Jaro 2024
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*
- *Elektro/fotoluminescenčí systémy*
- *Elektrochromie*
- *Piezoelektrické nanogenerátory*

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

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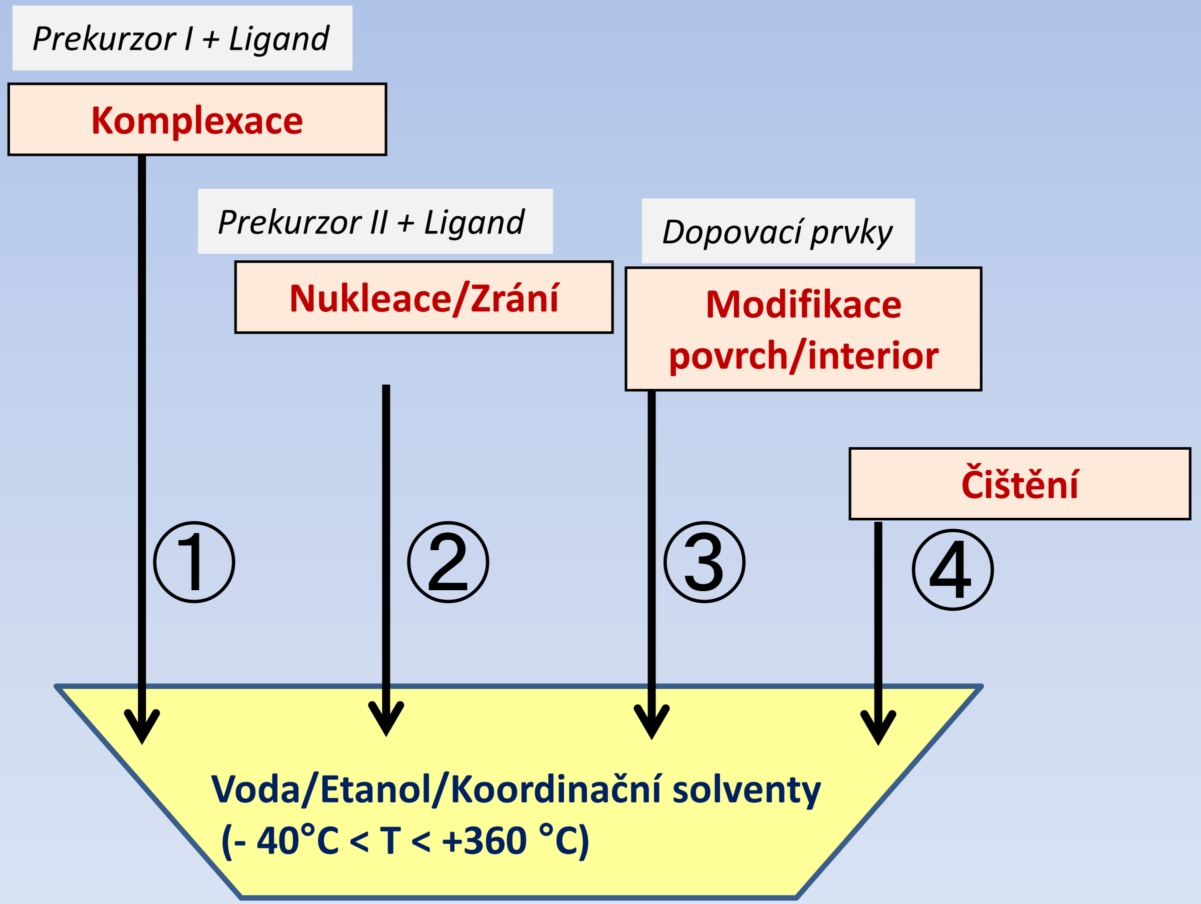
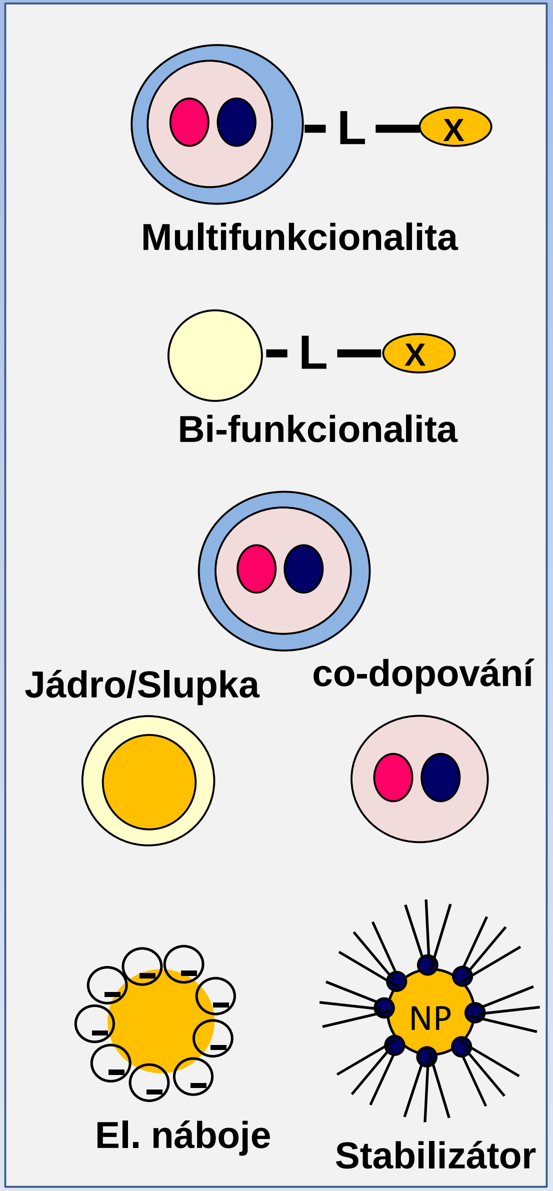
Chemické inženýrství anorganických nanokoloidů

Multiparametrální syntézy:
Cíl: Monodisperzita, stabilita, bez toxicity, jednoduchou cestou





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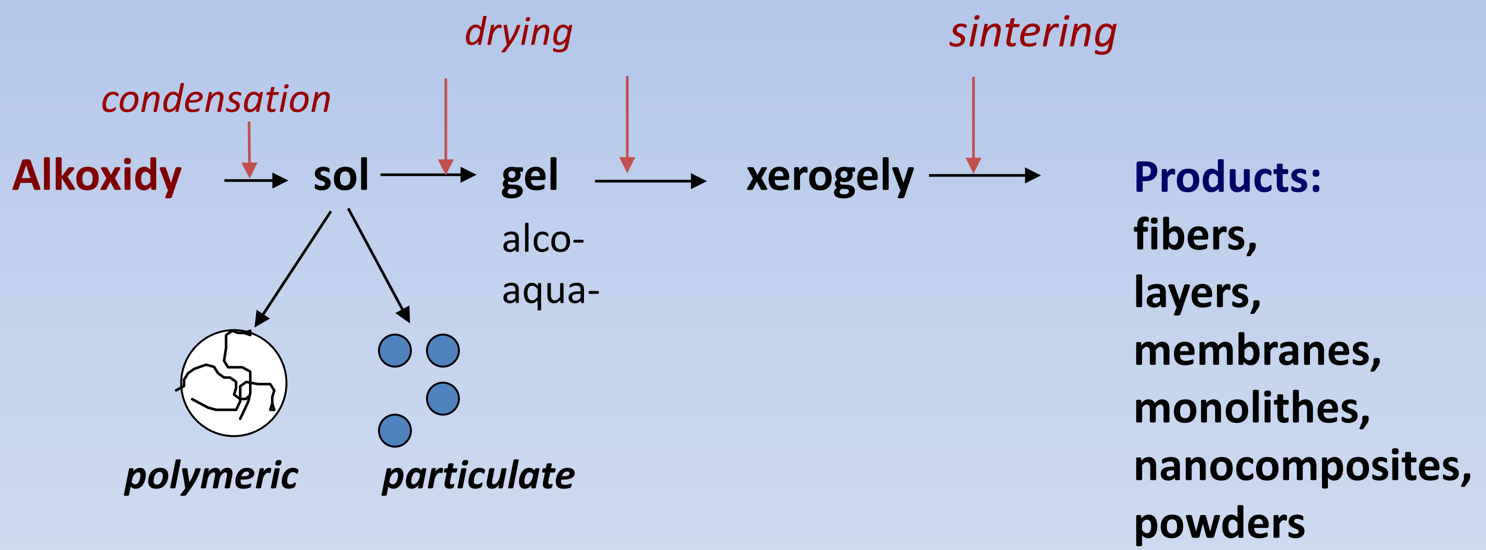
Sol-gelová Nanochemie

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



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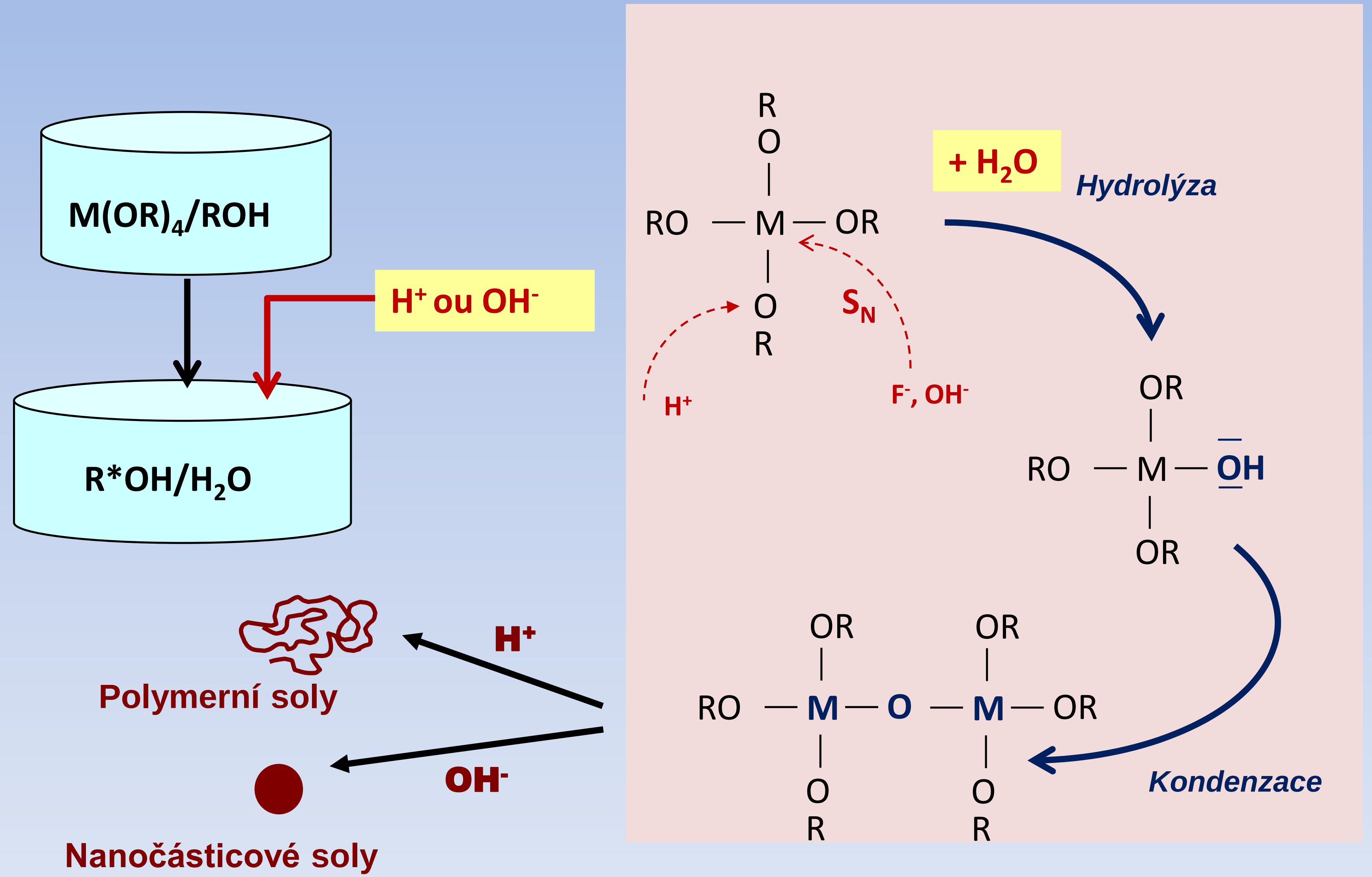
Oxidy kovů v alkoholu

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



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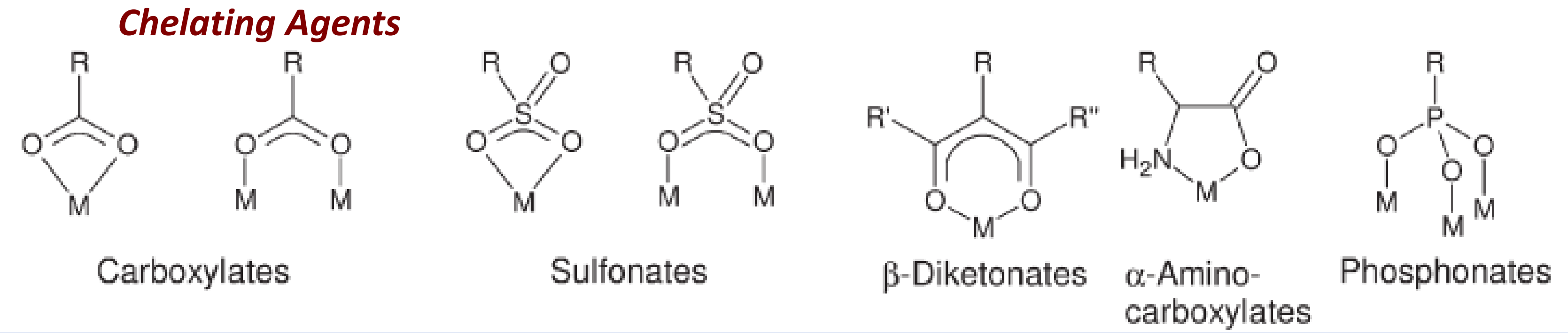
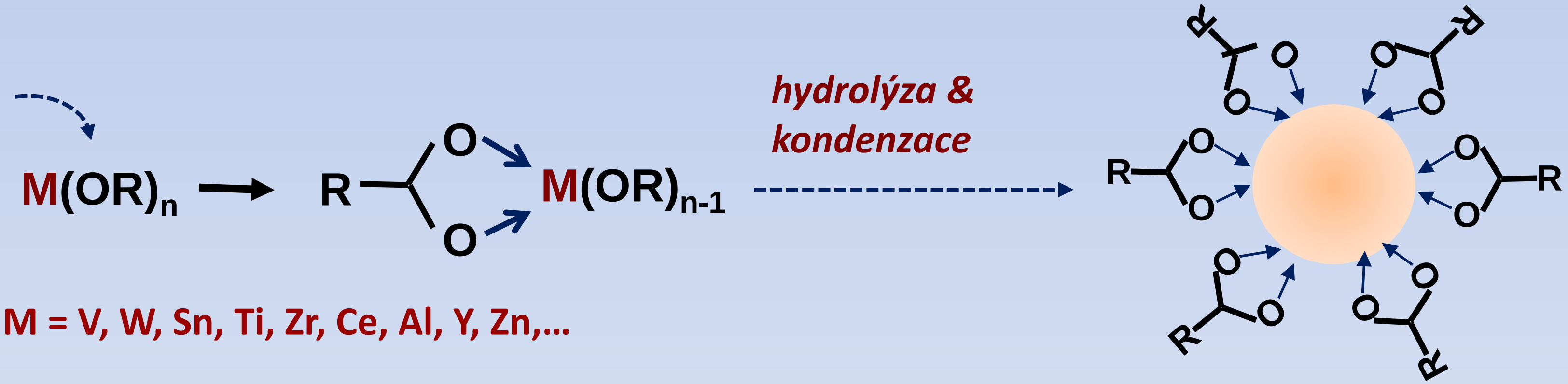
Komplexace alkoxidů

Snížení reaktivity a protekce vůči srážení





M = V, W, Sn, Ti, Zr, Ce, Al, Y, Zn,…

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Polymeric sols based on nano-$Zn_xTi_yO_z$ heterostructures (nano-alloys)

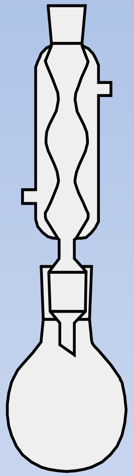
$$4\ Zn(Ac)_2 \cdot 2(H_2O) \xrightarrow{\text{EtOH ultrapure, 80°C}} 2\ HAc + 7\ H_2O + [Zn_4O](Ac)_6$$

TBT: $Ti(OBut)_4$

Chelation (HAc)
Esterification (HAc + EtOH)
Hydrolysis / Condensation (H_2O)

Sol polymérique
„Ti-O-Ti“ , „Ti-O-Zn-O-Zn“

EtOH
$Zn(Ac)_2\ 2H_2O$
TBT: $Ti(OBut)_4$



80-120°C

Z. Phys. Chem. 2007
Adv. Mater. 2006

applicable for other heteronanostructures pour les autres composites: $NiTiO_3$, $ZnFe_2O_4$, $ZnGeO_3$, $ZnGaO_2$, etc..

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Molekulární prekurzory sol-gelové nanochemie
Polymerizovatelné alkoxyláty kovů

M = V, W, Sn, Ti, Zr, Ce, Al, Y, Zn,…

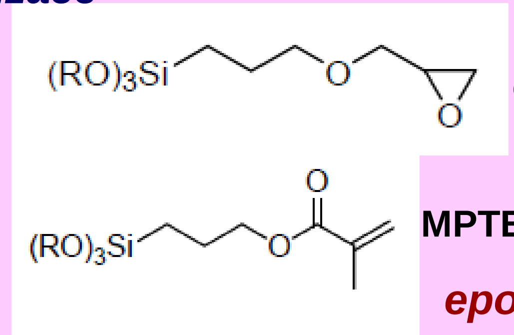
Opcionální použití inertních skupin

R_x
|
— **M** —
|
OR

Anorganické kondenzace

Anorganické kondenzace

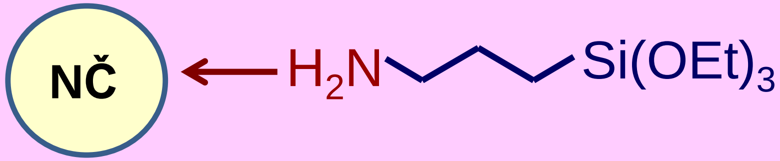
Organické polymerizace



GPTES

MPTES

epoxidy, metakryláty



Koordinační činidla

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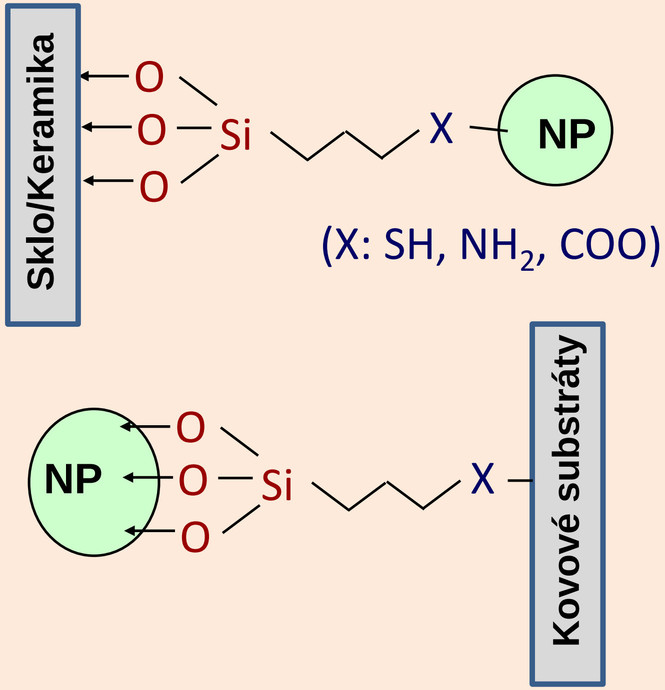
Strategie organizace nanočástic na substrátech

Adhéze !

Kovalentní vazby

Elektrostatické spojení



Tvorba tenkých vrstev

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

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

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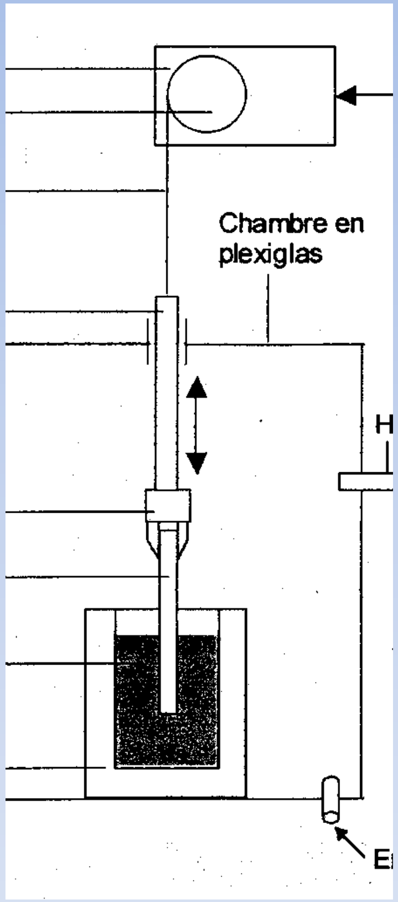
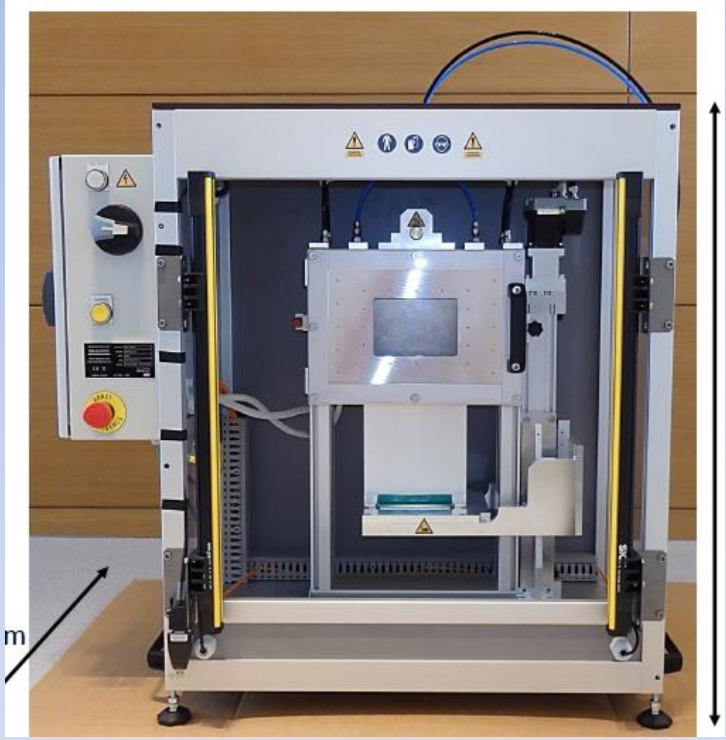
Kontrolované ponořování/tažení substrátu
(angl. dip coating)





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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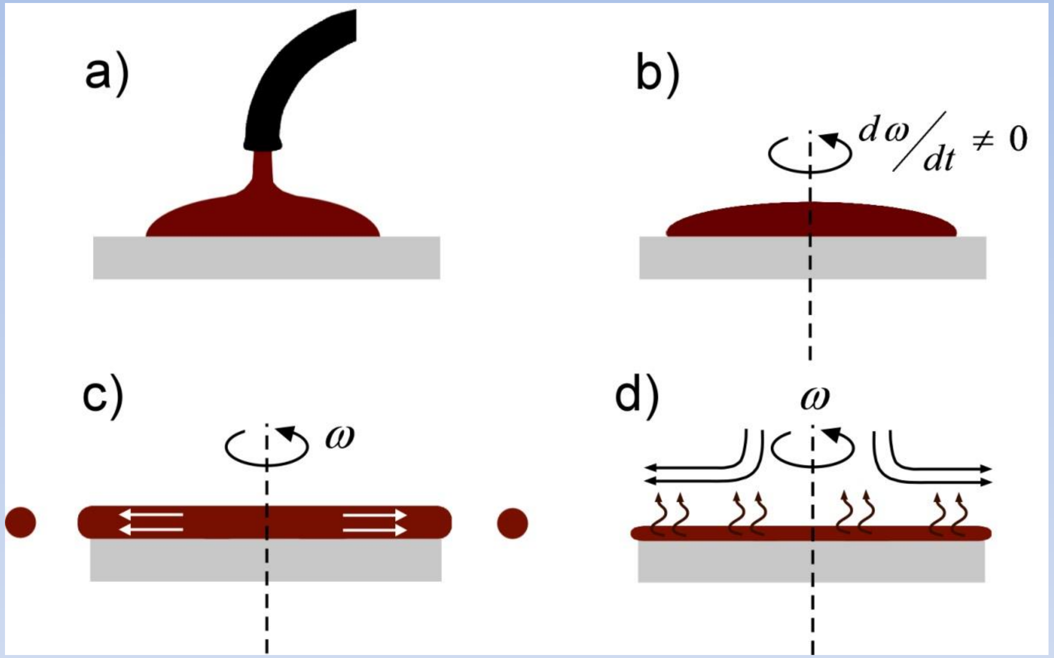
Centrifugální pokrytí :

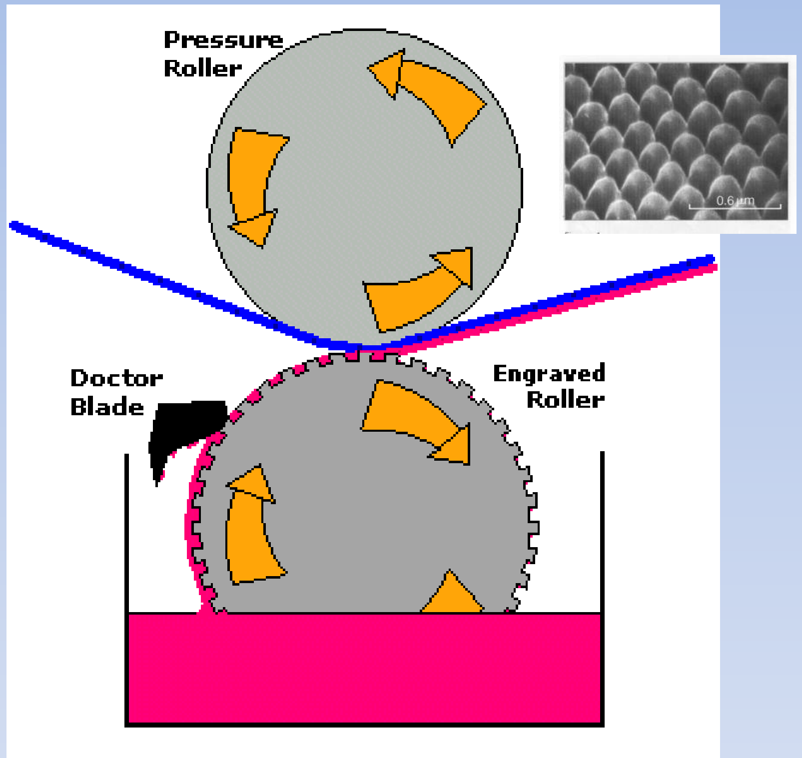
Roztok na rotujících substrátech, angl. Spin-on coating



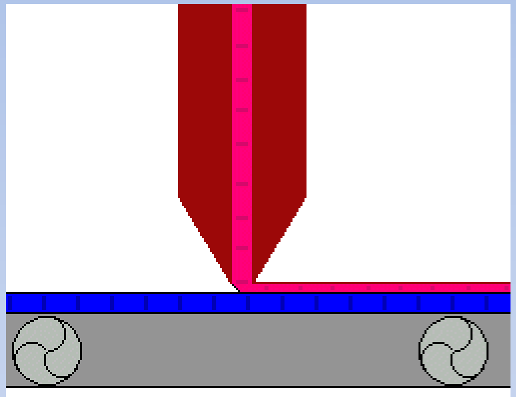
$$e[\mu m] = \frac{e_0}{\sqrt{1 + \frac{4 \cdot \rho \cdot \omega^2 \cdot e_0^2 \cdot t}{3 \cdot \eta}}}$$

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

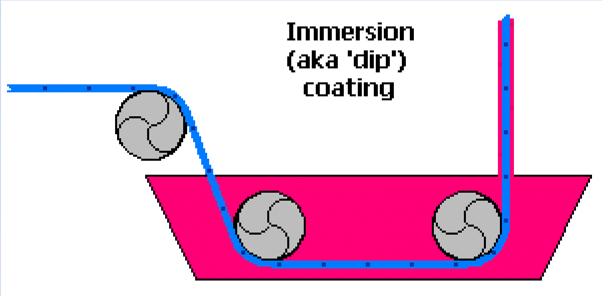
Doctor Blade, spray



Flexible substrates (textiles, plastics)



Steady substrates



mobile substrates

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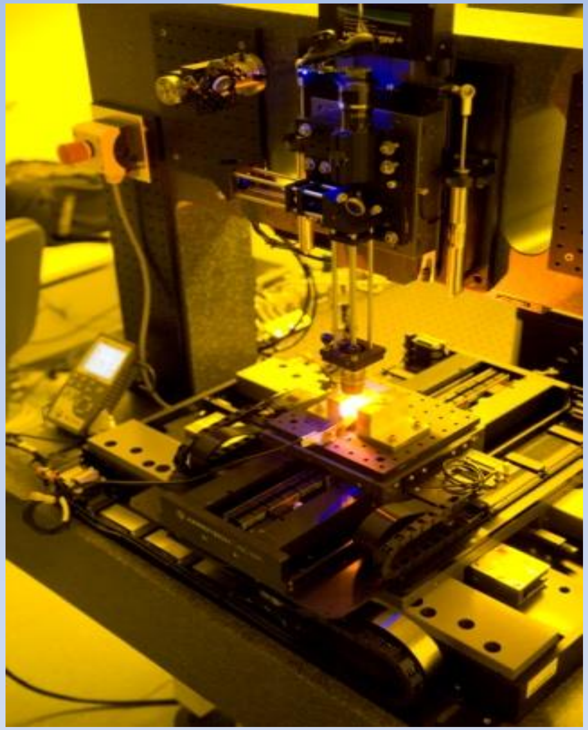
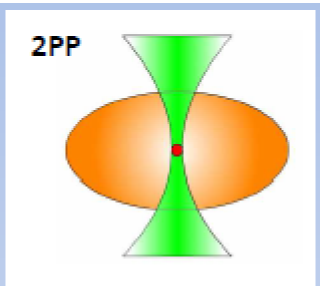
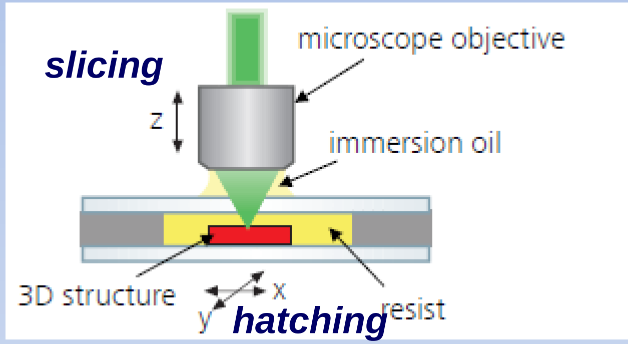
fs-Laser Printed Freeform 3D Structures (organosilicate inks via sol-gel)

Laser source: 100-400 fs, MHz-kHz

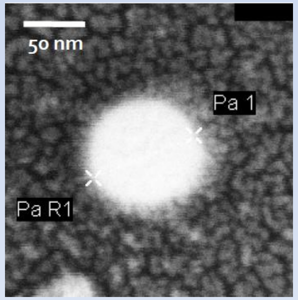
SHG $\omega \rightarrow 2\omega$ initiates 2PP (340 nm – 540 nm)







Sub-100 nm voxel



Low NA focus →

auditory ossicles human middle ear

S. Steenhusen, R. Houbertz
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Fraunhofer ISC

Institut des Sciences Chimiques de Rennes UMR CNRS 6226 V&C
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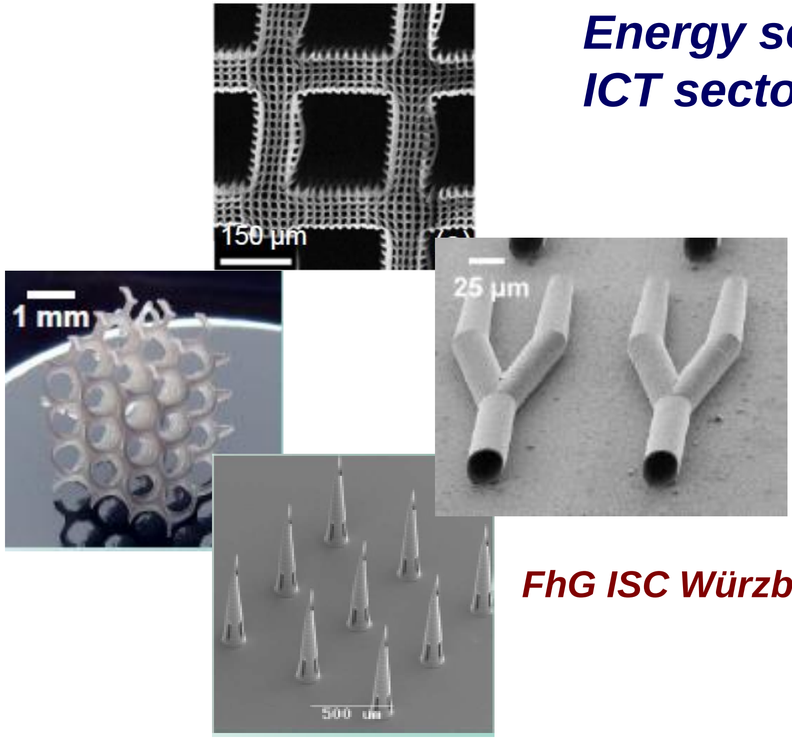
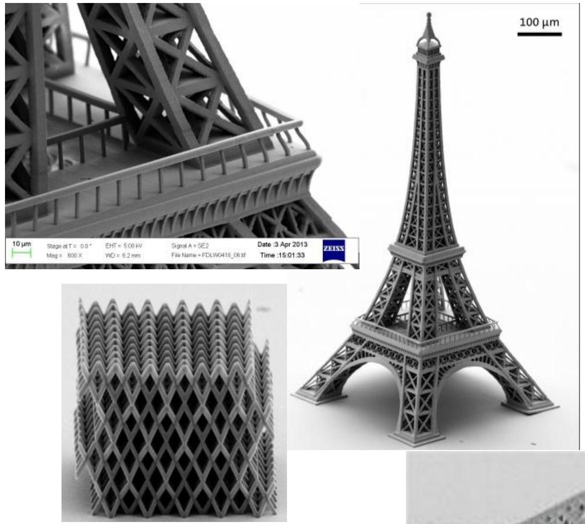
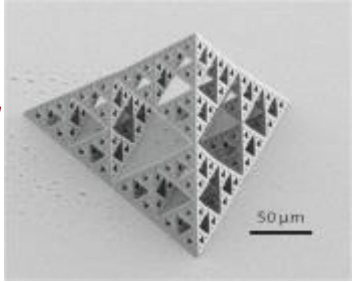
Targets:
Life sciences
Energy sector
ICT sector

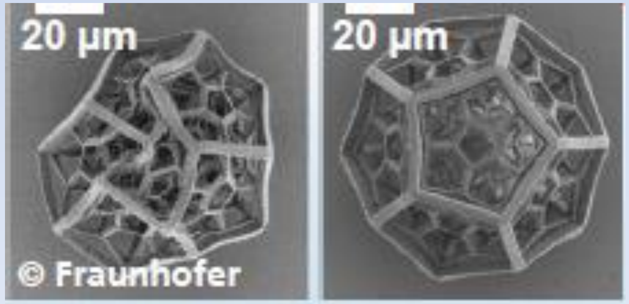


FhG ISC Würzburg



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, DRX, SAXS

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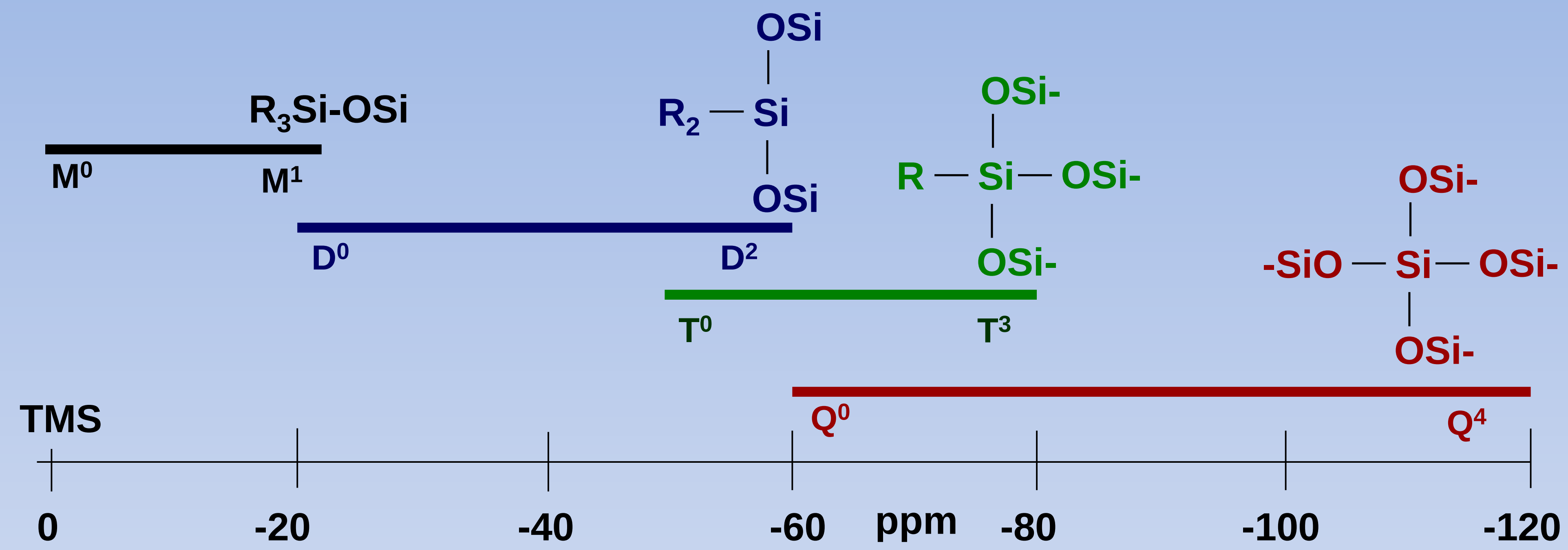
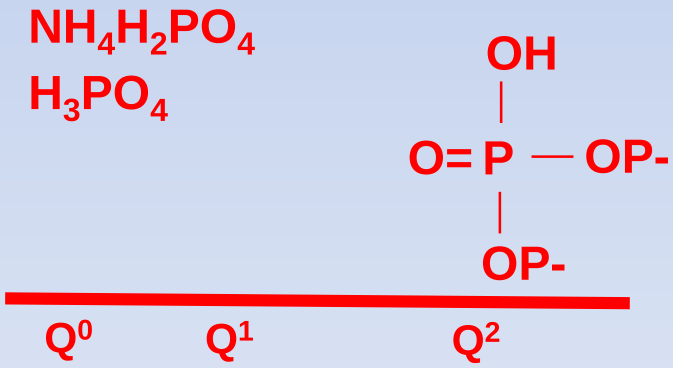
Nomenclature and chemical shift in ^{29}Si- and ^{31}P-NMR





Control question:

1. Indicate the structure of P_2O_5 and estimate the chemical shift position of the resonance
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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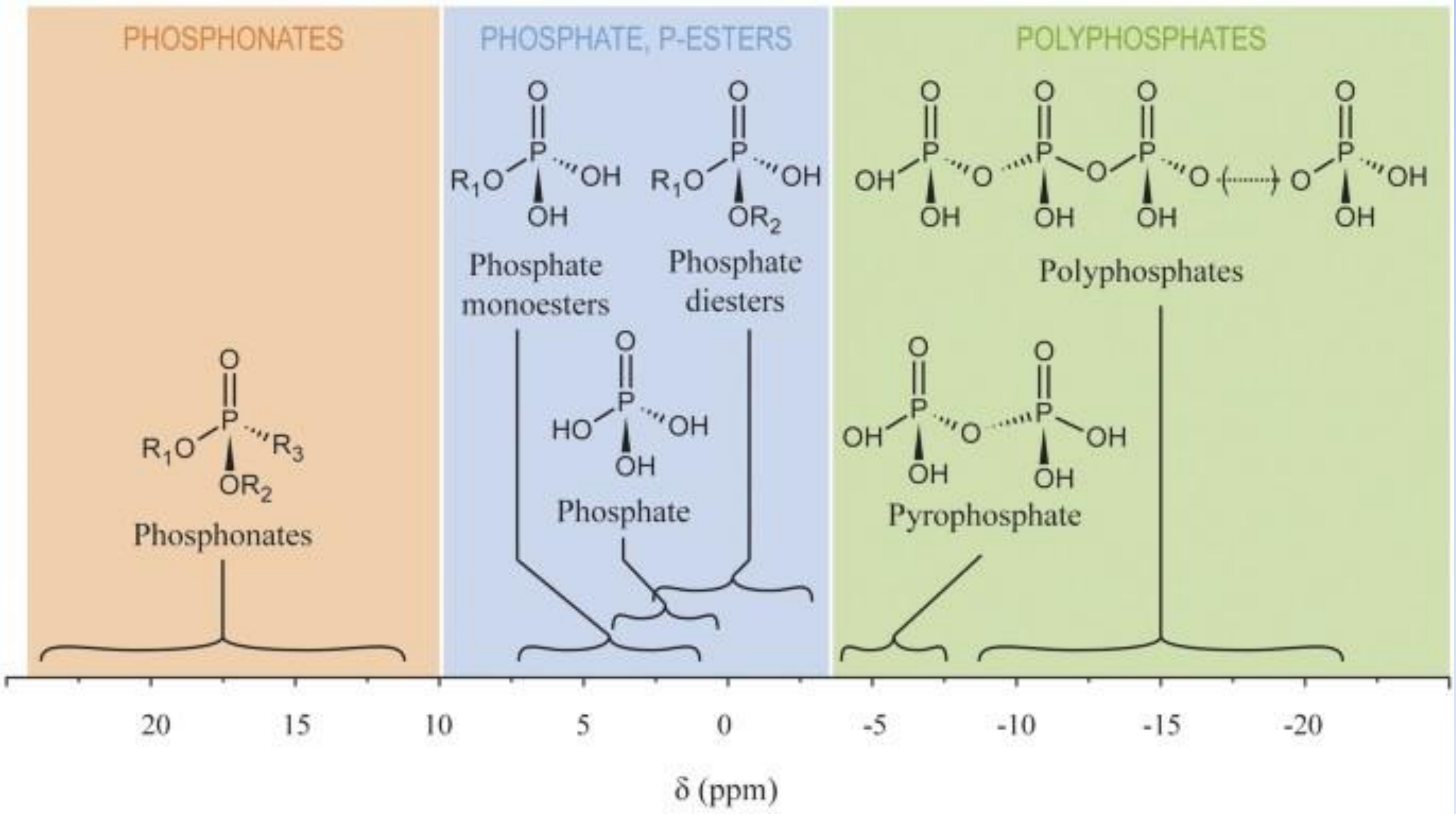
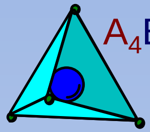
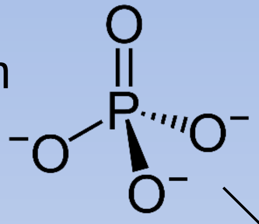
	Peak (ppm)	Phosphorus Atom
A ($P_3O_{10}^{5-}$)	-3.750, -3.904	A2
	-4.289	impurity
	-17.964, -18.118, -18.273	A1
	-20.059	impurity
B ($P_4O_{12}^{4-}$)	2.757	byproducts/impurity
	-22.137	B1
C ($P_2O_7^{4-}$)	-5.474	C1
D ($P_3O_9^{3-}$)	-20.93	D1



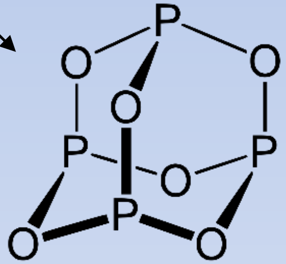


H_3PO_4

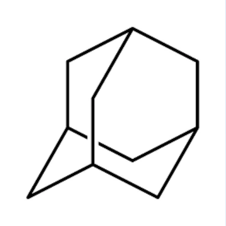
δ = 0 ppm



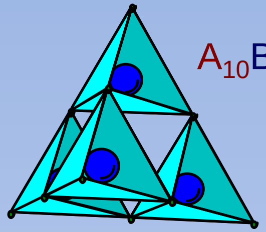
PO_4^{3-}

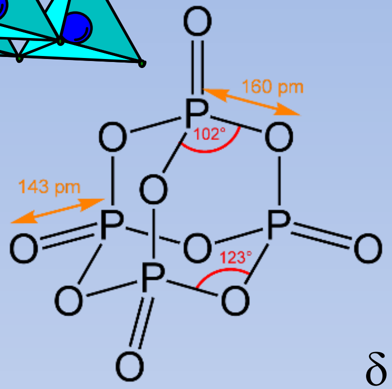


$P_2O_3 = P_4O_6$



Adamantane

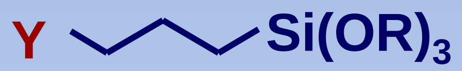




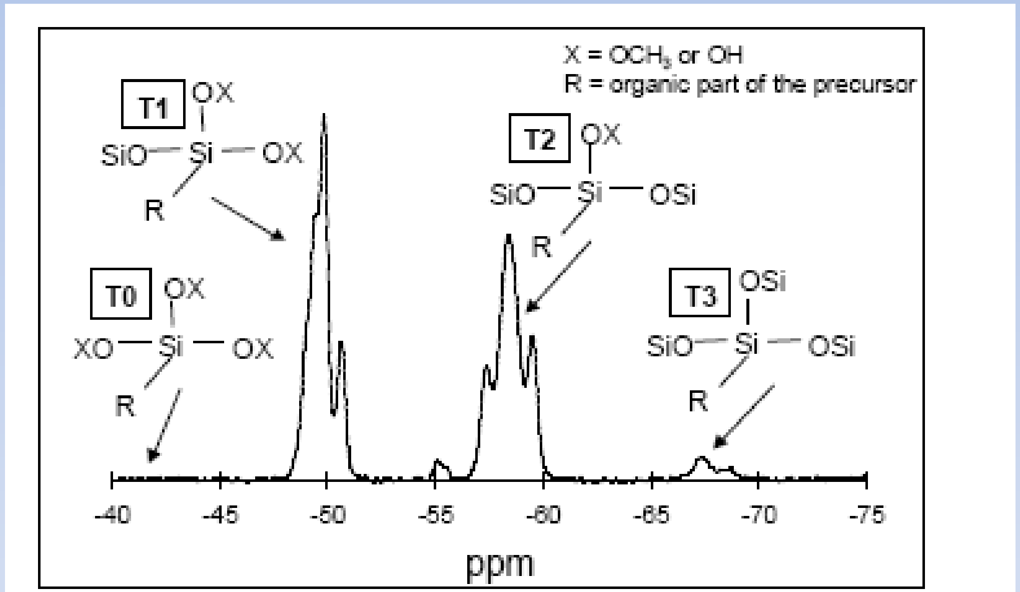
δ = - 53 ppm !

$P_2O_5 = P_4O_{10}$

Application of ^{29}Si - NMR



$T^1 \rightarrow T^3$

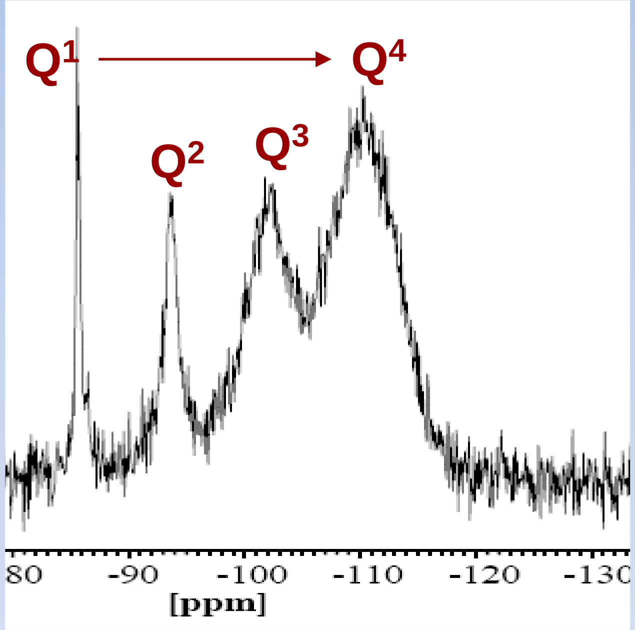


Condensation degree →

TEOS

H_2O ↙

OEt EtO – Si – OSi OEt	→	OSi SiO - Si - OSi OSi



Condensation degree →

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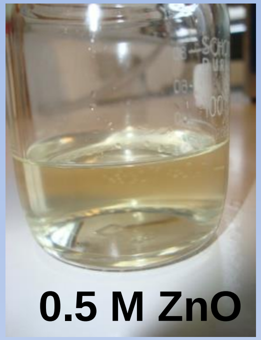
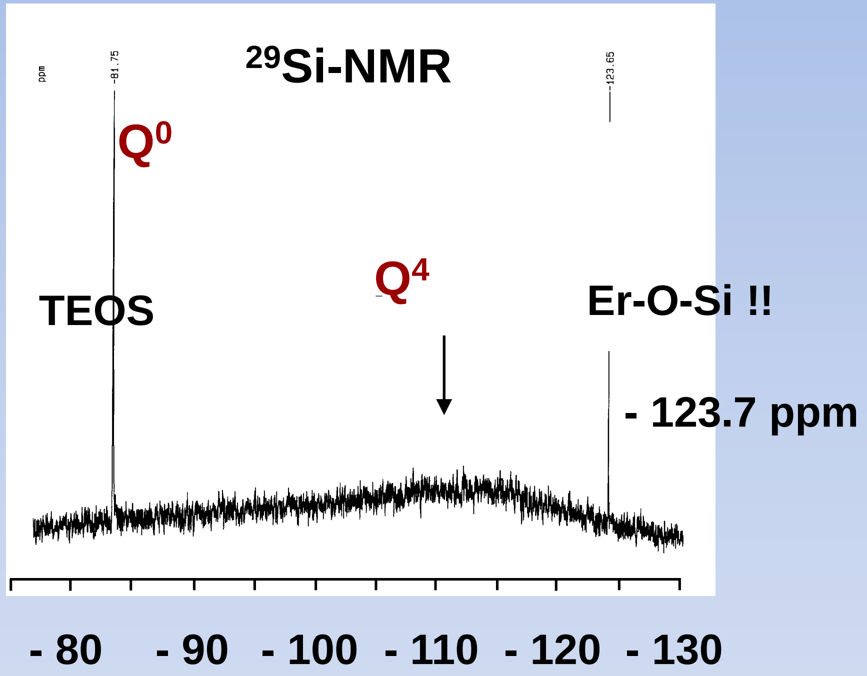
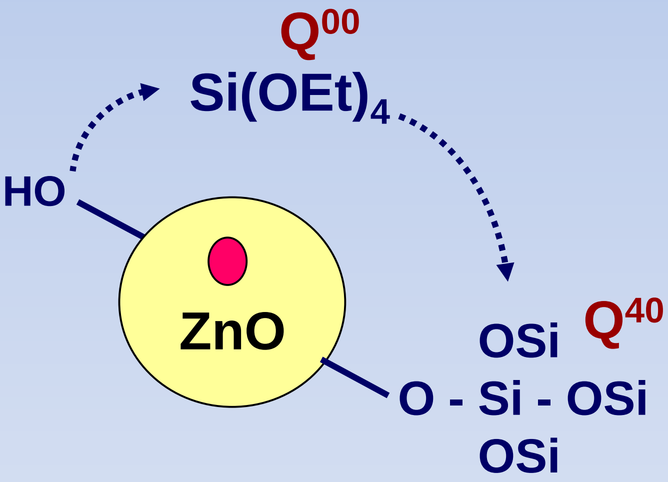
NMR-Spektroskopie nanokoloidu Er@ZnO



$ErAc_3$

TEOS





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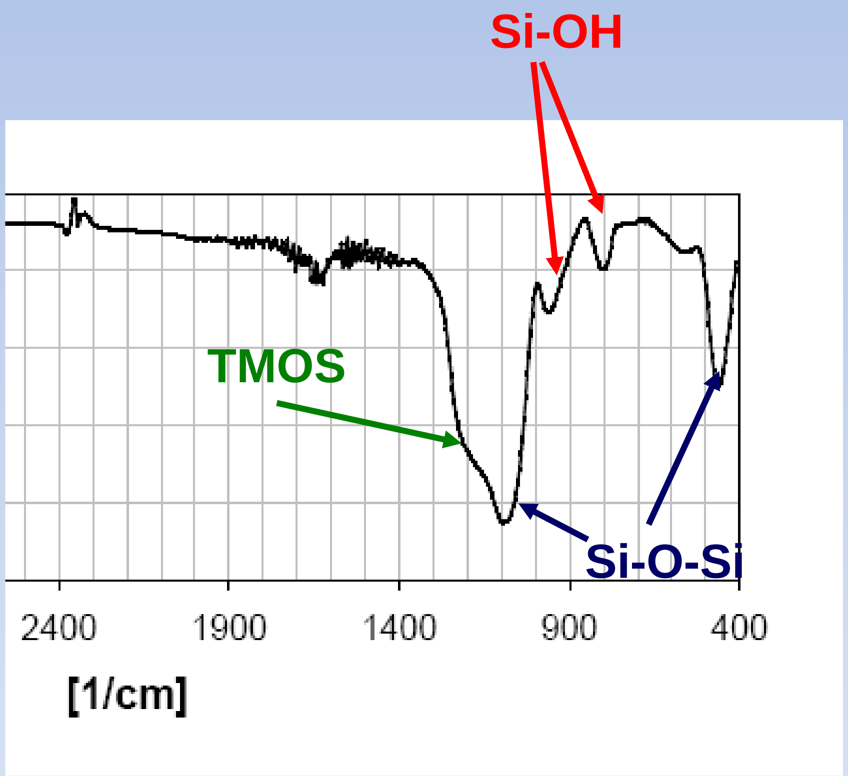
FTIR charakterizace

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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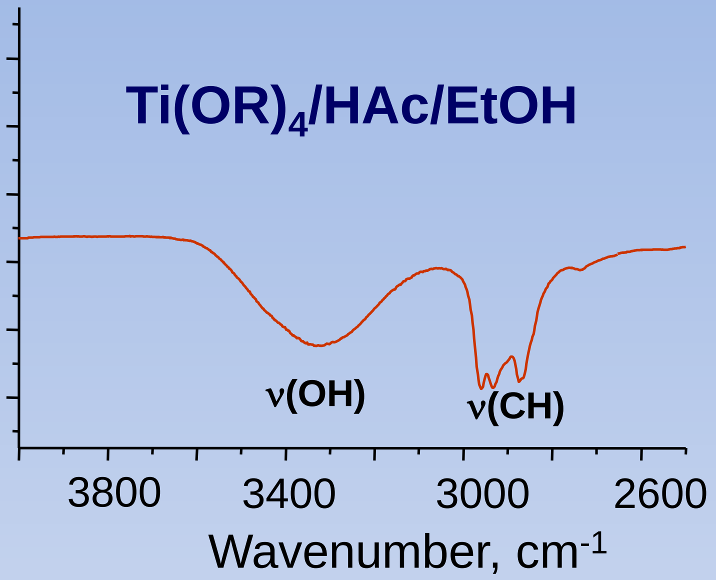
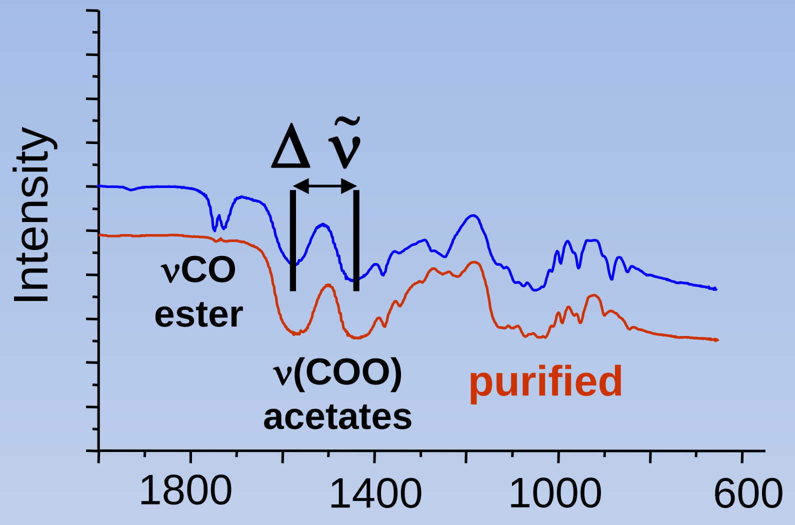
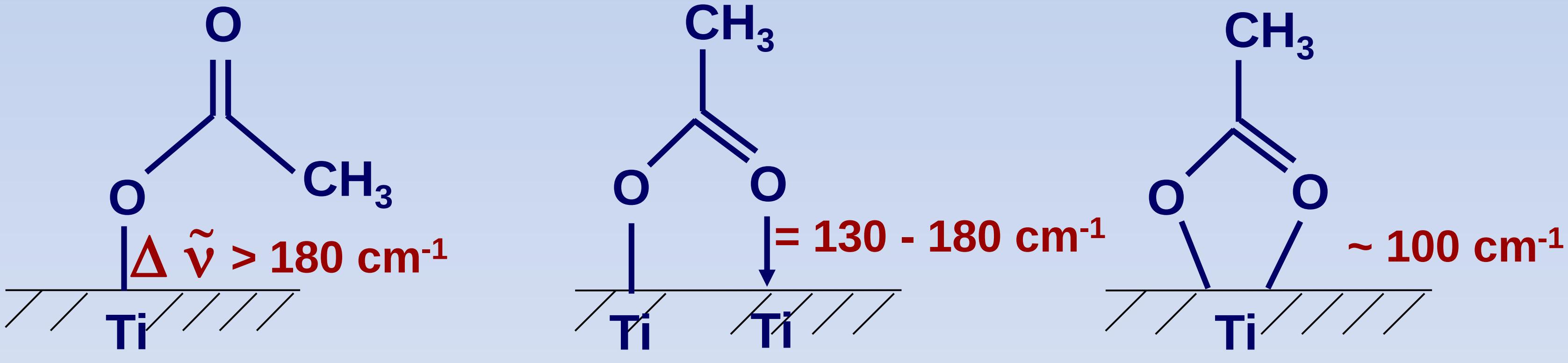
Interfacial chemistry of TiO_2 xerogel formed in ethanol







monodentate

bridging bidentate

chelate bidentate

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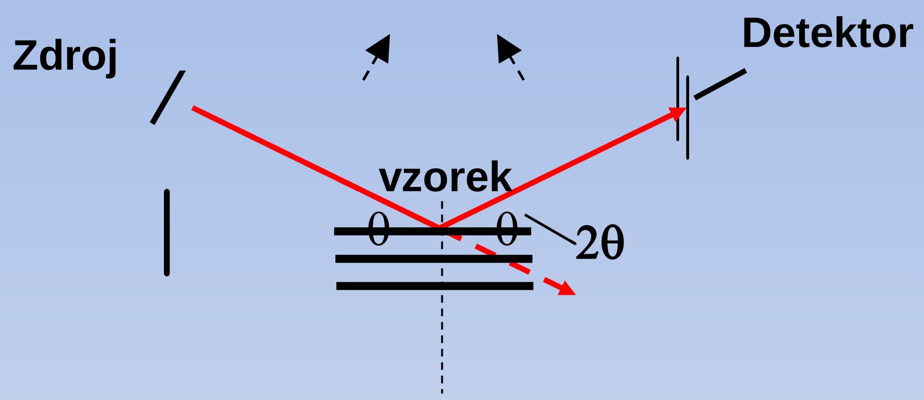
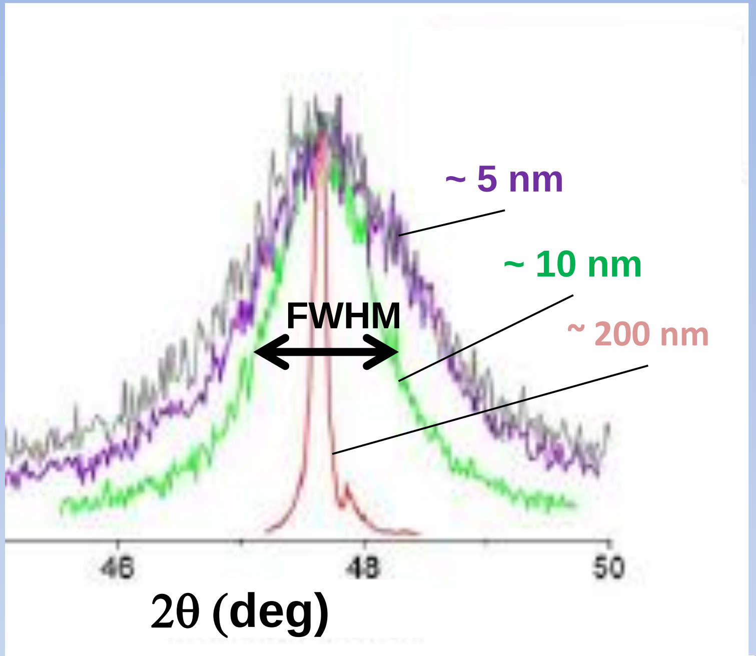
Identifikace nanokrystalinity a zjištění velikosti NČ metodou rentgenové difrakce (XRD)

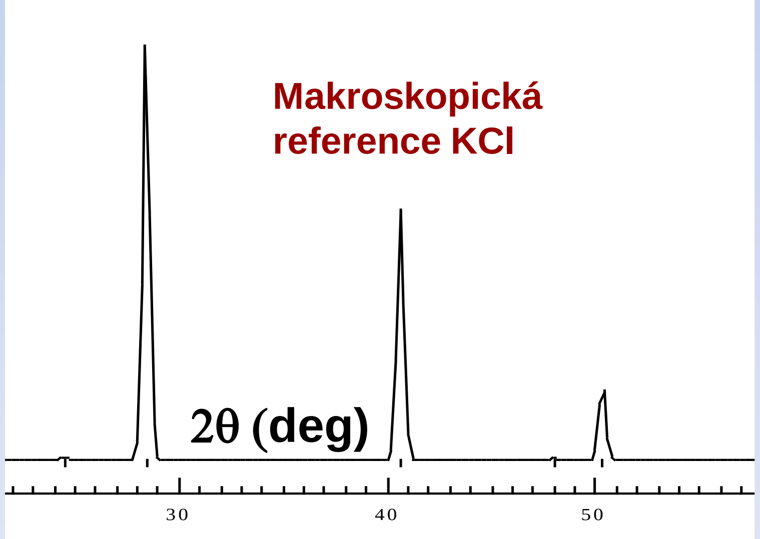




Bragova rovnice pro výpočet velikosti NČ

$$\mathbf{T} = \frac{\mathbf{K} \times \lambda}{\mathbf{LMH} \times \mathbf{cos}\,\theta}$$

T	střední velikost nanokrystalků
2θ	úhel pozorování
HWFM	šířka difrakčního peaku
λ	vlnová délka zdroje paprsků X



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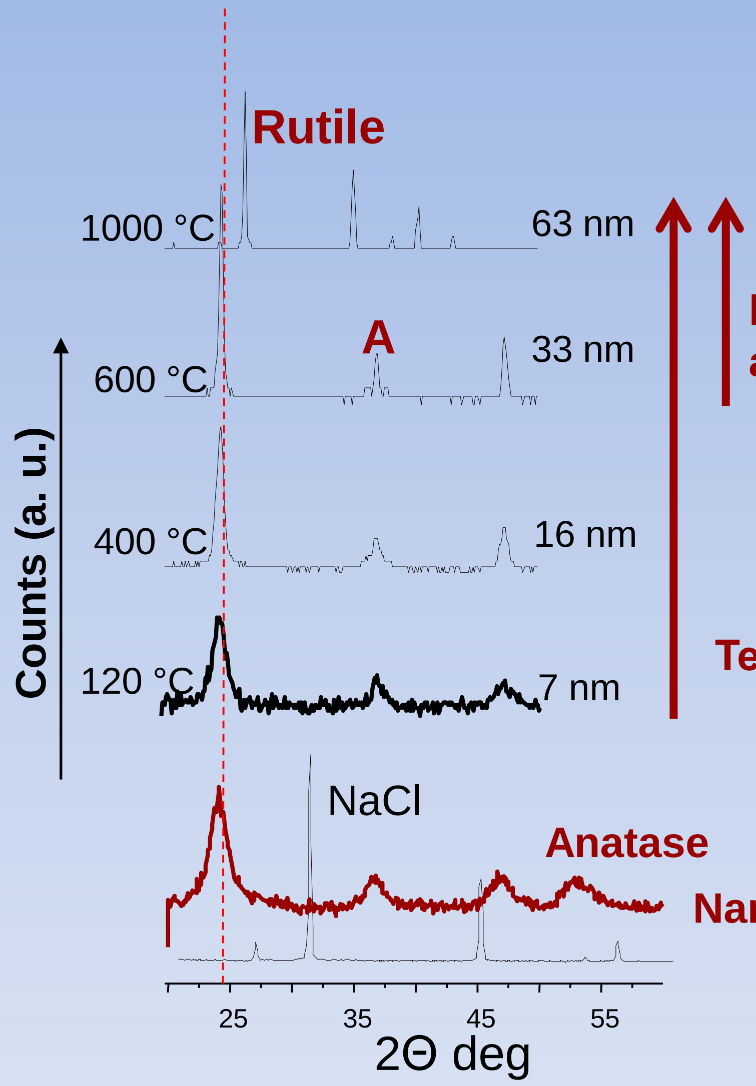
Protokol měření XRD s NČ TiO_2



Fázový přechod anatase→rutile

Termické spékání NČ v práškovém stavu

Nanoprášek izolový z koloidní fáze

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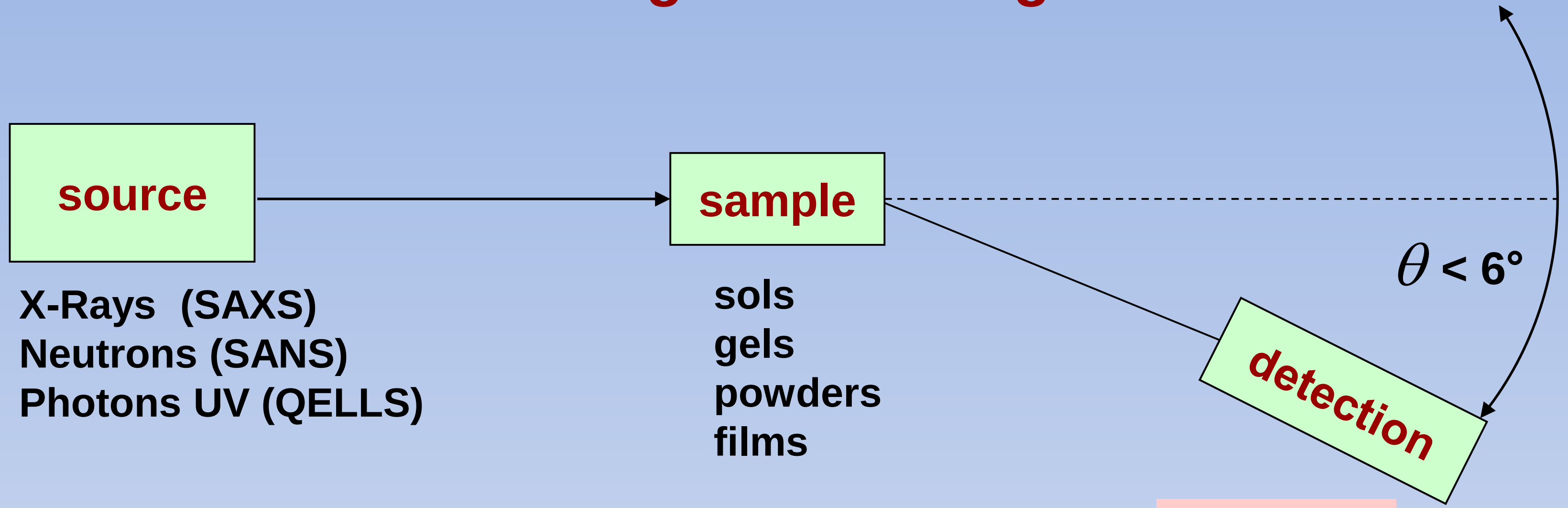
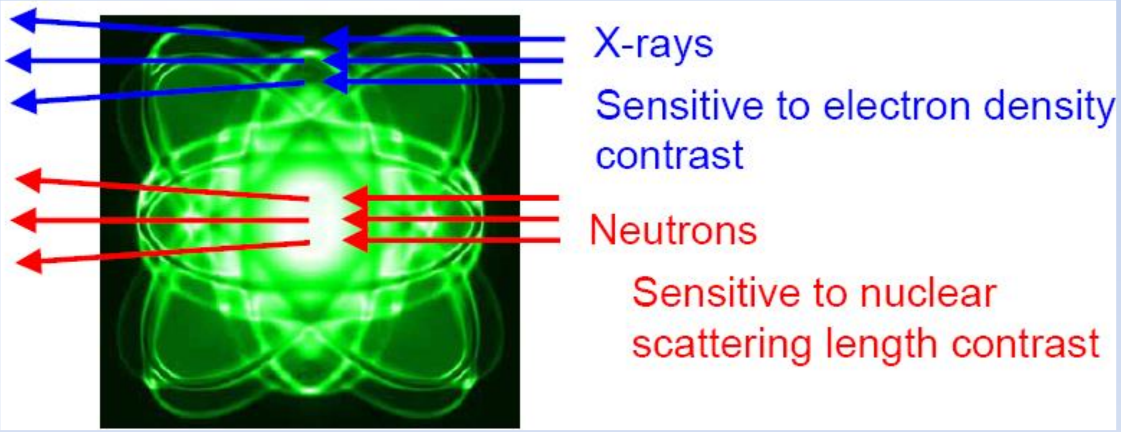
Small Angle Scattering





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

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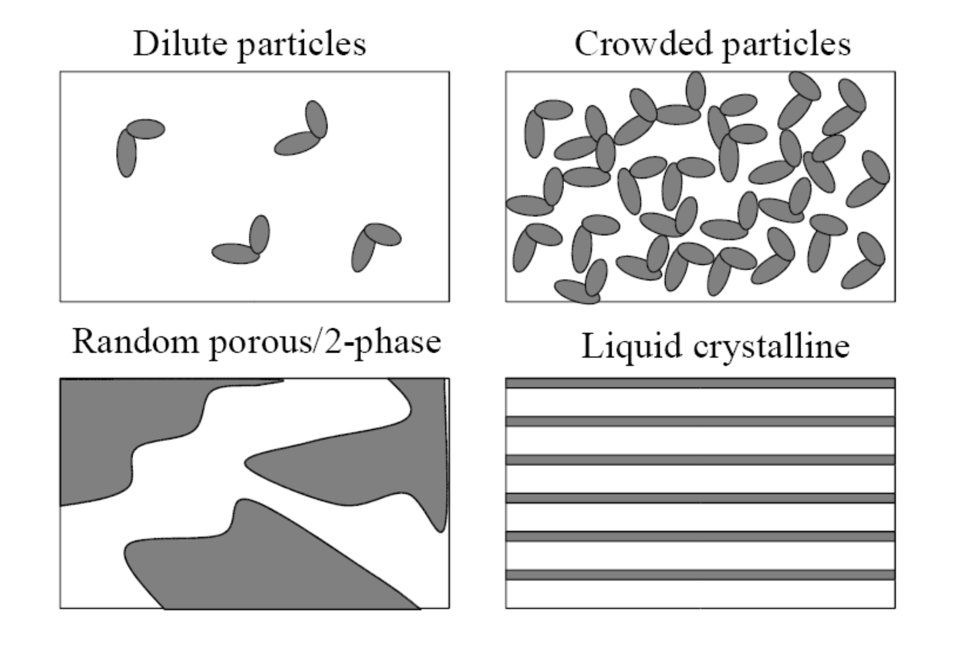
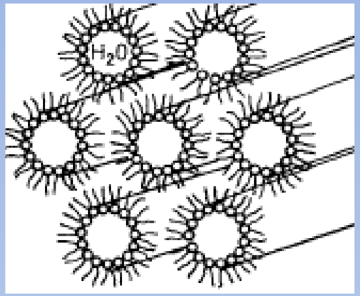
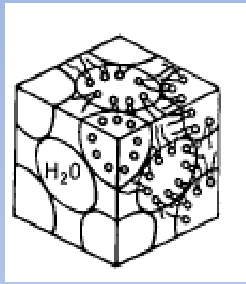
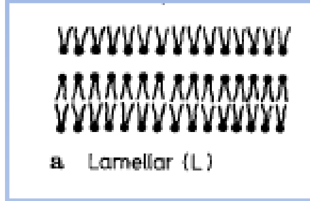
R_g – gyration radius
(primary particles and aggregates)
V_p – pore and particle volume
m_p – particle mass
A – specific surface area
D_f – fractal dimension
Shape of primary particles and aggregates

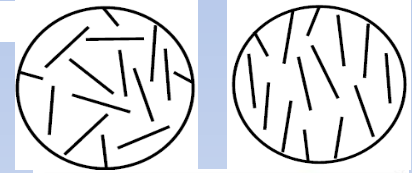








Orientation and self-organisation



Hydrated DNA

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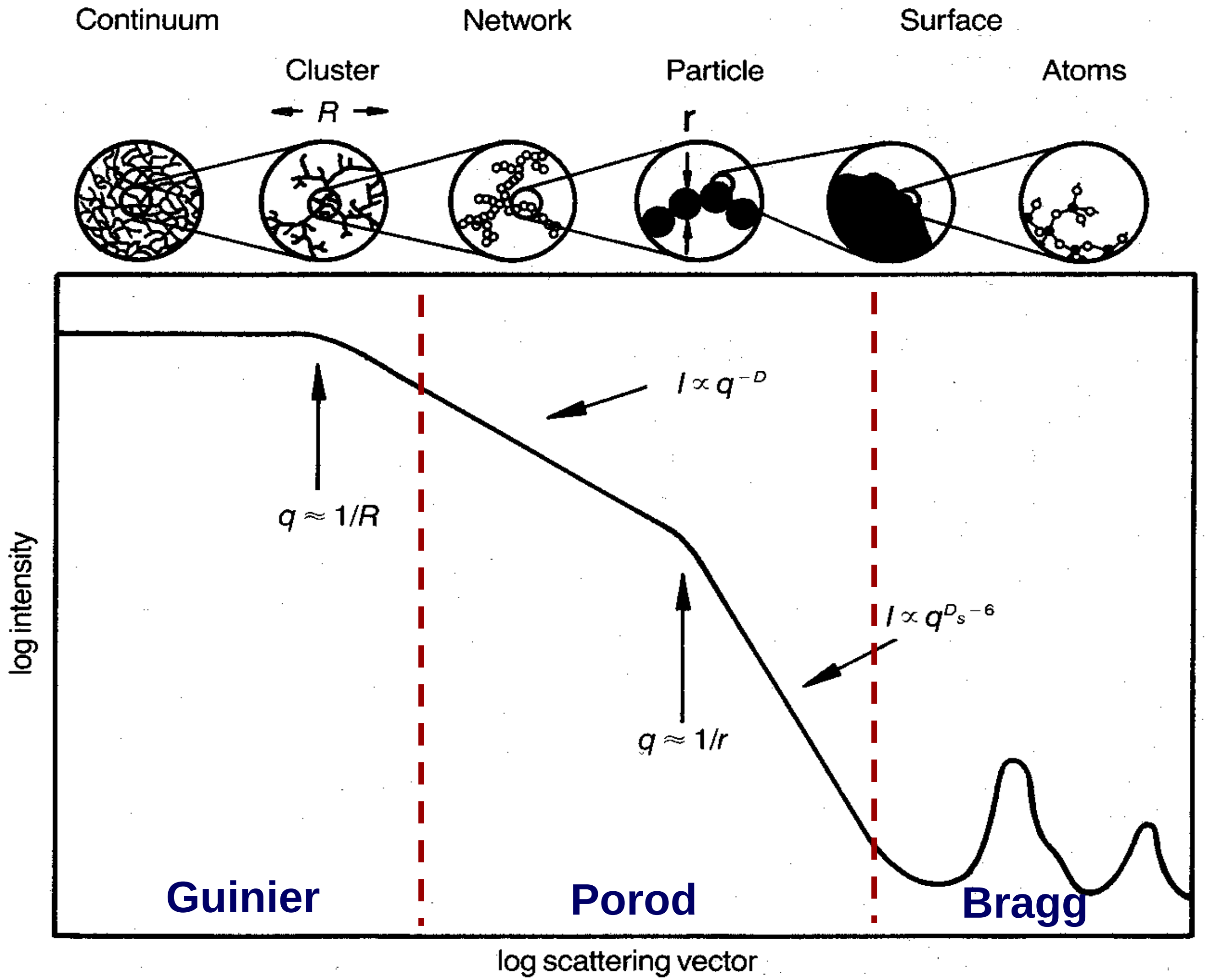

Fig. B2. Small-angle scattering curve for a disordered particle network. All structural features appear in the corresponding regions of scattering vector q. R and r denote a mean cluster and particle size, respectively; exponents D and D_S, determining a power-law decay, are a measure of the morphology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

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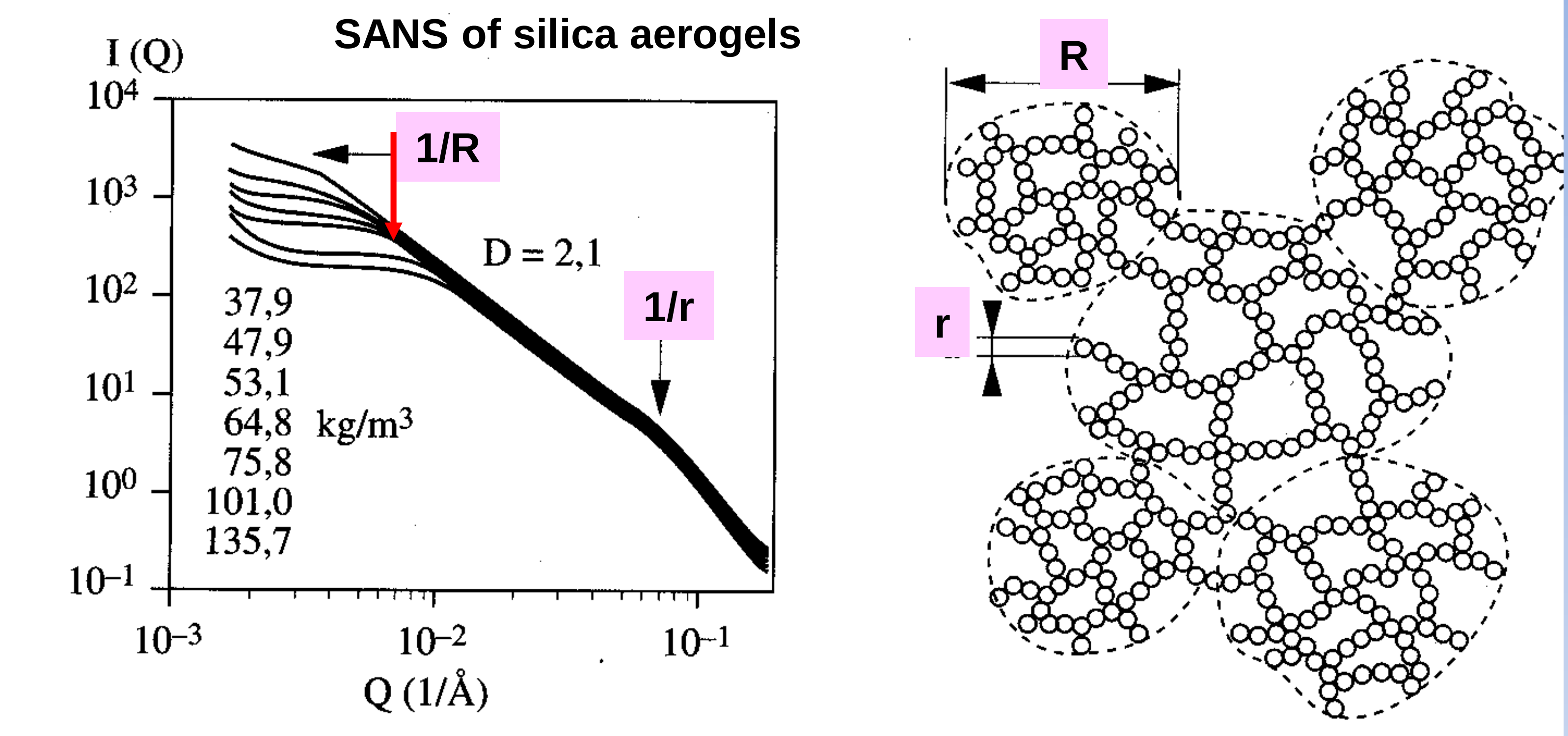

Note:

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;
   Suggest the principal chemical reactions taking place in the reaction mixture;
3. Using FTIR, various surface states of carboxylates can be identified; explain how?
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)

Jaro 2024
C9906

Spektroskopické metody charakterizace nanomateriálů

2. Polovodičové nanočástice v elektrotechnickém sektoru (ZnO, „CdZnSSe“)

- *Transparentní planární elektrody*
- *Elektro/fotoluminescenčí systémy*
- *Elektrochromie*
- *Piezoelektrické nanogenerátory*

Strategie prezentace

- *Teorie a kritické fyzikální parametry kontrolující kvalitu komponent*
- *Strategie syntézy a integrace nanočástic*
- *Srovnání Nano versus Macro*

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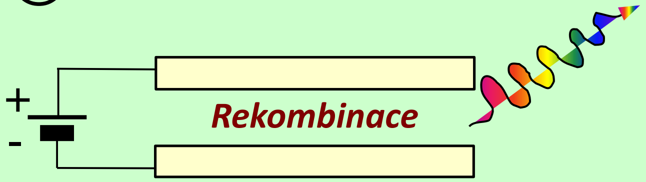
Přehled
Funkční principy

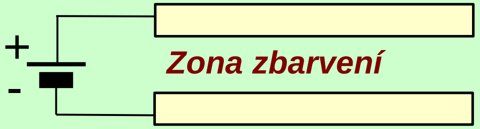
① *Transparentní elektrody*

TCO = transparent conducting oxides

② *Elektroluminescence*



③ *Elektrochromismus*



④ *Varistory*

⑤ *Piezoelektrické nanostruktury*

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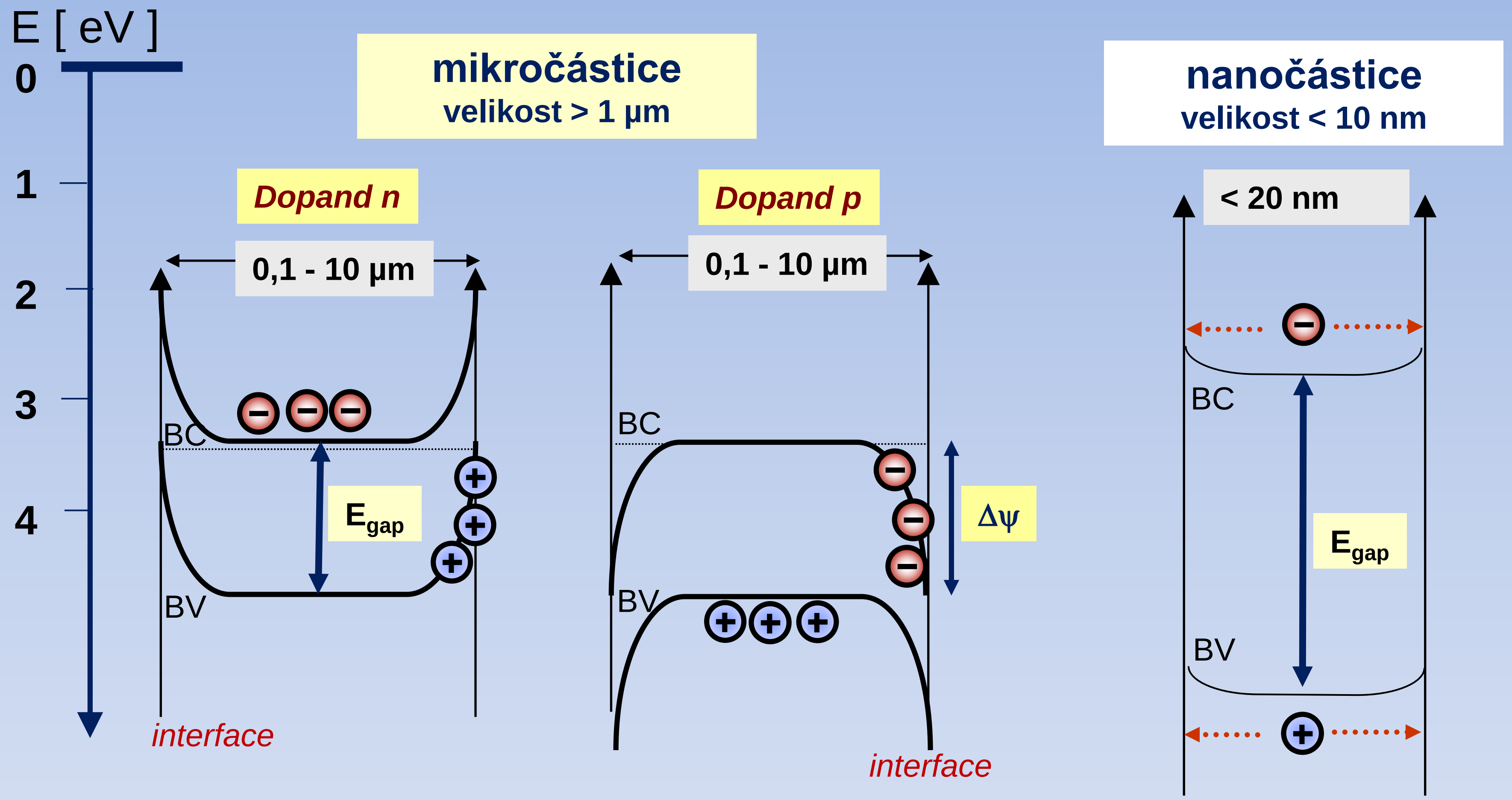
Srovnání energetických diagramů „*macro versus nano*“



Do notýsku:

Δψ = výška bariéry závisí na velikosti !

Kritické parametry:

N_e = koncentrace nositelů nàboje (v cm^3)

D_p = velikost částic

E = elektrické pole (V/cm)

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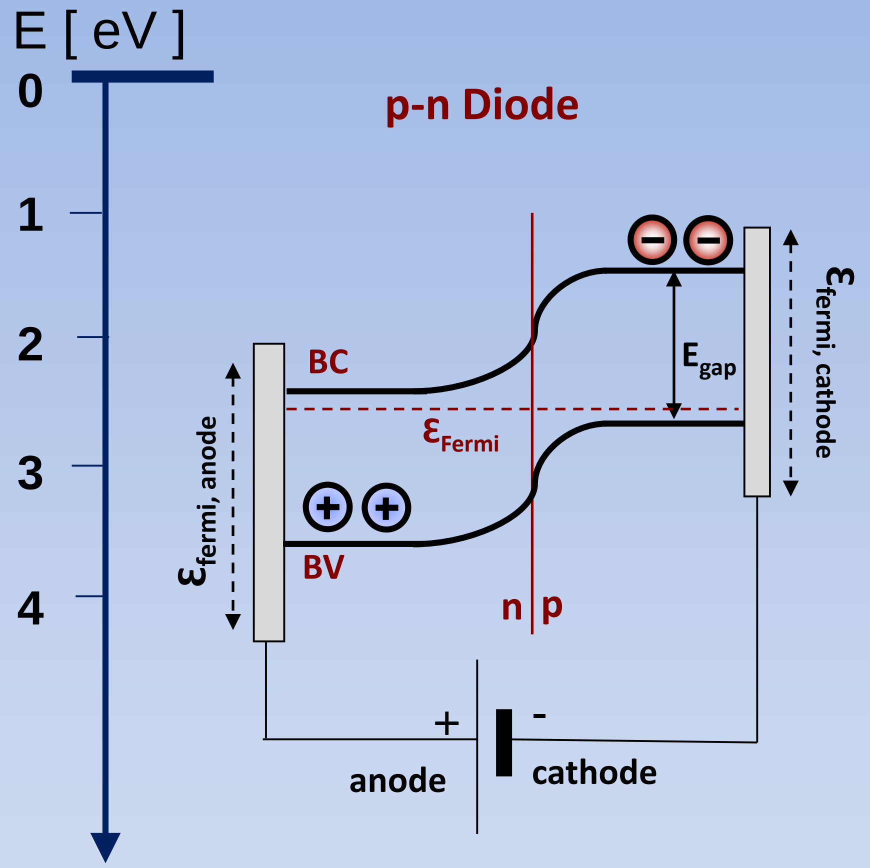
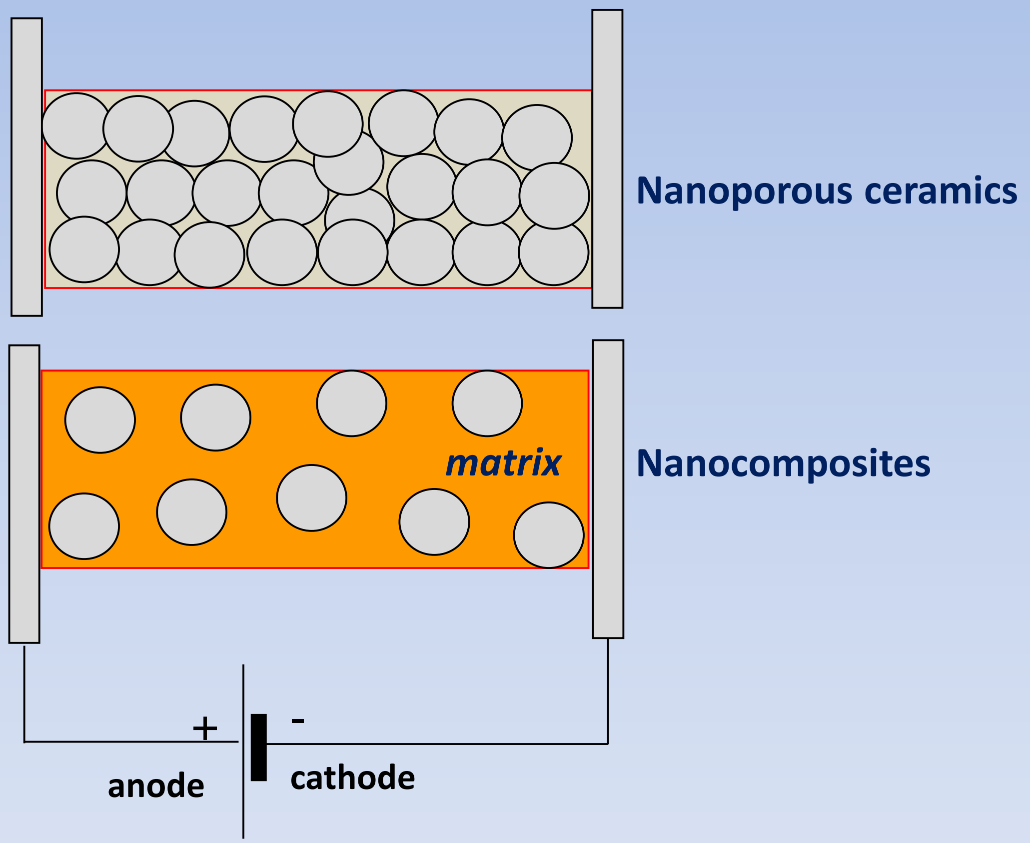
p-n Diode



Nanoparticulate aggregates



Note:
Surface chemistry, nanoporosity and NP size ar'e crucial parameters!

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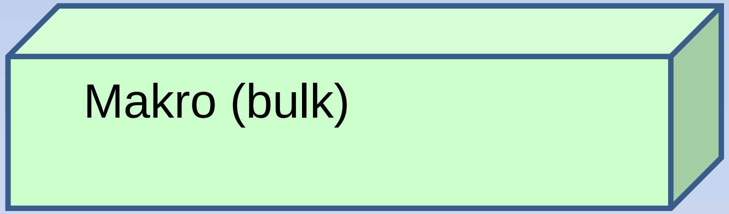
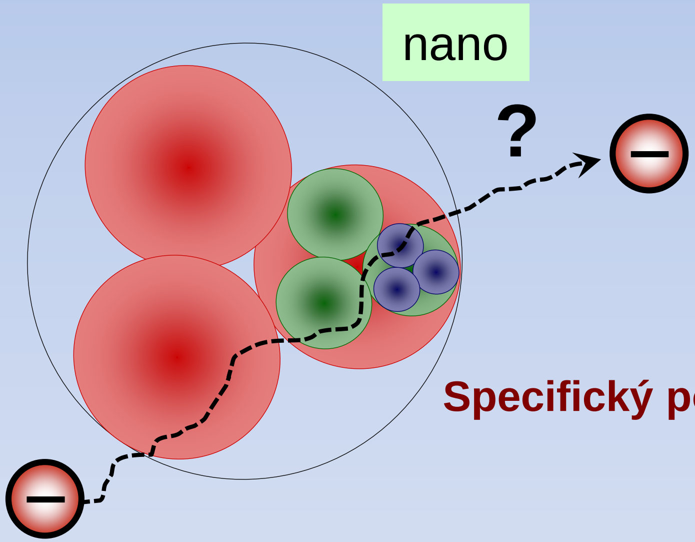
Transparentní elektricky vodivé oxidy

angl. « transparent conducting oxides TCOs »

Měřítko kvality ~ T / R_s

T = optická transmise (vis : 400-900 nm)
R_s = plošný odpor (< 20 Ω)





Specifický povrch!

T a R_s závisí na :
Morfologii (porozita, stupeň krystalizace)
Povrchové chemii (elektronické pasti, akceptory elektronů)
Mřížkové a povrchové defekty
Dopování

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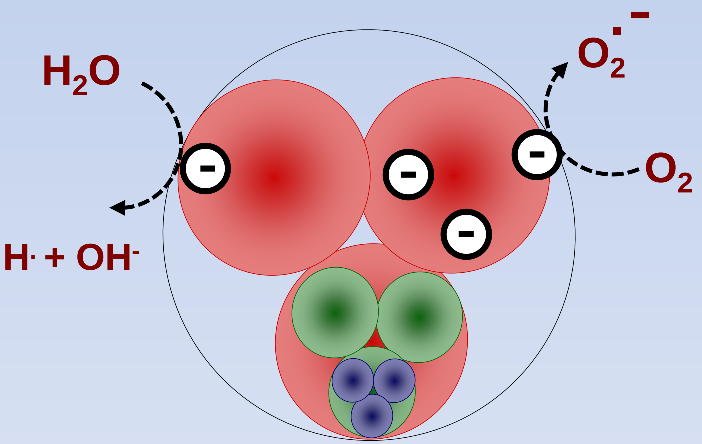
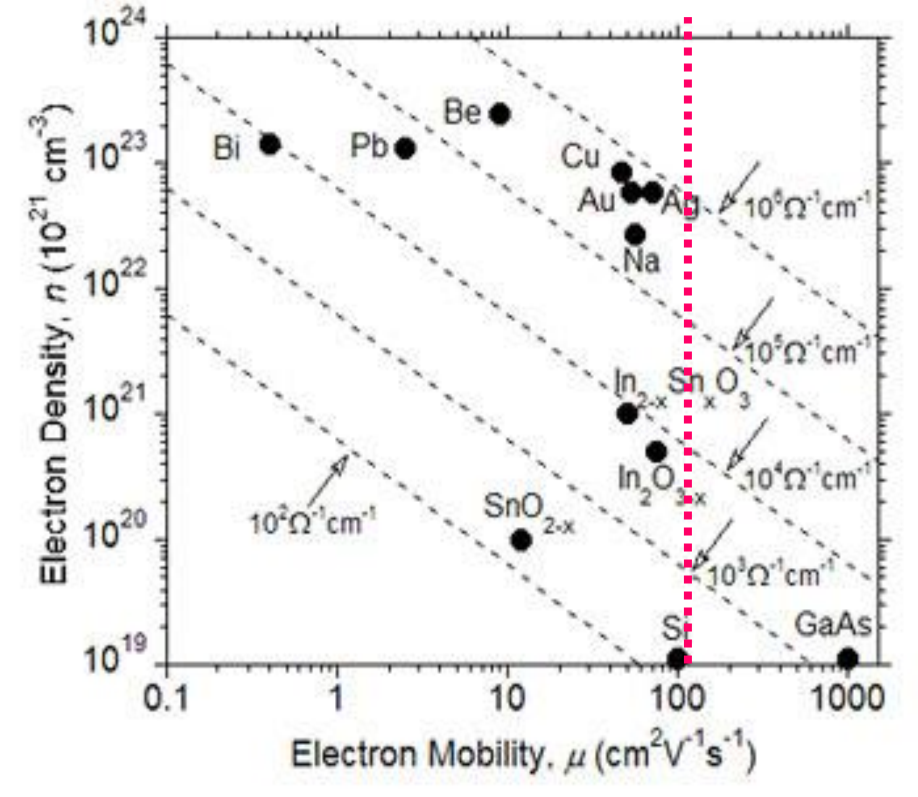
$R_s = \rho / t = 1 / e N_e \mu t$

R_s: plošný odpor (Ω/□)
ρ: relativní odpor (Ω cm)
t: tloušťka filmu
N_e: koncentrace volných elektronů ($1/cm^3$)
μ: mobilita elektronů ($cm^2V^{-1}s^{-1}$)
e: elementární náboj
N_e μ e = el. vodivost ($\Omega^{-1} cm^{-1}$)



↑μ morfologie & povrchová chemie



↑n_e : n doping

ITO : $In^{3+}_{2-x}Sn^{4+}_xO_3e^-_x$

ATO : $Sn^{4+}_{1-x}Sb^{5+}_xO_2e^-_x$

FTO : $Sn^{4+}O_{2-x}F^-_xe^-_x$

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

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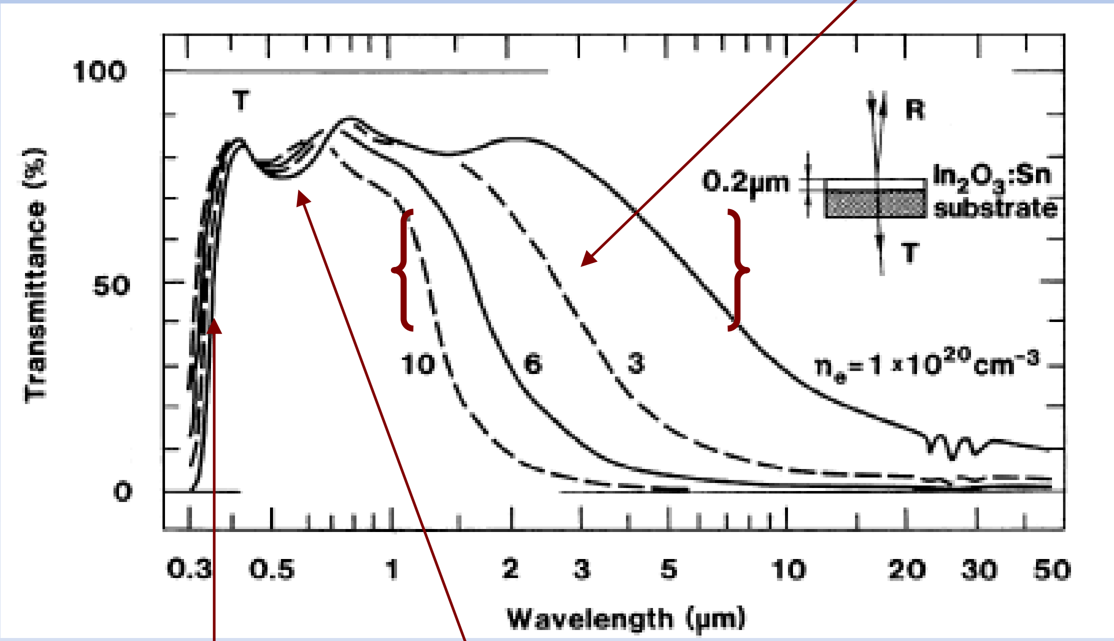
Optical spectral profile of TCO electrodes

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

Plasmon absorptions depending on free electron concentration



Interference fringes due to the different refractive indices of substrate and ITO film

Band gap around 3 eV

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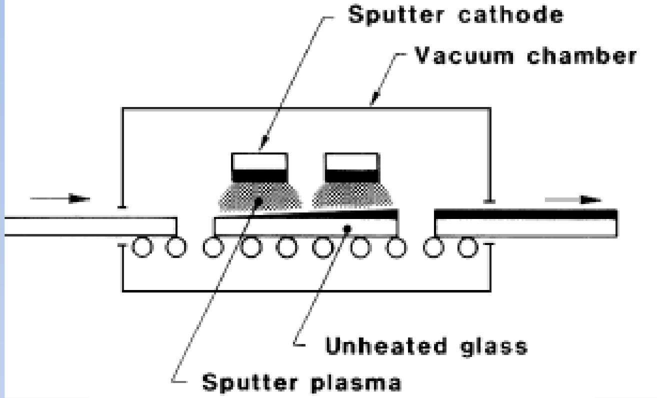
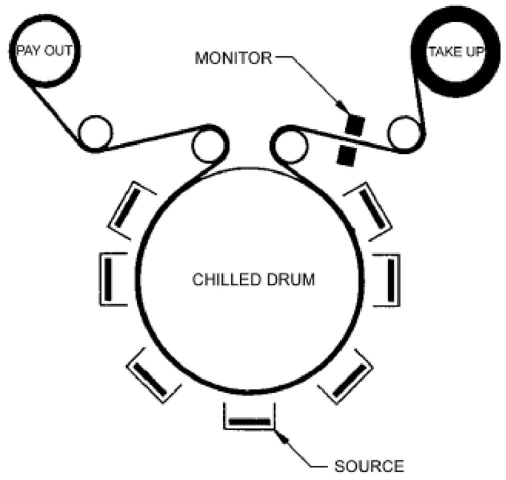
Elaboration methods

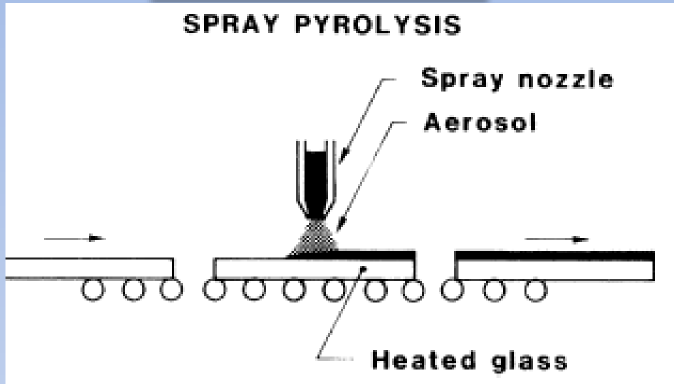
Pulsed Laser Deposition

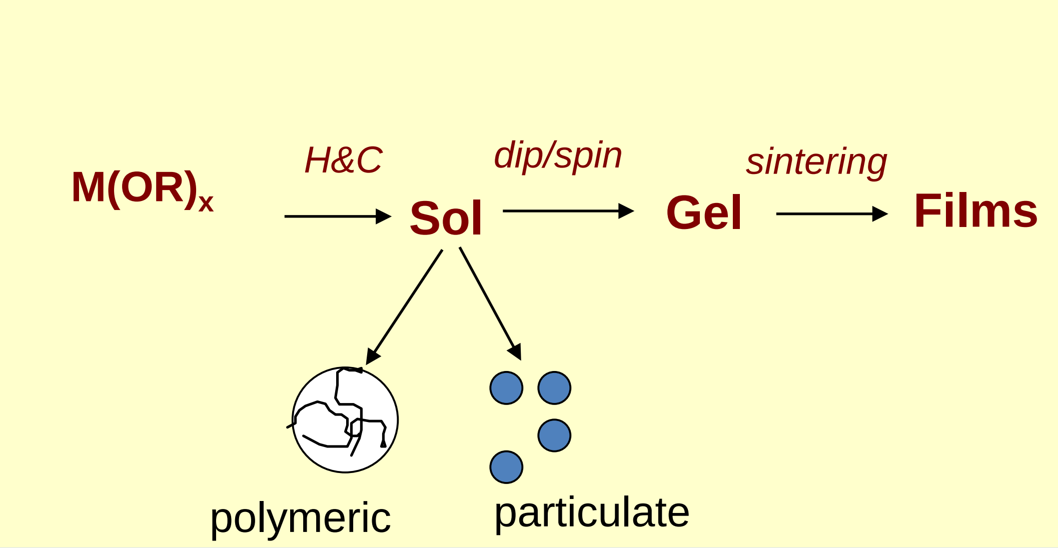
Sputtering





Spray pyrolysis





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Nano-ZnO

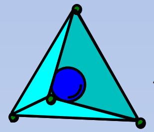
JACS 1991, 113, 2826

EtOH, 90°C

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

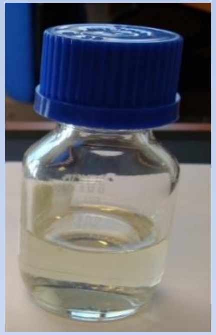
① *Nanoparticulate sol*

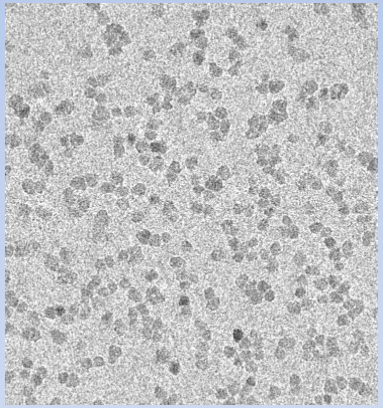
2.5 nm ≤ size ≤ 5 nm



$[Zn_4O](Ac)_6$

$LiOH \cdot H_2O$



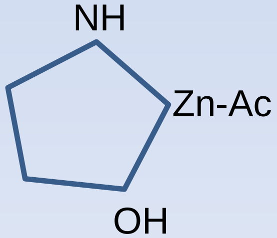


H_2O

② *Polymeric sol*

size ≤ 1 nm

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



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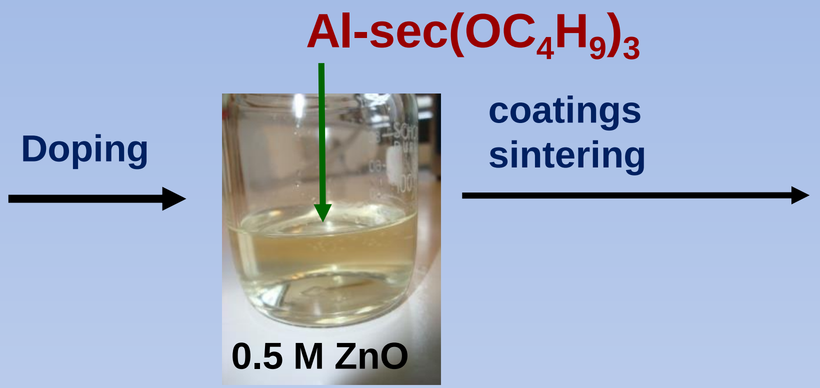
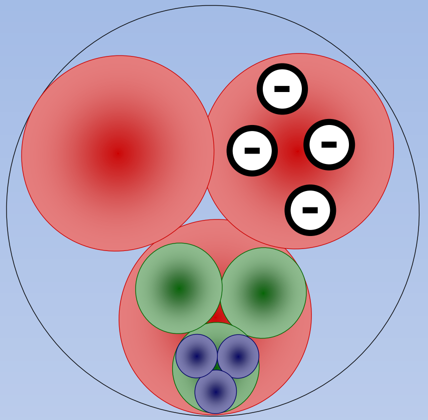
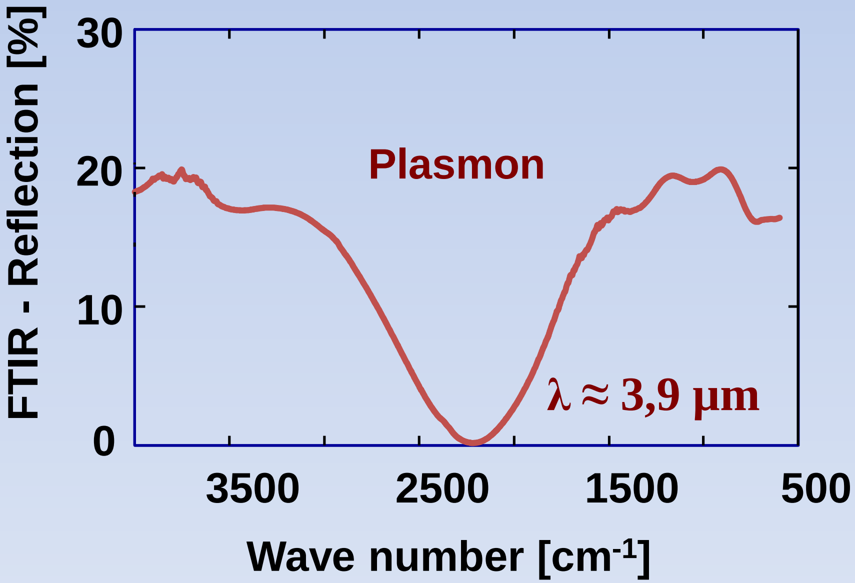
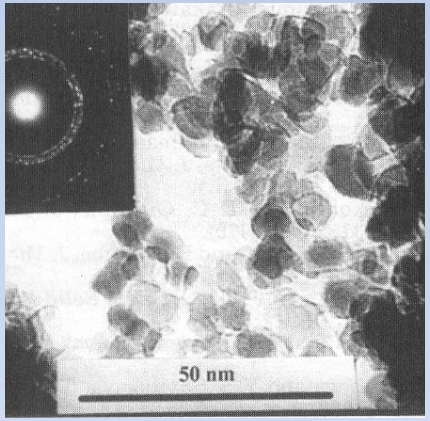
TCO based on ZnO/Al^{3+}





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





Do notýsku:

1. *Doped oxides behave like metal NP's (localized plasmon)*
2. *Nano- et mesoporous morphologies affect strongly the electron mobilities*

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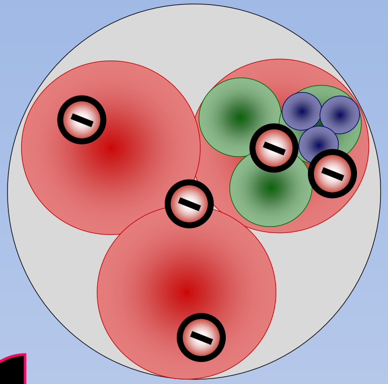
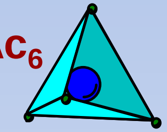
n_D ~ 1.7

μ = 0.001 cm^2/Vs



$(Zn_4O)Ac_6$

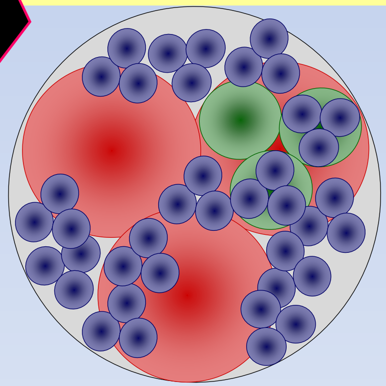


OH^-

Post-condensation:

1. **Pore filling**
2. **Elimination of O_2, H_2O**

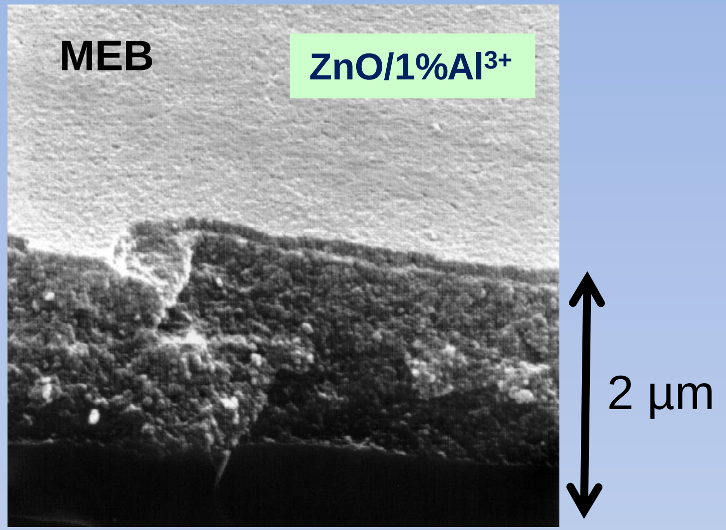
Creation of conducting chanels

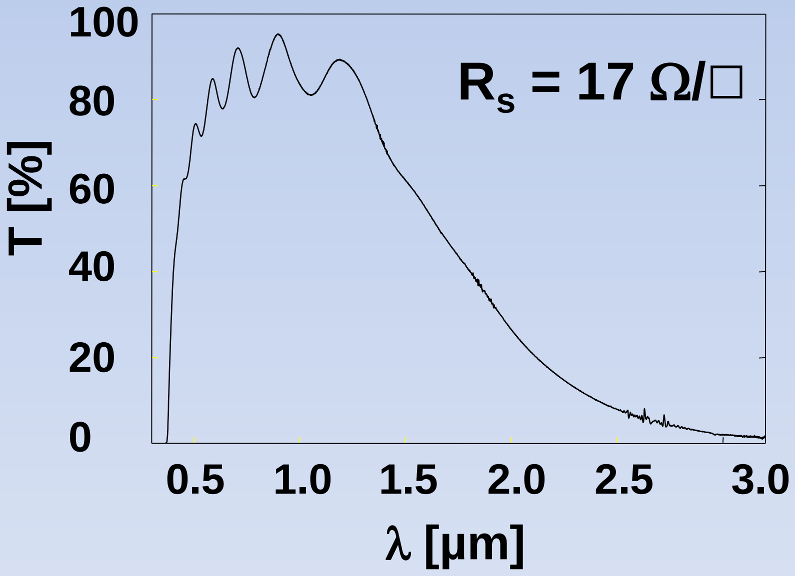


n_D ~ 2.1

μ = 9 cm^2/Vs

n_D = refractive index (ZnO bulk: = 2.1)





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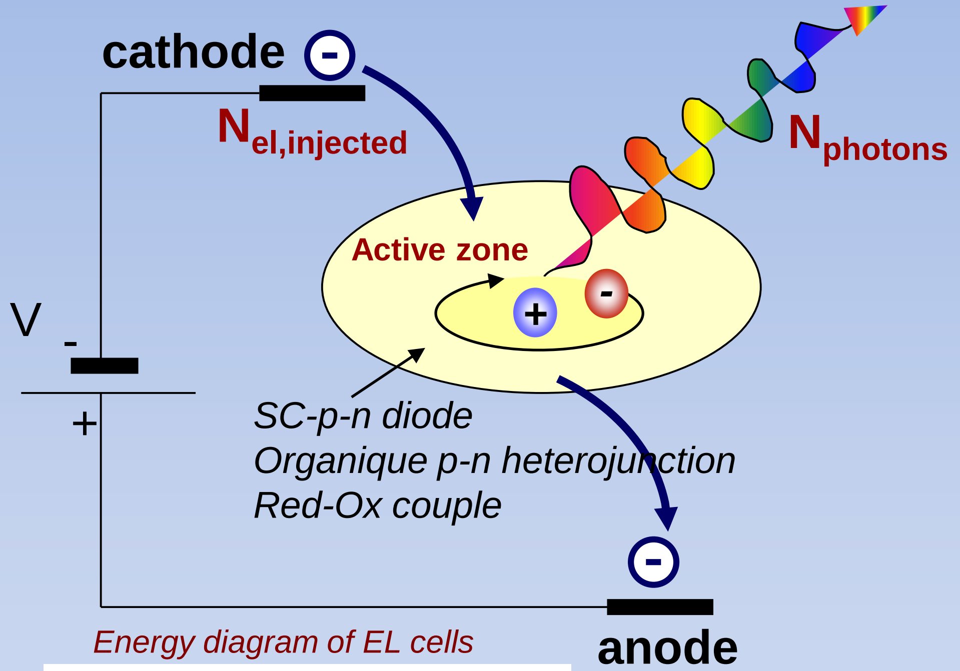
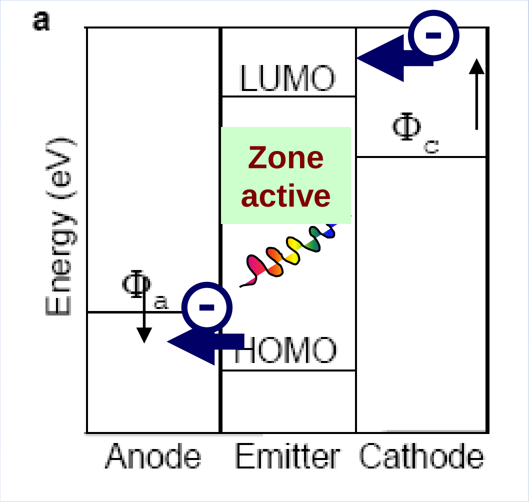
Electroluminescence



Energy diagram of EL cells



Electroluminescence yield

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

ou

$$\eta_{el} = 0,25\eta_{pl} \frac{W_r}{(1-W_r)+(j_{major}/j_{minor})}$$

Energy yield

$\eta_{energ} = \eta_{el}\, h\nu / eV$

⇓

Figure de mérite ~ ↑ $\eta_{pl} W_r / V$↓

η_{pl} = photoluminescence quantum yield
W_r = recombination probability (kinetics!)
V = applied electric voltage
e = elementary charge
$h\nu$ = photoenergy
j = current density

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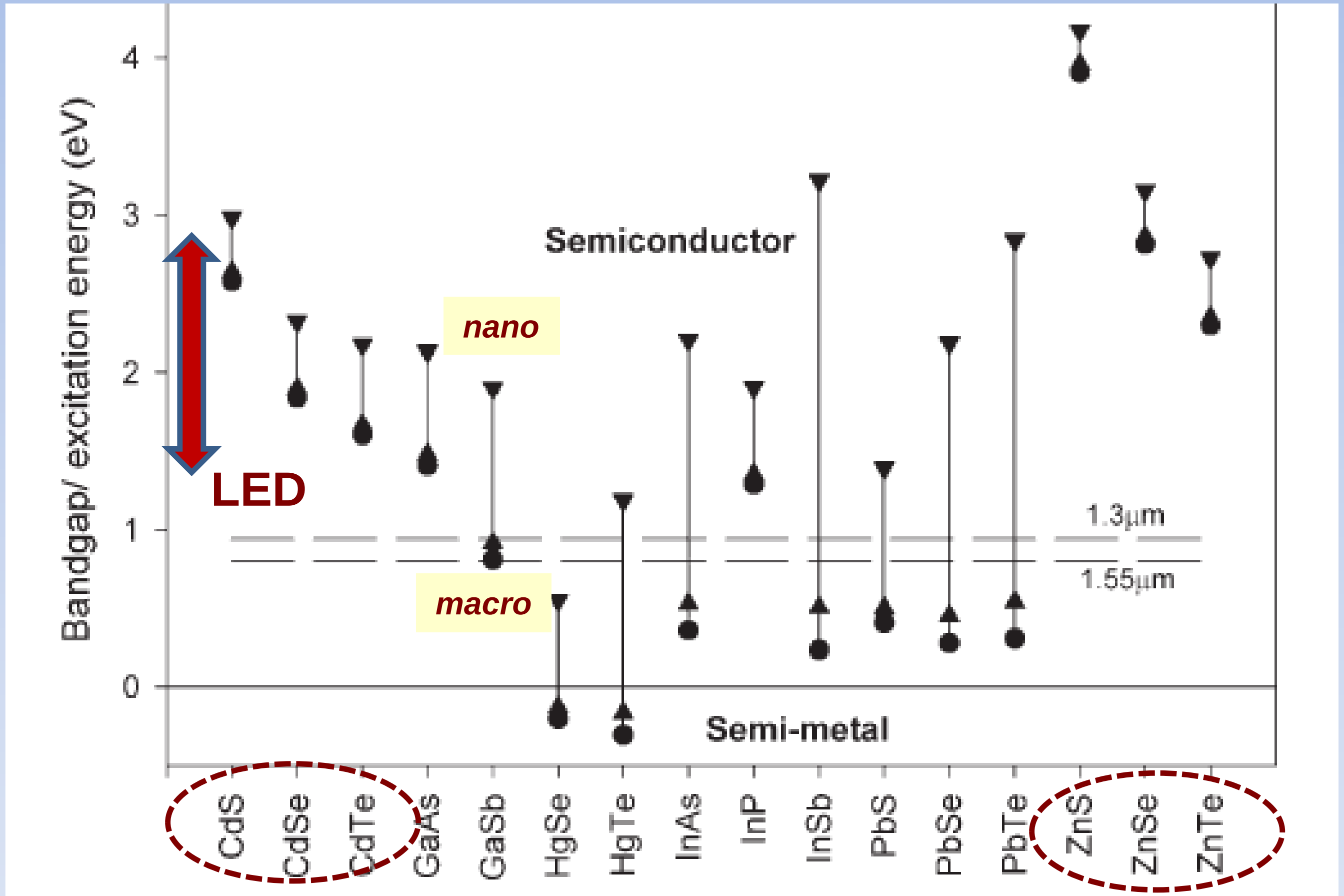
Strongly fluorescent SC nanostructures for Q-OLED's

« Band gap engineering »
Avarage size: 3 nm – 10 nm



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Calcul du diagramme de corrélation

gap optique (E en eV) vs. taille (diamètre en nm)

Approche mécanique-quantique pour NP-SC sphériques

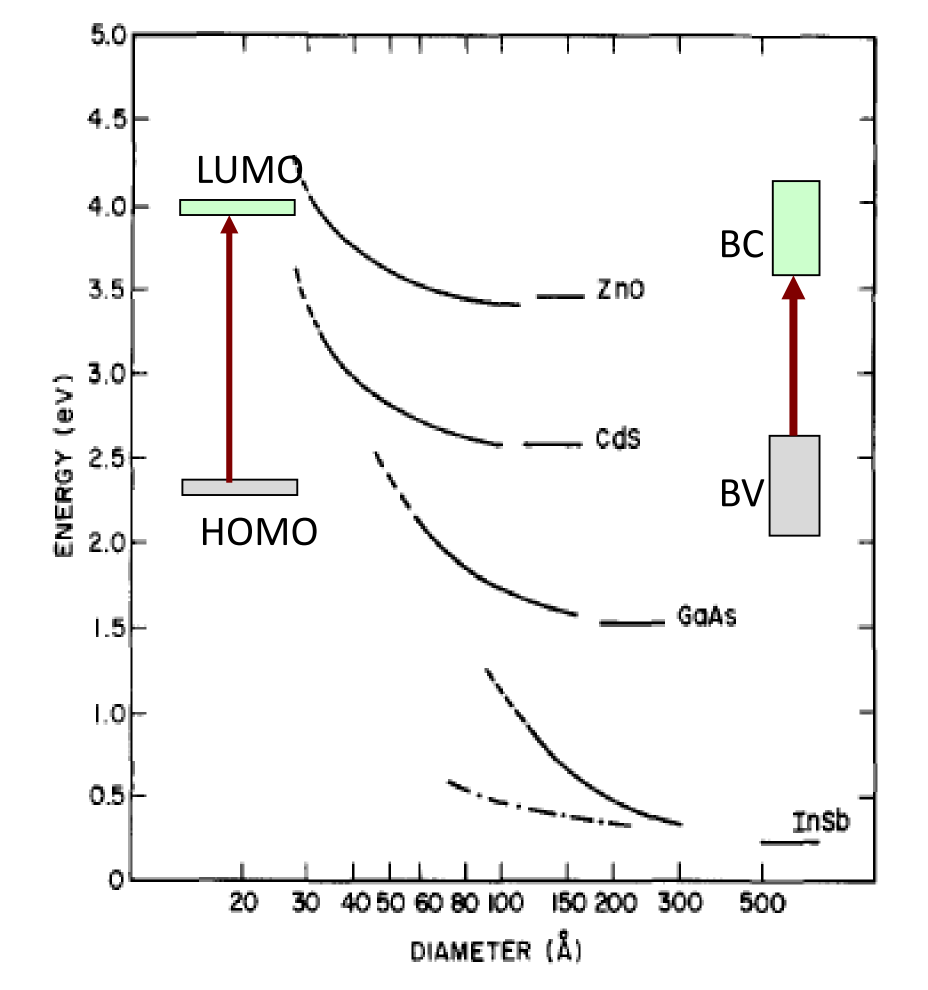
L. Brus

J. Chem, Phys. 80 (9), 1 May 1984

With the wave function Φ_0 the energy of the lowest excited state becomes

$$E \simeq \frac{\hbar^2\pi^2}{2R^2}\left[\frac{1}{m_e}+\frac{1}{m_h}\right]-\frac{1.8e^2}{\epsilon_2 R}+\frac{e^2}{R}\overline{\sum_{n=1}^{\infty}\alpha_n\left(\frac{S}{R}\right)^{2n}}, \quad (12)$$

$E_{cinétique}$ $E_{électrostat.}$ $E_{interface}$



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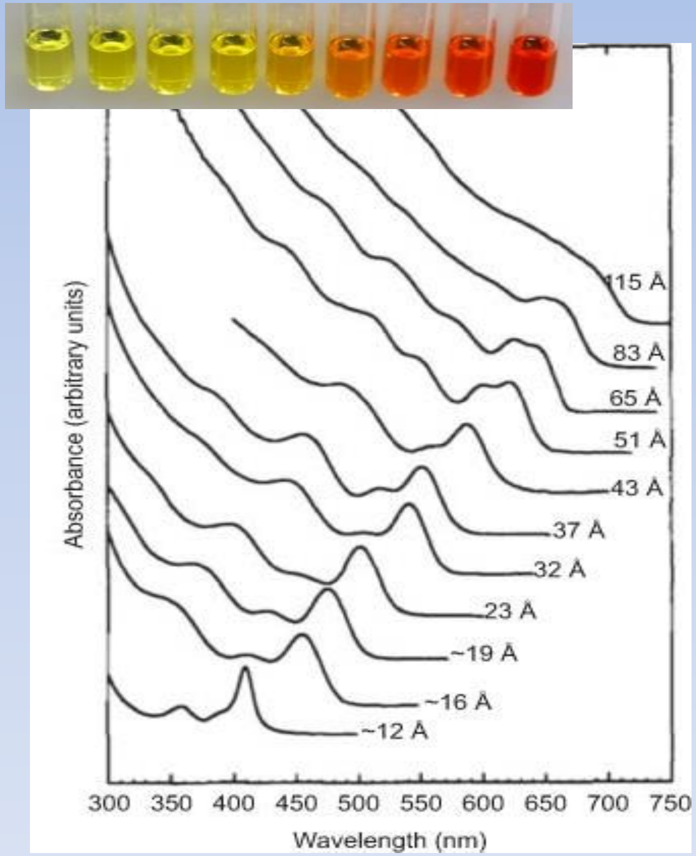
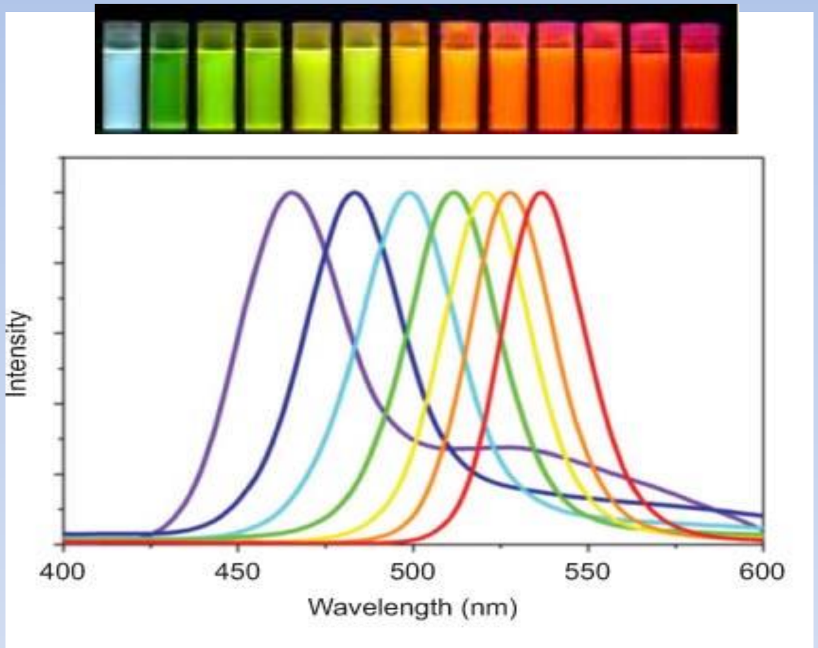
Etudes spectroscopiques UV-vis
Nanocolloïdes de CdSe

Observation à noter:

1. *taille↓ gap optique↑*
2. *Présence d'une bande d'absorption prononcée*
3. *Résonances multiples dans les spectres optiques*





Source
Gaponik N, et al, Small 2010;6:1364–78.
Talha Erdem and Hilmi Volkan Demir
DOI: https://doi.org/10.1515/nanoph-2012-0031

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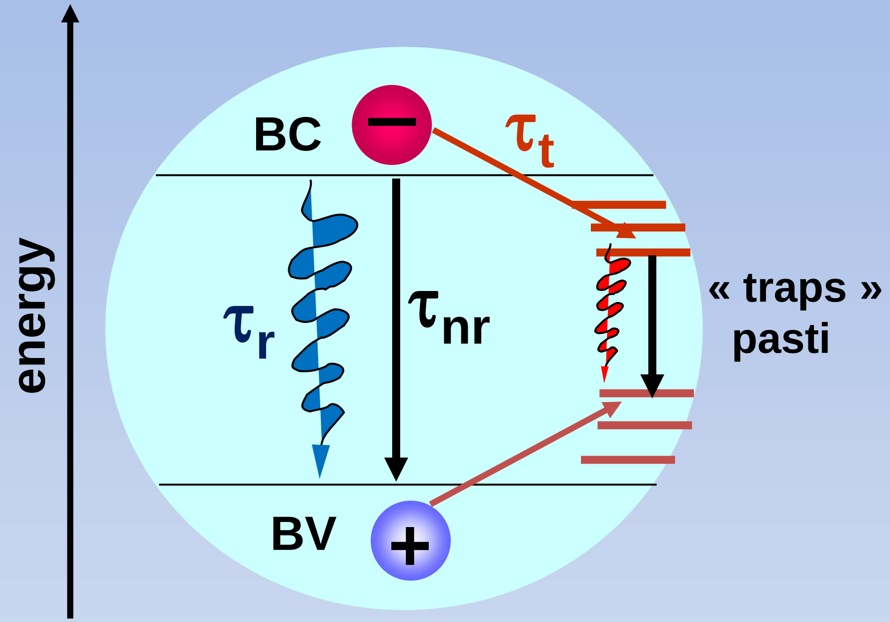
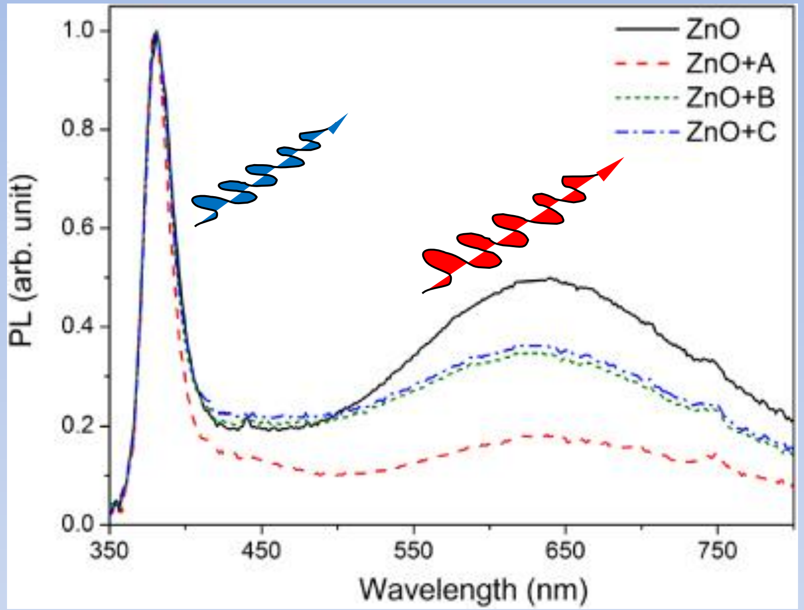
General remarks to luminescence





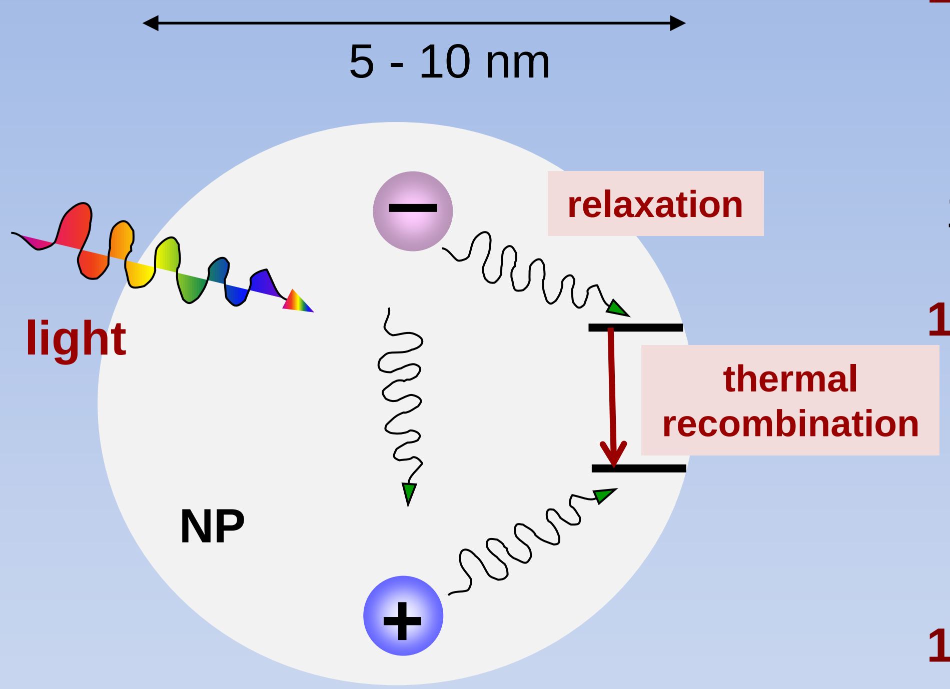
$$\tau_t \sim \tau_{nr} << \tau_r$$

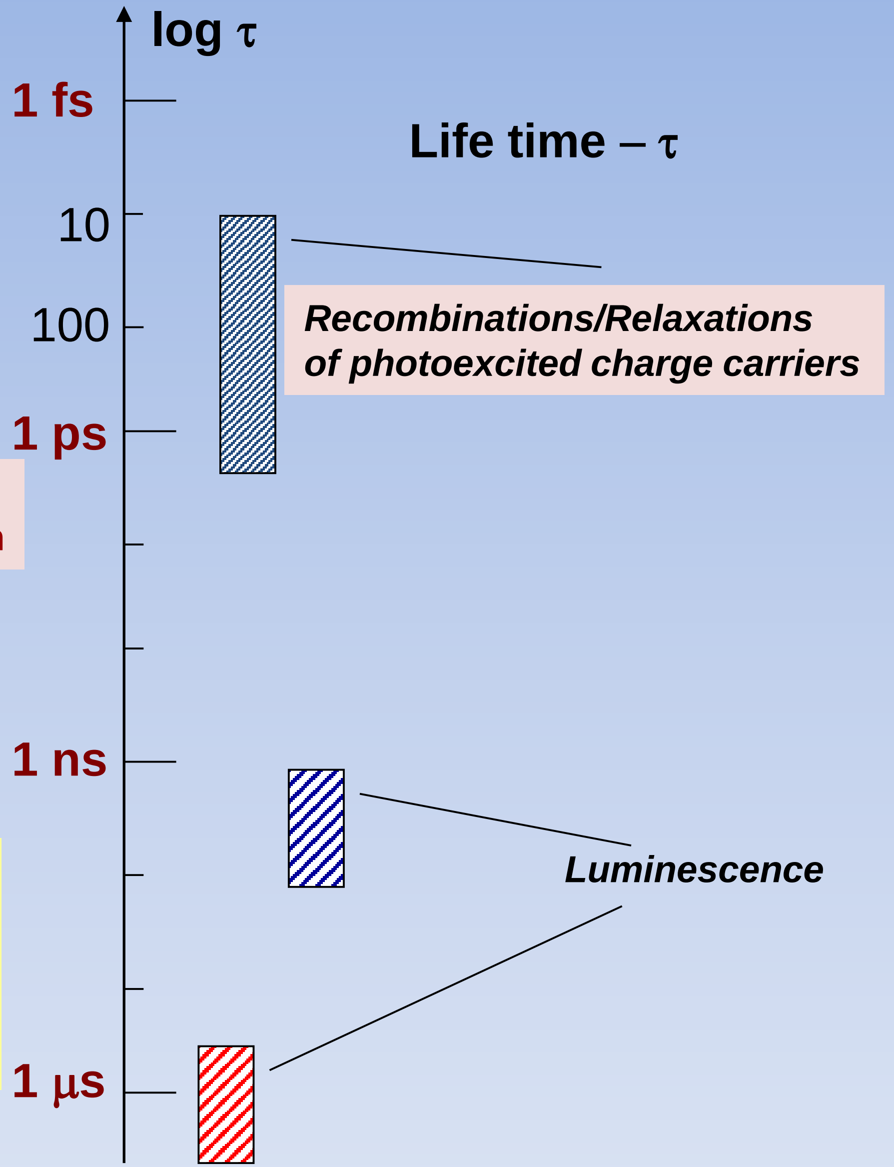
$\Phi < 0{,}1\%$

Quantum yield of luminescence Φ

$$\emptyset = \frac{photons\ émis}{photons\ absorbés}$$

Life time of charge carriers





Do notýsku:

Blocking of ultrarapid relaxation and recombination of electron/hole pairs is needed to activate luminescence

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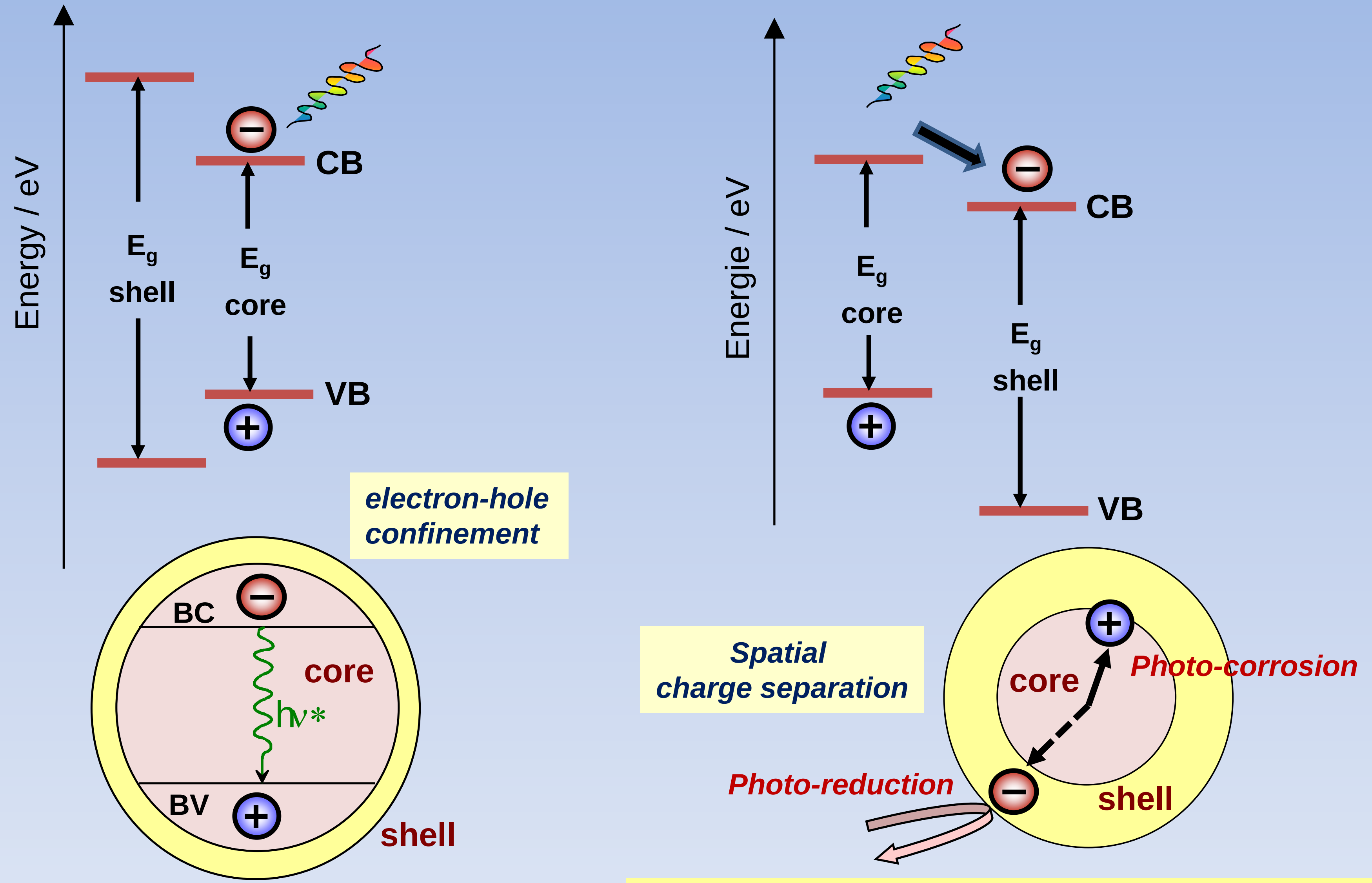
Thermodynamics of luminescence activation



Do notýsku:

1. ***Choice of SC to be coupled is important***
2. ***Chemical strategy of shell deposition is crucial***

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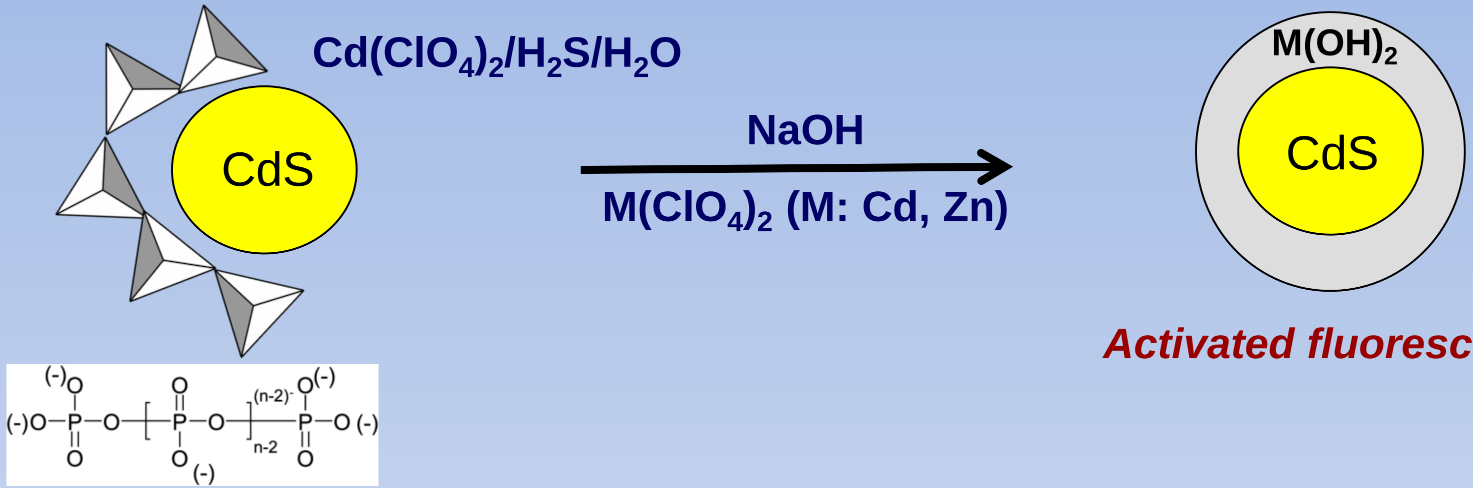
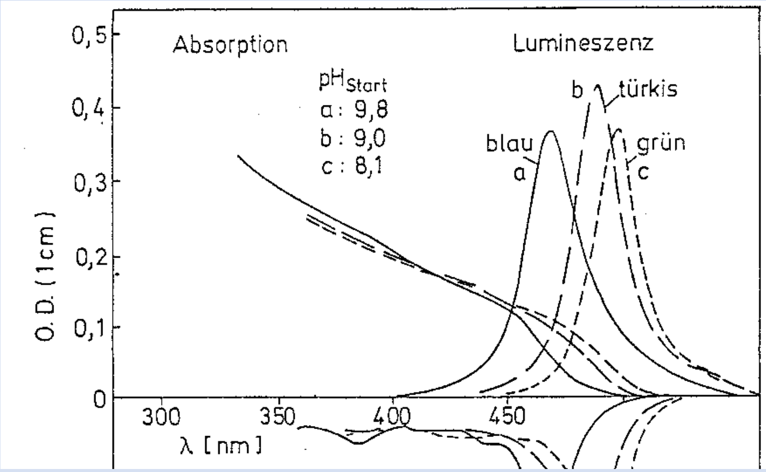
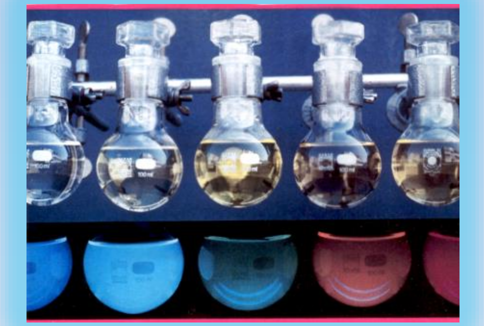
Nanocomposites “Core-Shell” CdS-$M(OH)_2$



Activated fluorescence (QY = 50%)





JACS 1987

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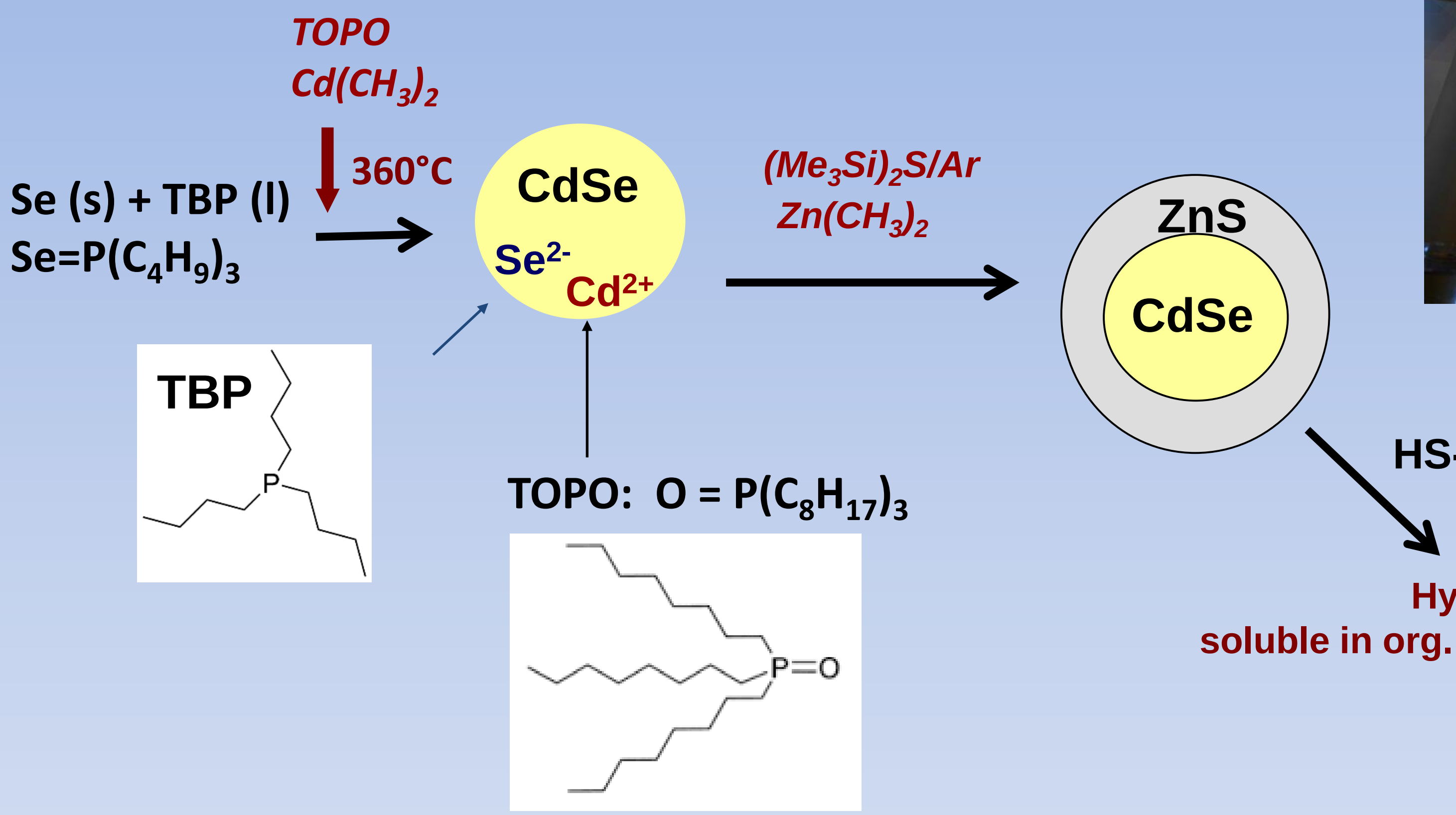
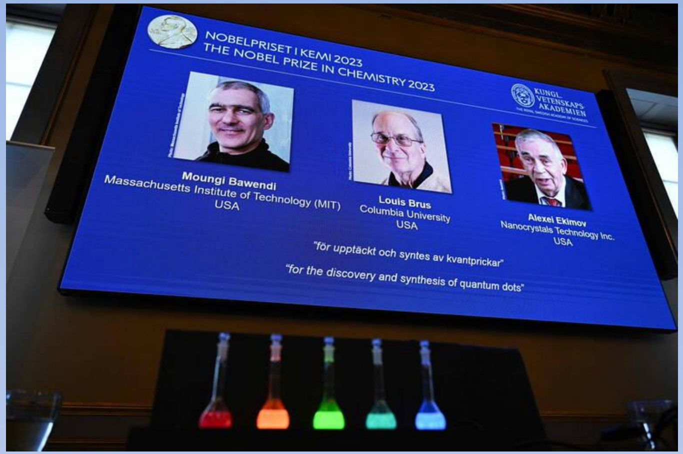
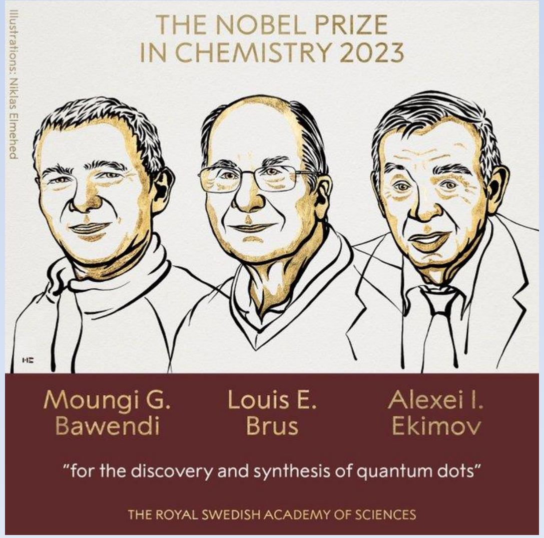
Core-shell activated luminescence

Bawendi et al, MIT; Alivisatos et al, Berkley



Hydrophobic,
soluble in org. solvents like toluene !!





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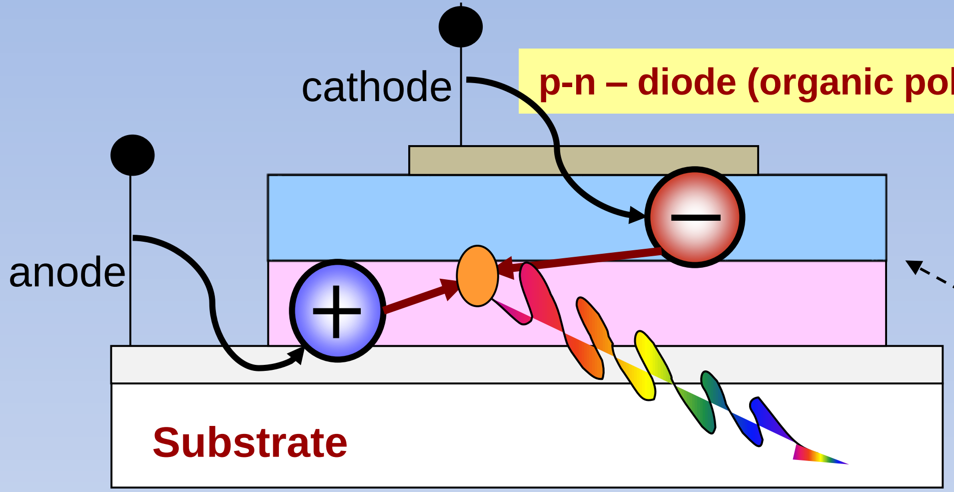
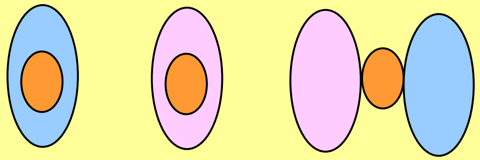
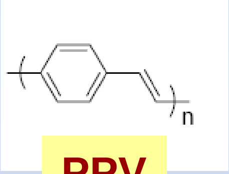
Design of EL components for intersectorial applications



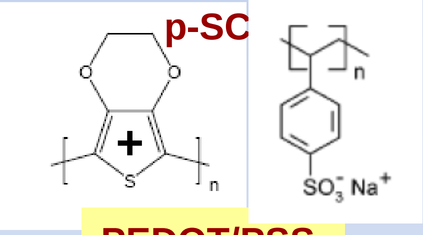
nanocomposites



Nanoparticles acting either as an antenna or as luminophore



PPV



PEDOT/PSS

PEDOT = poly-(3,4-ethylenedioxythiophene)
PSS = poly(styrene sulfonate)
PPV = poly(p- phenylene vinylene)

Luminophores and conductors p or n

Do notýsku:

1. Hybrid cells are useful for both, solar panels or electroluminescent displays
2. Most crucial is to control and to vectorize the transport of charge carriers

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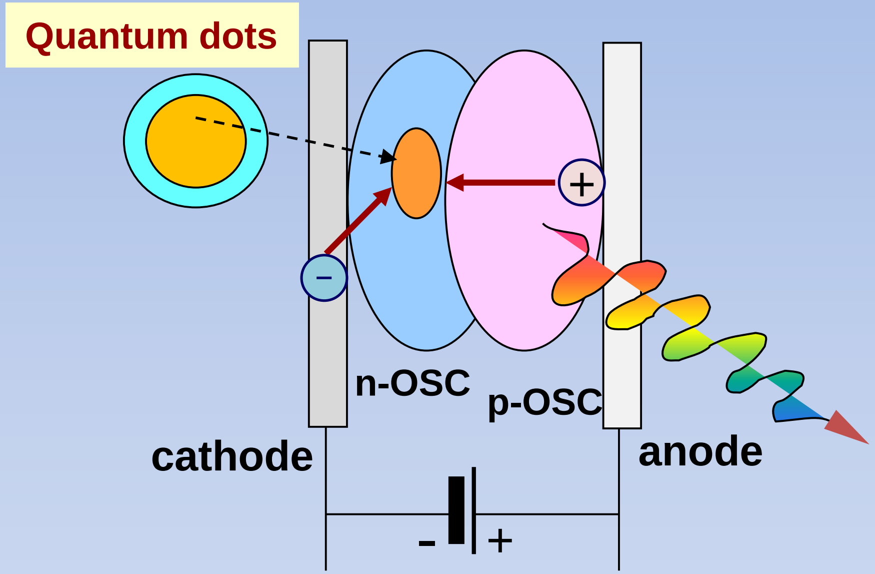
« Q-OLED »



OSC = organic semiconductors

PEDOT = poly-(3,4-ethylenedioxythiophene)
PSS = poly(styrene sulfonate)
PPV = poly(p- phenylene vinylene)

Source: QD Vision Texas

Source: SAMSUNG

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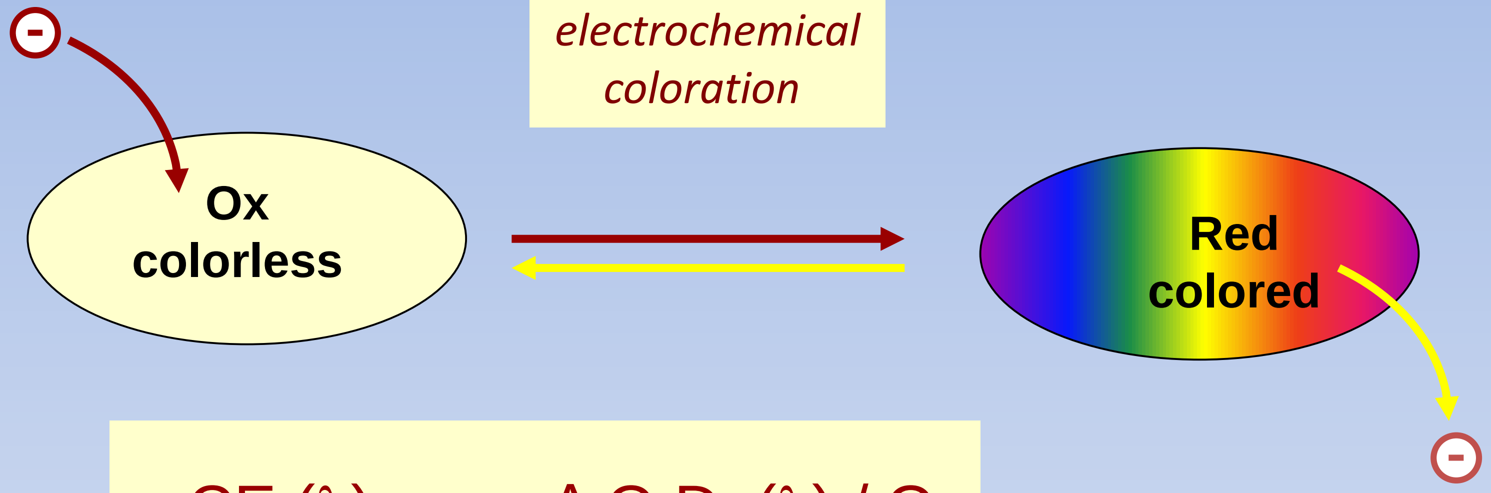
Electrochromic effect

Reversible electrochemical coloration



$$CE(\lambda) = \eta = \Delta\, O.D.(\lambda) / Q$$

η = CE = conversion efficiency
O.D. = optical density
Q = charge carriers involved (C/cm^2)

Cathodic coloration :

WO_3, MoO_3, V_2O_5, Nb_2O_5, TiO_2, Cu_2O

blue

$WO_3 + ne^- + n\,M^+ \leftrightarrow M_nWO_3$

W^{6+}-O^{2-}-W^{6+} $\qquad$ W^{6+}-O^{2-}-H^+(W^{5+})

Yellow to blue

Anodic coloration :

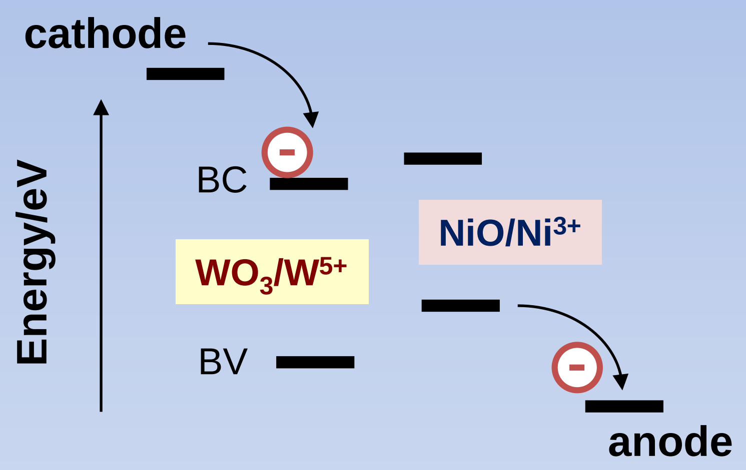
NiO, CoO, Cu_2O, IrO_2

coloré

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

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

Pale green to brown



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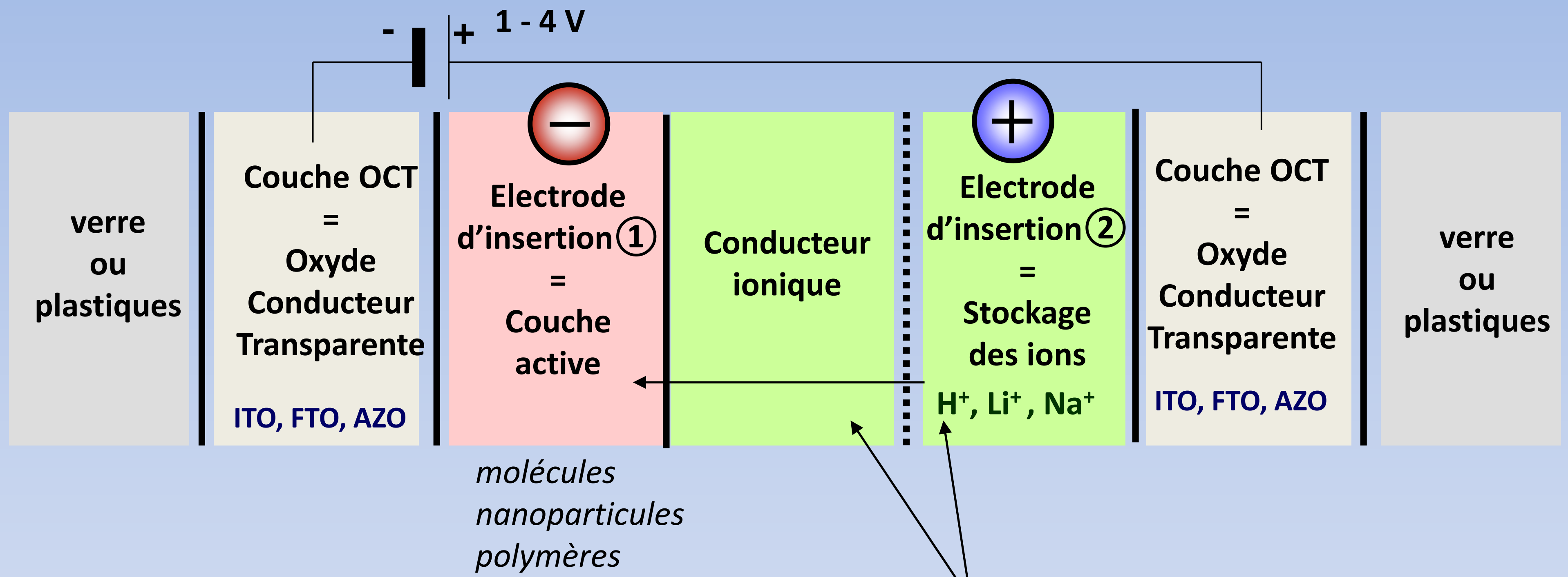
Cellules multicouches électro-chromiques



Paramètres critiques:

Maîtrise de la conductivité électronique and ionique
Durée de vie: 10^4 – 10^5 cycles (5-20 ans)
Dynamique de la coloration/décoloration – ms, sec, min)
Température : entre - 50°C et + 100°C
Transparence optique des multicouches minces

Conducteurs ioniques:

Gels, membranes (organo)céramiques
- ZrO_2, Ta_2O_5
- Hybrids organominéraux
- polyelectrolytes: PEO, PVA

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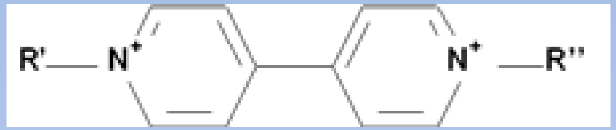
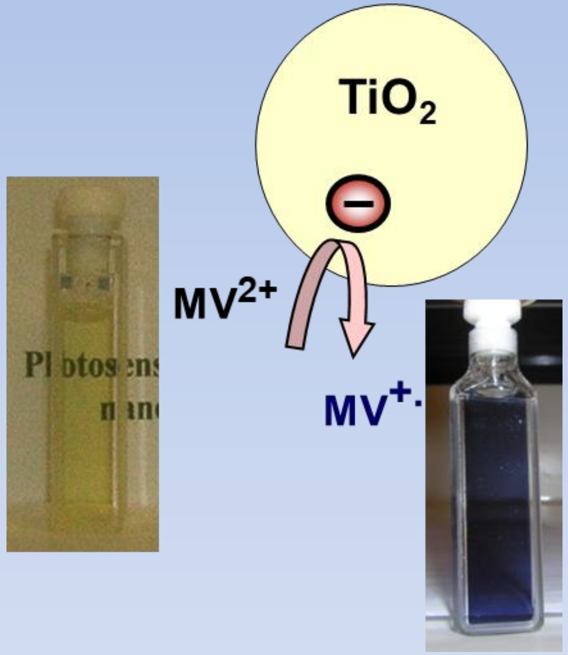
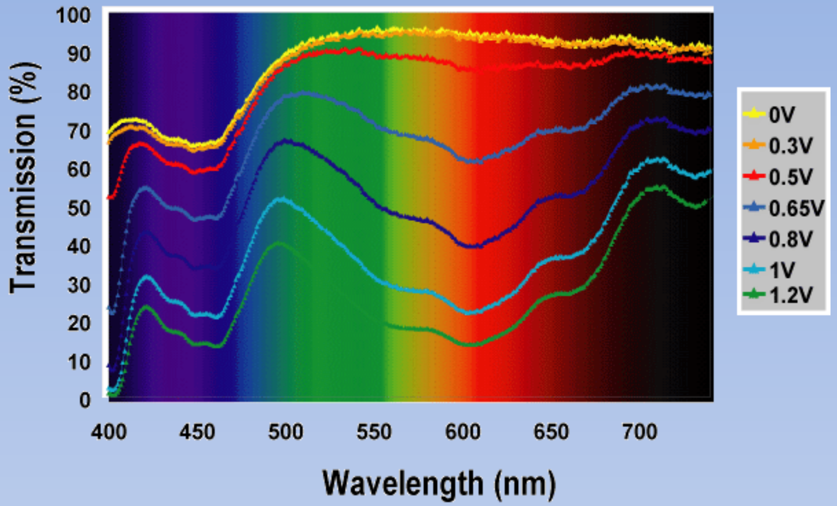
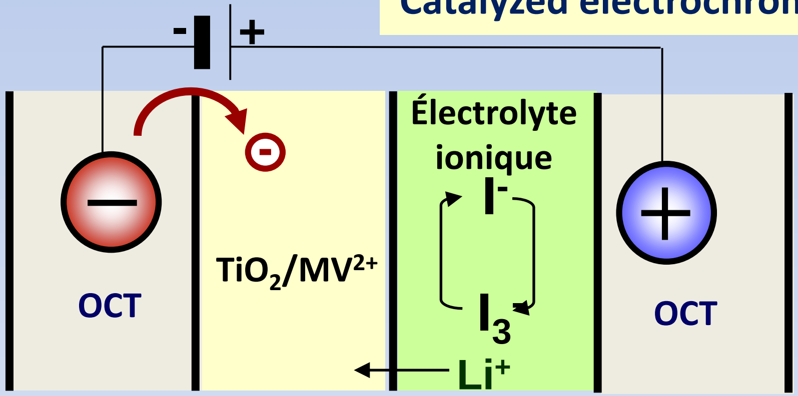
Alkyl viologenes grafted on TiO_2 NPs







Catalyzed electrochromy



TiO_2/MV^{2+} + LiI

décoloré

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

coloré

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Synthesis approaches and electrochromic decorations

1. *rf-sputtering*
2. *CVD (organo-compounds 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 etc…

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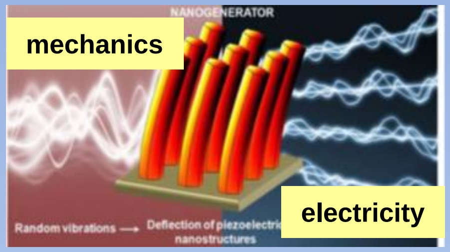
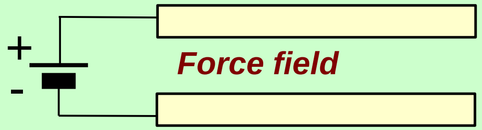
Piezoelectric Nanostructures (PEN)





Electromechanically triggered PEN

Physical key parameters

$$P_i = d_{ijk}\,\sigma_{jk}$$
$$d_{33} \sim \varepsilon_r D_p \uparrow$$

s = strain (N/m^2)
$\mathbf{d_{33}}$ = piezoelectric coefficient (C/N ou pm/V)
$\mathbf{P_i}$ = induced electric polarisation (C/m^2)
ε_r = dielectric permittivity
D_p = nanoparticle size

Structural key parameters

- *anisotropy*
- *size, shape and orientation of nanostructures*

Classification

Perowskites (cubic anisotropic class)
$Pb(ZrTi)O_3$ (PZT), $BaTiO_3$ (BT)

Wurtzite (hexagonal anisotropic class):
ZnO, GaN, AlN, Hydroxyapatite

Piezopolymers (synthtic and nartural)
Poly-vinylidene-fluoride (PVDF)
poly(l-lactic acid) (PLLA)
Kollagen, Keratin, muscles, etc.
Nanocomposites :
(tubes, spirales, plates, etc.)

Applications:

1. **Piezovoltaics, piezotronics**
2. **Biomedicine (théranostique, tissue regeneration, etc..)**
3. **Telecommunication (sonar, smartphone speakers etc.)**

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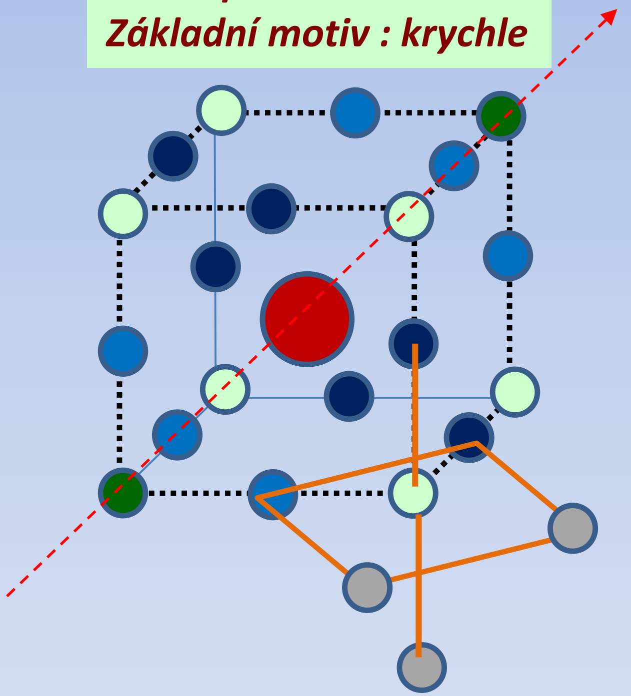
Struktura Perowskitů
ABO_3

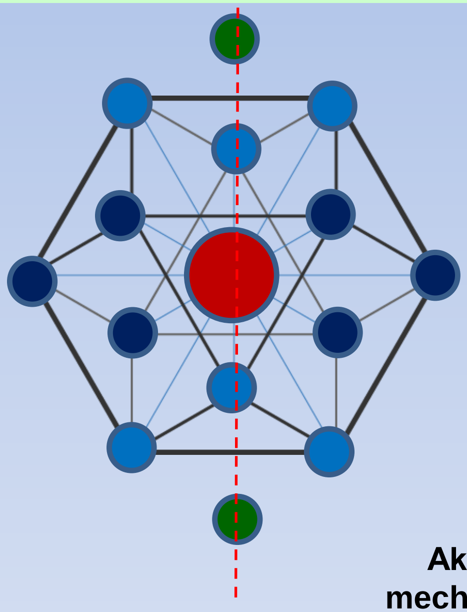
A : Na, K(I); Ca, Sr, Ba, Pb(II); La, Y(III)
B : Nb (V); Ti, Zr, Sn(IV);
O^{2-} = kyslík

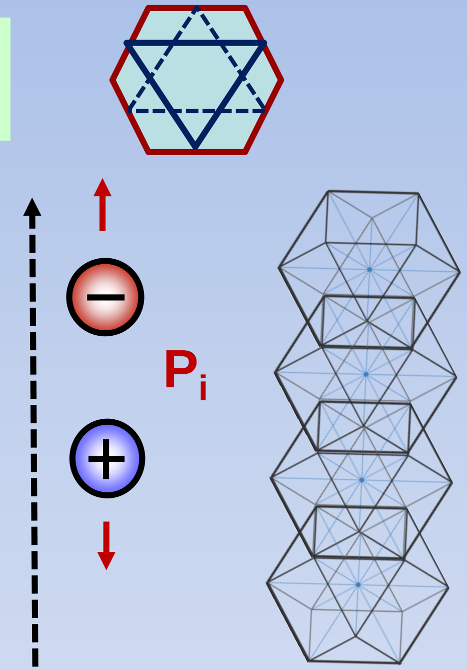
KČ (A) = 12 O
= 8 B
KČ (B) = 6 O

Běžná prezentace
Základní motiv : krychle



Staronová Fullerova prezentace
Kuboktaedr





Akční osa mechanické síly
σ

Do notýsku:

1. *Faktor tolerance – t určuje aktivitu PE:*
   $t \sim (R_O + R_A)/(R_O + R_B)$
   t = 1, ideální kubická isotropie, PE je neaktivní
   t < 1, anisotropie, předpoklad PE aktivity
2. *Kontribuce iontových a kiovalentních vazeb kontroluje směr PE*

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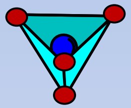
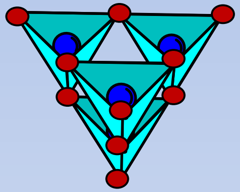
Wurtzite and Zincblende

« AB »
cations: Zn, Cd, Pb, Hg, Al, Ga, B
anions : O, S, Se, Te, N; etc

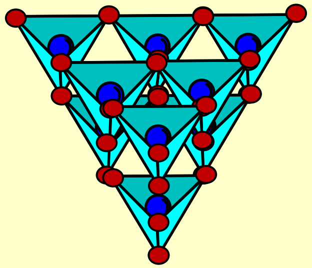


Building stone
AB_4 ou A_4B

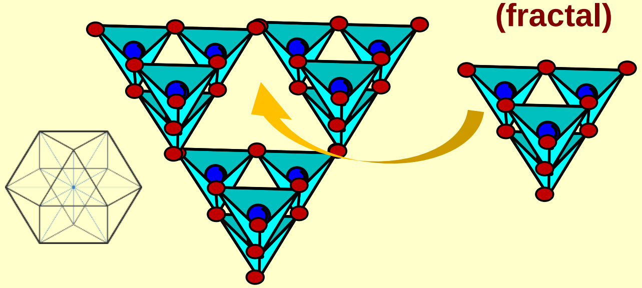
Octahedral cage



Cubic network (Euclidien)

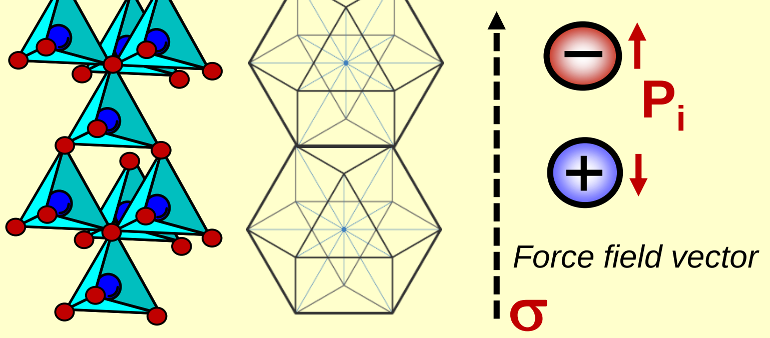


Cubic network (fractal)



Cuboctahedral cavity (cage)

Hexagonal anisotropy



To note:
Hexagonal nanostructures are PE actif
Growth along the c-axis (002)
Fractality is the origin of PE

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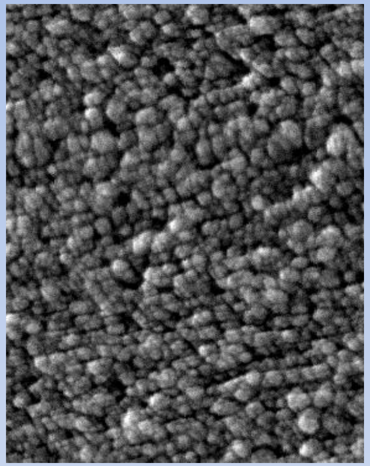
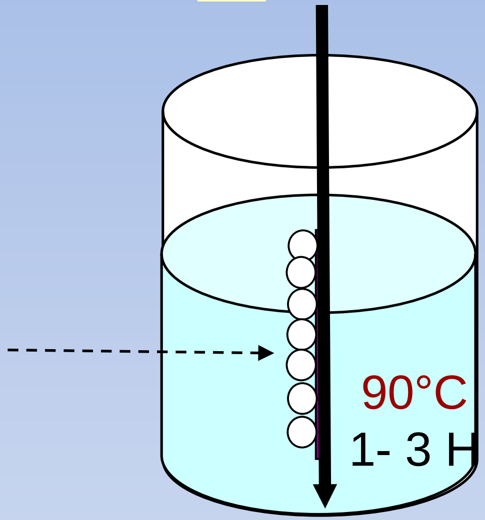
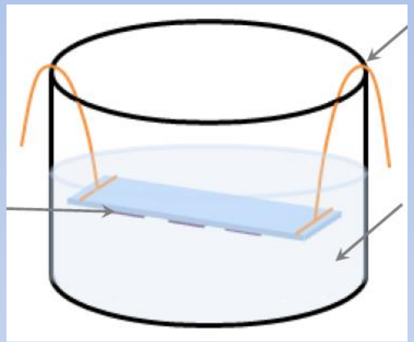
Synthesis of ZnO nanorods in water

1 *Seed layer via Sputtering or Sol-Gel*

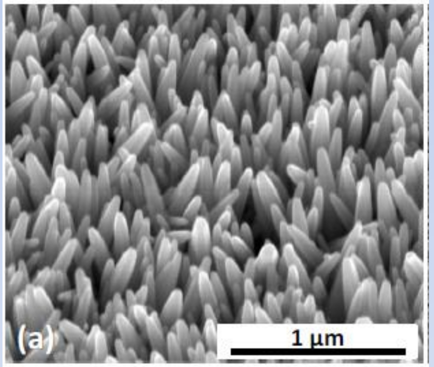


2 *Dip*





$Zn(NO_3)_2$ / $R\text{-}NH_2$ / H_2O



$$Zn^{2+} + 4OH^- = [Zn(OH)_4]^{2-}$$

$$Zn[(OH)_4]^{2-} = ZnO + H_2O + 2OH^-$$

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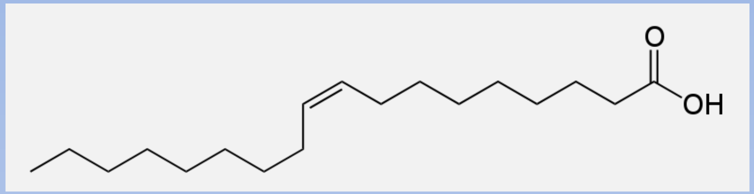
ZnO nanorods in hexane

$Zn(Ac)_2 \cdot 2(H_2O)$

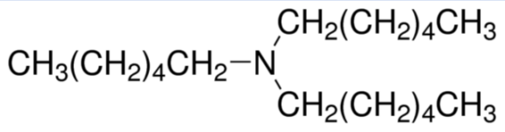


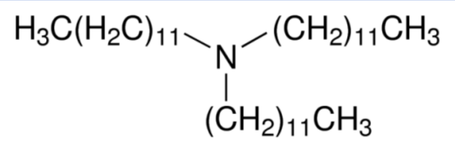
Ligand: kyselina olejová, C18, b.p. 360°C
Solvent: trihexylamin, C6, b.p. 270°C
tridodecylamin, C12, b.p. 300°C

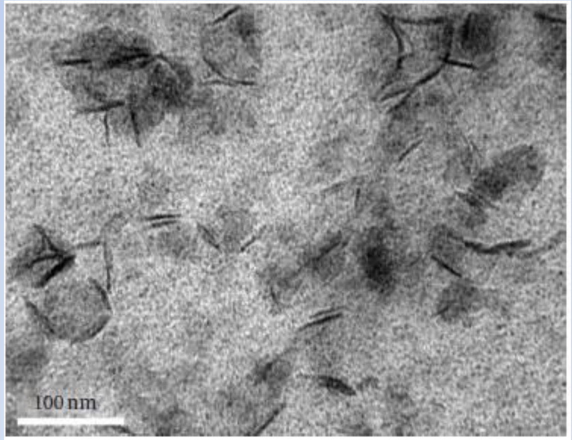
280°C
Argon

Tvorba a srážení
Ultracentrifugace

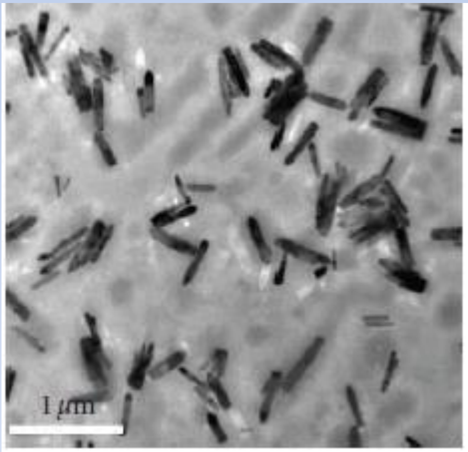
Do roztoku hexanu







tlouštka: ~ 3 nm



~ 60 nm

Group d'O'Brien
Journal of Nanomaterials
Volume 2007, Article ID 73824,
doi:10.1155/2007/73824

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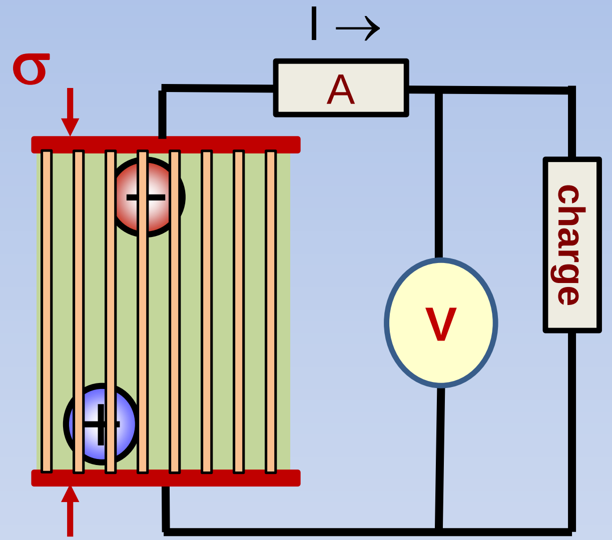
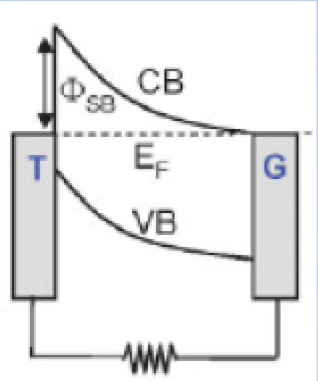
Exemple of piezoelectric nanogenerator

Vertical or horizontal alignment inside of insulating polymeric matrix

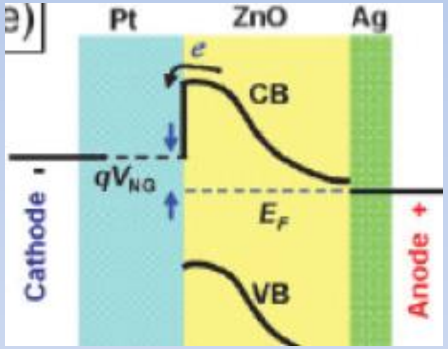


electrodes

Conventional energy diagram of a Schottky junction



Ground state



Applied force field with el. charge flow

Measured parameters:
V_{oc}-tension (till 1 V)
I_{sc}-current (till 2 mA/cm^2)
Electricity output ~0.4 mW/cm^2

Réf.: Pr. Wang
Georgia Tec 2006

Control question:
How the energy diagram of a Schottky nano-junction would look like?

Revision, questions:

0. Understanding the differences in energy diagrams of macro versus nano
1. Knowledge of crucial phys. parameters governing the performance of TCO electrodes
2. Strategy of controlling mobility and concentration of free electrons
3. Address the key physical parameters controlling the efficiency of piezoelectricity
4. Explain principle functioning (structure related rules) as well as the energy diagram of piezoelectric nanogenerator
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. Describe the component design and chemical composition of catodic and anodic electrochromy device

Jaro 2024
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*
- *Elektro/fotoluminescenčí systémy*
- *Elektrochromie*
- *Nanovaristory*
- *Piezoelektrické nanogenerátory*

3. TiO_2 v solárním nanosektoru

- *Úvod do solární technologie*
- *Fotokatalytické systémy*
- *Nanofotovoltaika*

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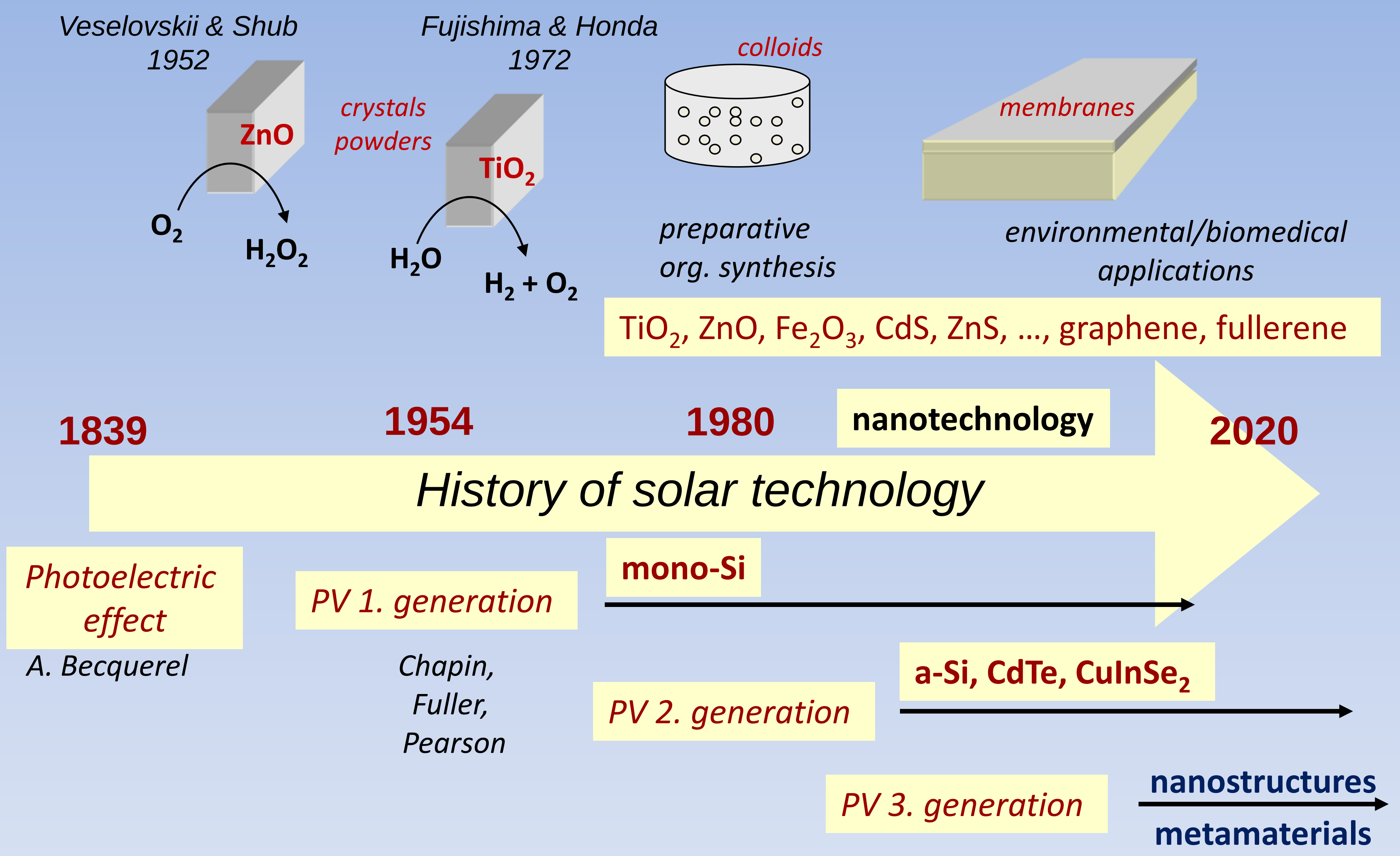
Veselovskii & Shub
1952
ZnO
O_2
H_2O_2
crystals
powders
Fujishima & Honda
1972
TiO_2
H_2O
$H_2 + O_2$
colloids
preparative
org. synthesis
membranes
environmental/biomedical
applications
TiO_2, ZnO, Fe_2O_3, CdS, ZnS, …, graphene, fullerene
1839
1954
1980
nanotechnology
2020
History of solar technology
Photoelectric
effect
A. Becquerel
PV 1. generation
Chapin,
Fuller,
Pearson
mono-Si
PV 2. generation
a-Si, CdTe, $CuInSe_2$
PV 3. generation
nanostructures
metamaterials

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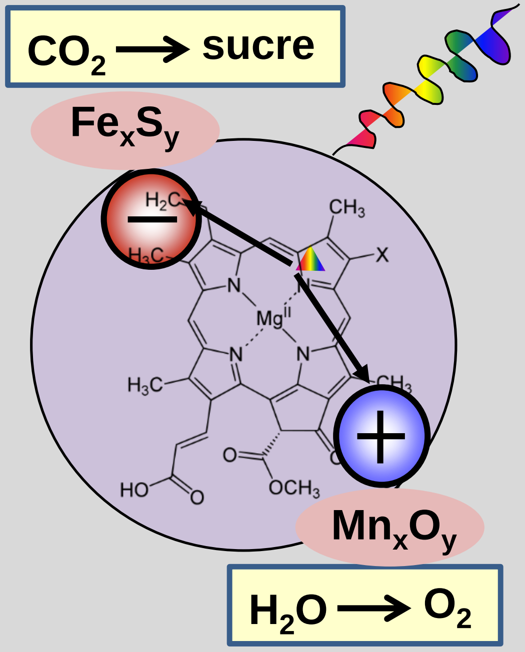
Solar energy harvesting

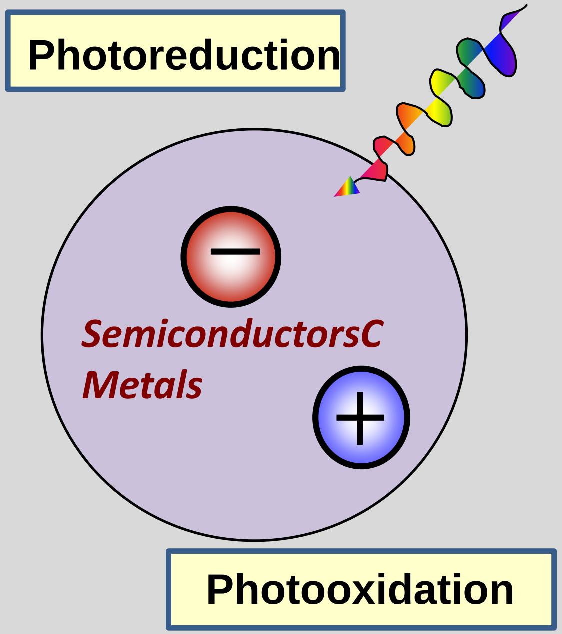
Sun induced charge creation in Nature, laboratories and some future visions

Photosynthesis (~2%)

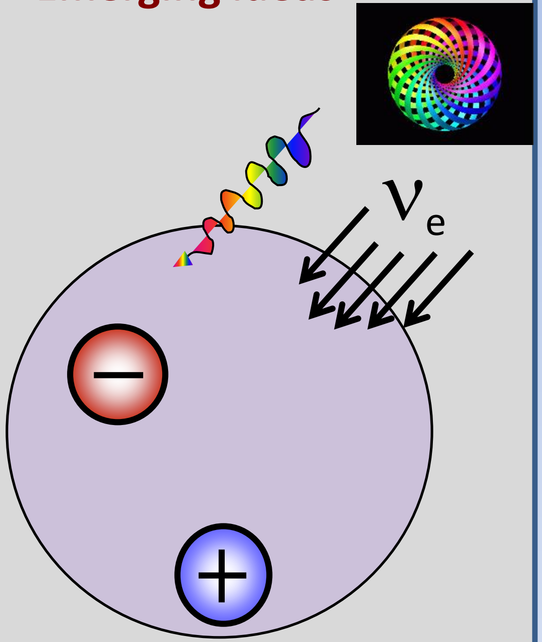


10^{17} photons/cm^2 sec !

Photocatalysis (~ 80%)



Neutrinolysis
Emerging ideas



10^{11} neutrinos/cm^2 sec !

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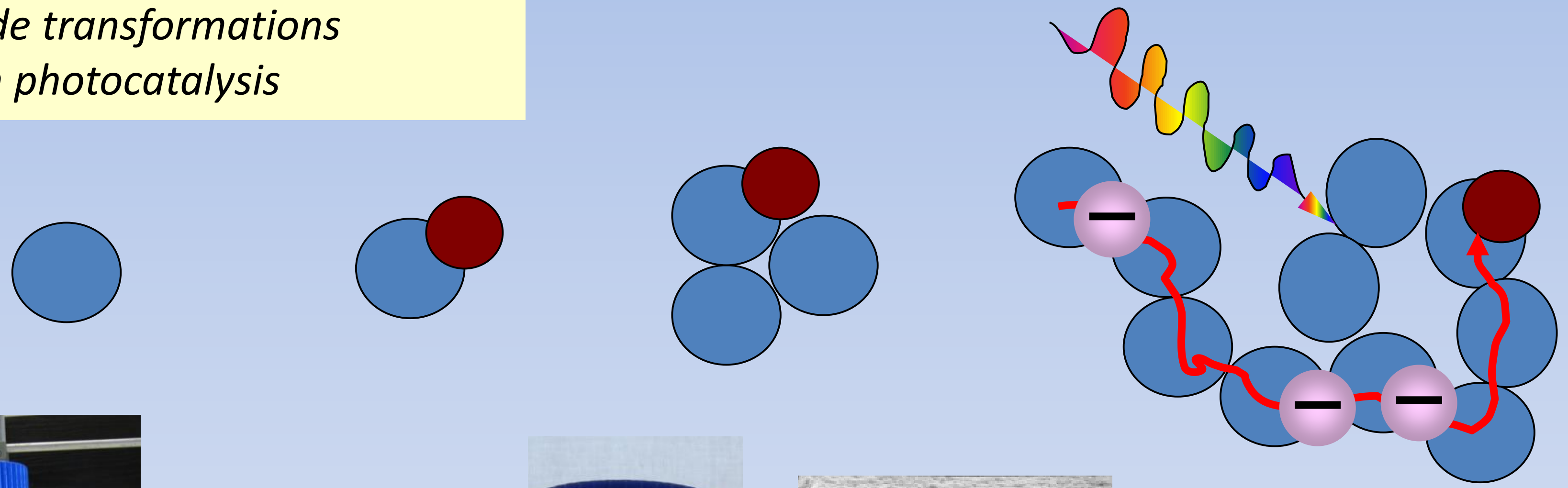
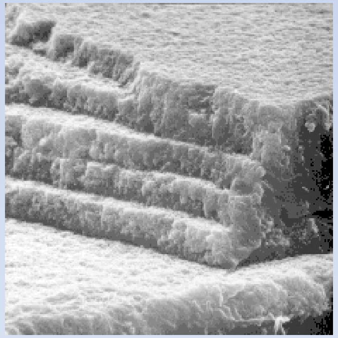
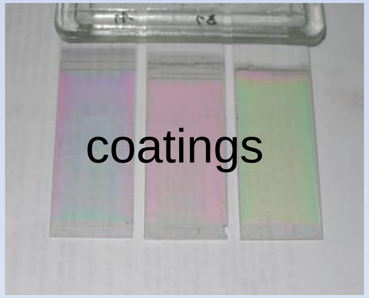
Photocatalysis applications

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**

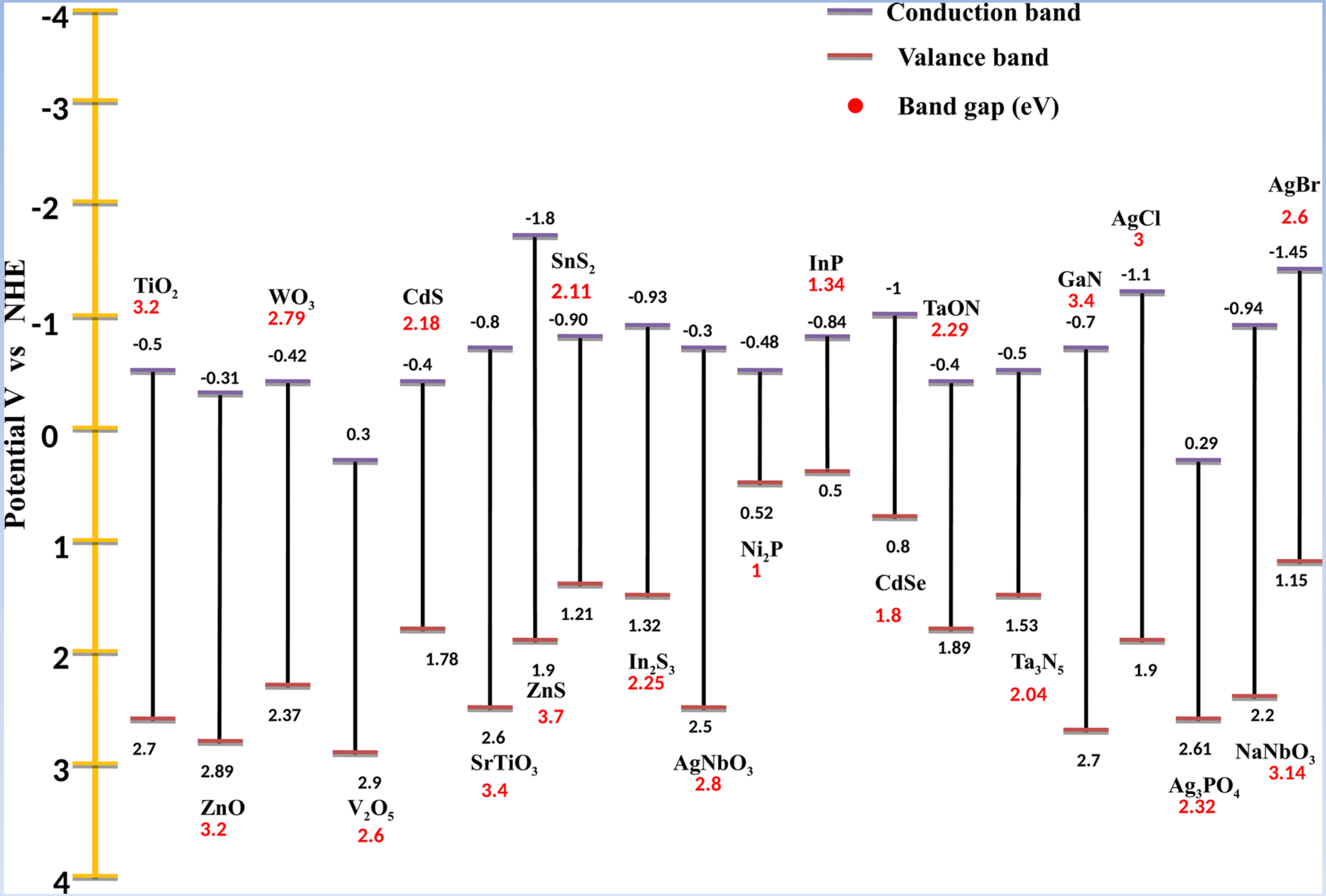
heterostructures, dopings and surface modifications

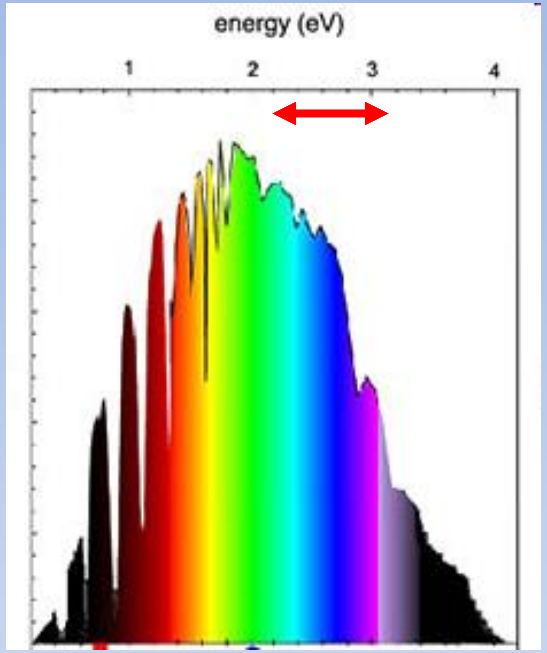
► **morphology of immobilized nanostructures**

particle shapes, aggregate architectures and mesoporosity

►**integration into photoreactor prototypes on various scales**

nanocolloids, powders, thin coatings, photoreactor design





Note:
Photo-corrosion problems limit the materials choice (AgX, CdS, Fe_2O_3)

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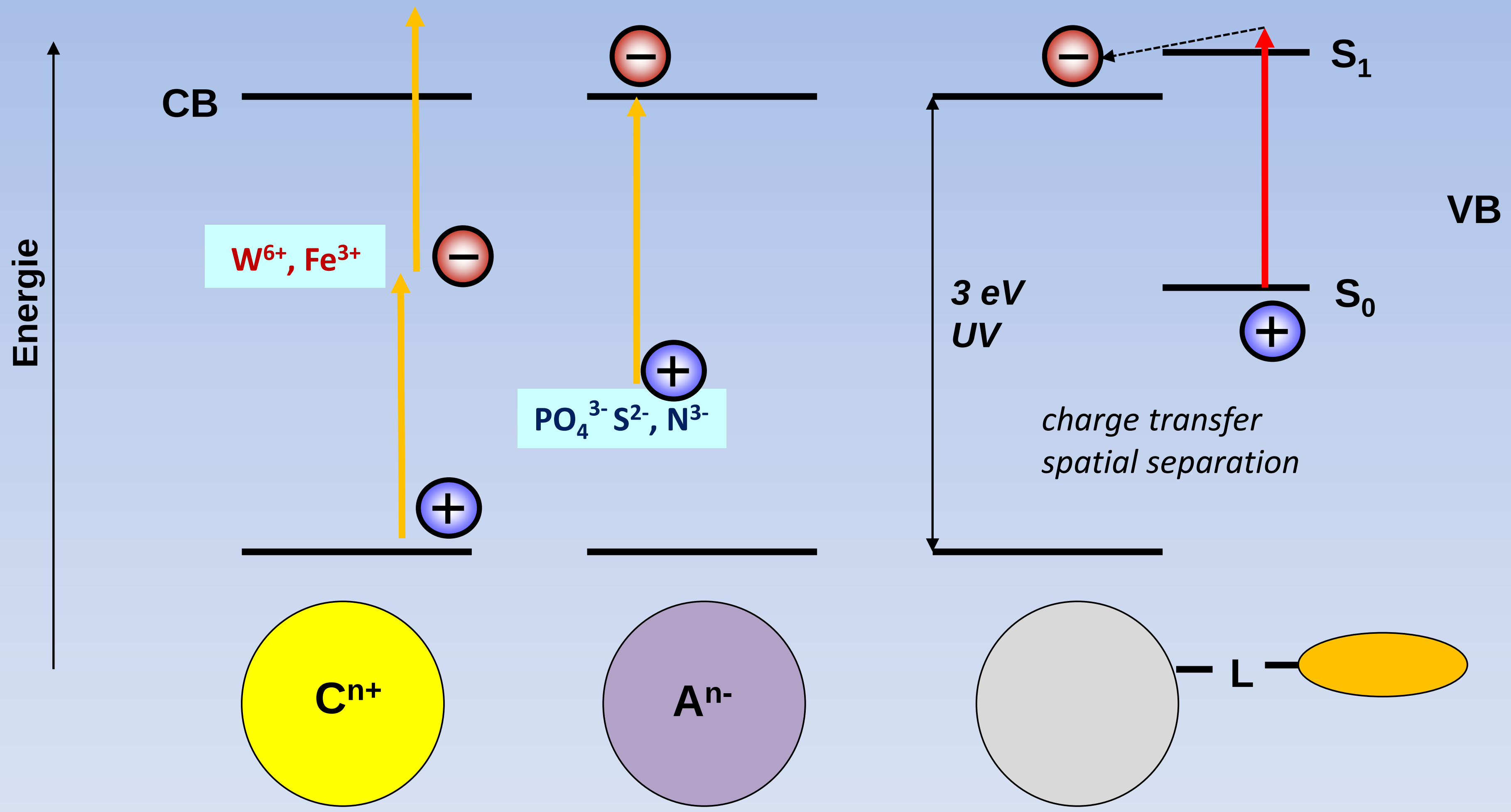
Doping and spectral sensitization of photocatalytic oxides: TiO_2, ZnO, $ZnTiO_3$



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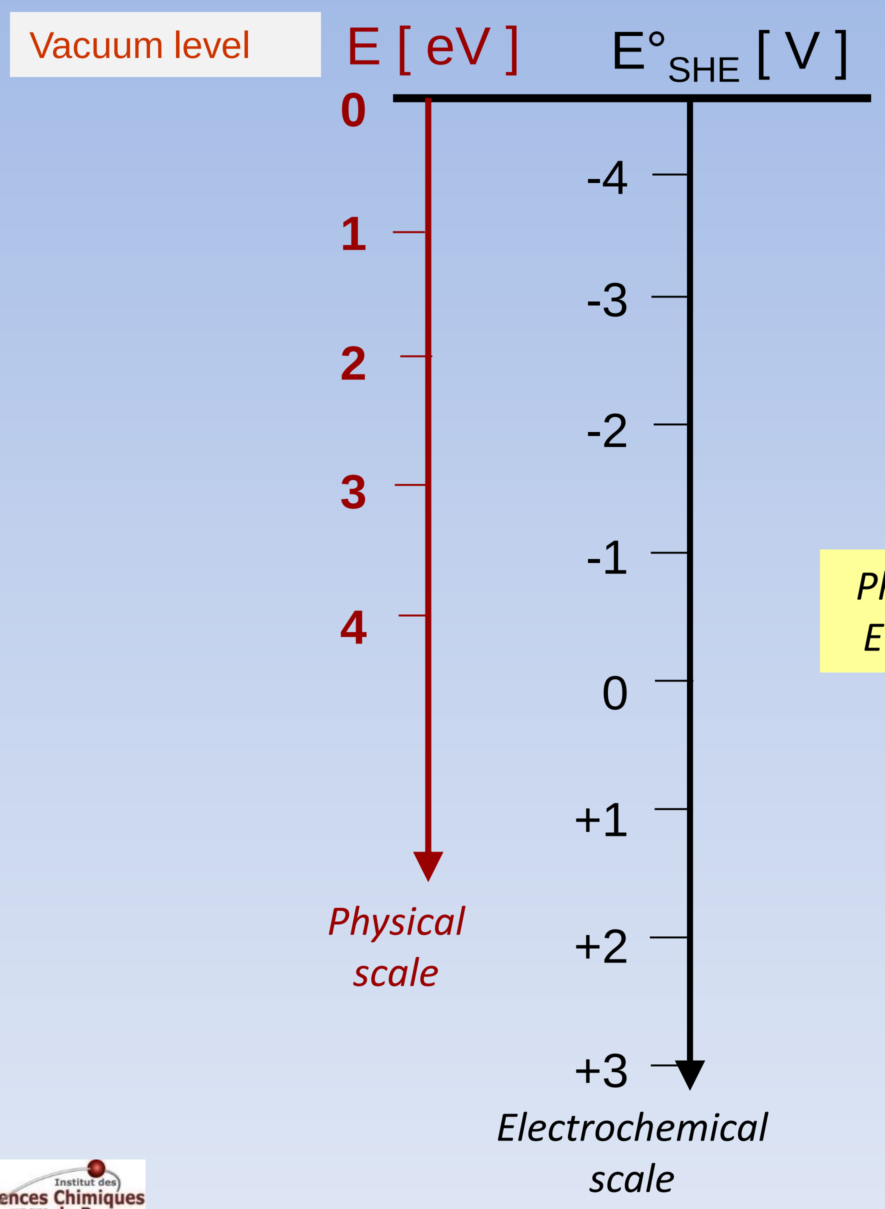
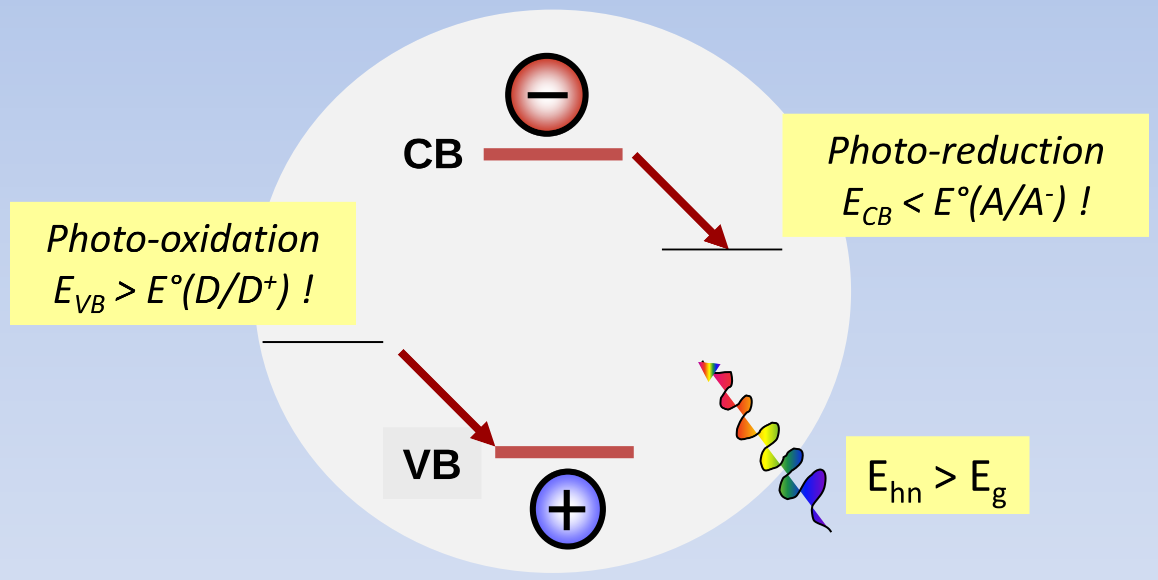


Thermodynamics of charge carrier transfer



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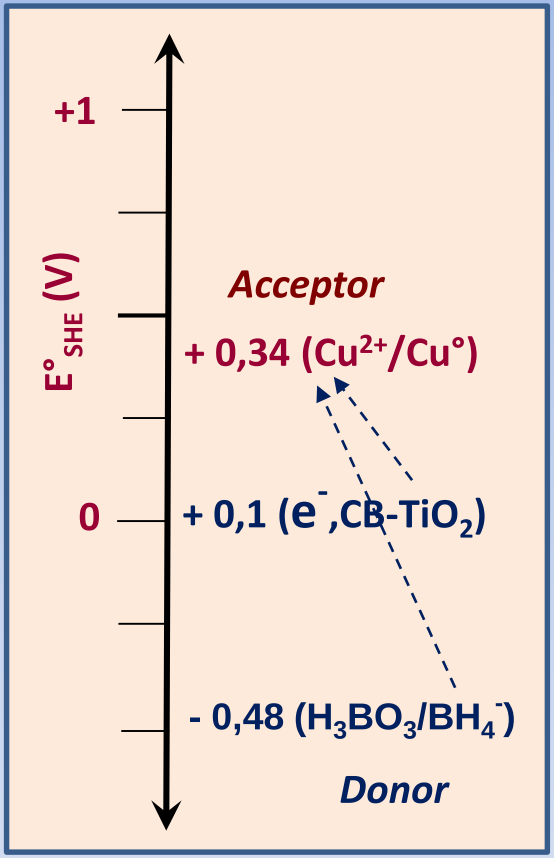
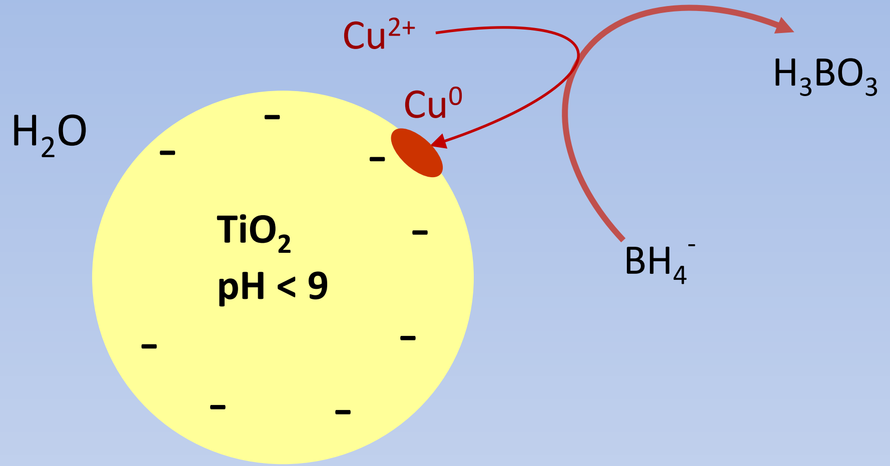
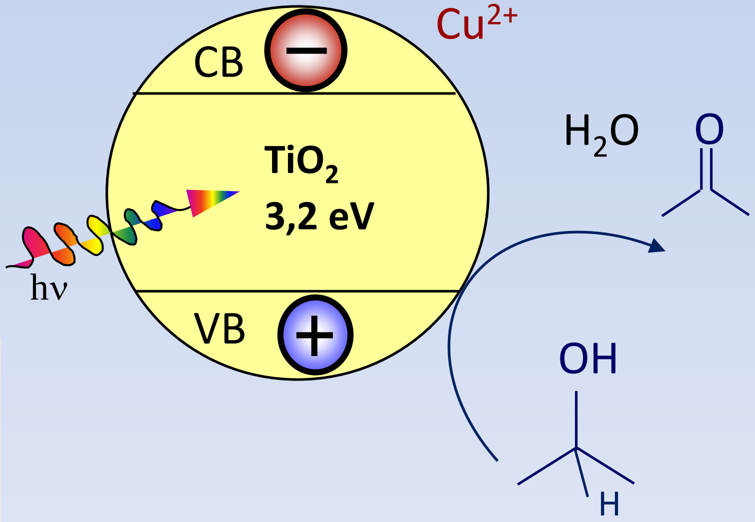
Example: formation of Cu nanoislands on TiO_2

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







$$Cu^{2+} + 2\,e^- \rightarrow Cu° \qquad (\times 4)$$

$$BH_4^- + 3\,H_2O \rightarrow H_3BO_3 + 7H^+ + 8\,e^-$$

$$BH_4^- + 4\,Cu^{2+} + 3\,H_2O \rightarrow H_3BO_3 + 7H^+ + 4\,Cu°$$

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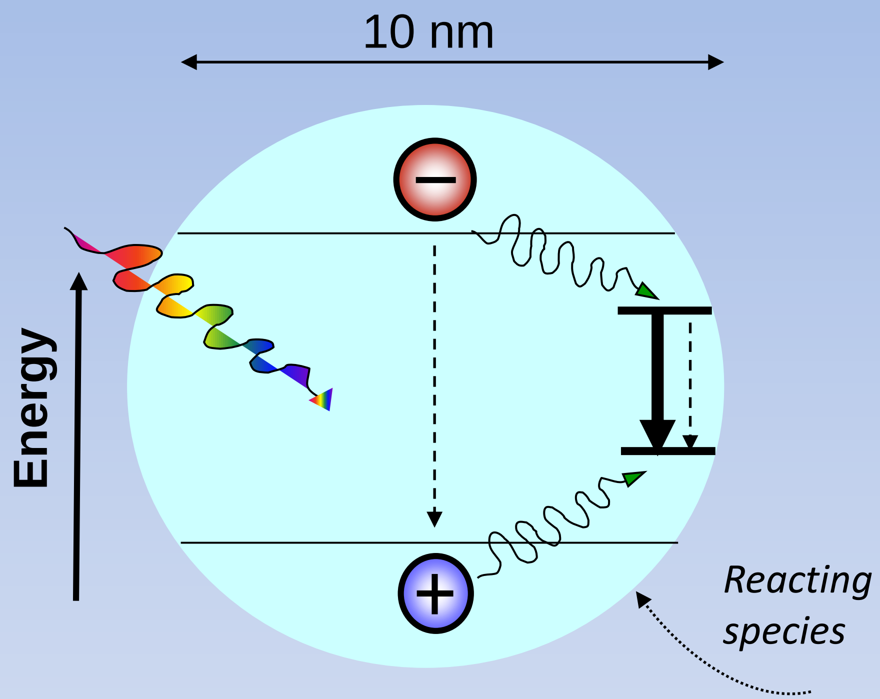
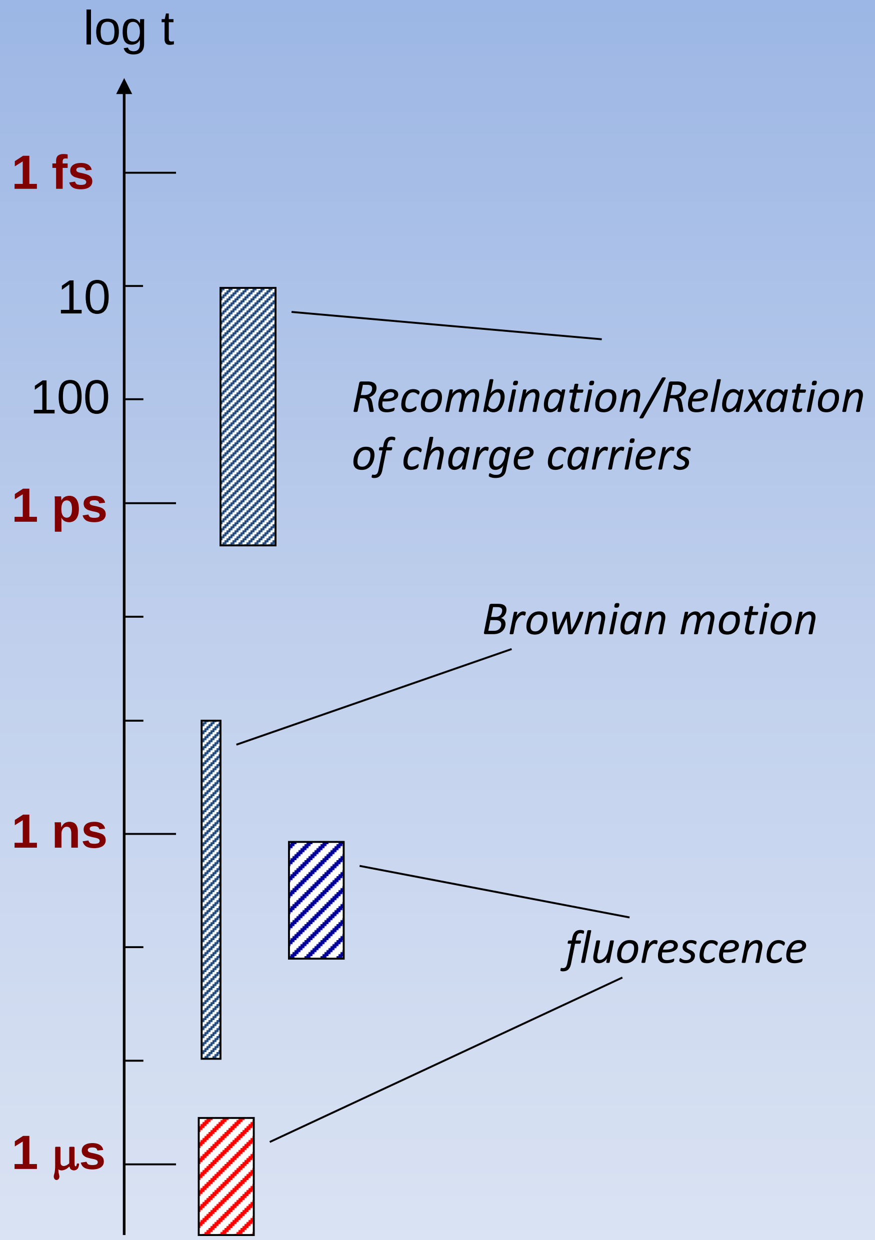
Kinetics and photocatalysis





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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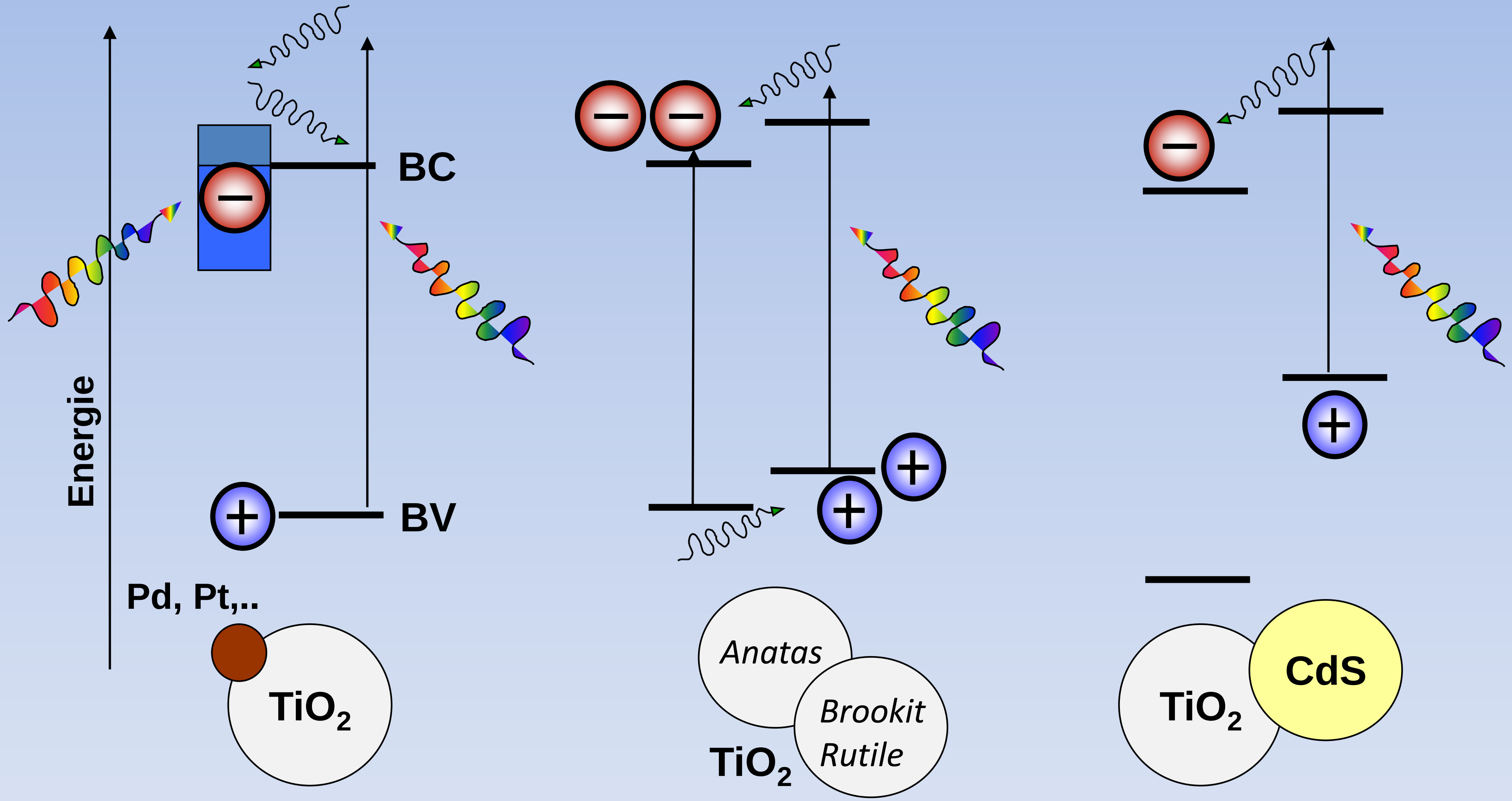
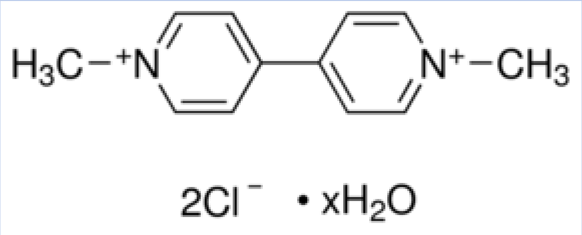
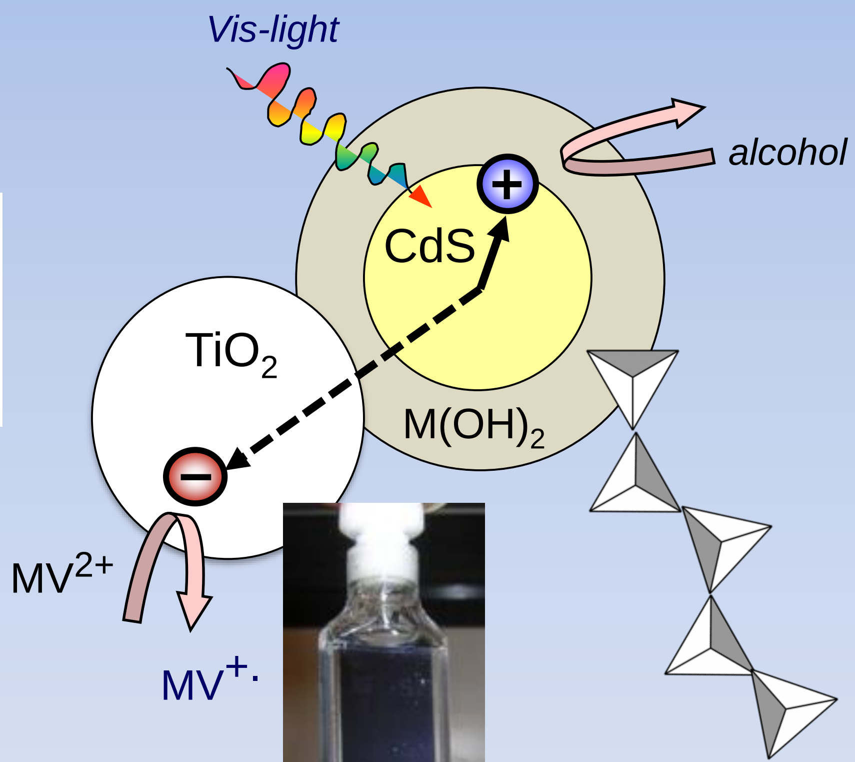
Spatial separation of charge carriers

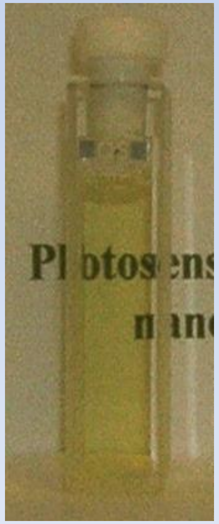


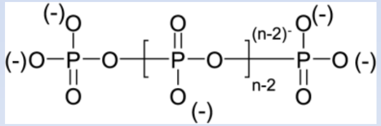
Highly efficient photoreactions in nanocolloidal CdS/TiO_2 (ZnO) - heterojunctions

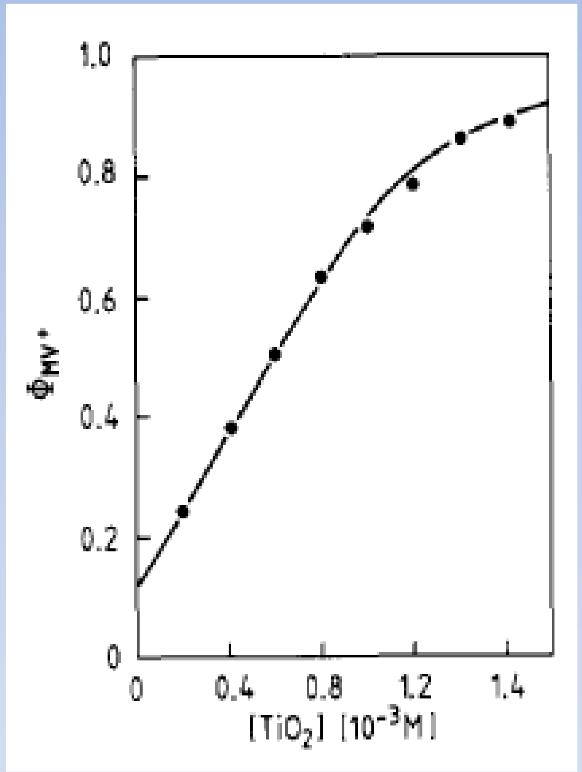
Paraquat herbicide











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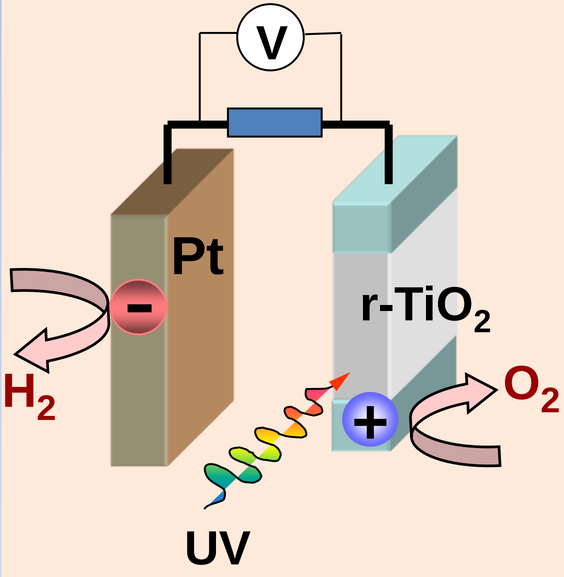
Solar water splitting

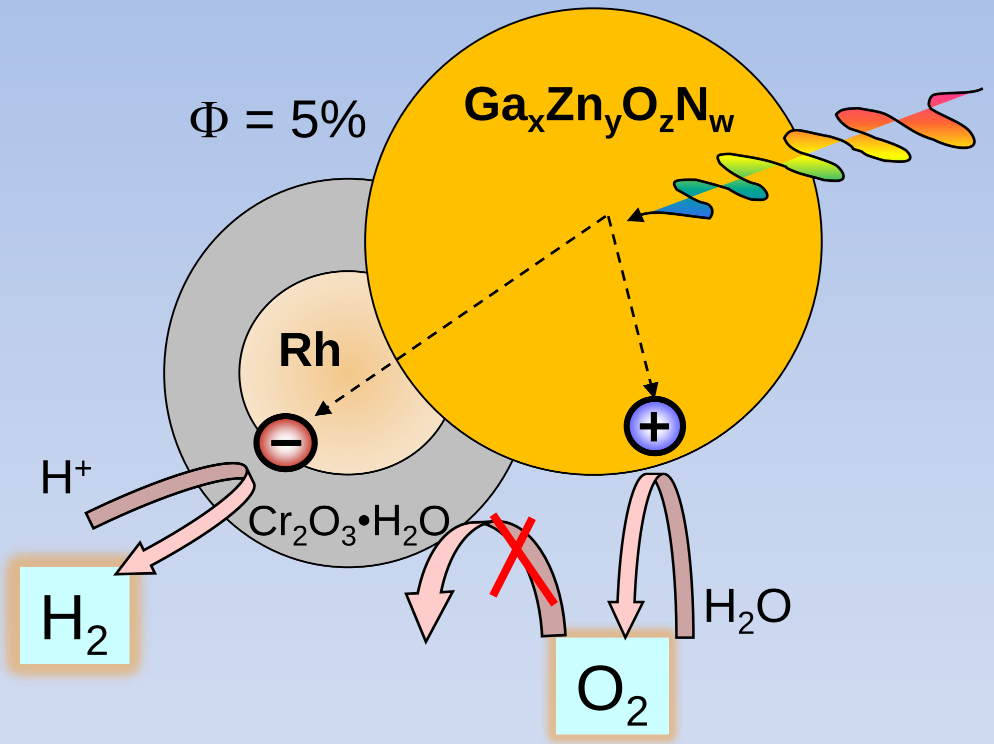
Fujishima-Honda

Quantum yield < 0,1%



Nature 1972, 238, 37

K. Maeda et al, Nature 2006



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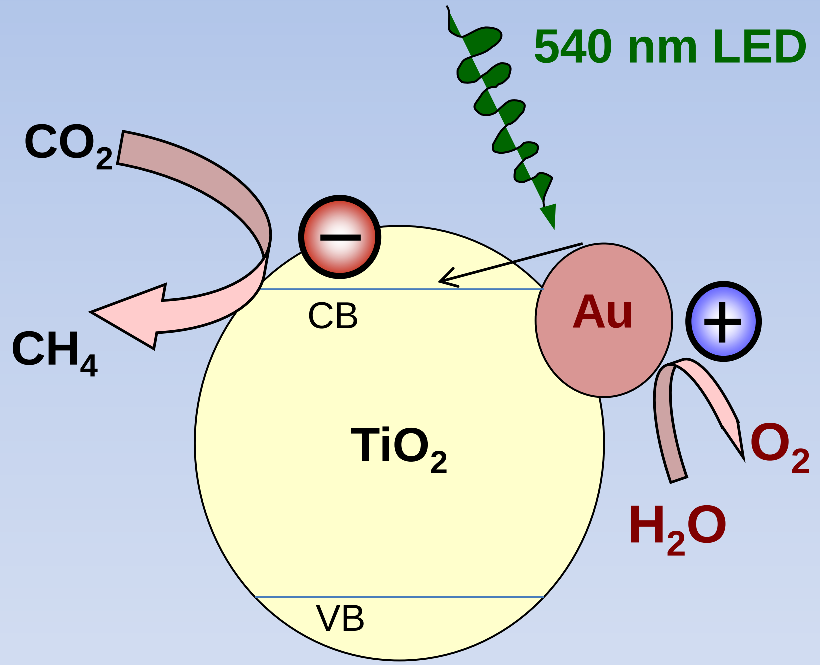
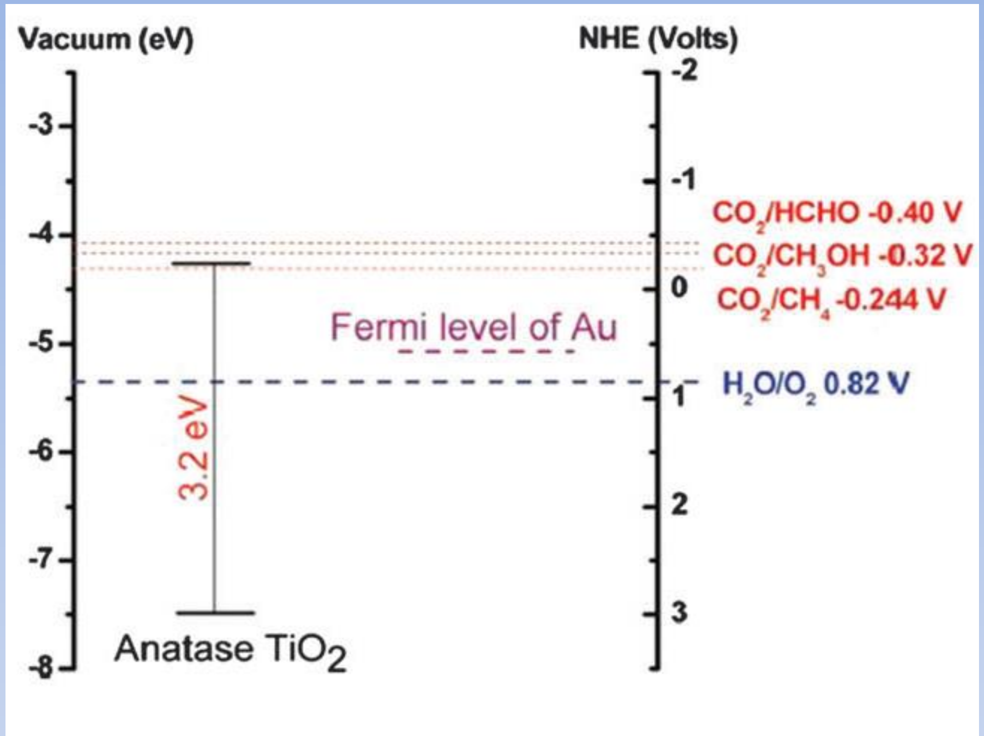
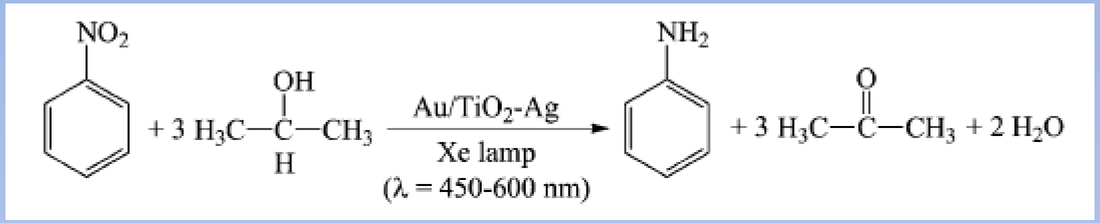
CO_2 photo-transformations via surface plasmons

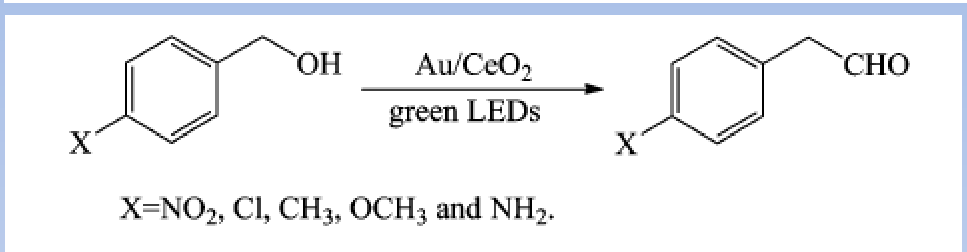


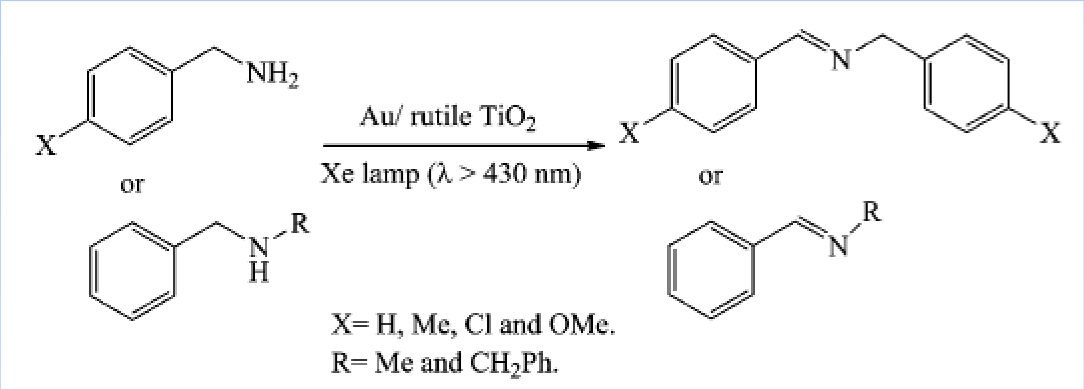
D. Astruc, Univ. Bordeaux
RSC-Chem. Soc. Rev. 2014, 43, 7188

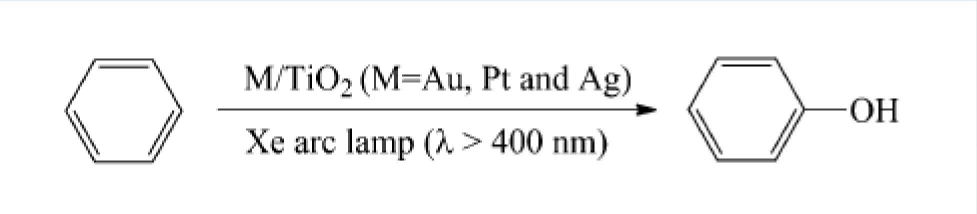


reaction
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO$
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH$
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4$

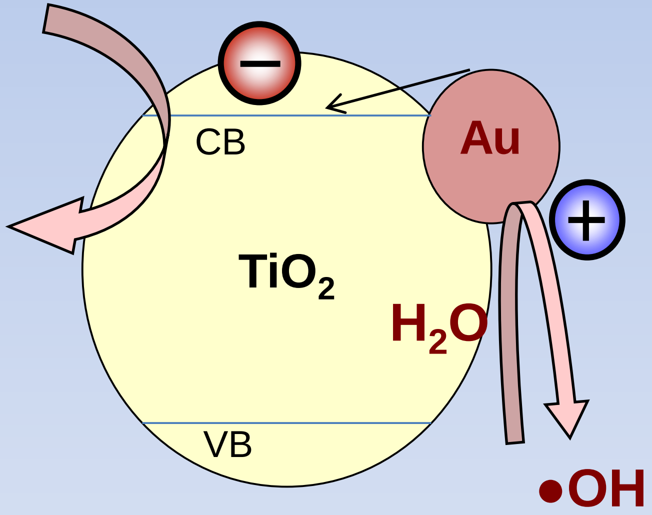








In most cases:
Yield > 50%
Selectivity > 90%



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

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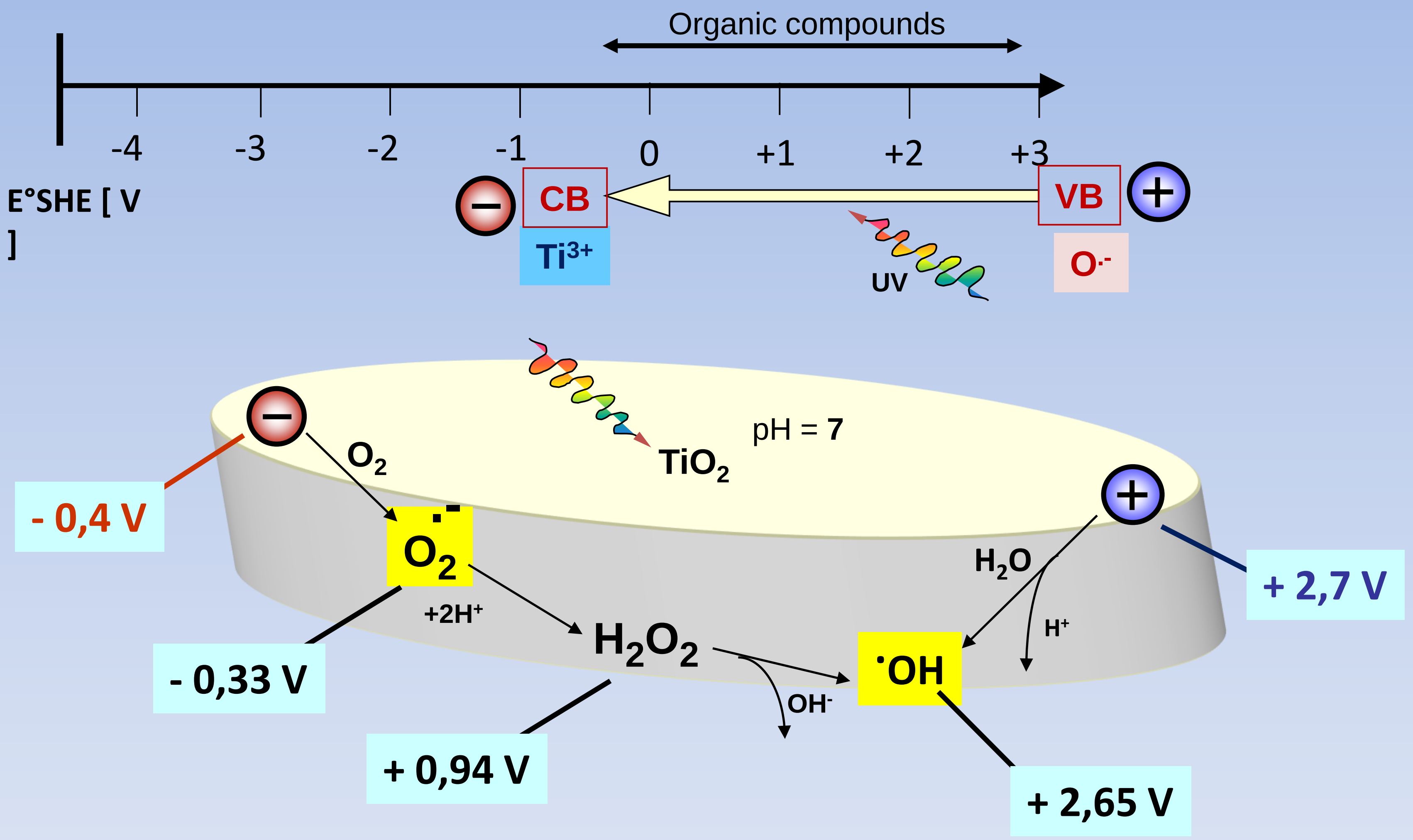
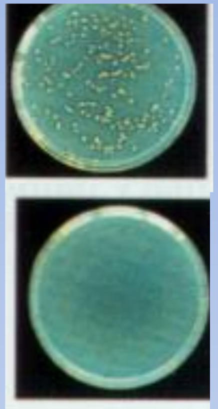
Environmental Photocatalysis

TiO_2 + UV + oxygen + water

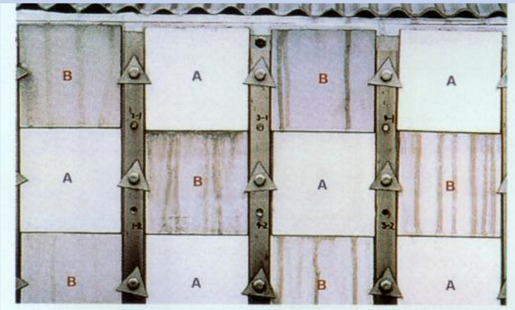


Super-Hydrophilicity in the car industry

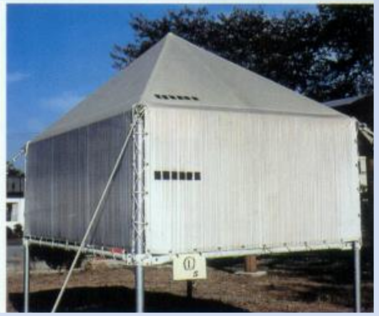
Bacteria killing

Super-Hydrophilicity in building constructions

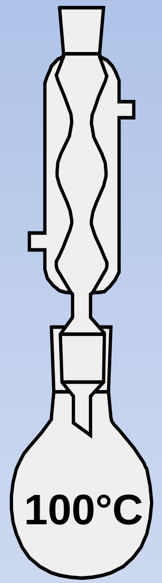


Self-cleaning and sterilisation of textiles




Polymeric sol route to nanostructured xerogels and coatings $Zn_xTi_yO_z$

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



$Zn(Ac)_2\ 2H_2O$

$Ti(OBut)_4$

EtOH

Complexation
$Ti(OBut)_4$

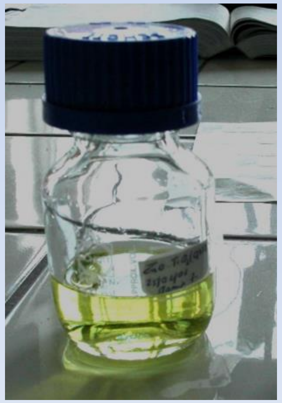
$AcTi(OR)_3$

Esterification
EtOH

H_2O

Hydrolysis
Condensation

„Ti-O-Ti“
„Ti-O-Zn-O-Zn“



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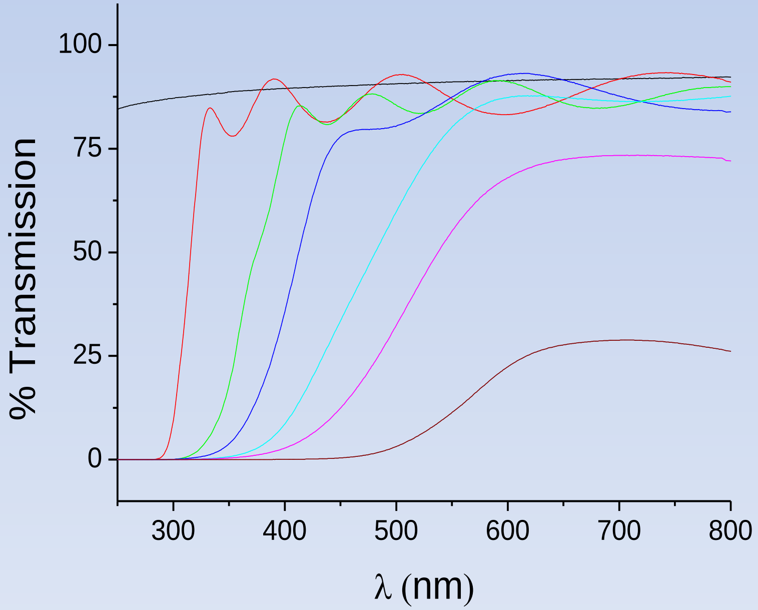
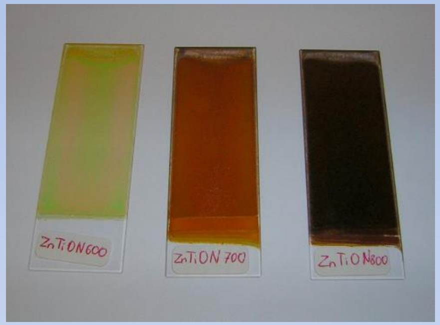
Growth of spinel nanophases in thermal nitridation process

Polymeric sol
2 M $Zn_xTi_yO_z$

Coatings on glass

Sintering in NH_3





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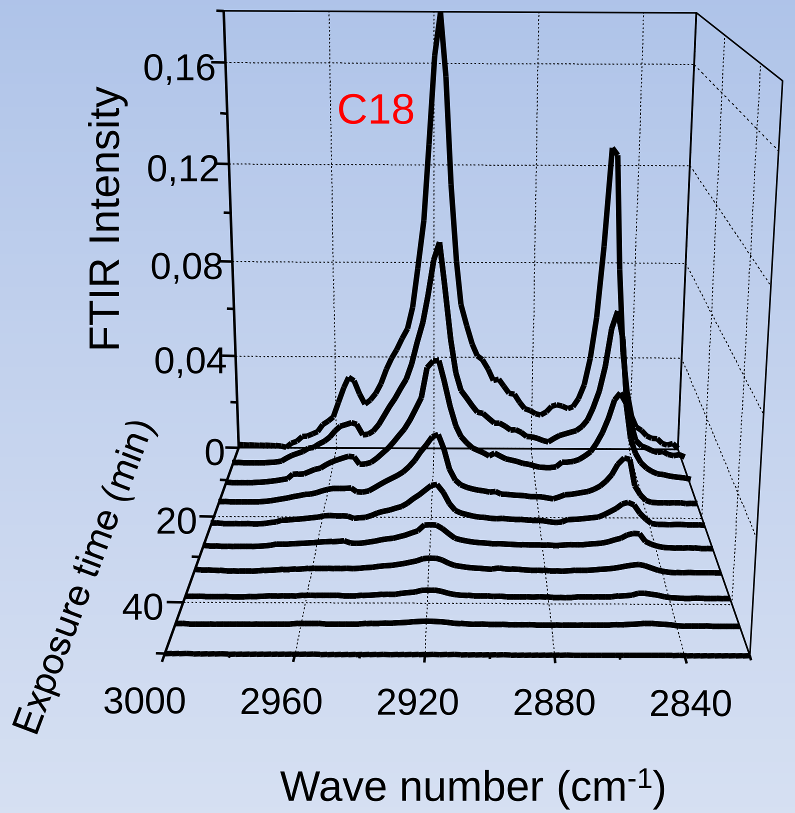
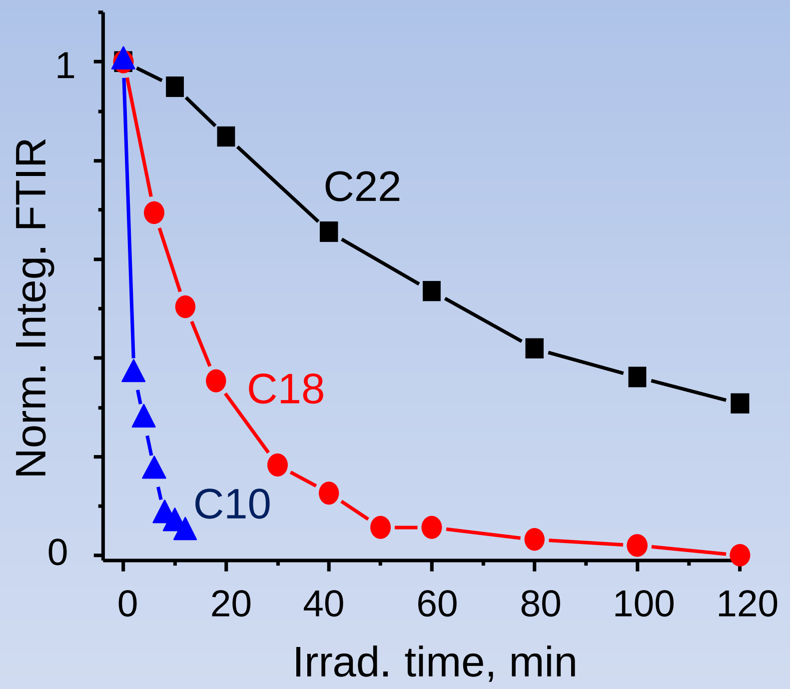
Superhydrophilic $ZnTiO_3/TiO_2$ films in Photocatalysis

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





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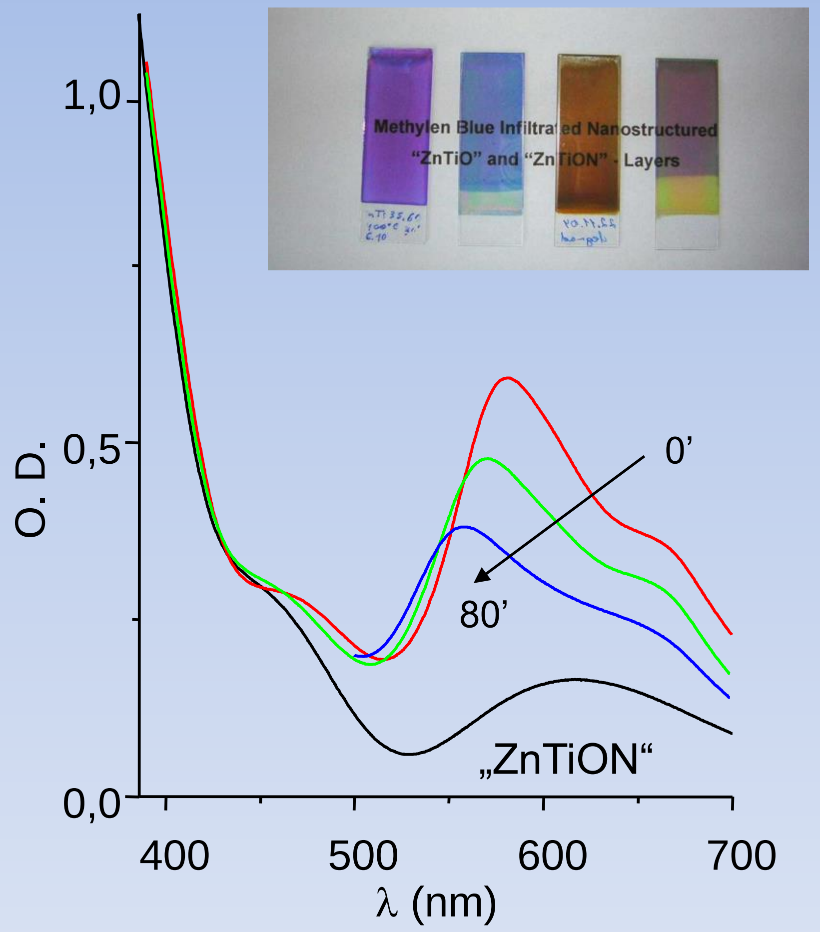
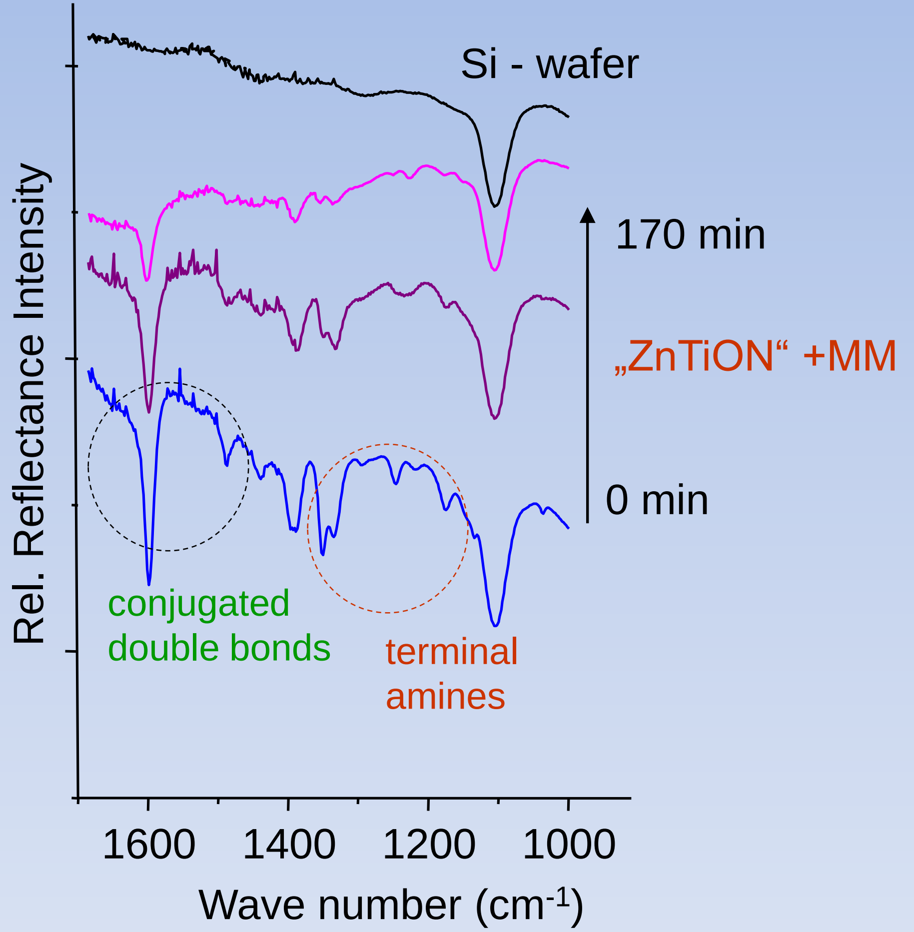
Methylene Blue photodegradation on “$Zn_2TiO_{4-x}N_x$”-Spinel layers

(λ_{ex} > 430 nm, Xe – Lamp, humid air)





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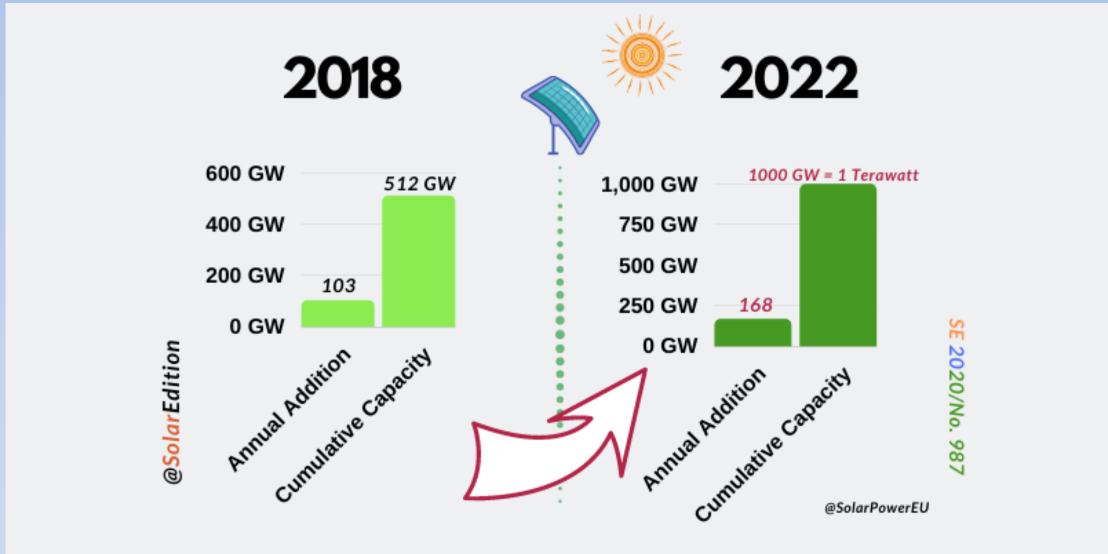
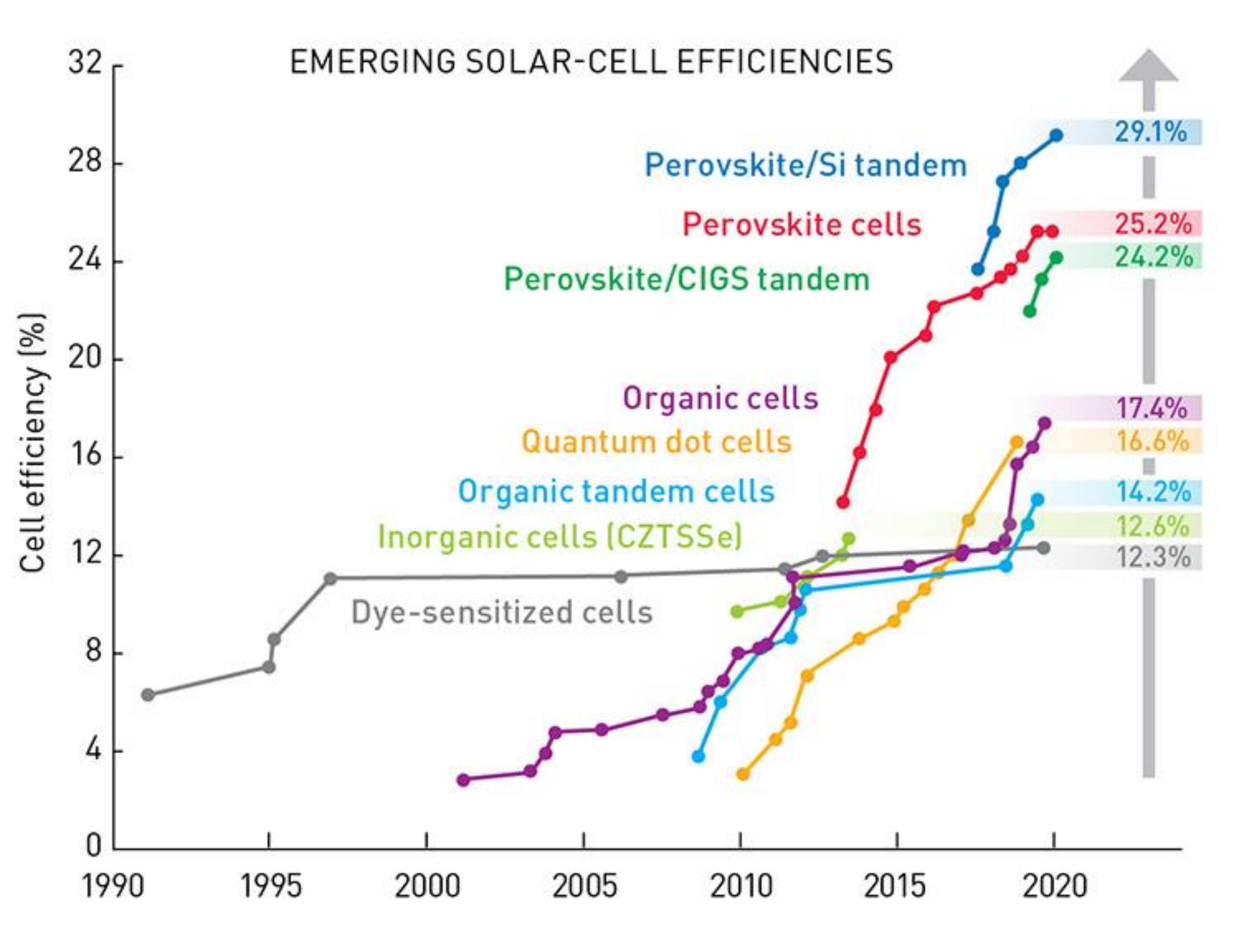
Photovoltaics: forecasts and actual efficiency statistics





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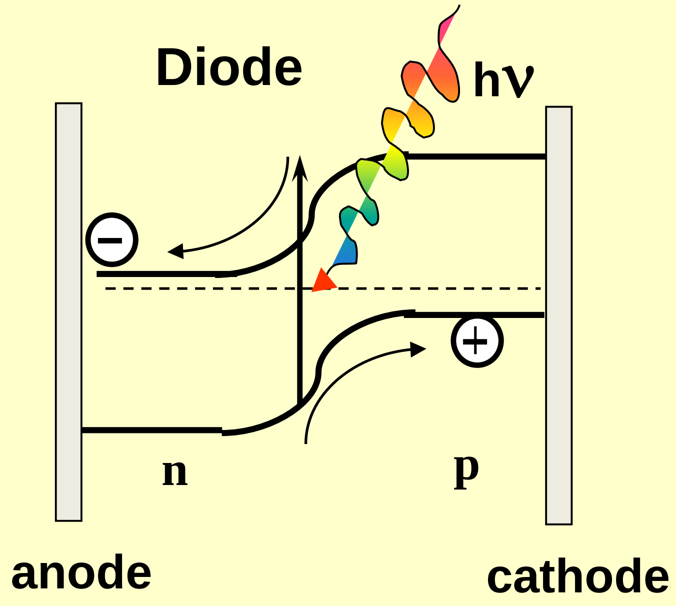
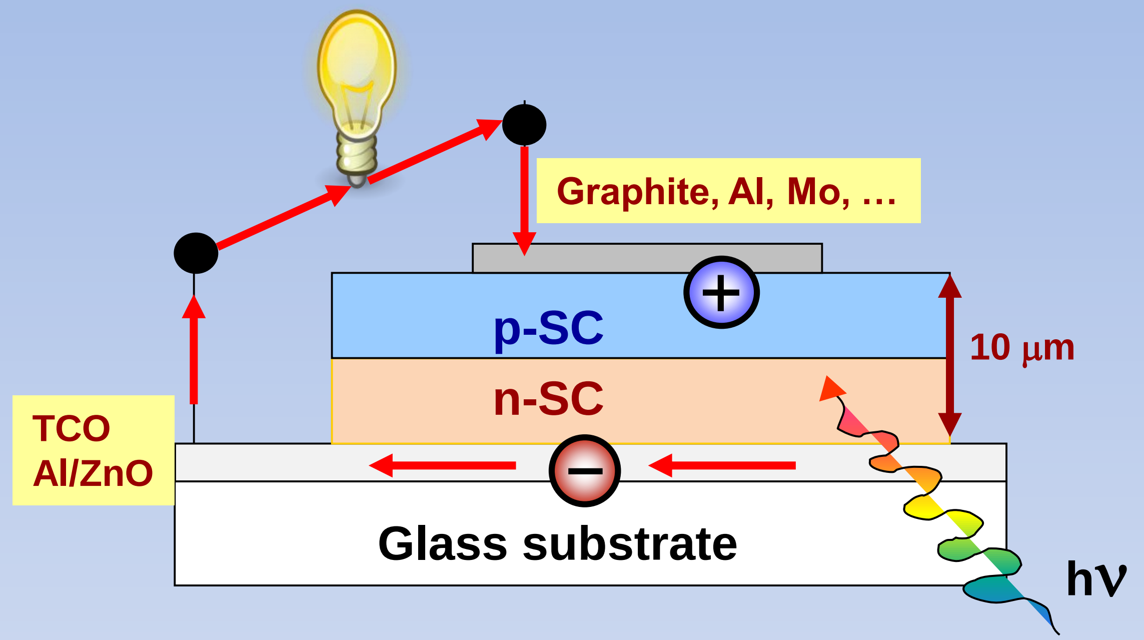
Introduction to photovoltaics



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

η_{stc} = 15 – 50 %



Conversion efficiency
stc = standard test condition

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

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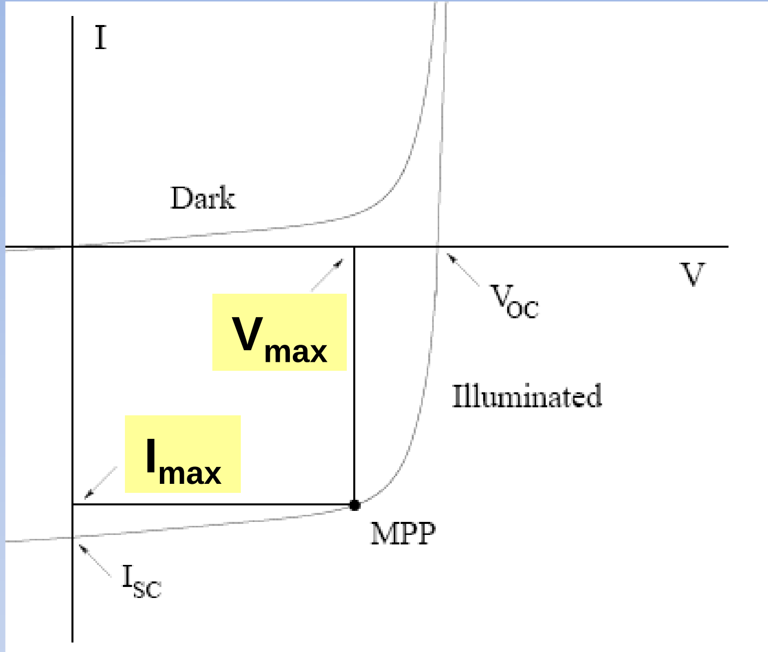
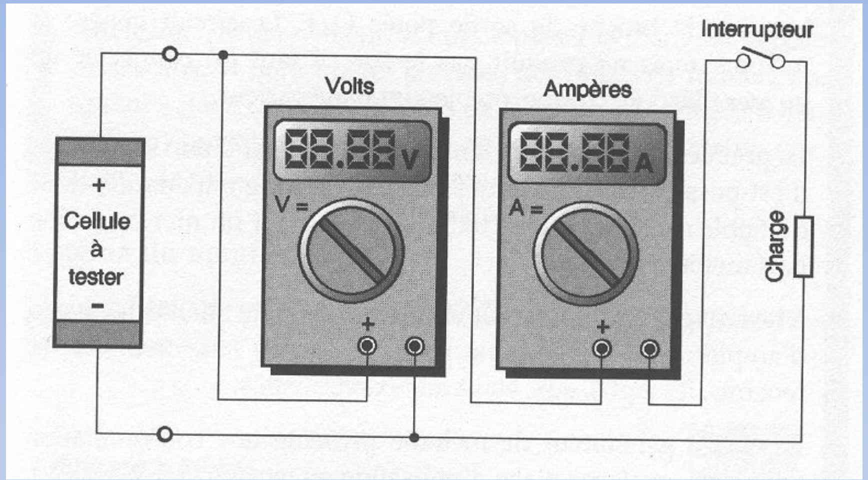
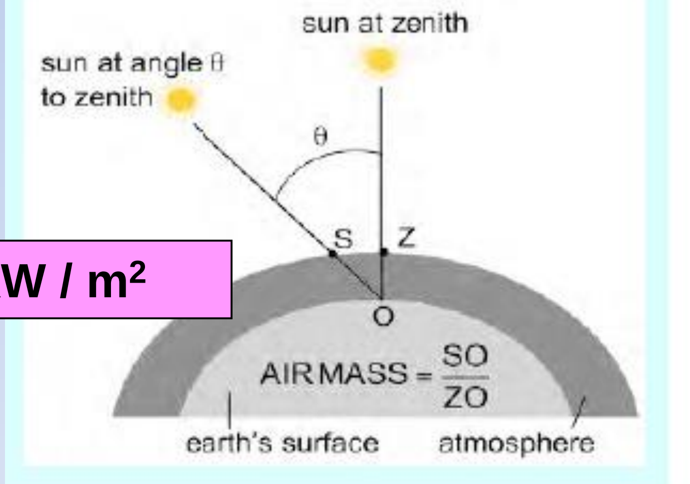




$$\eta = FF\frac{V_{oc}I_{sc}}{P_{in}} = \frac{V_{max}I_{max}}{P_{in}}$$

P_{in} = 1 kW / m^2



η = conversion efficiency (0 - 1)
FF = fill factor
V_{OC} = open circuit voltage (V)
I_{SC} = short circuit current (A/m^2)
P_{in} = solar input power (W/m^2)

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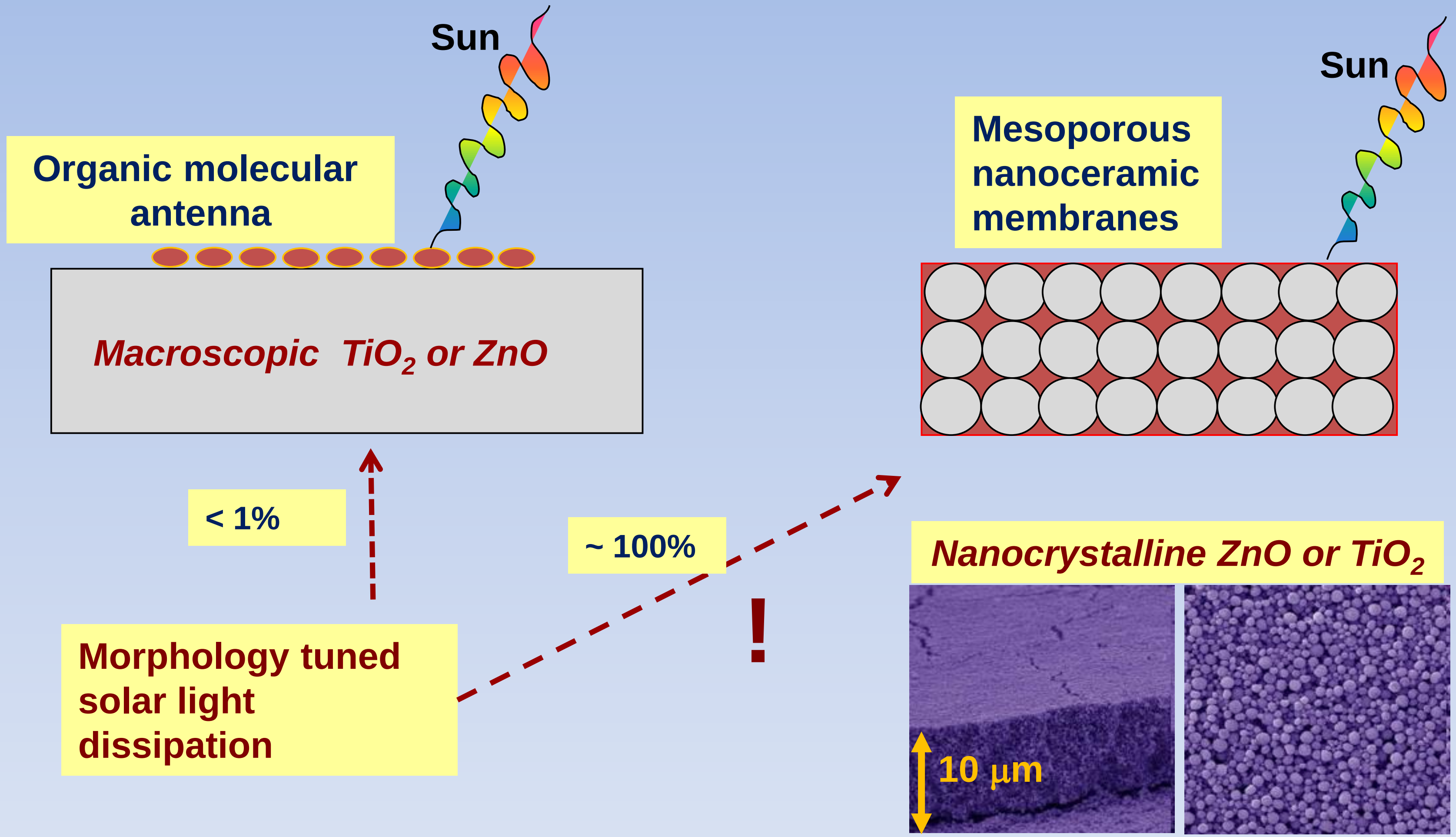
Nanostructured solar cells



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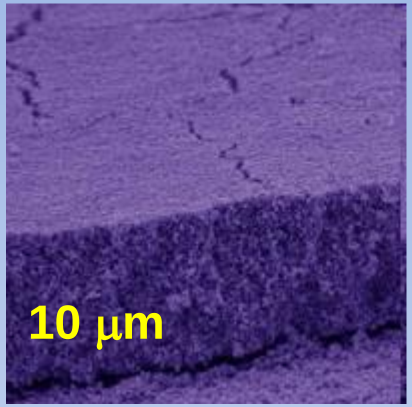
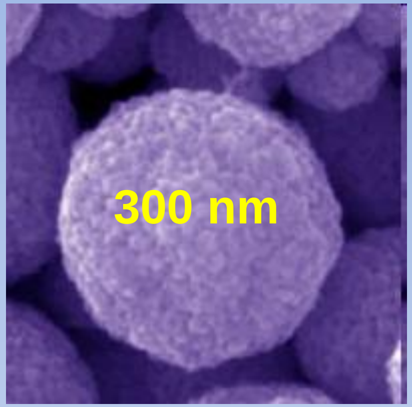
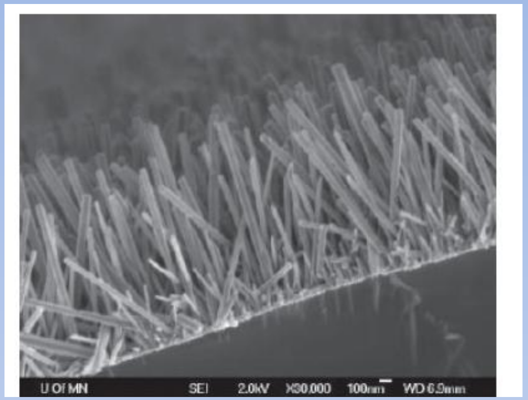
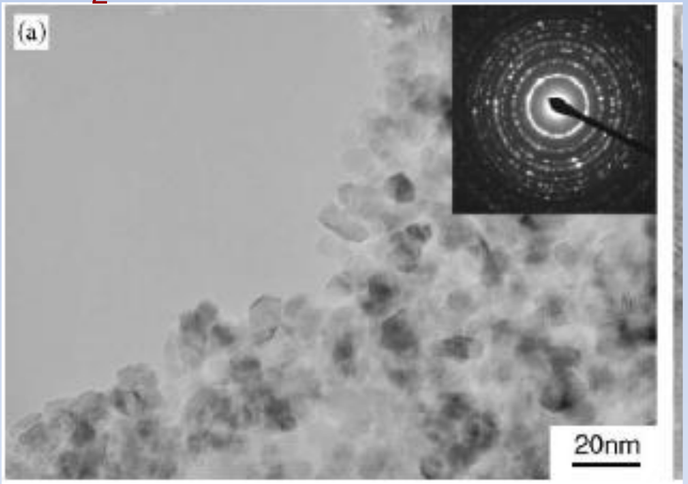
ZnO

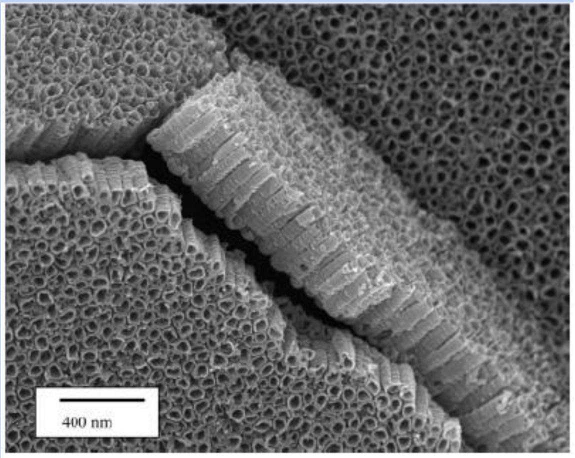


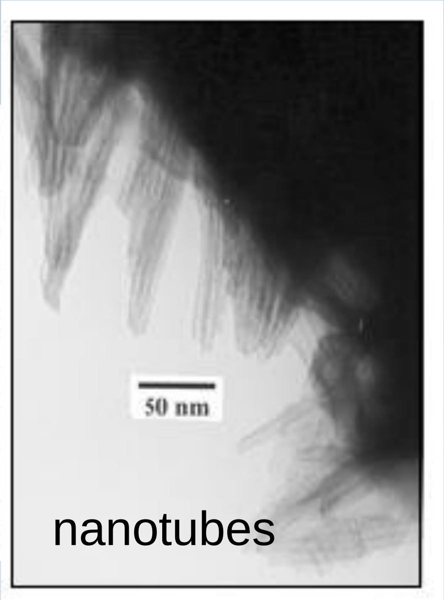




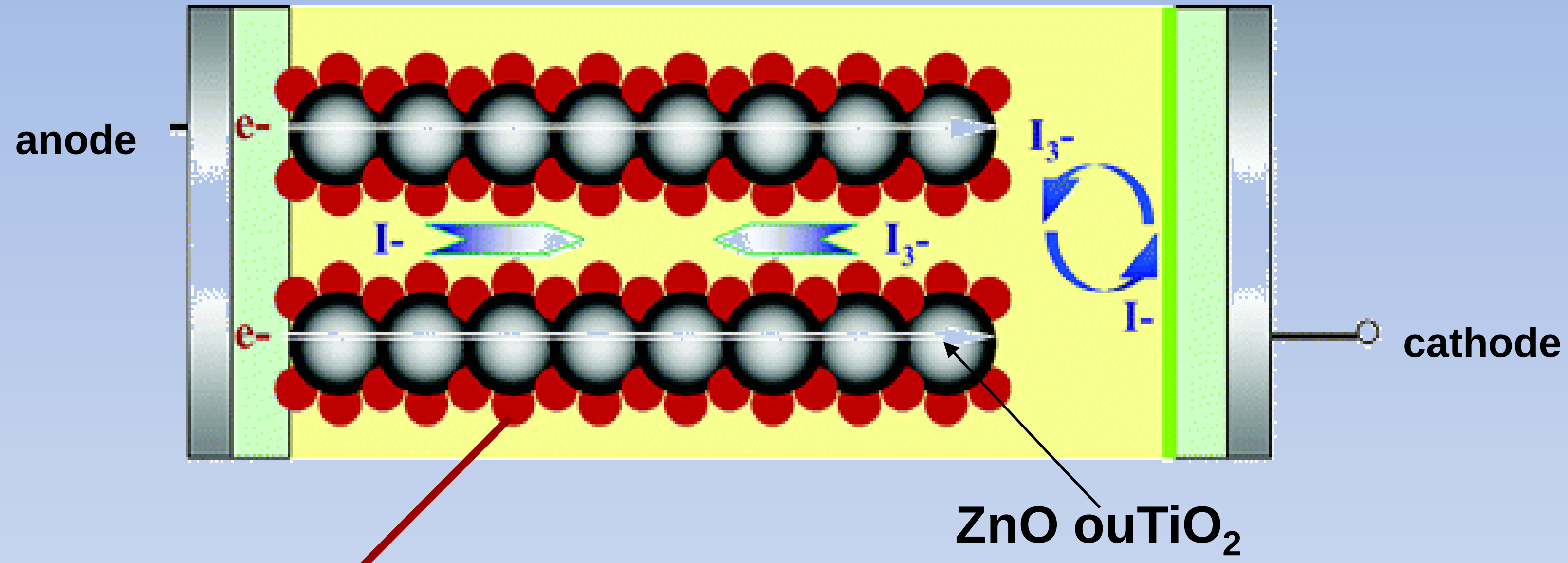
TiO_2



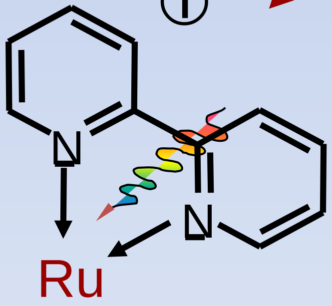




Concept of regeneration in photo-sensitized cells

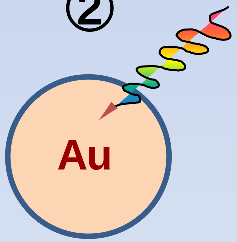


①



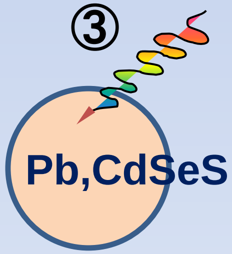
12% (1987)

②



5% (1995)

③

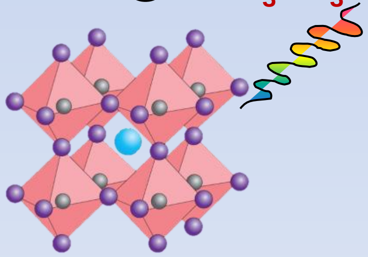


8% (1987)

④

Perovskite

$CH_3NH_3PbI_3$



29% (2024!)

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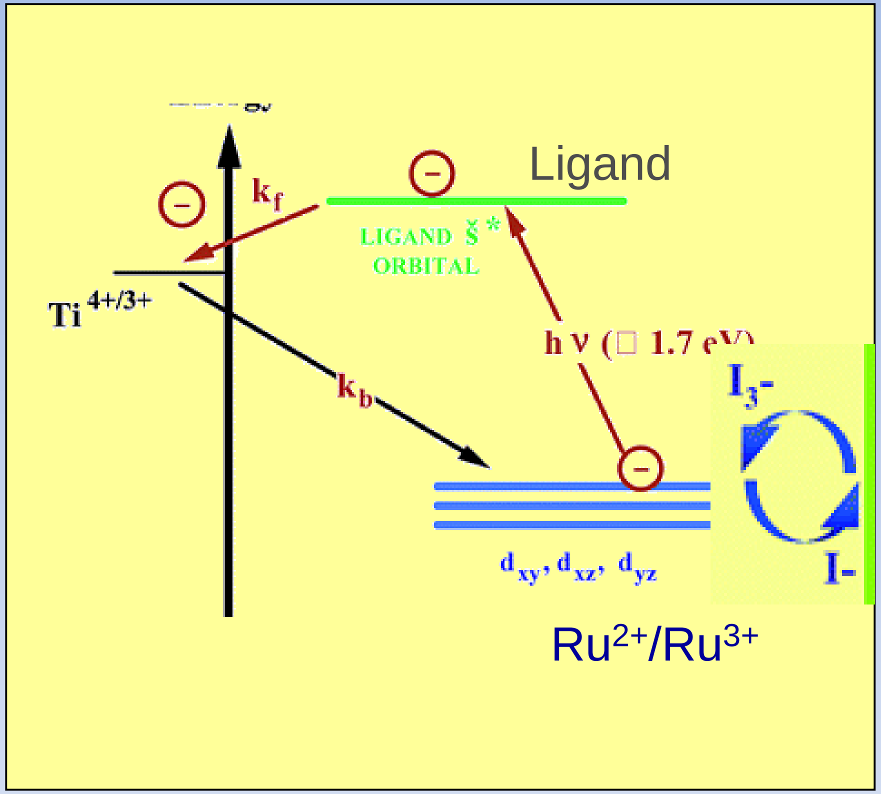
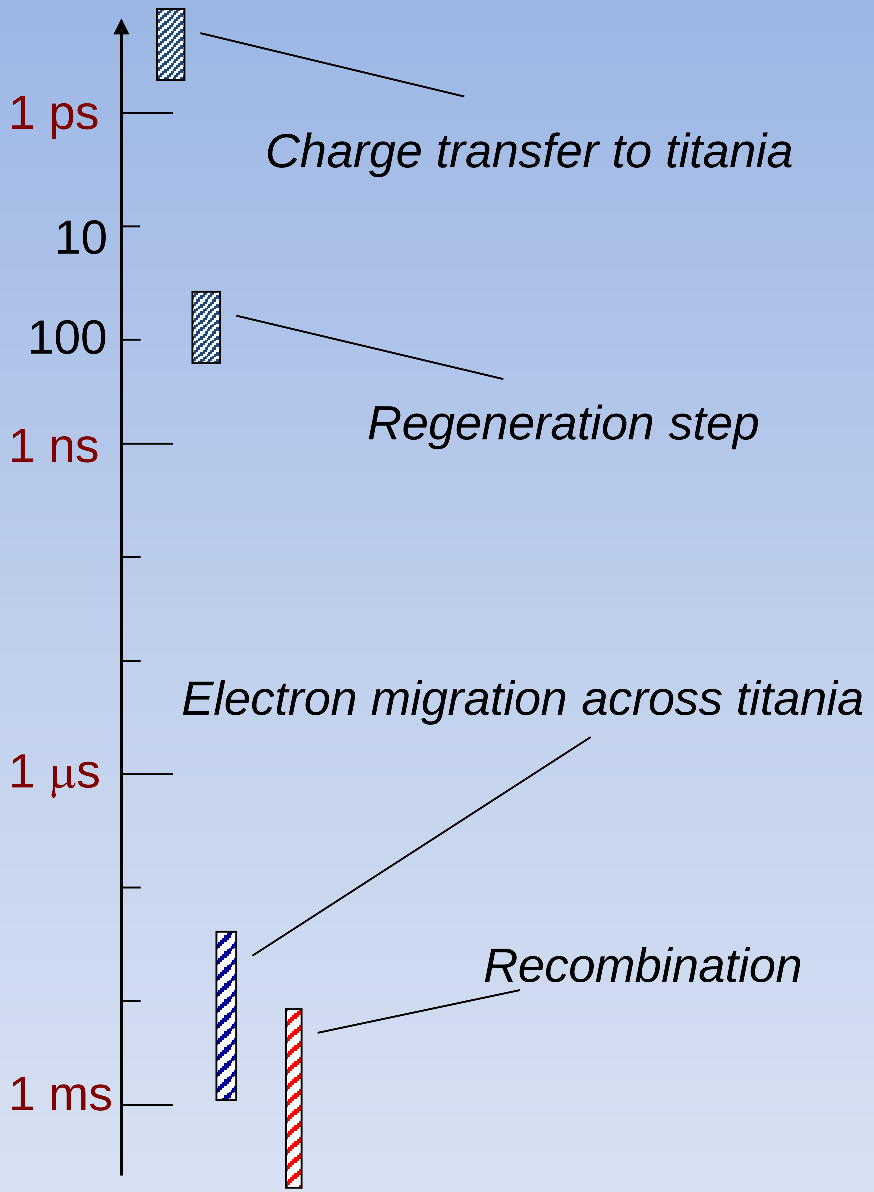
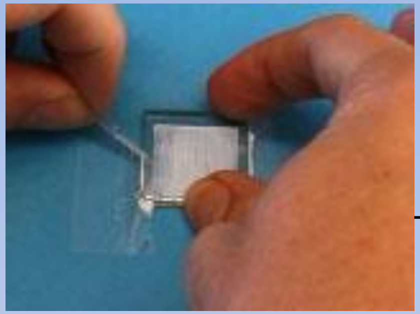
Kinetics of Grätzel cell





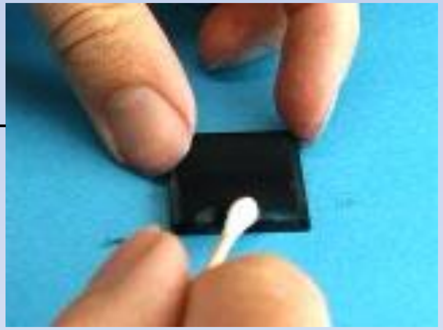
Construction rapide d’une cellule d’après Grätzel

Degussa P 25 TiO_2



Verre avec FTO

Dye infiltration



Carbone electrode

Infiltration du KI_3

Mesure photoélectrique

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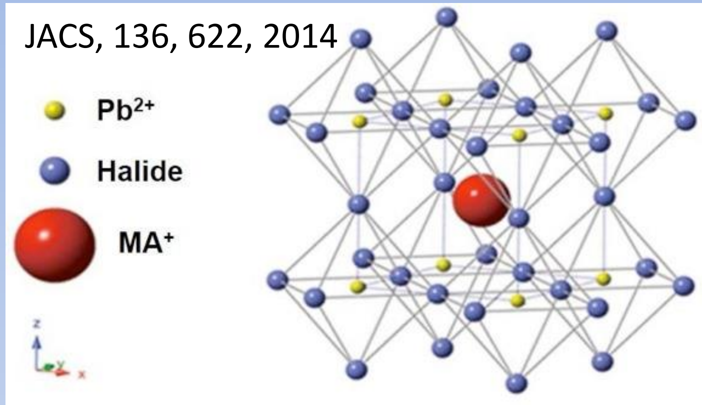
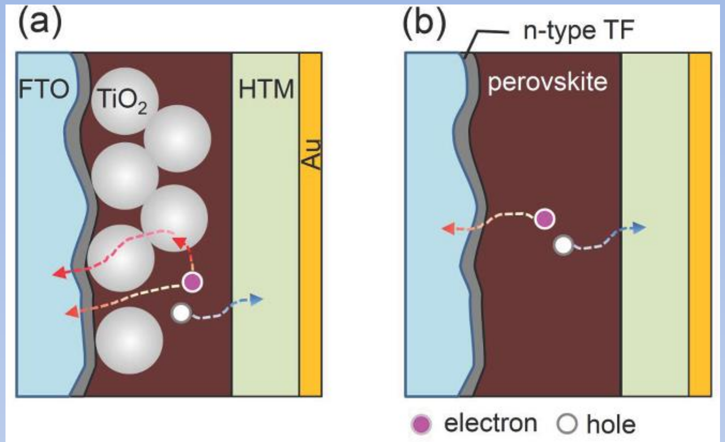
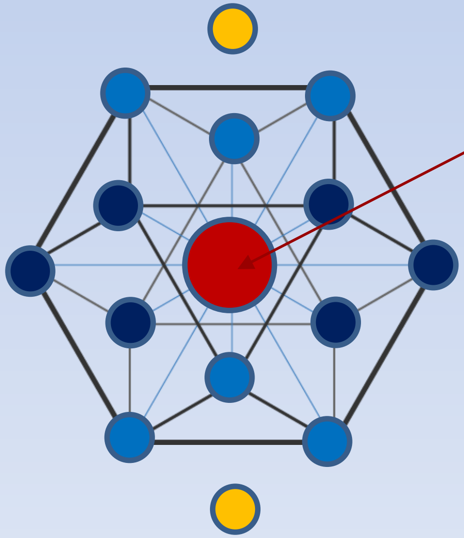
Organic Perowskite solar cells (AMX_3)

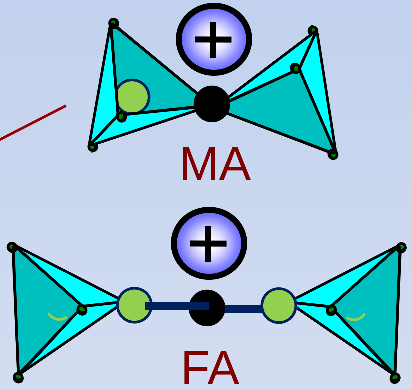
HTM = hole transporter zone
Organic polymers



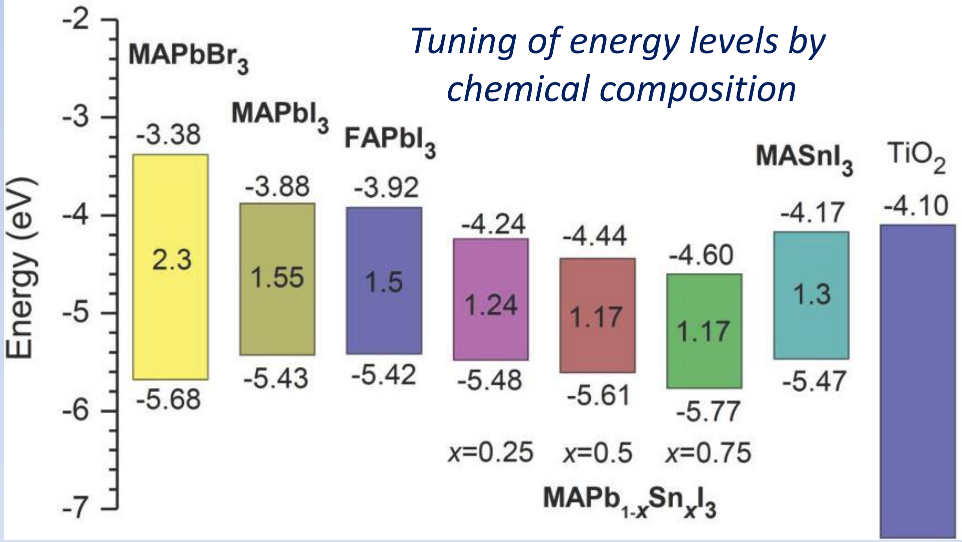


Methylammonium (MA)





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



Tuning of energy levels by chemical composition

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

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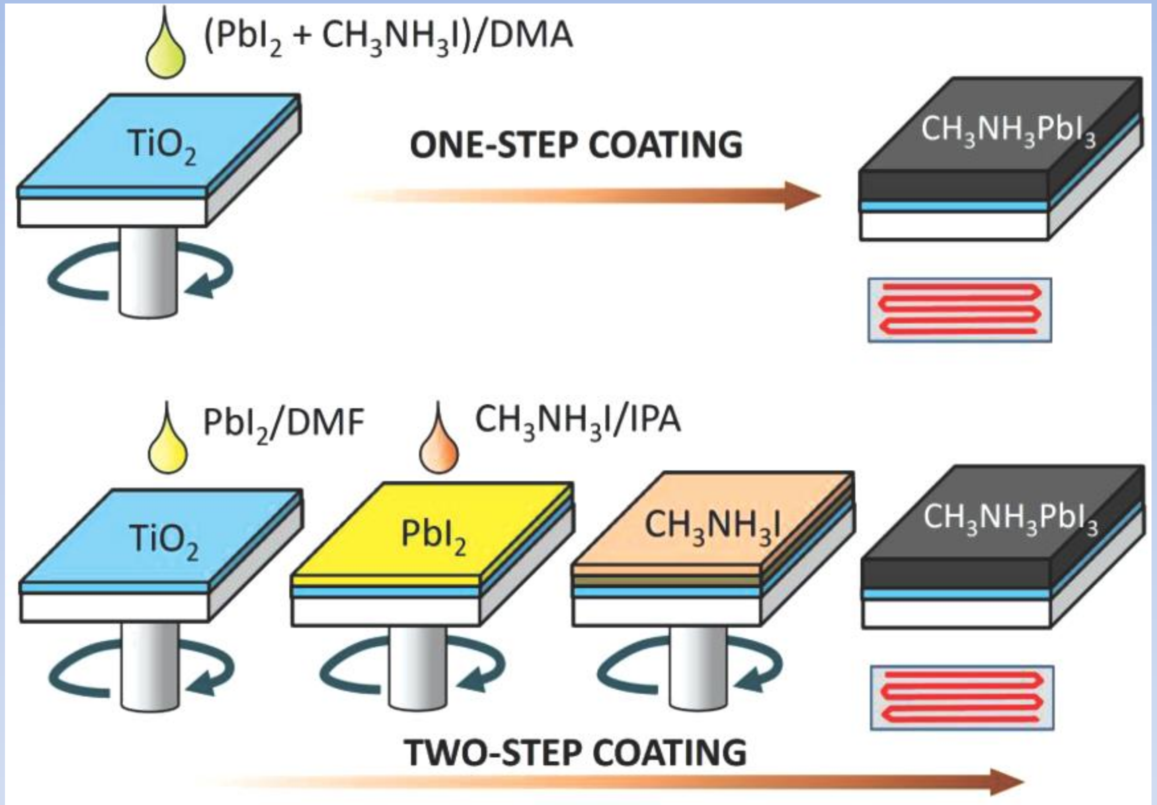
Préparation simple de cellules de Pérovskite

Small
Volume 11, Issue 1, pages 10-25, 30 OCT 2014 DOI: 10.1002/smll.201402767
http://onlinelibrary.wiley.com/doi/10.1002/smll.201402767/full#smll201402767-fig-0005



Crucial points 1. photostability and toxicity of Pb
2. Mechanism is not clear

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 and modern nanoscaled solar cells;
5. Solar antennas used in nanoscale photovoltaics;