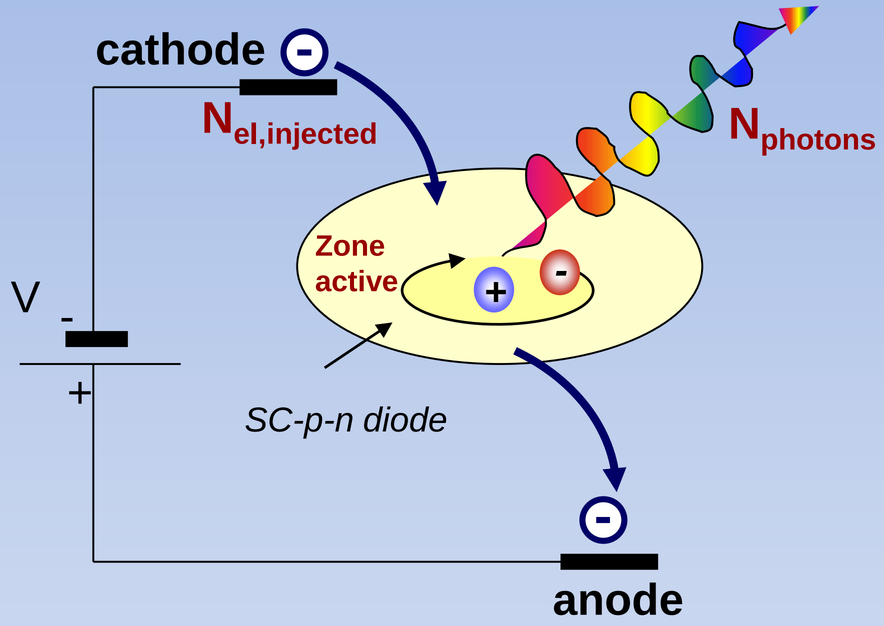
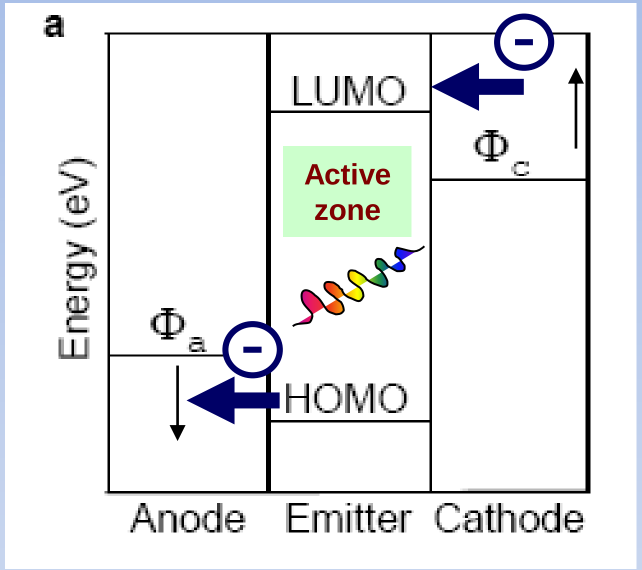
Electroluminescence



EL - Energy diagram



EL- Figure of merit

$\eta_{el} = \eta_{el}\ ,\ N_{photons} / N_{el,injected}$

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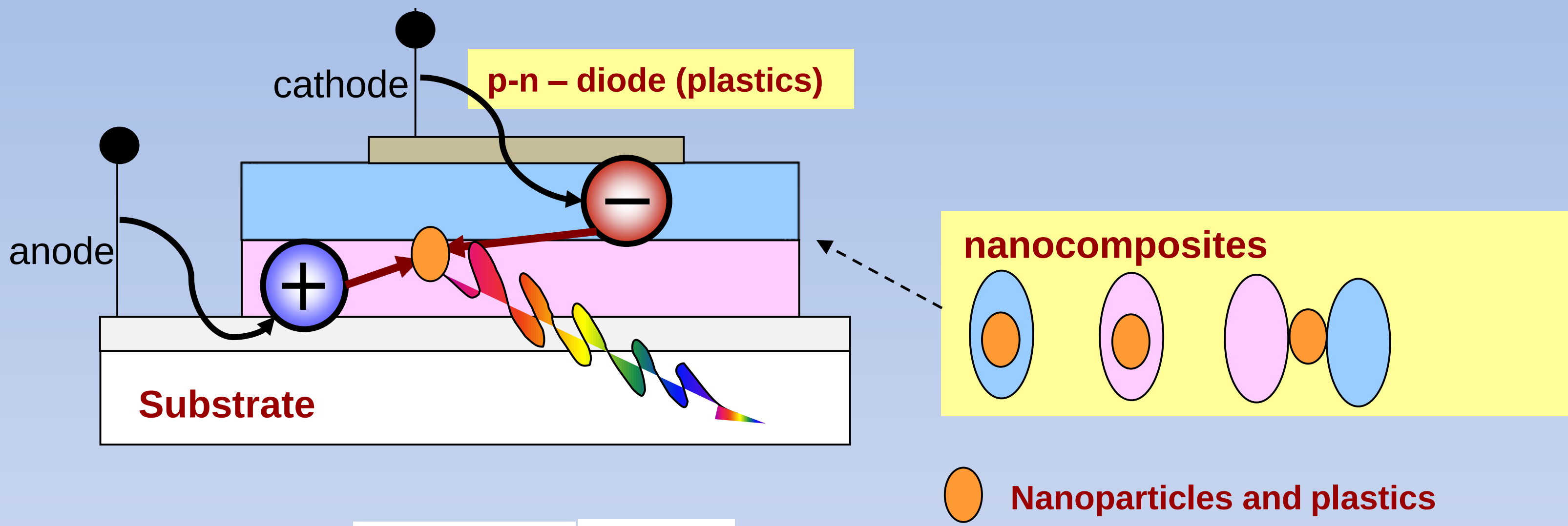
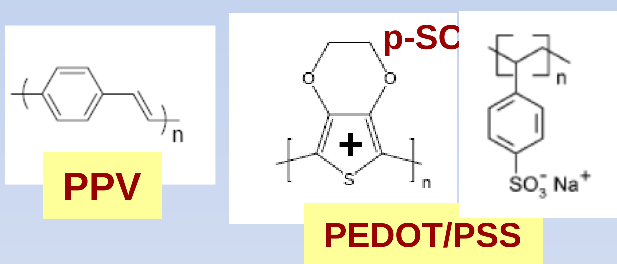
Global design of hybrid cells for intersectorial applications





PEDOT = poly-(3,4-ethylenedioxythiophene)
PSS = poly(styrène sulfonât)
PPV = poly(p- phénylène vinylène)

Luminophors et conductors p or n

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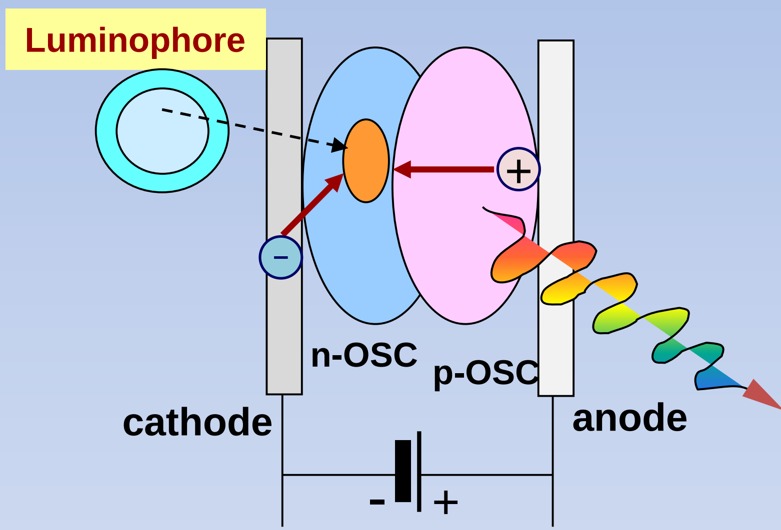
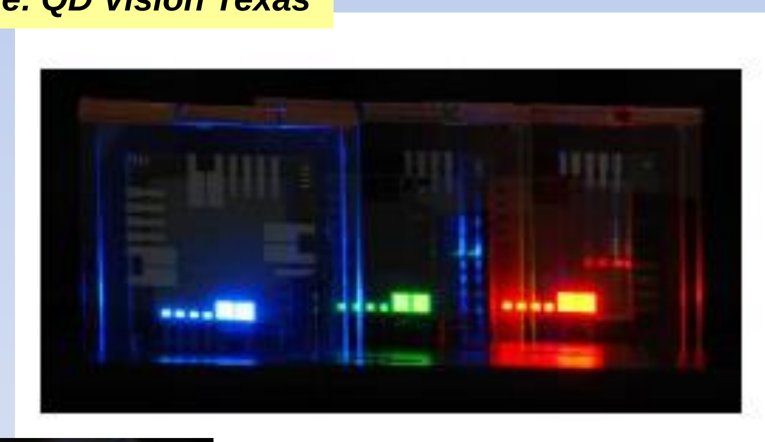
« Q-OLED »



Source: SAMSUNG

Source: QD Vision Texas



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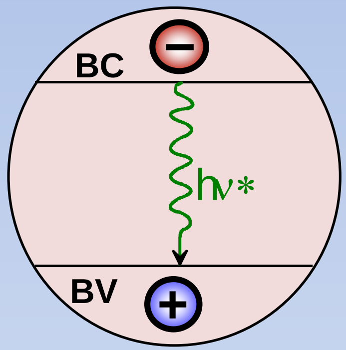
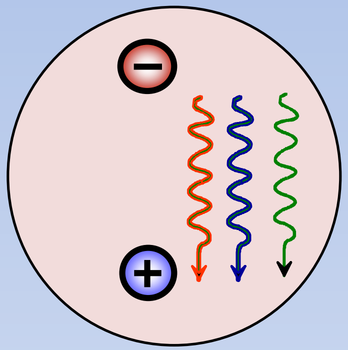
Photoluminescing nanoparticles

① SC-Quantum dots



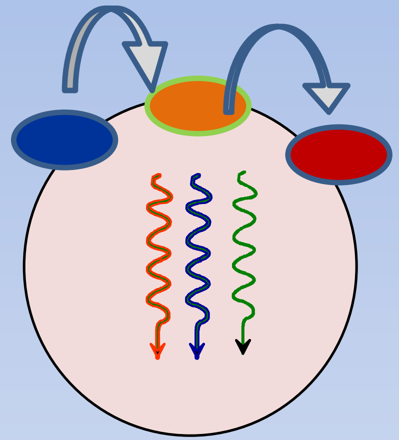
CdS, CdSe, ZnS,
CdTe, ZnTe,
Silicium, Carbon! etc…

② NP carriers of lanthanides



Cations TR (III): Er, Yb, Tm
ZnO, CdSe, $NaYF_4$

③ NP carriers of FRET



Silica, Au, Ag
Organic chromophors
(Er, Yb)@$NaGdF_4$

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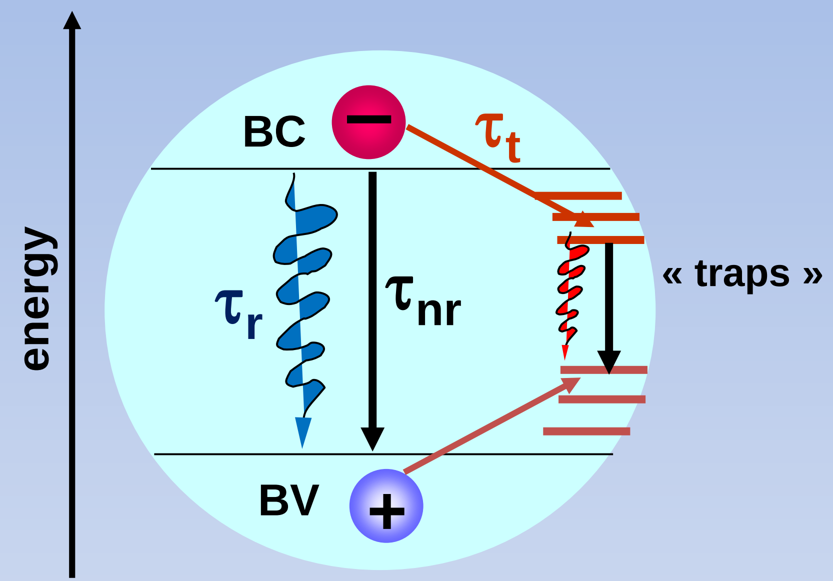
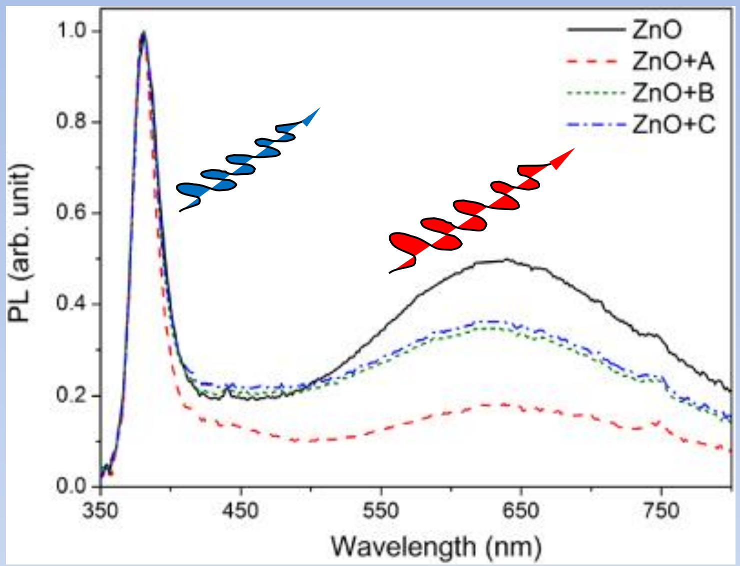
❶ General introduction





$$\tau_t \sim \tau_{nr} << \tau_r$$

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

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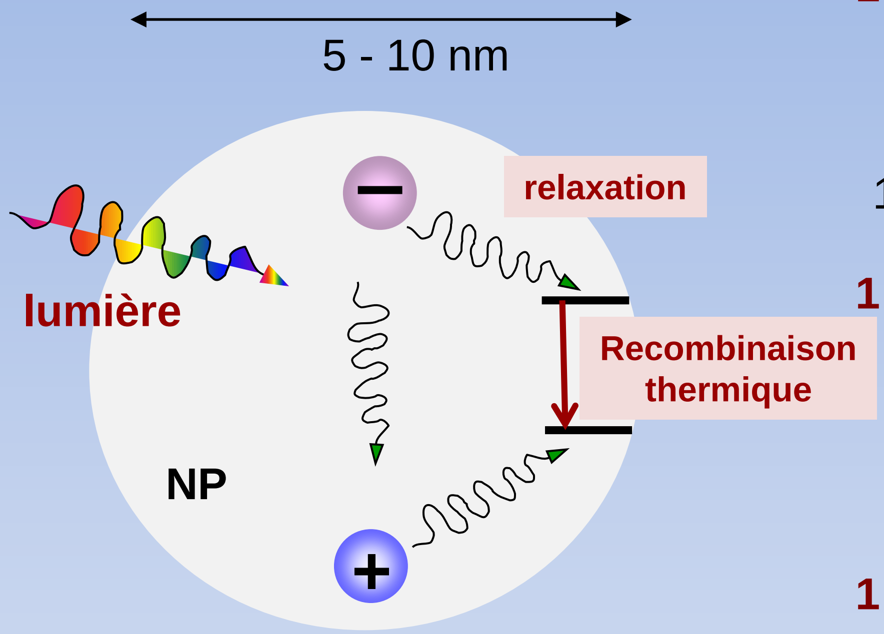
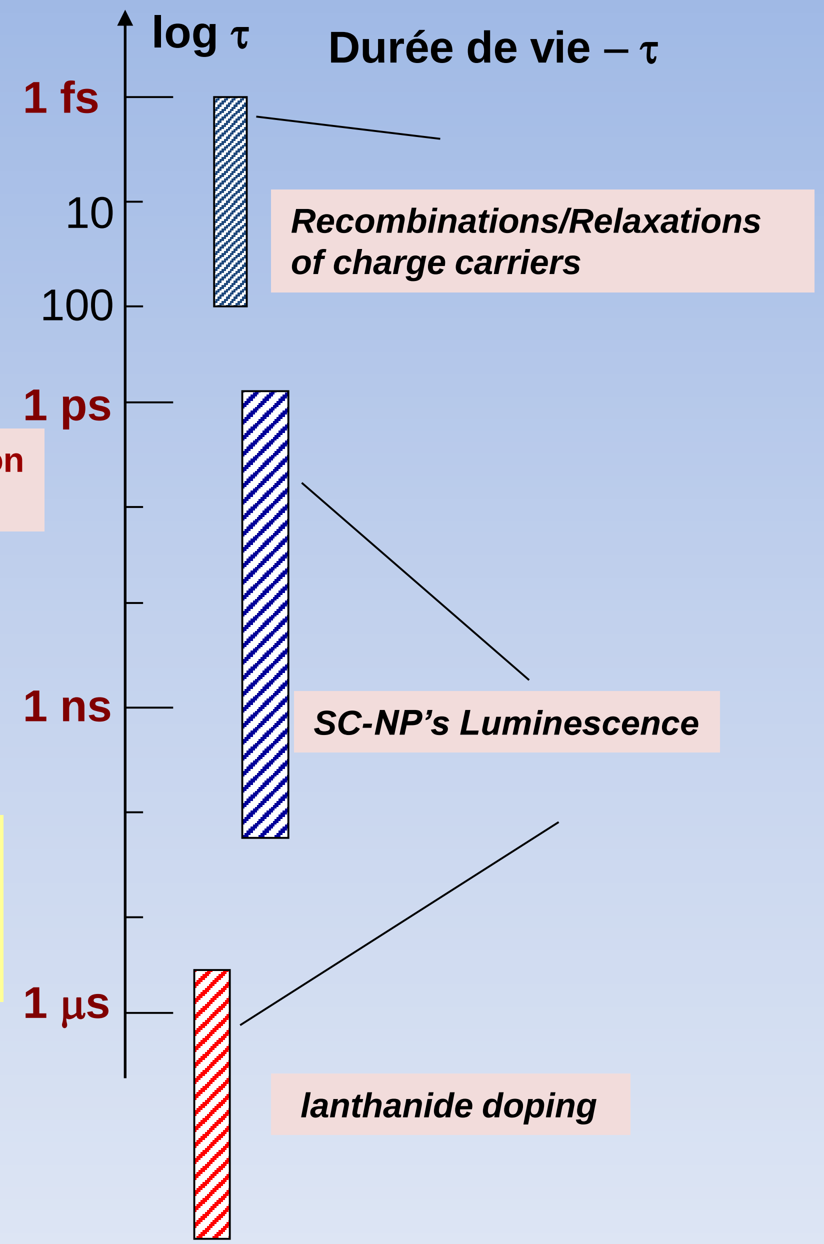
Life time of charge carriers in SC-NPs





Note:

Blocking of ultrarapid thermal recombinations is needed

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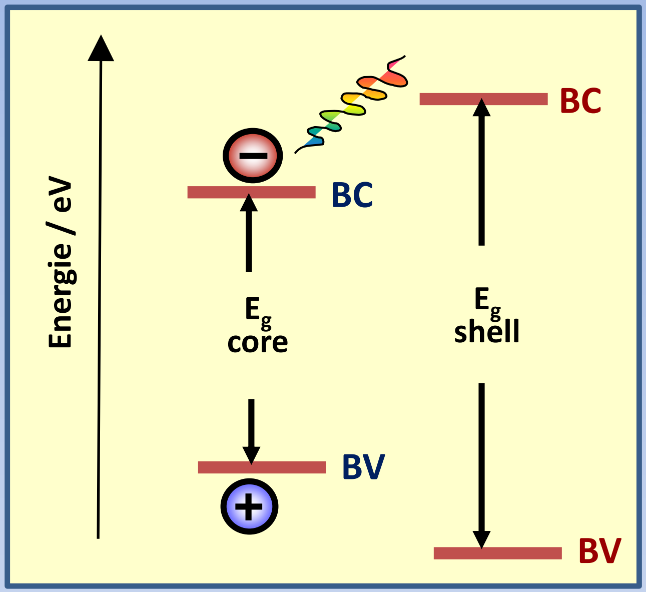
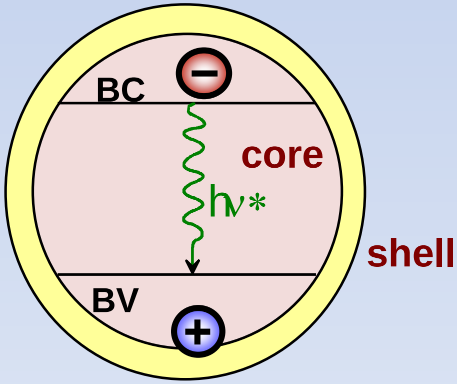
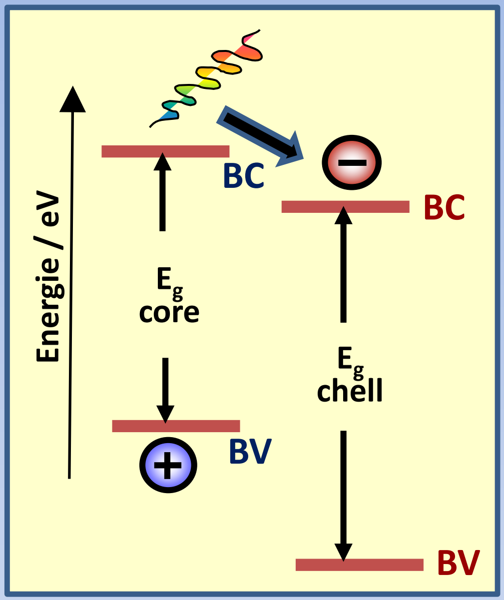
Luminescence Activation via « core-shell »

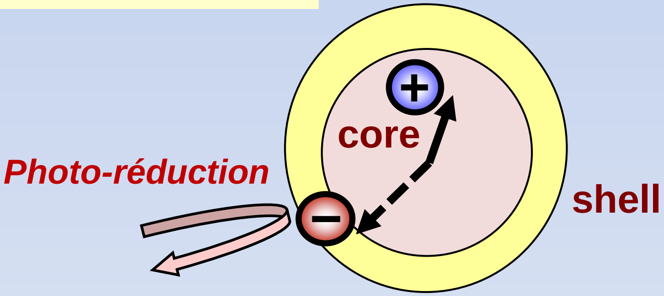


Light confinement





Spatial charge separation



Note:

1. *Choice of SC-couple*
2. *Shell nanochemistry (epitaxy, strong chemical bonds)*

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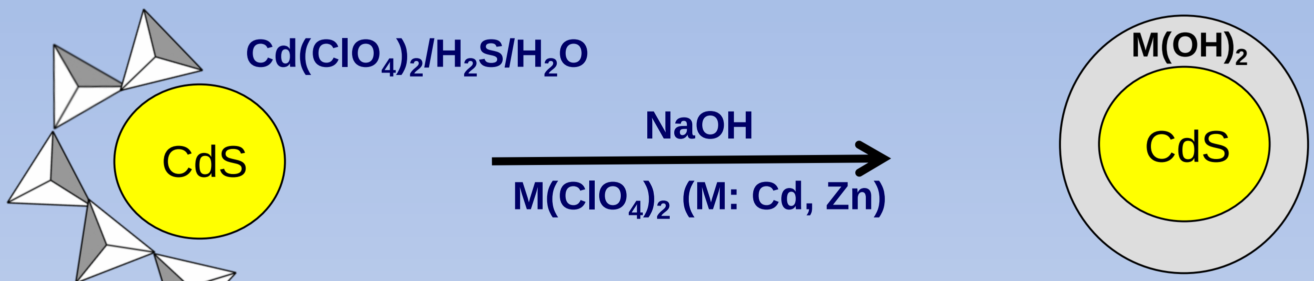
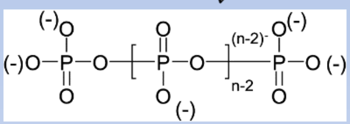
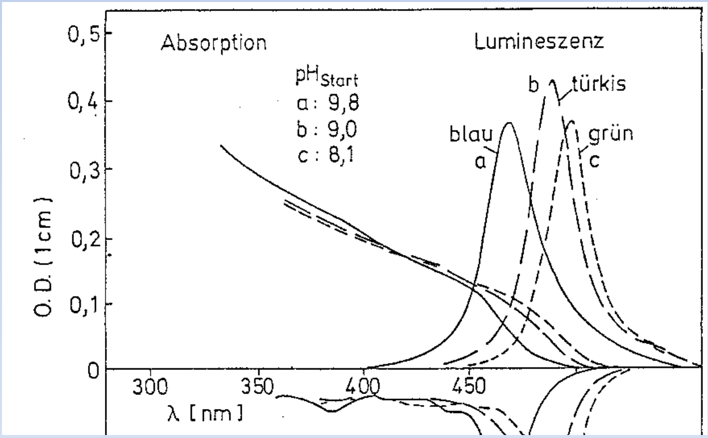
Nanocomposites “Core-Shell” CdS-M(OH)$_2$





acivated



JACS 1987

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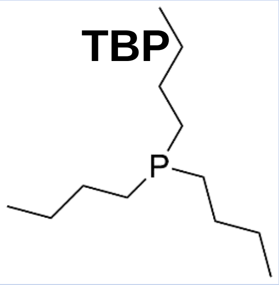
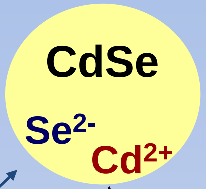
Core-shell activated luminescence

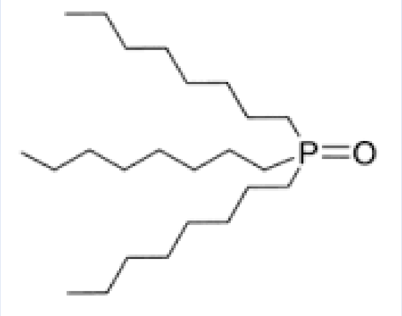
TOPO
$Cd(CH_3)_2$
360°C

Se (s) + TBP (l)
$Se{=}P(C_4H_9)_3$

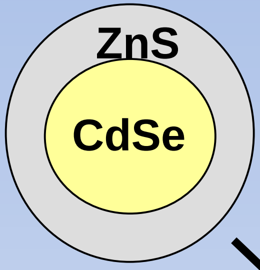




TOPO: $O = P(C_8H_{17})_3$



$(Me_3Si)_2S/Ar$
$Zn(CH_3)_2$



$HS\text{-}C_{12}H_{25}$

Hydrophobic,
soluble in toluene !!

Bawendi et al, MIT; Alivisatos et al, Berkley

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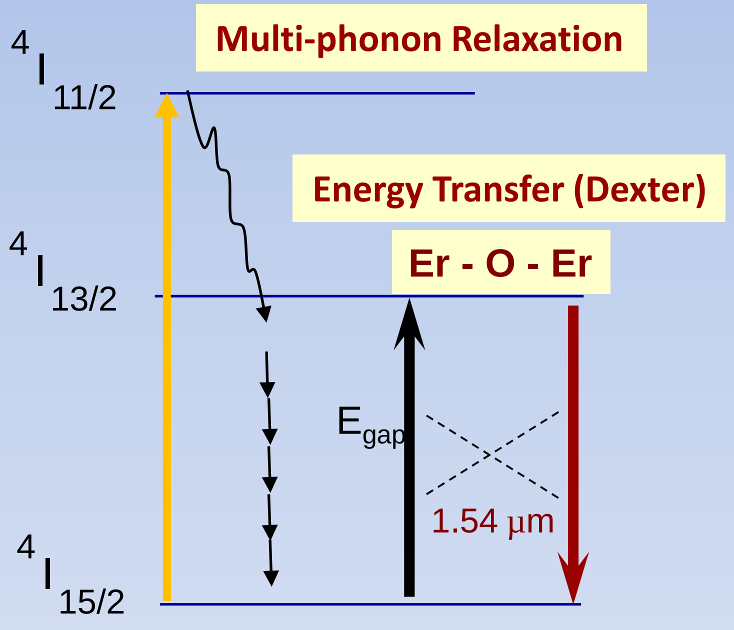
❷ Lanthanide doped Nanoparticles (Ln@NP's)

Figure of merit ~ N_{Ln} (cm^{-3}) τ (ms) T (%) / η (p_{phonon})

1. $N_{Ln} = 10^{20} - 10^{21}$ Er^{3+}/cm^3
2. τ = life time of luminescence
   Er^{3+}: 10-25 ms
3. Film transparency
4. Luminescence efficiency
   (phonon energy!)



1.54 µm (0,8 eV) = 6537 cm^{-1}

Luminescence efficiency

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

W_r = probability of recombination (radiative)
W_{nr} = Probabilité de la recombination (non-radiative)
p = number of phonons bridging the fundamental gap
A,B = empirical constantes

À savoir:
Phonon = *elastic waves produced by collective atomic vibrations*

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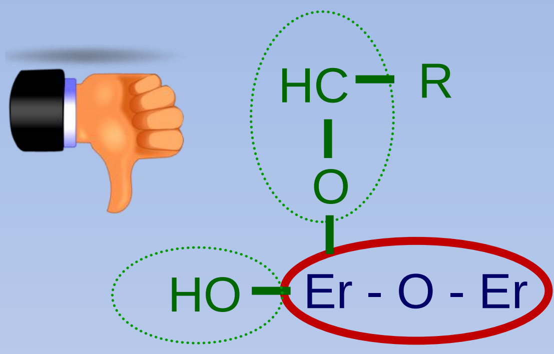

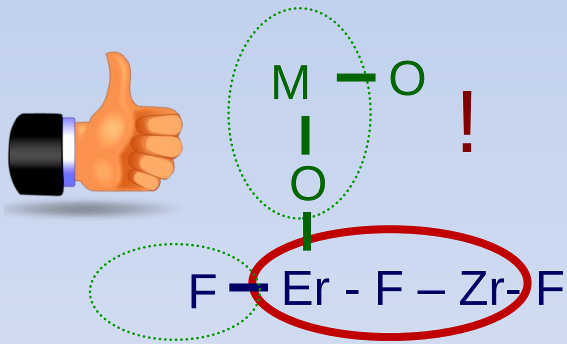

$$p = \Delta E/ \hbar\omega = 6537\ cm^{-1} / \hbar\omega$$

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_xO_y M_xChalc_y	300-800	8-20
fluorides	200-400	15-30

Note:

To maximize the fluorescence intensity

1. **Avoid Ln- ionic agregations**
2. **Avoid high energy phonons (OH, CH)**

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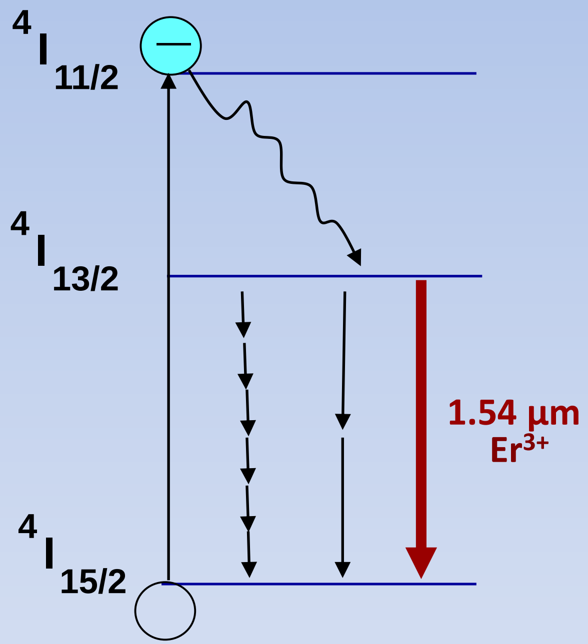
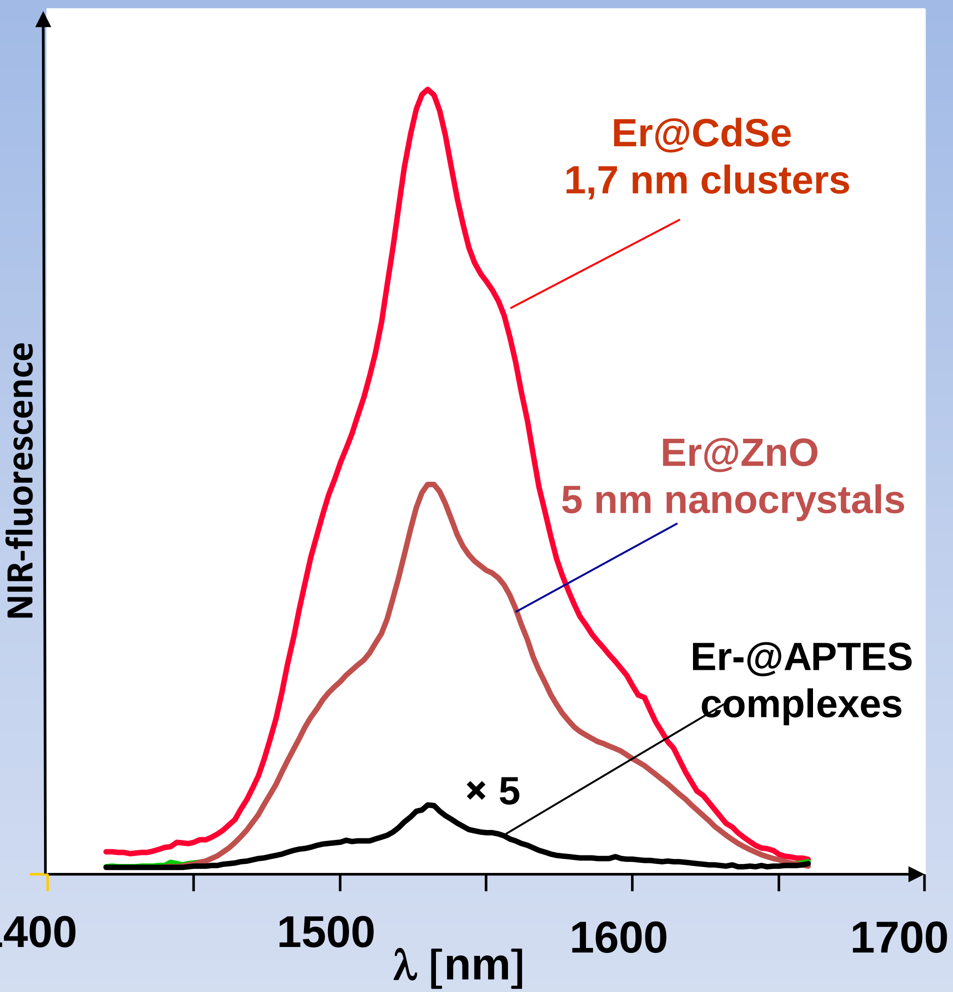
Multiphonon relaxation in ethanolic nanocolloids





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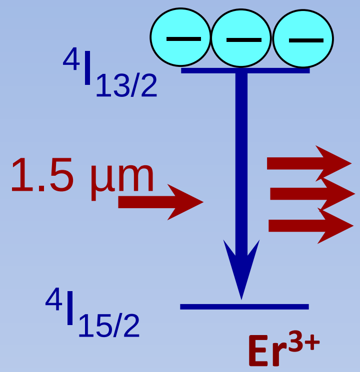
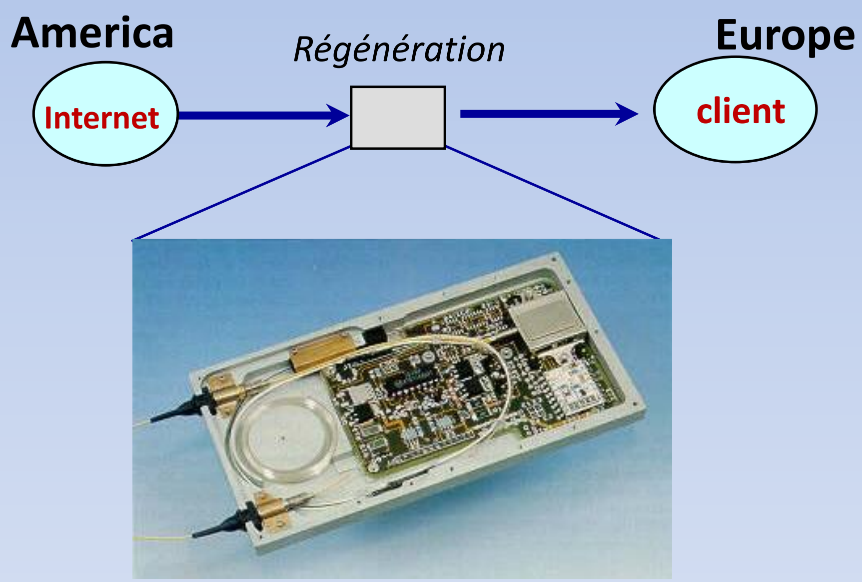
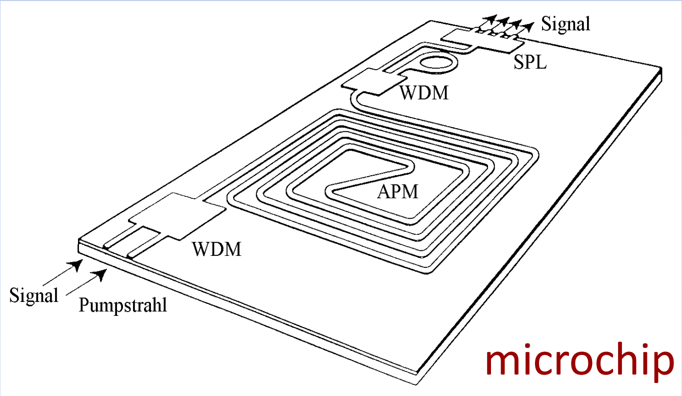
NIR amplifier modules in web







Local networks

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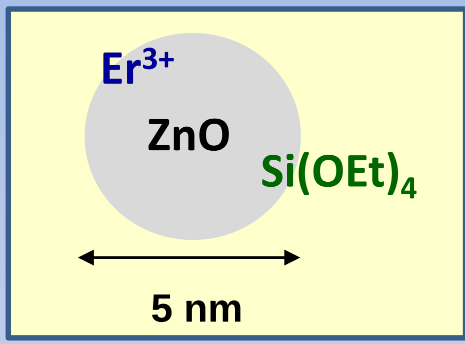
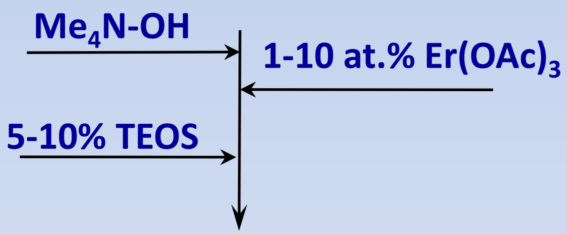
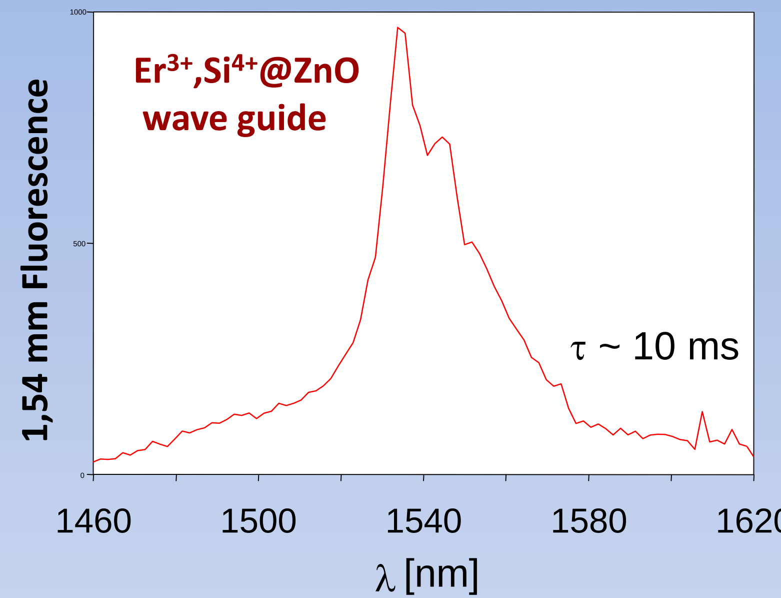
„Er,Si-co-doping“ of nano-ZnO

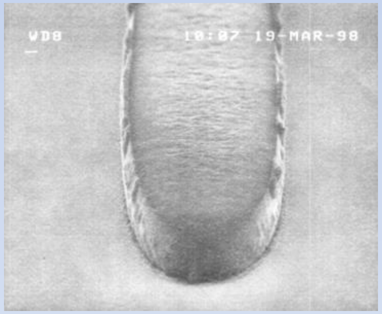


$Zn(OAc)_2$
in 1-Propanol



2-3 M Er,Si@ZnO-Sol
for dip coatings





UNIVERSITAS MASARYKIANA BRUNENSIS
Institut des Sciences Chimiques de Rennes UMR CNRS 6226 V&C
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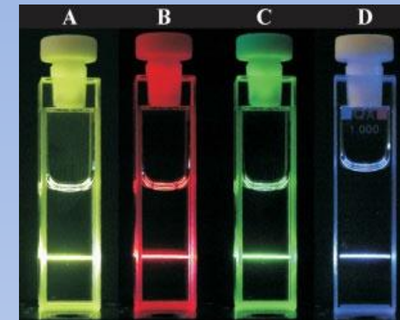
Highly Efficient Multicolour Upconversion Emission in Transparent Colloids of Lanthanide-Doped $NaYF_4$ Nanocrystals**

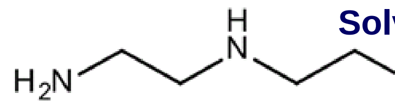
By *Stephan Heer*, *Karsten Kömpe*, *Hans-Ulrich Güdel*, and *Markus Haase**

Adv. Mater. 2004



$NaYF_4$/Ln

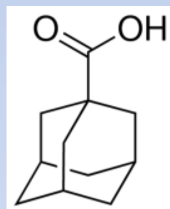
$LnCl_3$ $6H_2O$, Ln : Y, Yb, Er, Tm in methanol



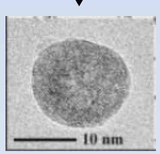
Solvant

Na

Ligand!

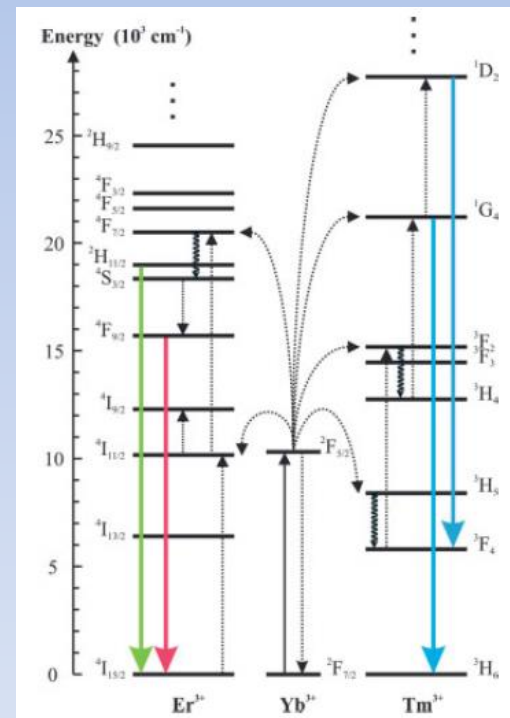


NH_4F



$NaYF_4$/Ln

DMSO
Chloroform



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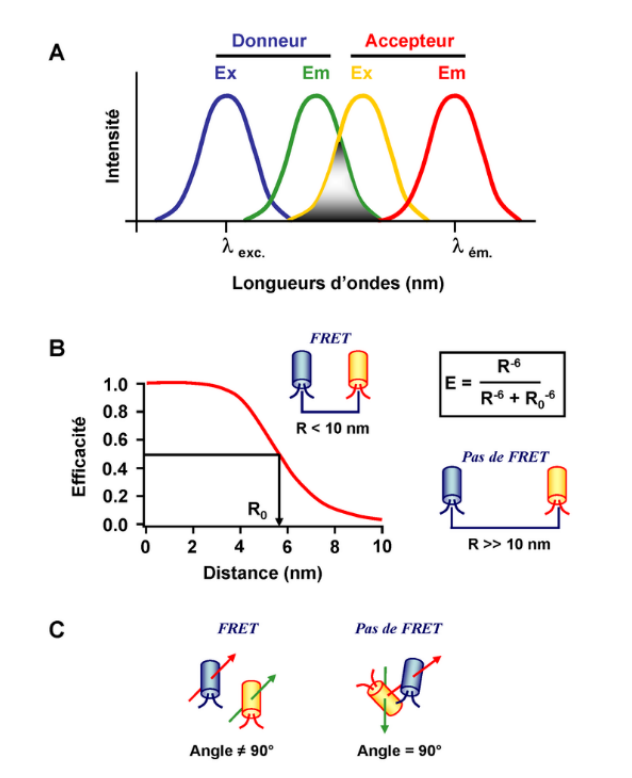
❸ Nanoparticles = Carriers and Activateurs of FRET

FRET = « Förster resonant energy transfer »

Critical parameters FRET:



Wikipedia

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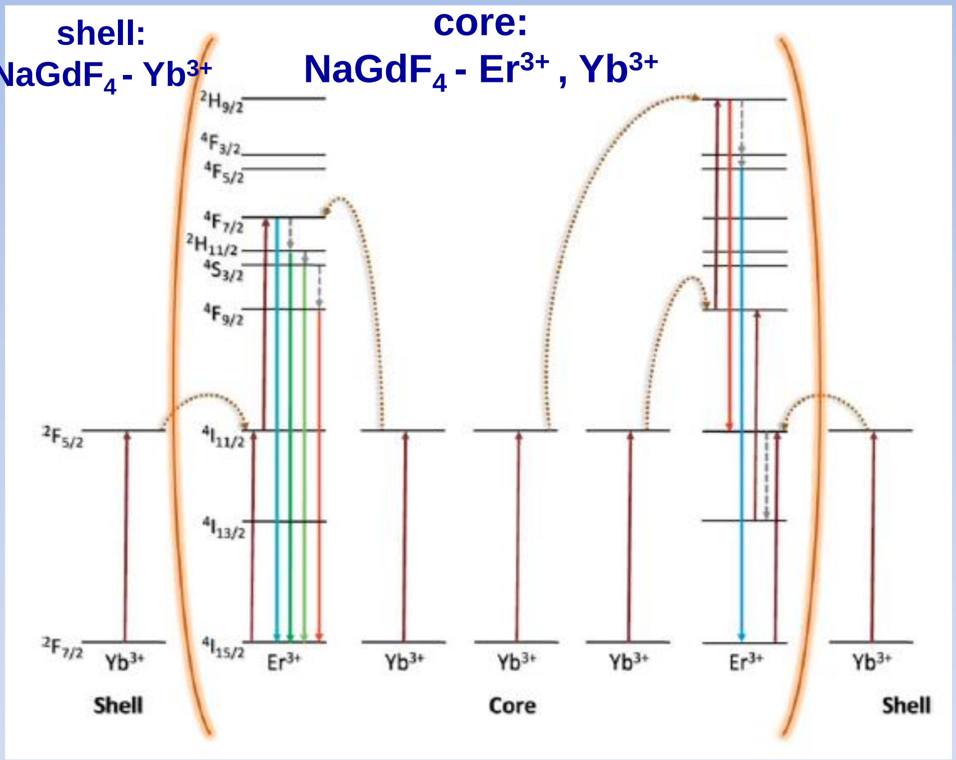
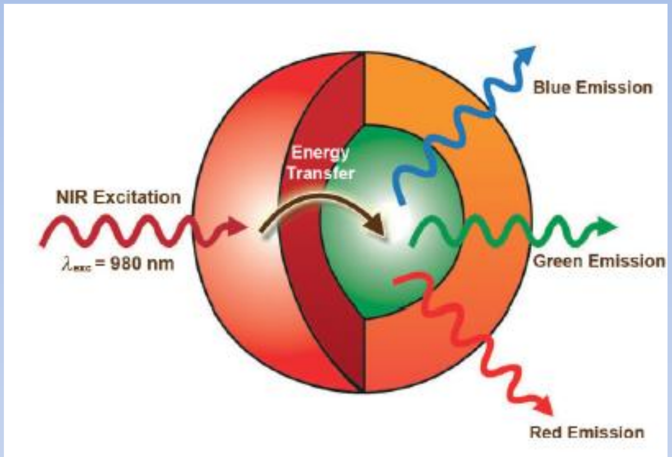
Nanoparticules de $NaGdF_4$ dopées par Er^{3+} et Yb^{3+} pour l'upconversion de la luminescence

Vetrone et al, Adv. Funct. Mater. 2009

shell: $NaGdF_4$ - Yb^{3+}

core: $NaGdF_4$ - Er^{3+}, Yb^{3+}





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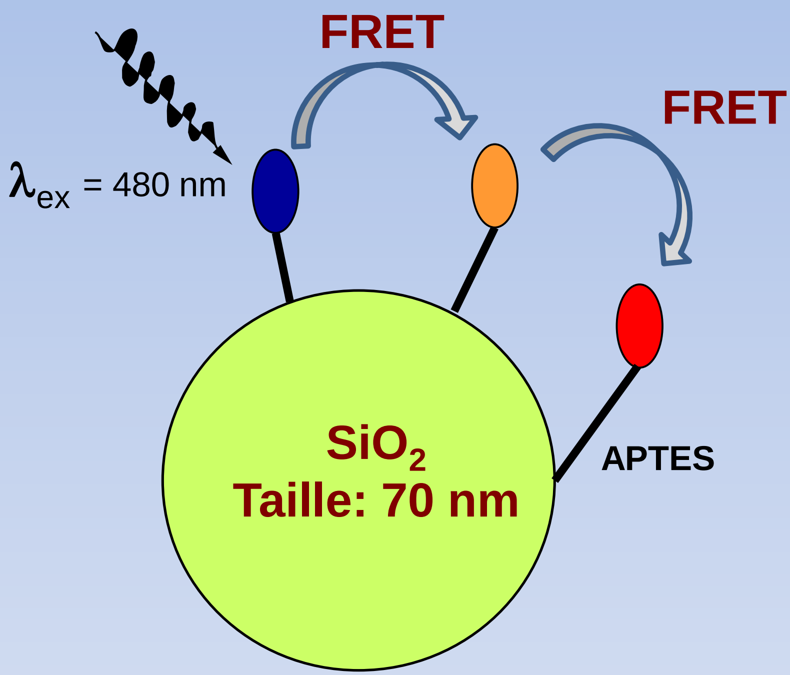
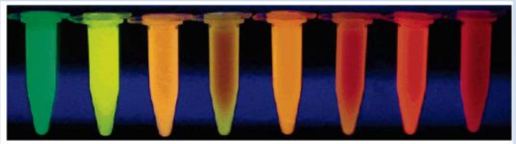
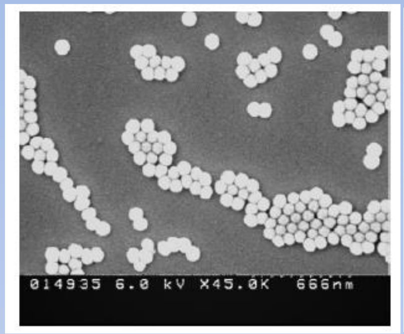
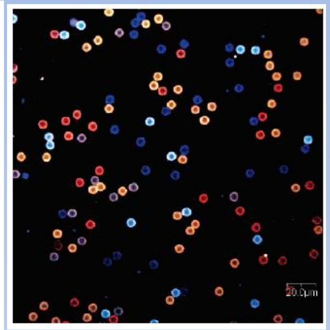
Wang&Tang, Nanoletters 2006

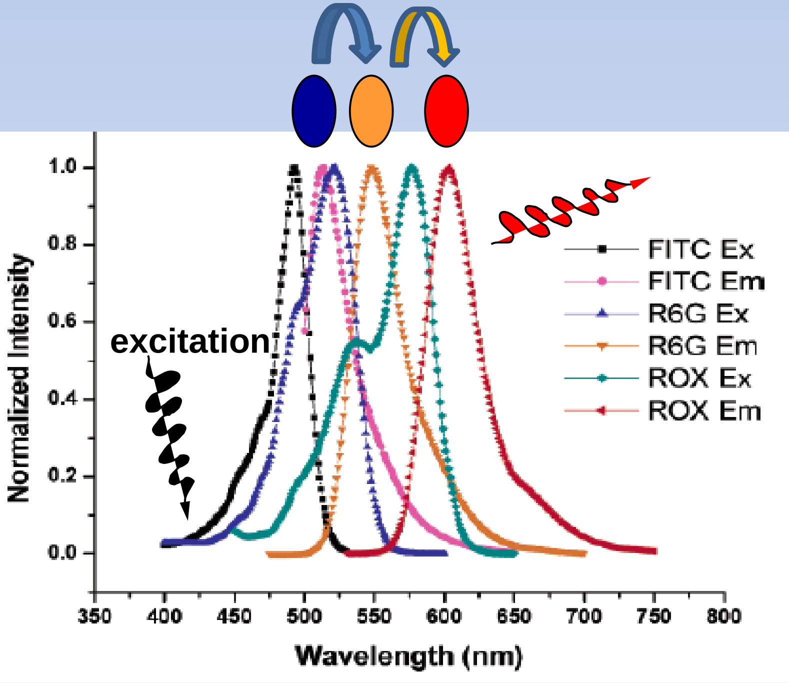
Greffage de trois chromophores organiques en tandem sur les NP de la silice











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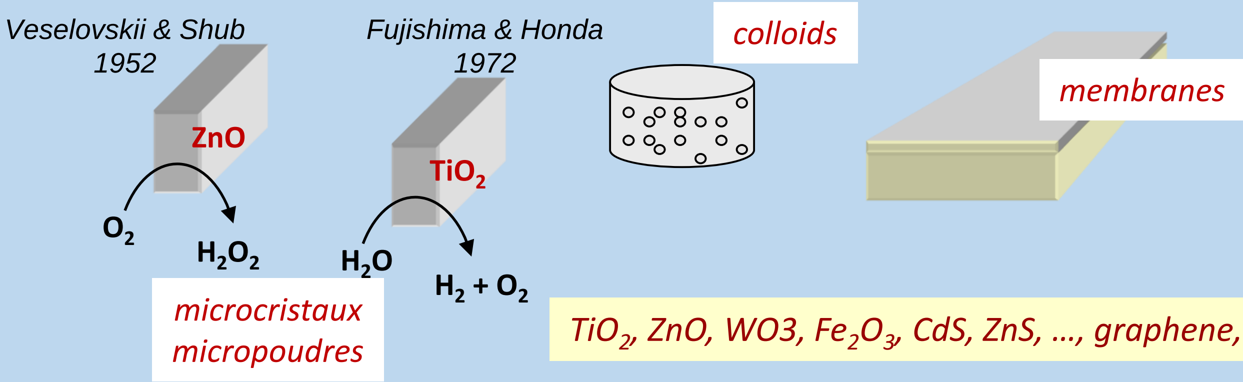
Chapter 2. Revision, questions:

1. Explain energy diagram differences between macro- and nanoelectrodes in contact with electrolyte
2. Knowledge of crucial phys. parameters governing the performance of TCO electrodes
3. Strategy of controlling mobility and concentration of free electrons
4. Describe the component design and chemical composition of catodic and anodic electrochromy device
5. What are the competing processes taking place in photoexcited semicondutor nanoparticles?
6. What are the strategies of photoluminescence activation?
7. Explain the energy diagramme of strongly luminscent SC NP's
8. Explain the close relation between photovoltaics and electroluminescence
9. What are the crucial parameters of lanthanide based luminescing devices?



TiO_2, ZnO, WO3, Fe_2O_3, CdS, ZnS, …, graphene, fullerènes

nanotechnology →

1839 **1954** **1980** **2020**

History of solar technology

Phénomène photoelectrique

Becquerel France)

1. Génération : mono-Si

Chapin, Fuller, Pearson (USA)

2. Génération: couches minces à base de a-Si, CdTe, CuInSe2 (CIS)

3. Génération: nanostructures, metamatériaux

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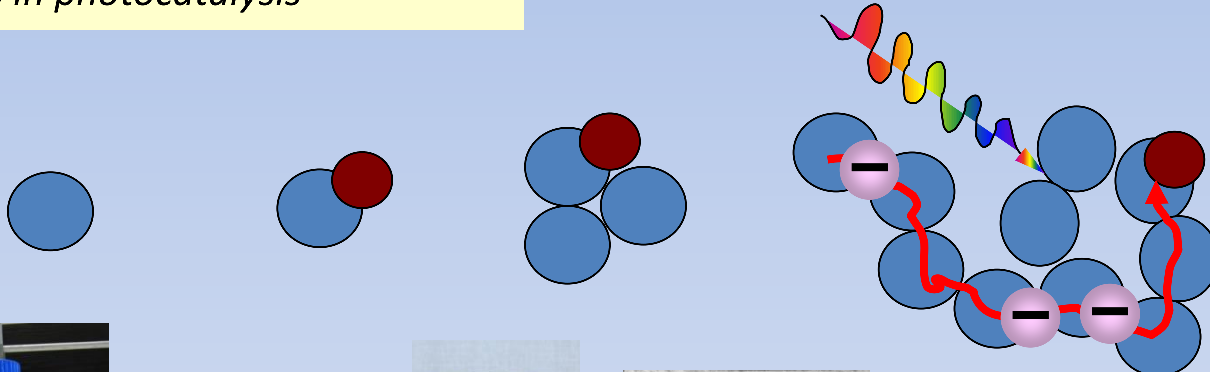
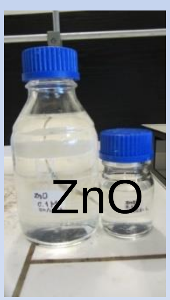
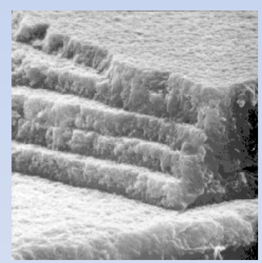
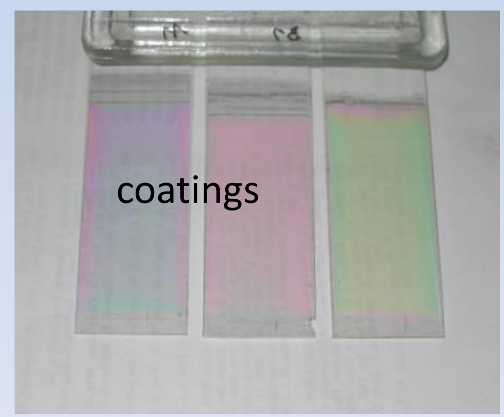
Photocatalysis applications

1. *Organic preparative synthesis*
2. *Environmental detoxification*
3. *Self-cleaning windows*
4. *Solar water splitting (solar fuels, O_2, H_2)*
5. *Carbon dioxide transformations*
6. *Biosystems in photocatalysis*









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Crucial parameters and issues in Nanophotocatalysis

► **spectral profile based selection**
visible light active nano's are needed (400 – 600 nm)

► **thermodynamics based selection**
comparison of band energy levels with redox potentials

► **kinetics oriented selection**
heterostructures, dopings and surface modifications

► **morphology of immobilized nanostructures**
particle shapes, aggregate architectures and mesoporosity

► **integration into photoreactor prototypes on various scales**
nanocolloids, powders, thin coatings, photoreactor design

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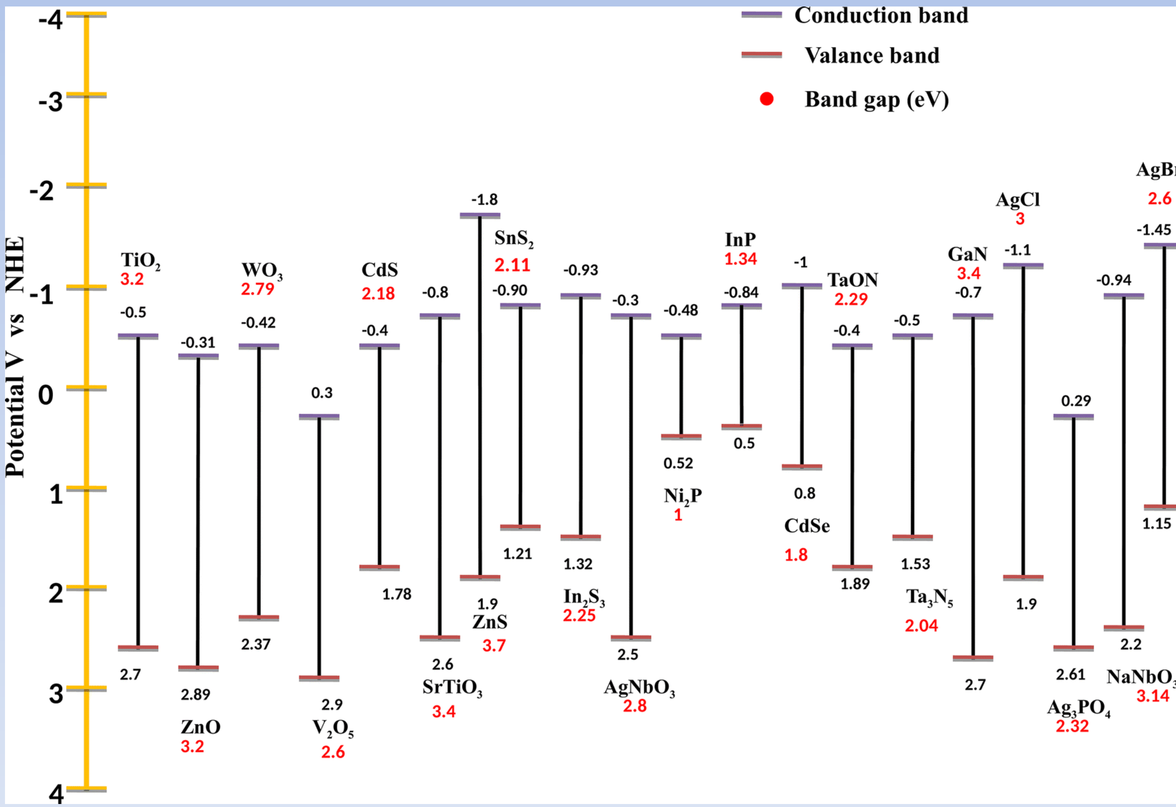
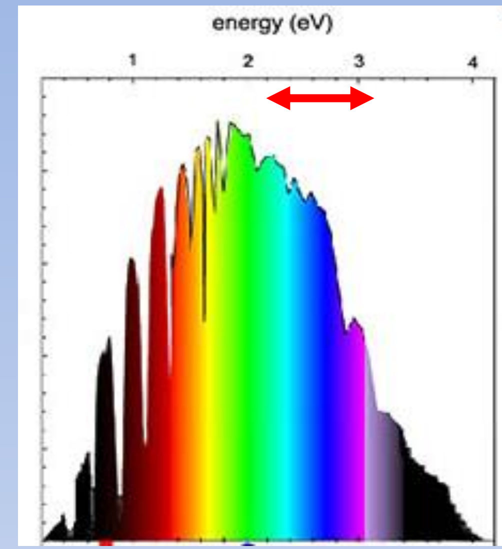
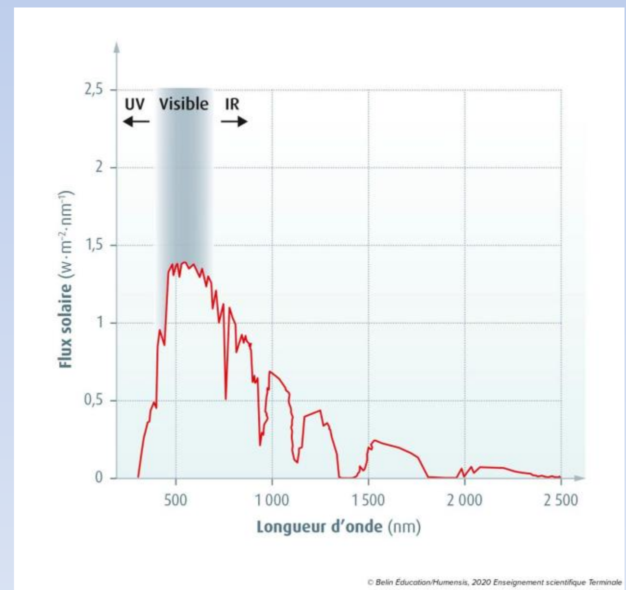
Photocata selection :

1. *Optical Gap*
2. *Energy levels of VB and CB*
3. *Photostability*
4. *Toxicity*
5. *Applications (energie/environnement/preparative synthesis*







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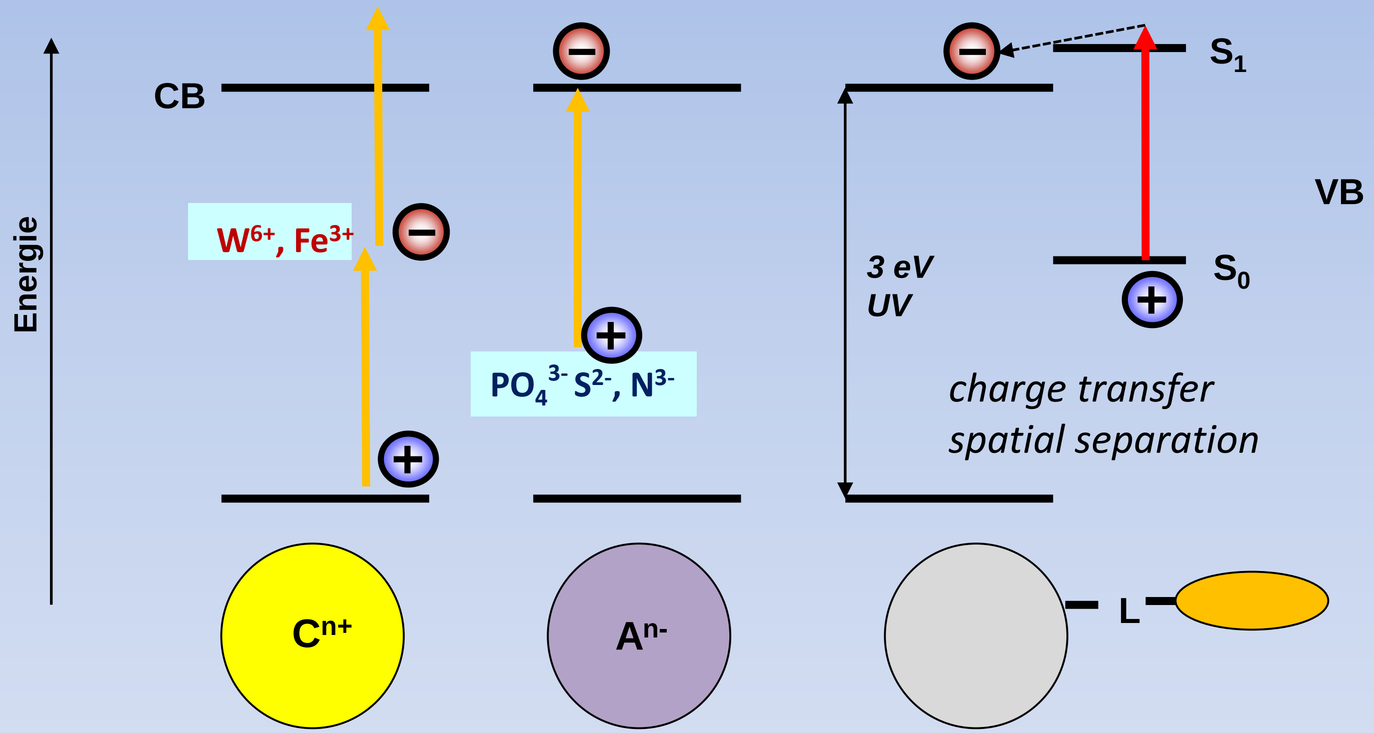
Doping and spectral sensitization of photocatalytic oxides: TiO_2, ZnO, $ZnTiO_3$



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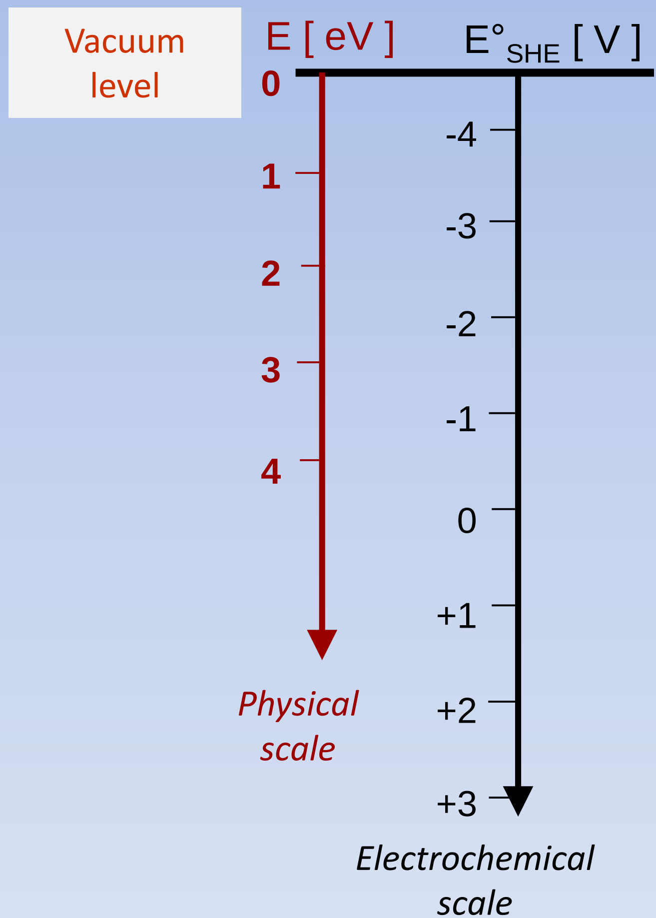
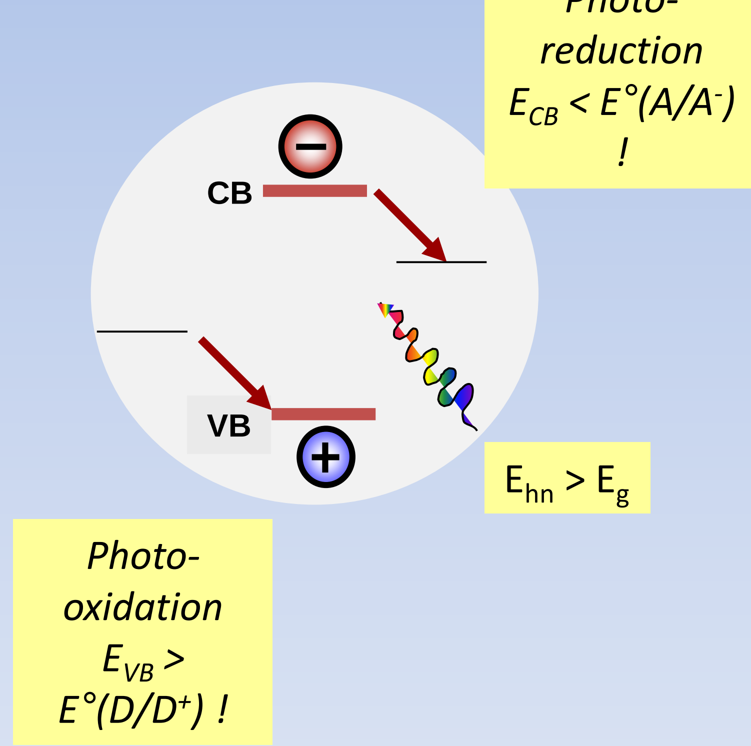
Thermodynamics of charge carrier transfer





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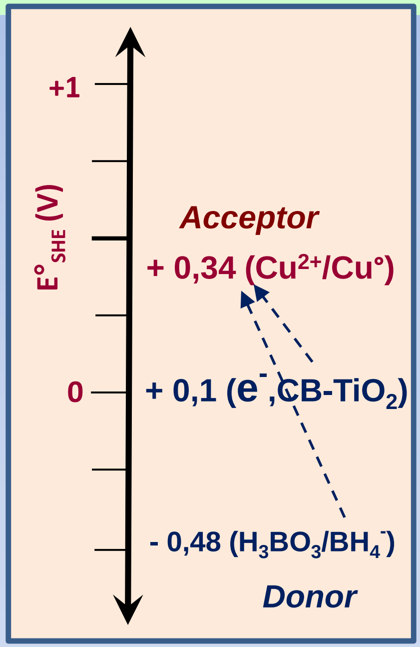
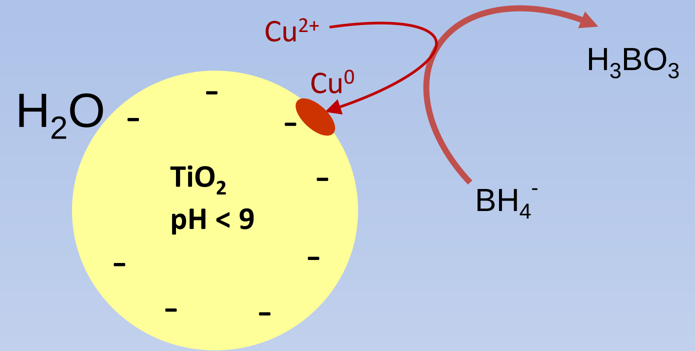
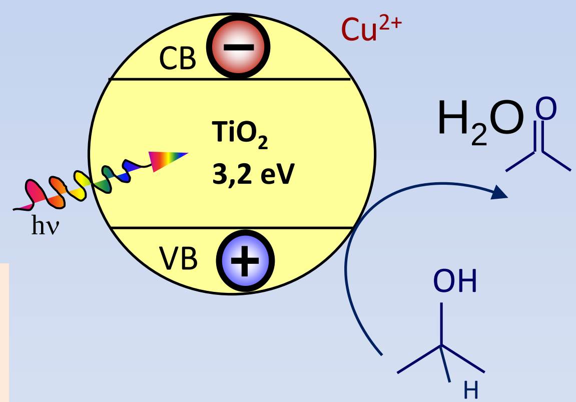
Example: formation of Cu nanoislands on TiO_2

1. $Cu2+$, $NaBH_4$
2. $Cu2+$, isopropanol in water UV-light



$$Cu^{2+} + 2e^- \rightarrow Cu^\circ \qquad (\times 4)$$
$$BH_4^- + 3\,H_2O \rightarrow H_3BO_3 + 7H^+ + 8\,e^-$$
$$\overline{BH_4^- + 4\,Cu^{2+} + 3\,H_2O \rightarrow H_3BO_3 + 7H^+ + 4\,Cu^\circ}$$





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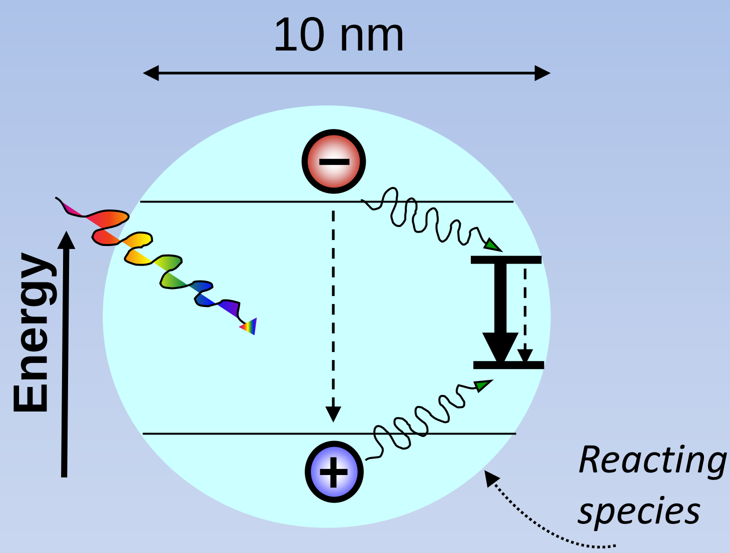
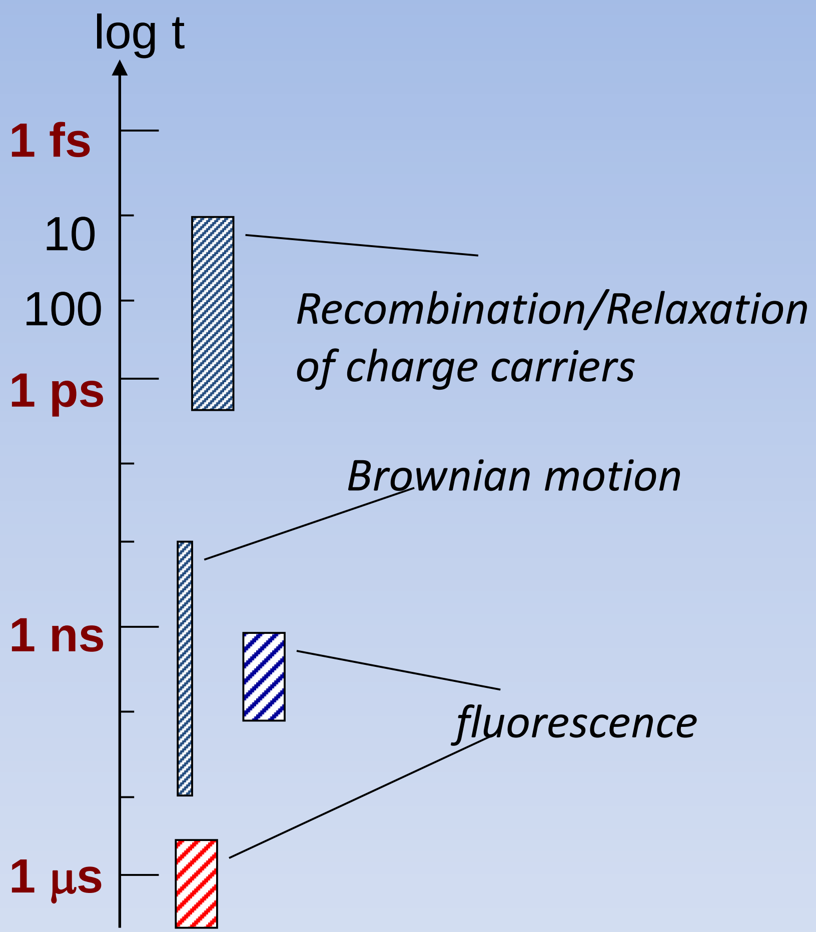
Kinetics and photocatalysis





Note:

1. *To eliminate the rapid thermal relaxations and recombination's is the biggest challenge*
2. *Efficient photo catalysis requires a closed contact (covalent, electrostatic) at the interface NP/molecule*
3. *The best actual approach is the spatial charge separation*

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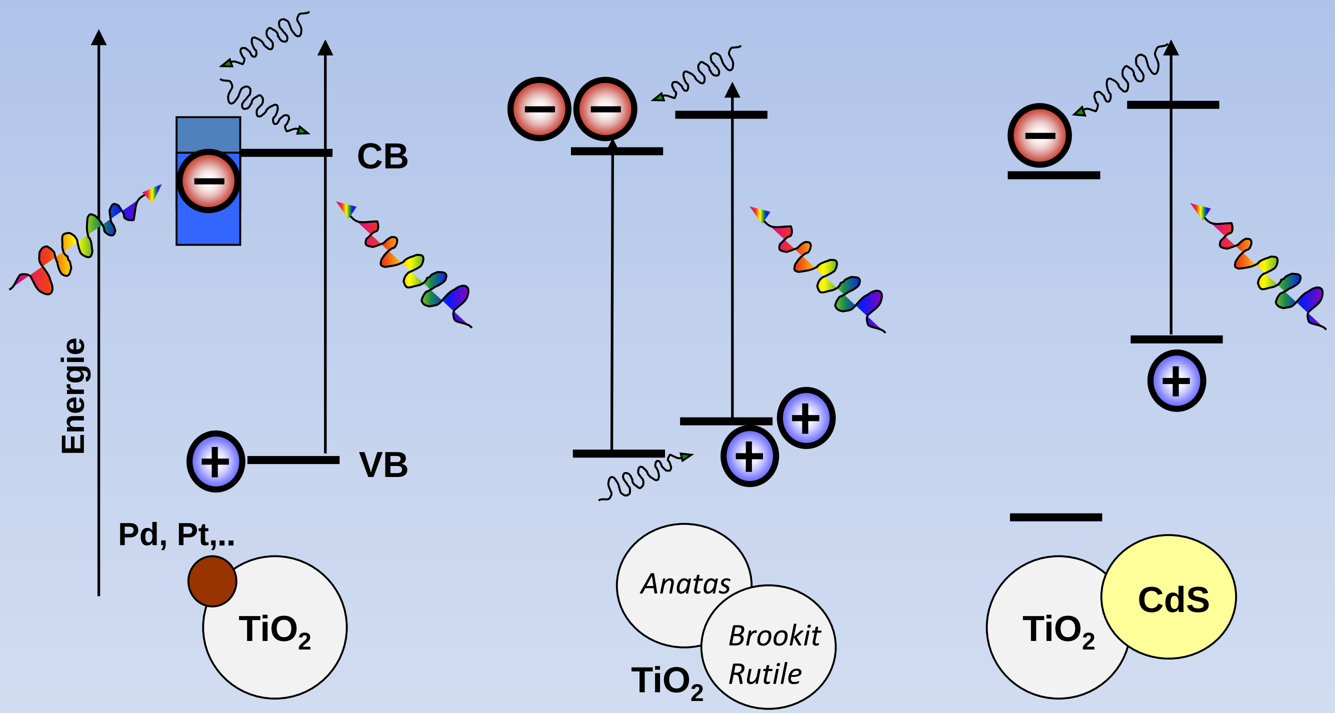
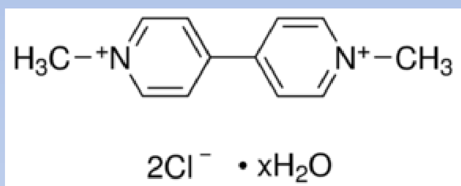
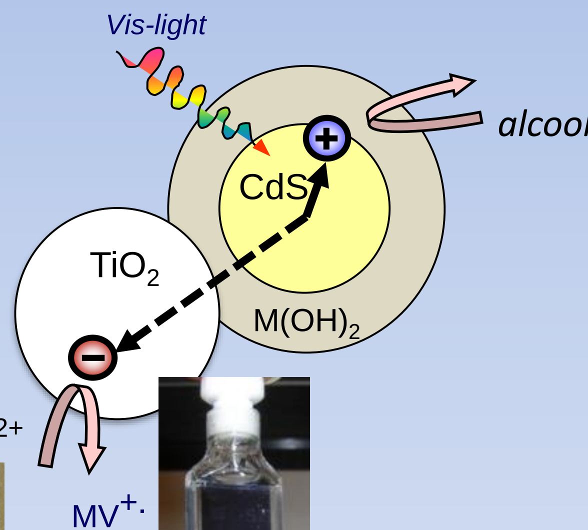
Spatial separation of charge carriers

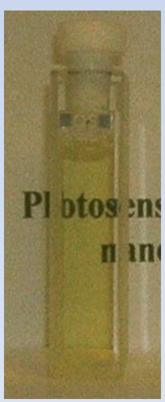


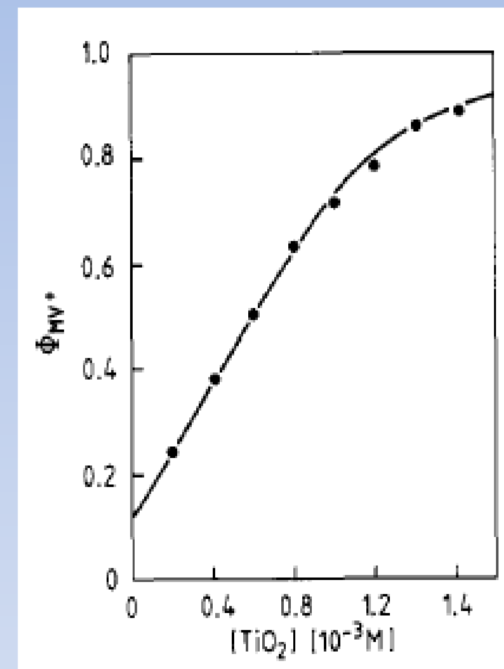
Viologen photoreduction in CdS/TiO$_2$

Paraquat herbicide









JACS 1987

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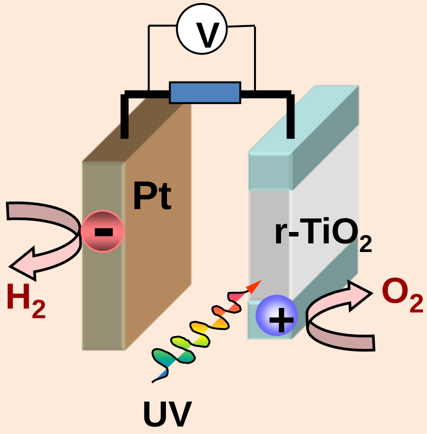
Solar water splitting

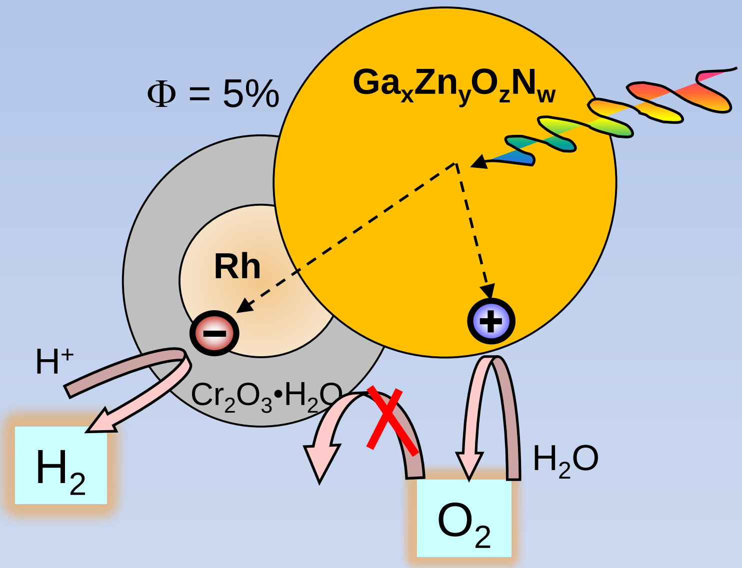
Fujishima-Honda

Quantum yield < 0,1%



Nature 1972, 238, 37

K. Maeda et al, Nature 2006



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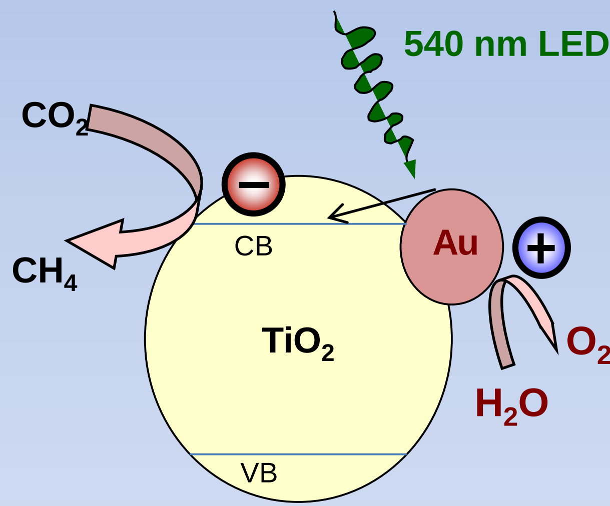
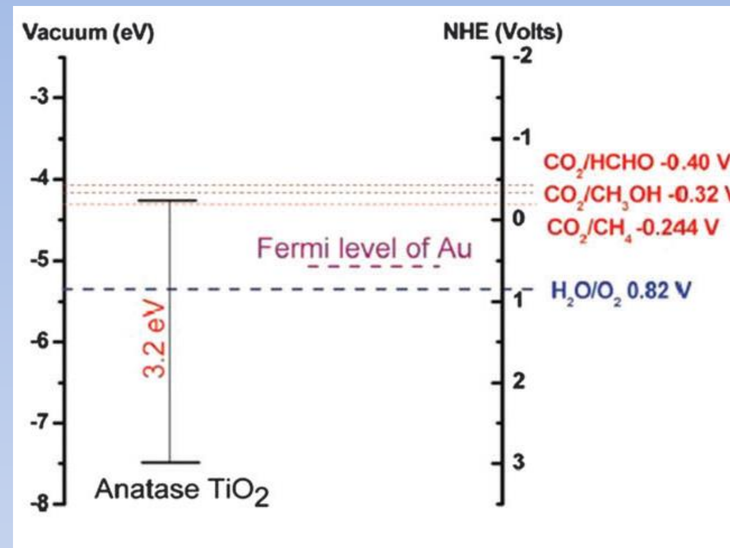
CO_2 photo-transformations via surface plasmons



D. Astruc, Univ. Bordeaux
RSC-Chem. Soc. Rev. 2014, 43, 7188



reaction
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO$
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH$
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4$

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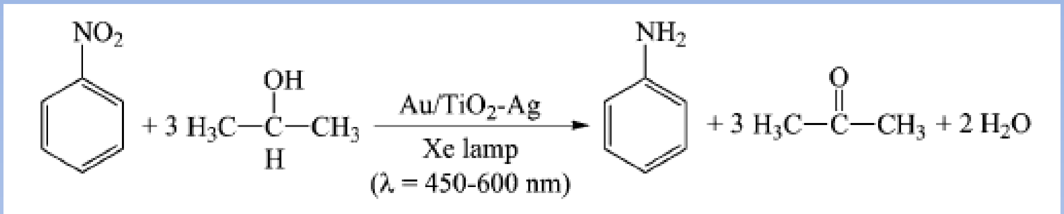
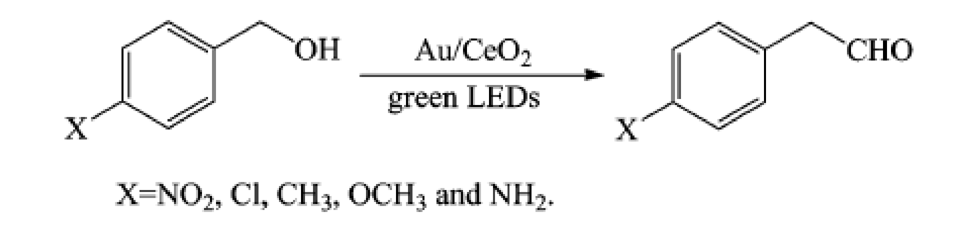
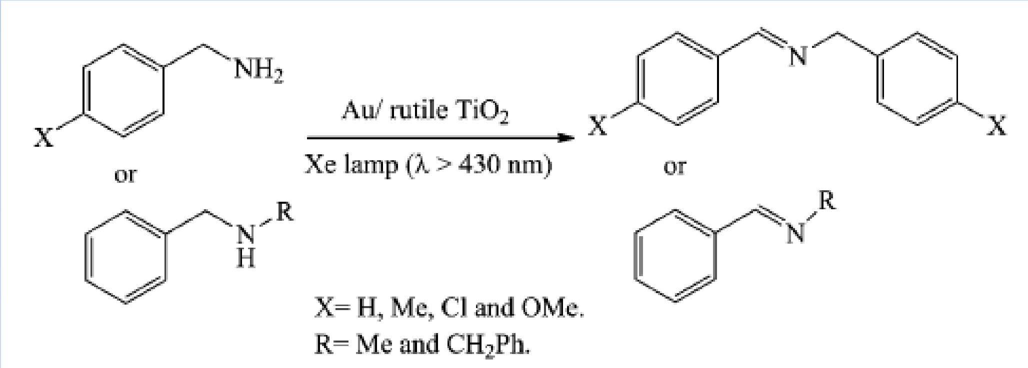
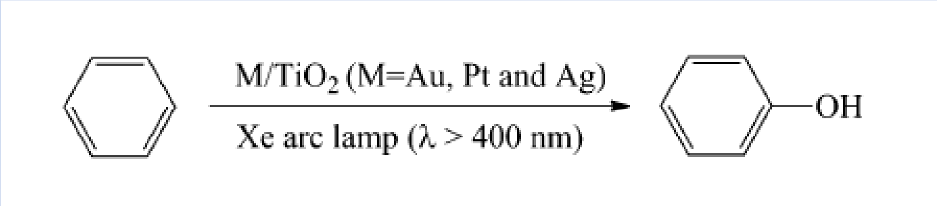
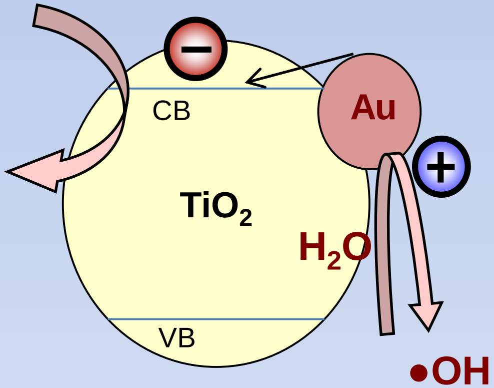








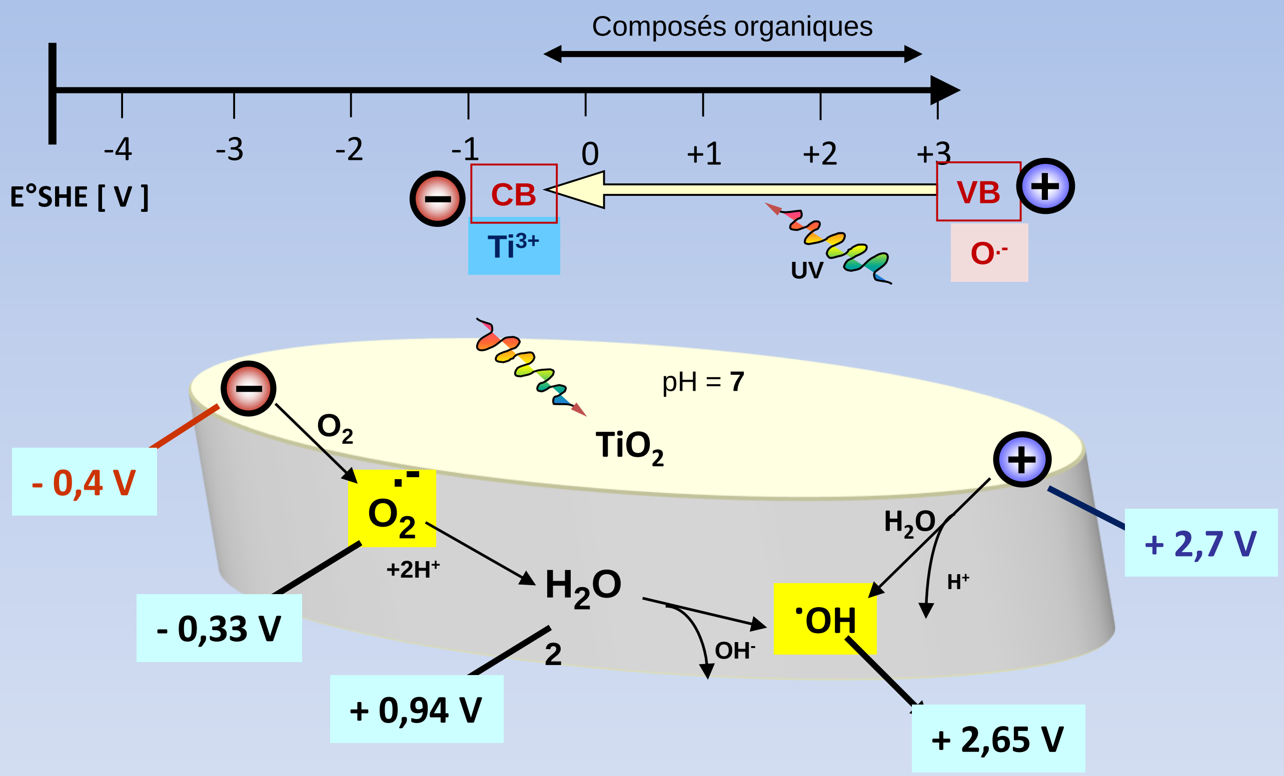
Note:
Yield > 50%
Selectivity > 90%



D. Astruc, Univ. Bordeaux
RSC-Chem. Soc. Rev. 2014, 43, 7188

Photocatalyse environnementale

TiO_2 + UV + dioxygène + l'eau



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Photocatalyse environnementale

Photo-minéralisation de polluants organiques

$C_xH_yCl_z$ → → CO_2 + HCl + H_2O

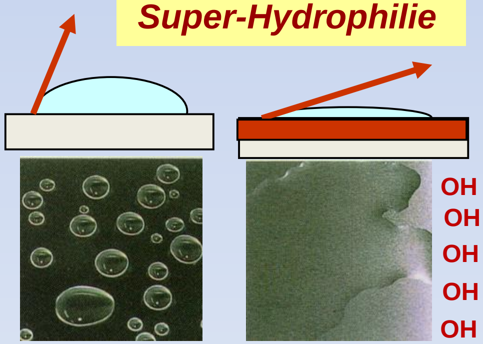
$C_xH_yP_z$ — phosphates

$C_xH_yN_z$ — nitrates

$C_xH_yS_z$ — sulphates

Purification des eaux industrielles

Super-Hydrophilie



Auto-nettoyage et stérilisation solaire
Interfaces résistantes aux bactéries et virus

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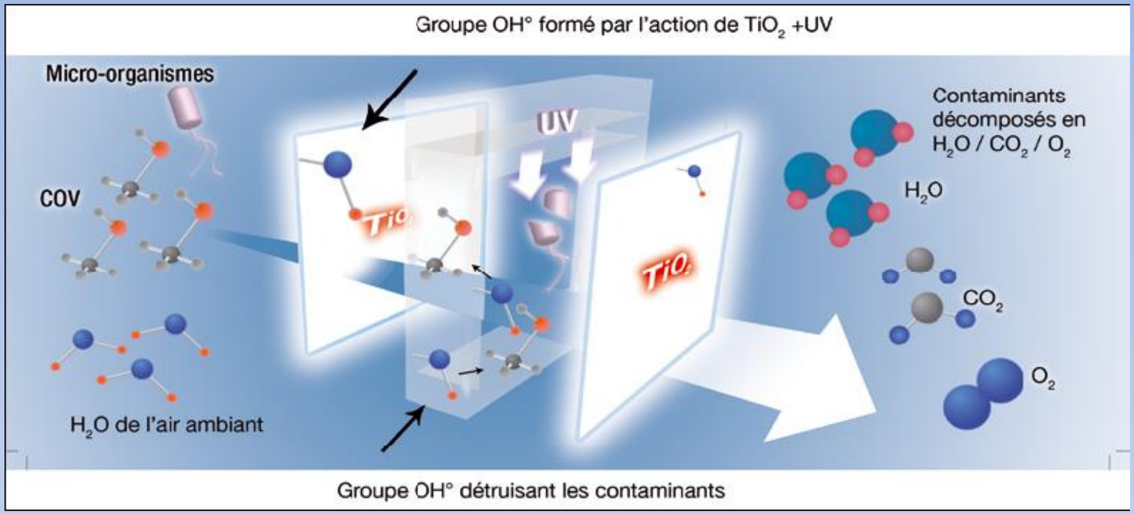
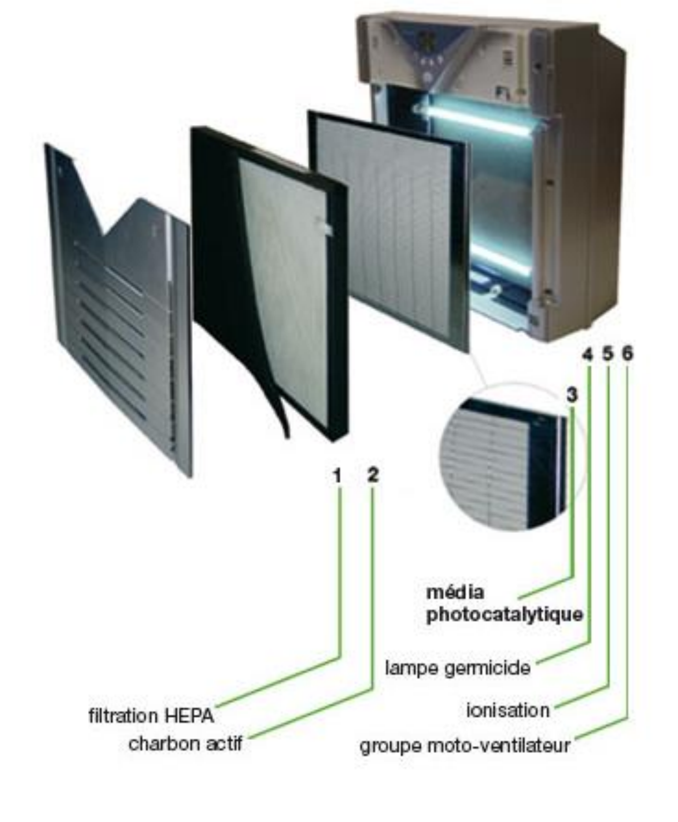




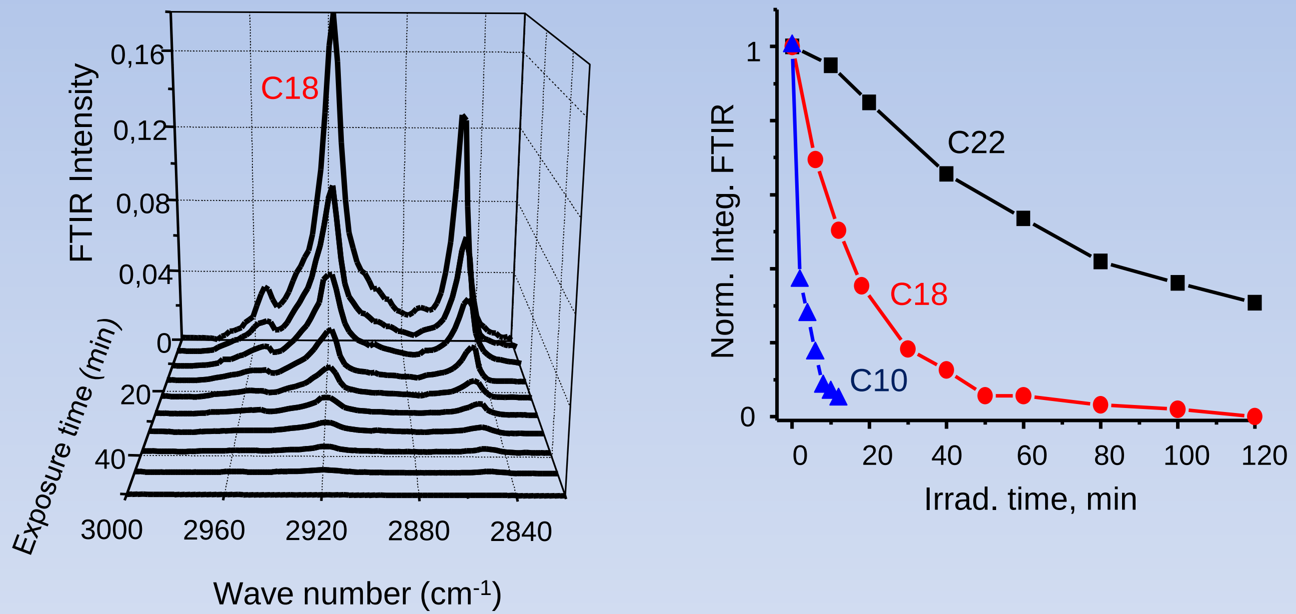
photoclean® QUARTZ

de l'air propre à l'air pur

Florence Benoit, Toulouse

Superhydrophilic $ZnTiO_3/TiO_2$ films in Photocatalysis

Photodegradation of Fetty Acids, Xe-lamp, air, rel. humidity: 80%



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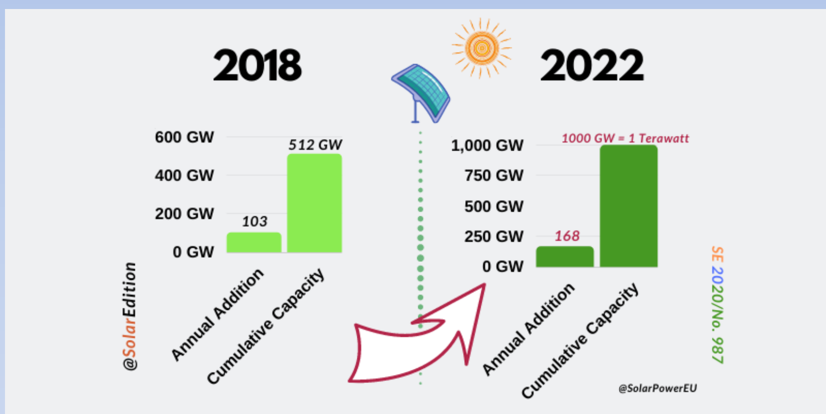
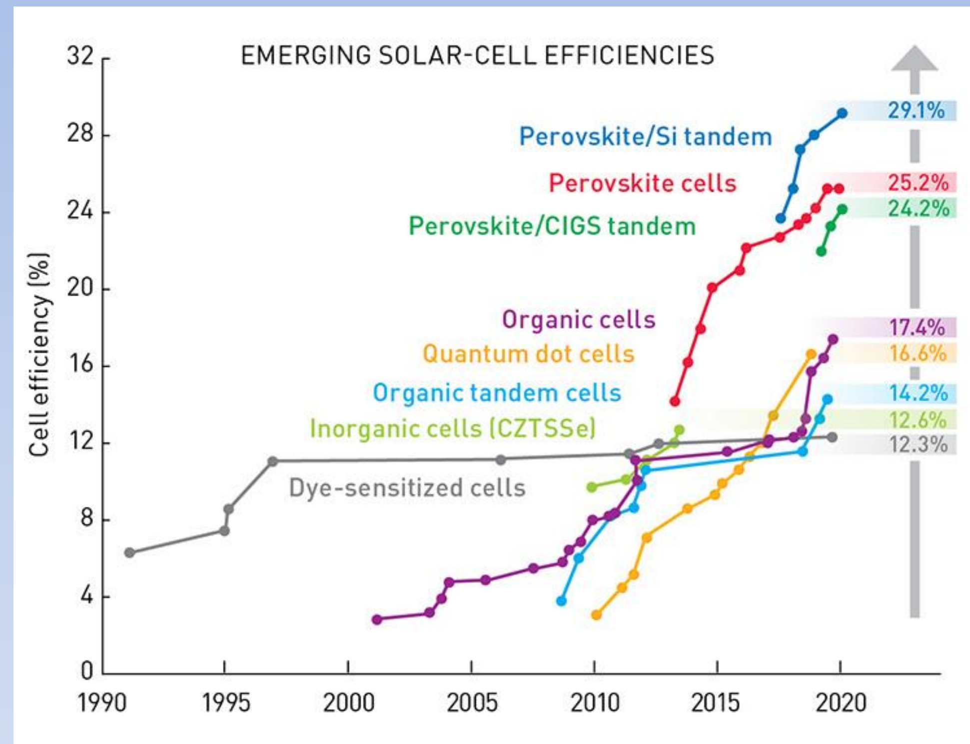
Photovoltaics: forecasts and actual efficiency statistics





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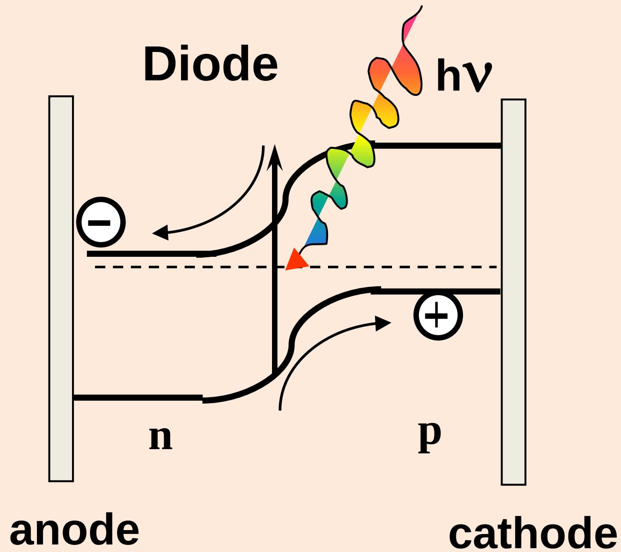
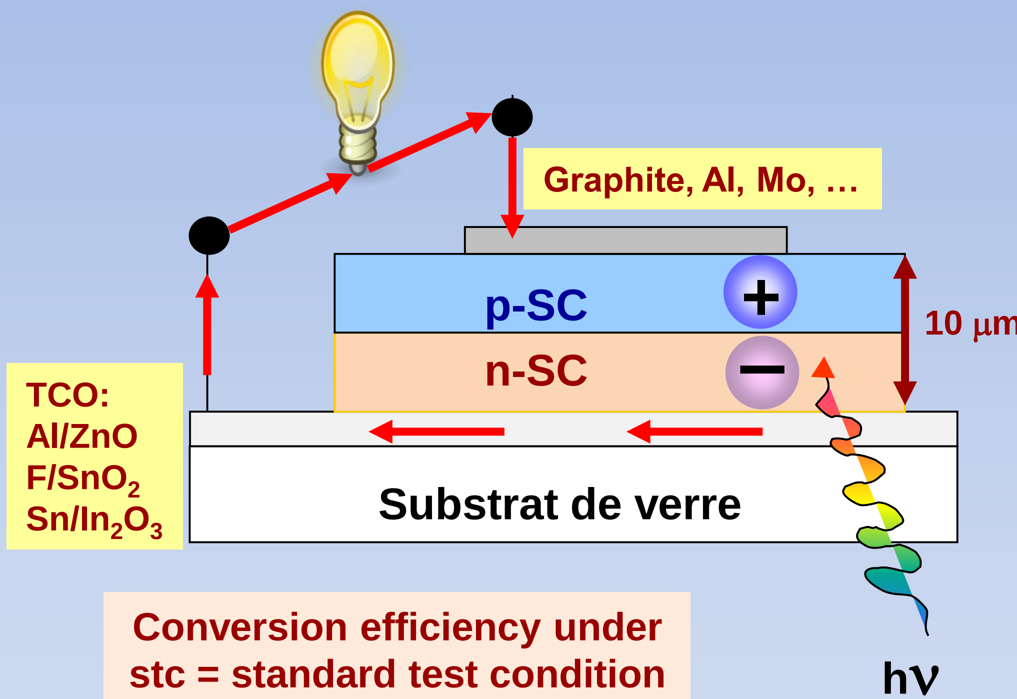
General introduction to solar cells



n-Si/p-Si
n-GaAs/p-GaAs (InP)
n-CdS/p-CdTe
n-CdS/p-CuInSe$_2$

η_{stc} = 15 – 50 %



Conversion efficiency under stc = standard test condition

$$\eta_{stc} = \frac{P_{el}(W/m^2)}{P_{reçu,stc}(1kW/m^2)}$$

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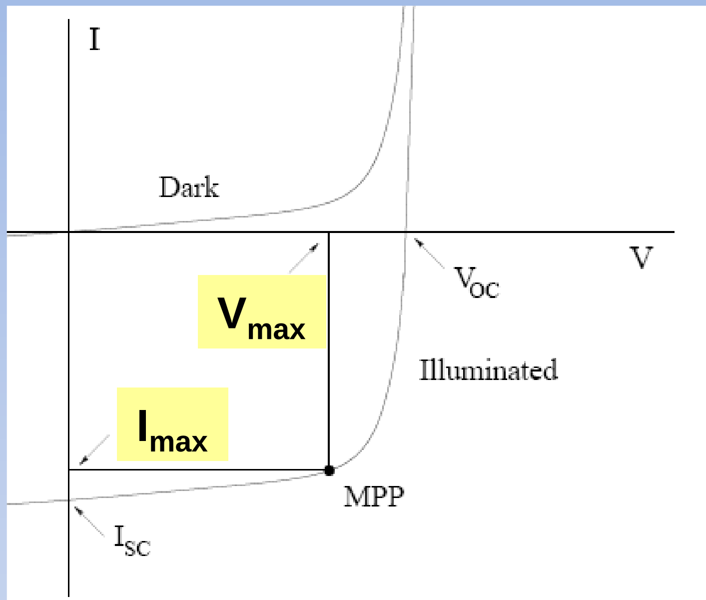
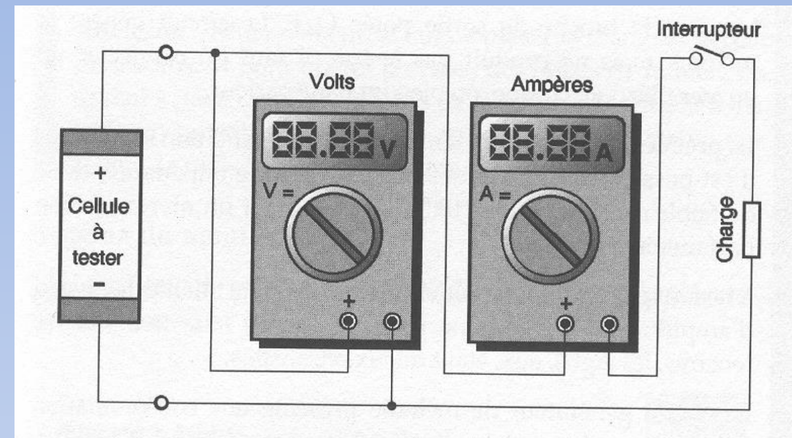
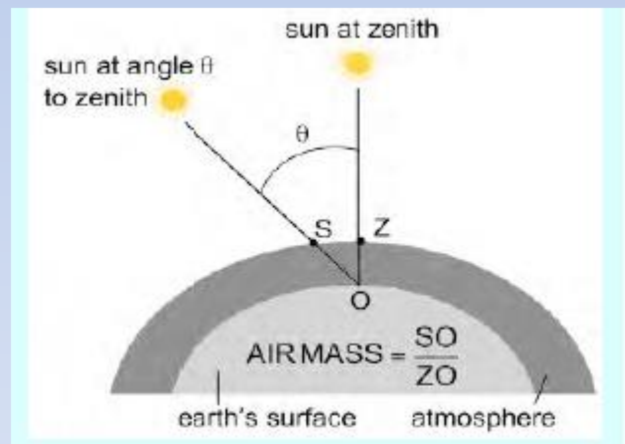
Characterisation of solar cells





$$\eta = FF\frac{V_{oc}I_{sc}}{P_{in}} = \frac{V_{max}I_{max}}{P_{in}}$$



Convention internationale

P_{in} **= 1 kW / m²**

η = rendement de la conversion

MPP = facteur de remplissage

V_{OC} = tension à circuit ouvert (V)

I_{SC} = curant à circuit fermé (A/m²)

P_{in} = puissance solaire (W/m²)

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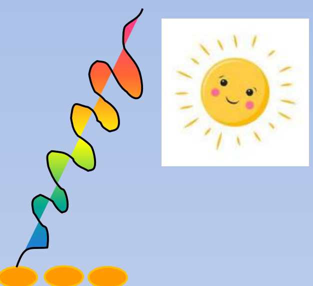
Cellules solaires à base de semiconducteurs oxydes photo-sensibilisés

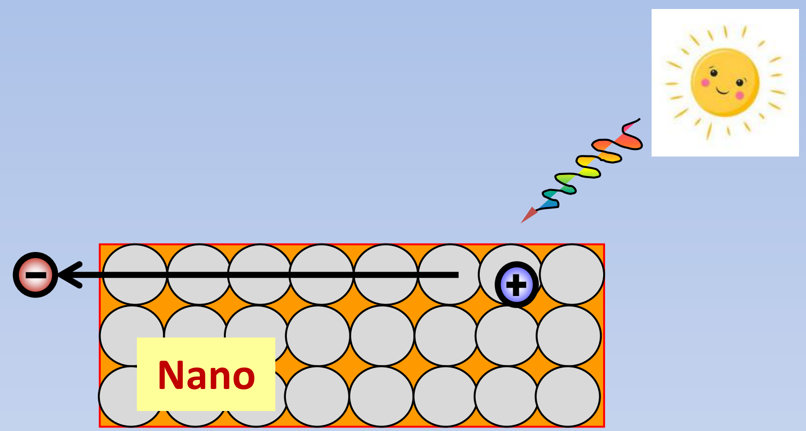


Chromophore organique

Electrode monocristalline massif

TiO_2 ou ZnO

Pr. Gerischer et al (Berlin 1960-1970)



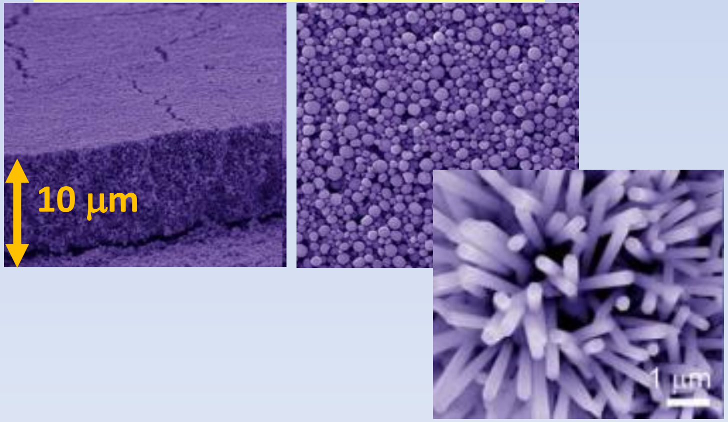
Pr. Grätzel et al (EPFL Lausanne depuis 1990)

< 1%

~ 100%

!

Nanocristaux de ZnO ou TiO_2



Rayonnement solaire dissipé par l'antenne solaire

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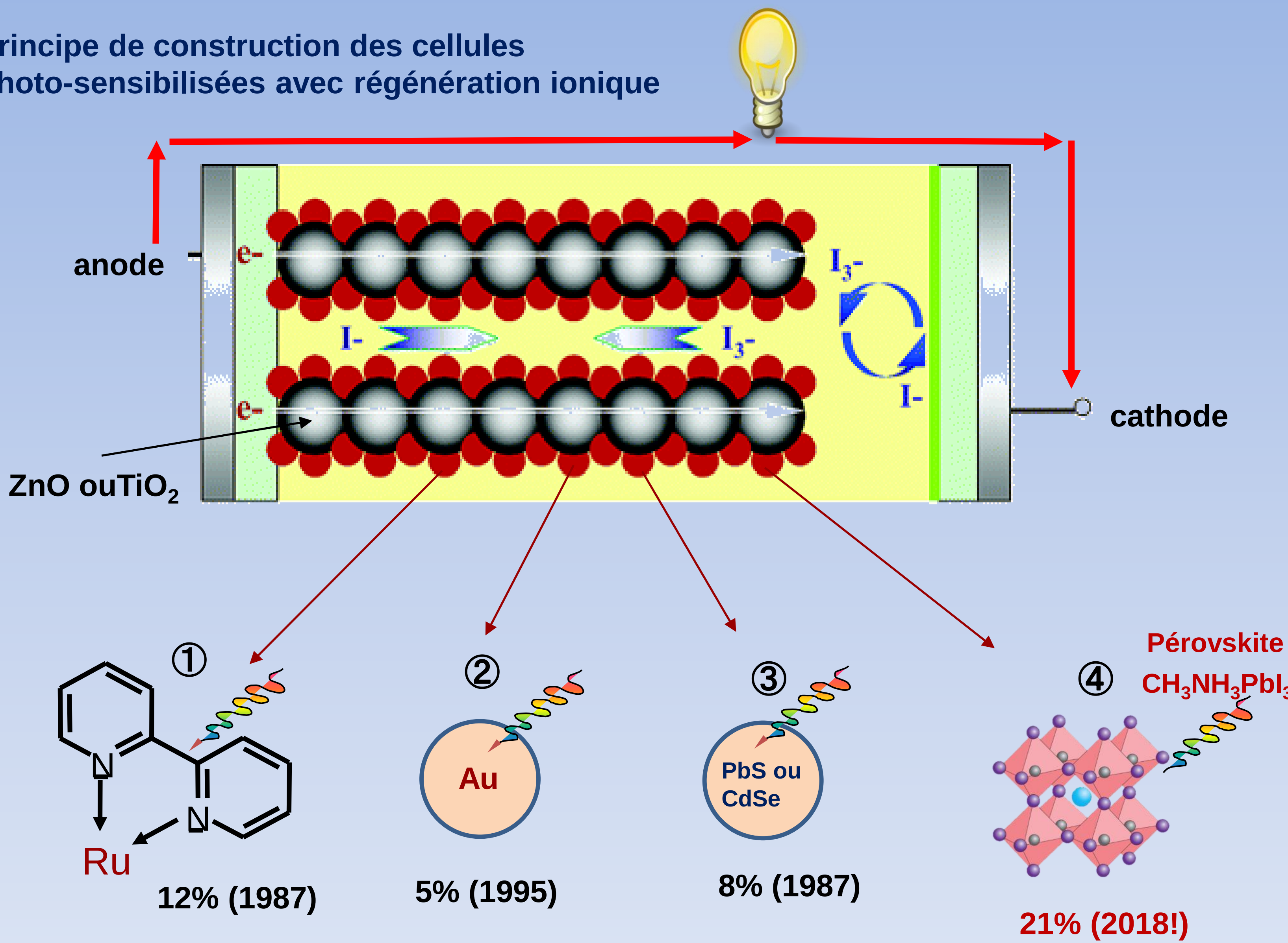
Principe de construction des cellules photo-sensibilisées avec régénération ionique



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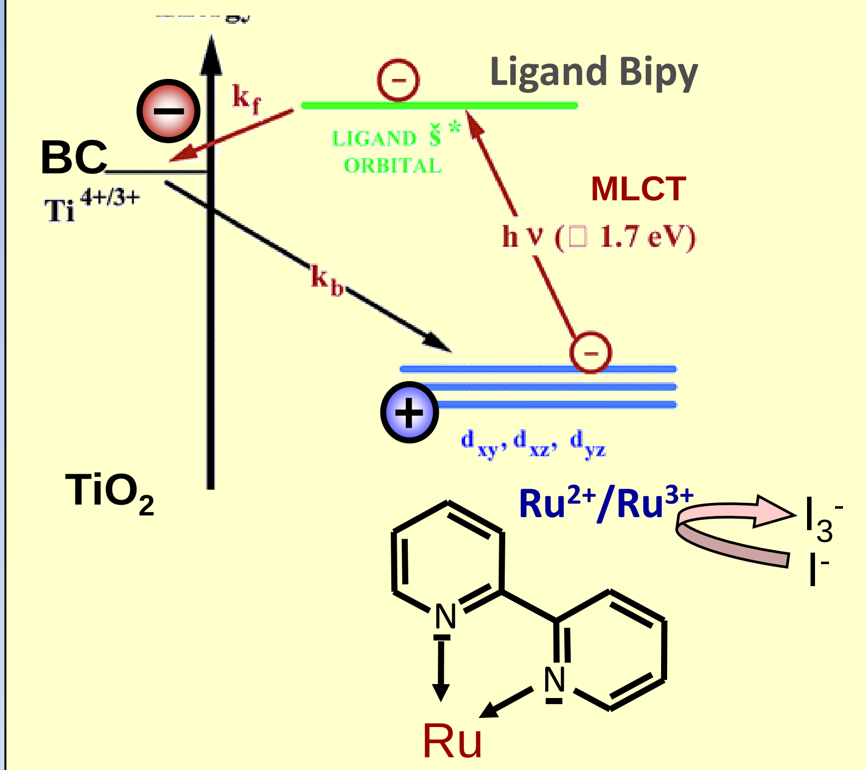
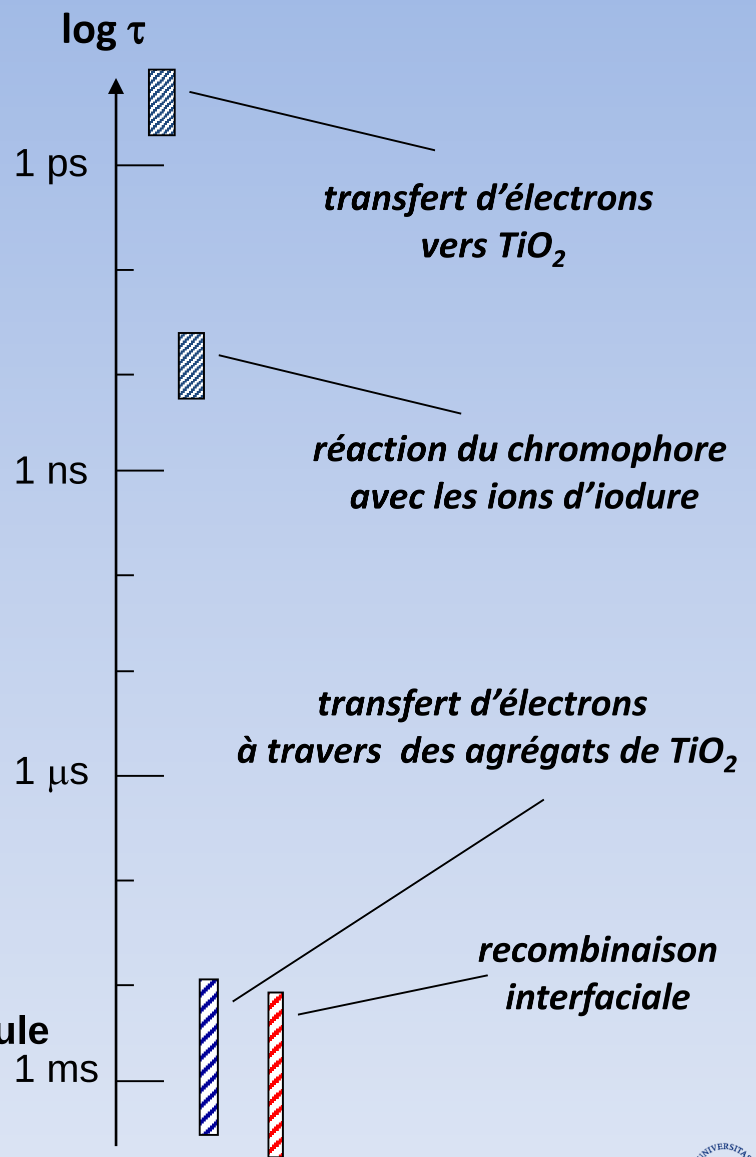
L’analyse cinétique
de la cellule photo-sensibilisée



Couple (I_3^-/ I^-) est le régénérateur clé de la cellule



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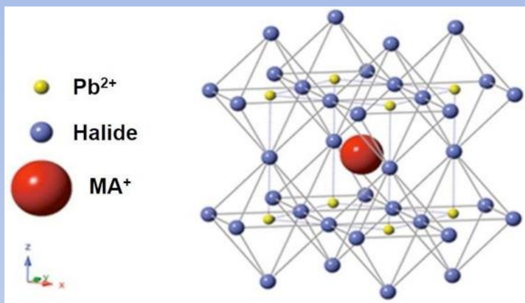
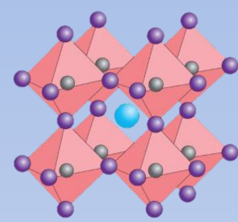
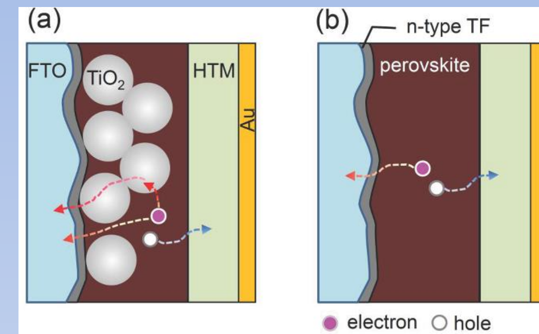
Organic Perowskite solar cells (AMX_3)

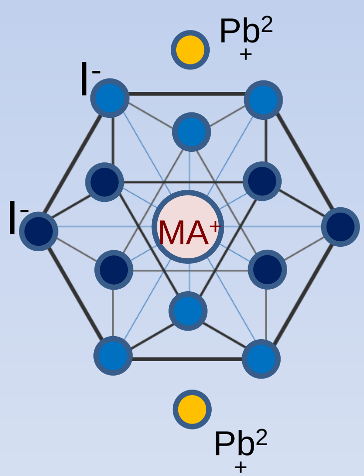
HTM = hole transporter zone
Organic polymers

JACS, 136, 622, 2014

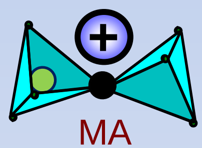




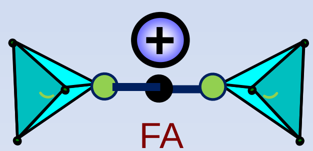


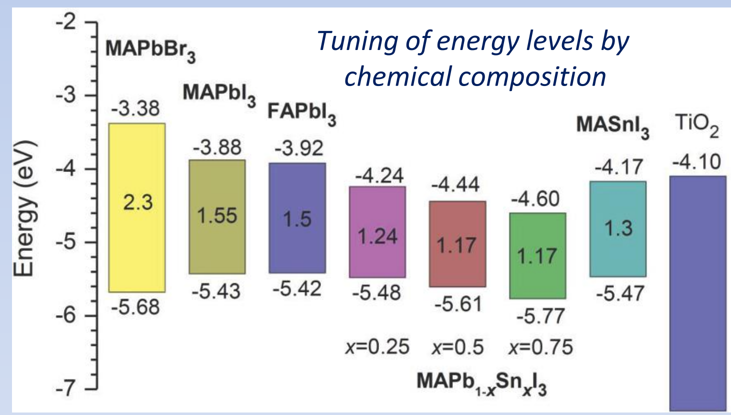


MA: Methylammonium $(CH_3NH_3)^+$



FA: formamidinium $HC(NH_2)_2^+$





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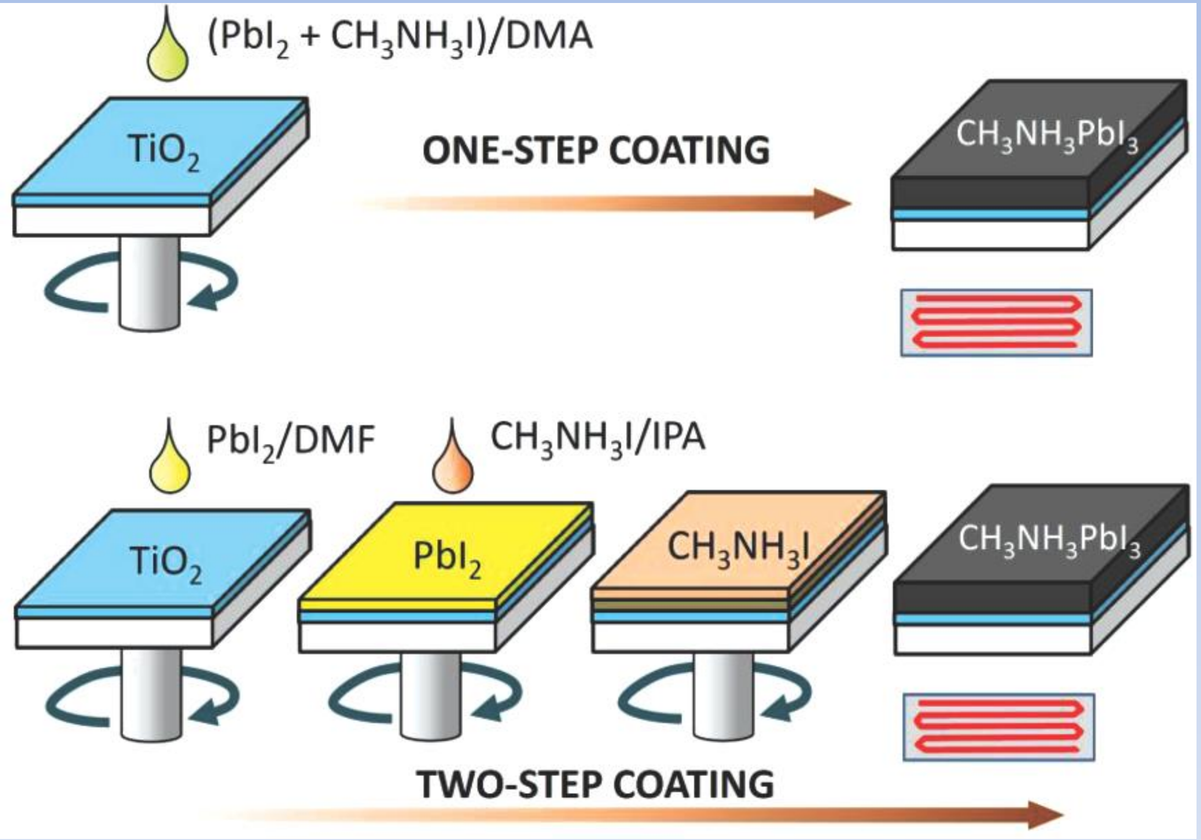
Préparation simple de cellules de Pérovskite

Small Volume 11, Issue 1, pages 10-25, 30 OCT 2014



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Chapter 3. Questions, revision

1. Difference between « nano versus macro » in semiconductor photocatalysis.
2. How many elementary charges are needed to transform :
    a) water into hydrogen and oxygen
    b) CO_2 into CH_4?
3. What are the essential radical states formed in photoexcited titania? Which applications are related to this process?
4. How function classical macroscopic and modern nanoscaled solar cells?
5. Give ay least three solar antennas used in nanoscale photovoltaics.

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