

Inorganic nanoparticulate materials: Characterization and applications

1. MFNP & Optical methods

- in situ UV-vis growth monitoring
- global approach to separation and analysis
- applied NP - ligand strategies
- Eco/Life sciences:
- surface chemistry,
- plasmon, luminescence

2. Solar sector

- NP-thermodynamics/kinetics
- Photocatalysis
- Solar cells

3. ICT sector

(Information and communication technology)

- Transparent conductors
- electrochromy/electroluminescence
- planar wave guides and web amplifiers

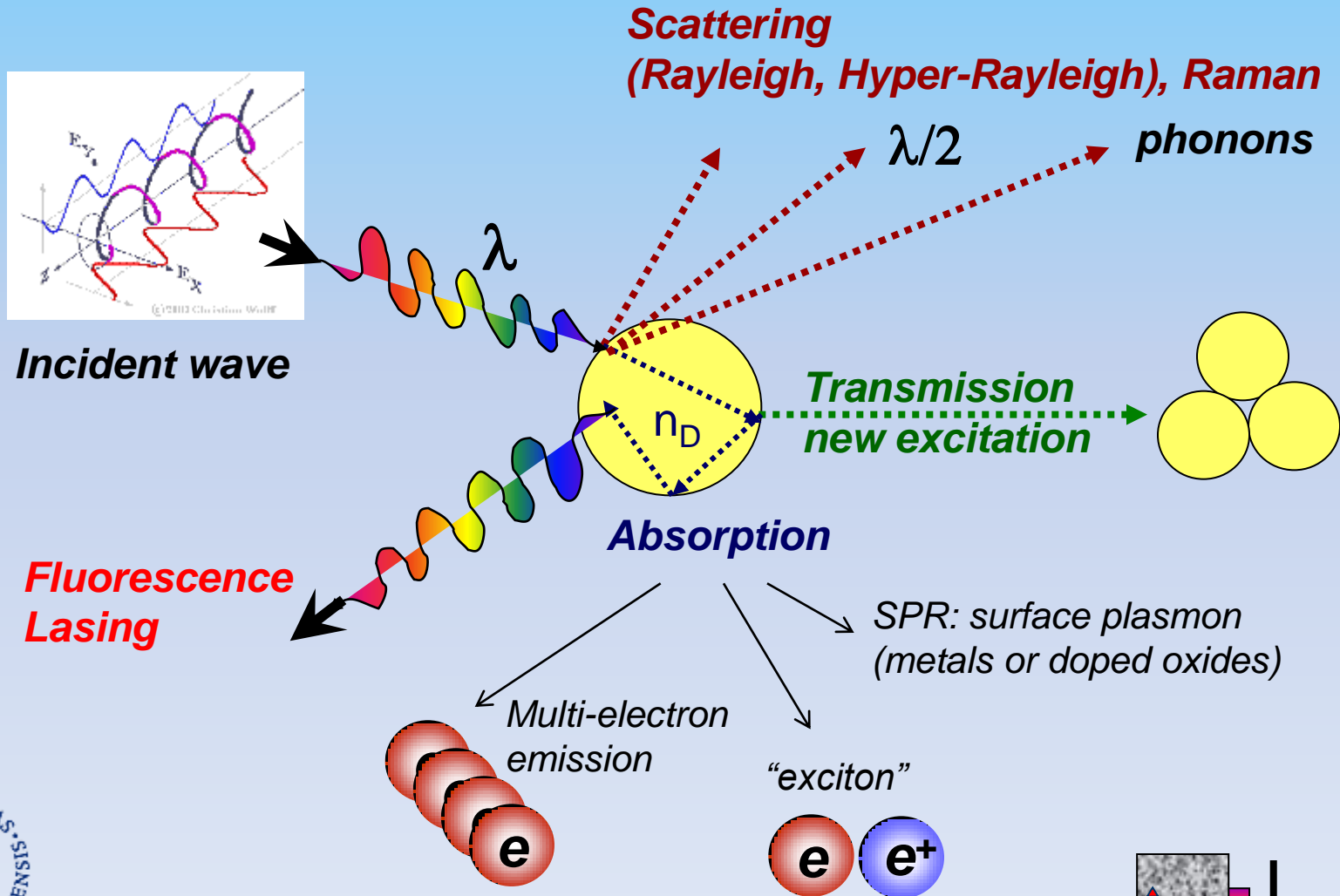
4. Fractal approach to analysis

- introduction to fractals
- concept of fractal dimension
- examples of D_f determination



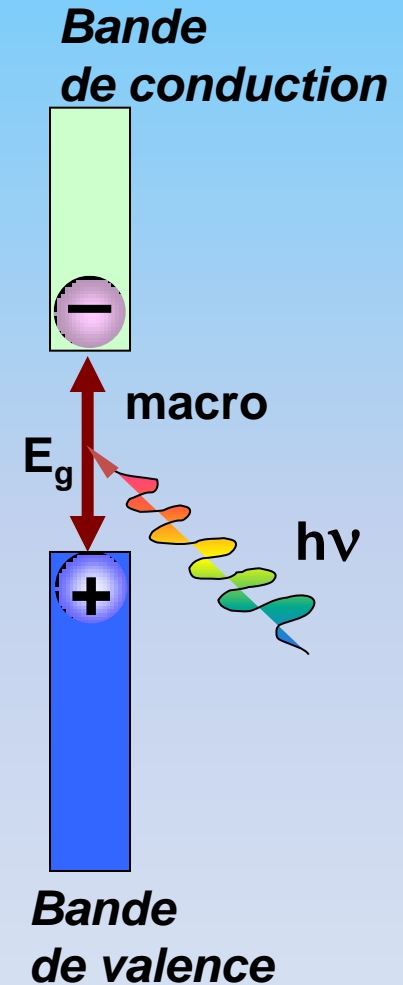
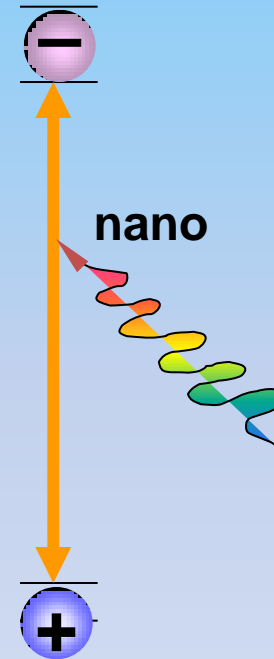
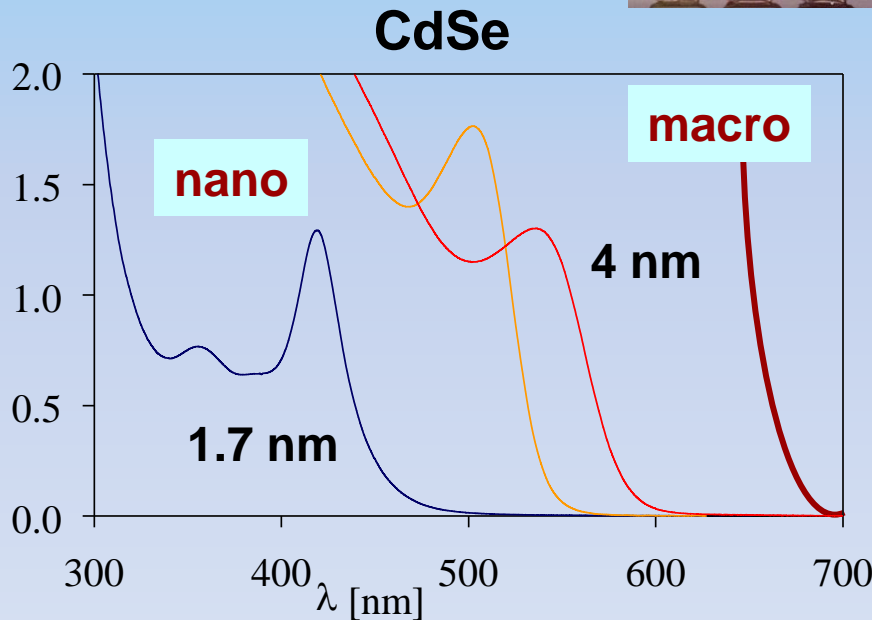
L. Spanhel

Ch 1. Optical monitoring, total analysis and tailoring multifunctional nanoparticles MFNP (sizes $\ll 100$ nm)

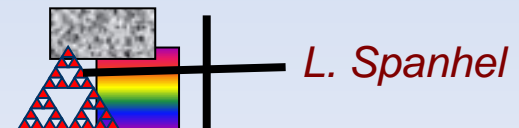


Nanostructures semi-conductrices :

Le gap optique varie avec la taille des particules!!



$$E(\text{eV}) \sim 1240 / \lambda (\text{nm})$$



Optical absorption in ZnO et TiO₂



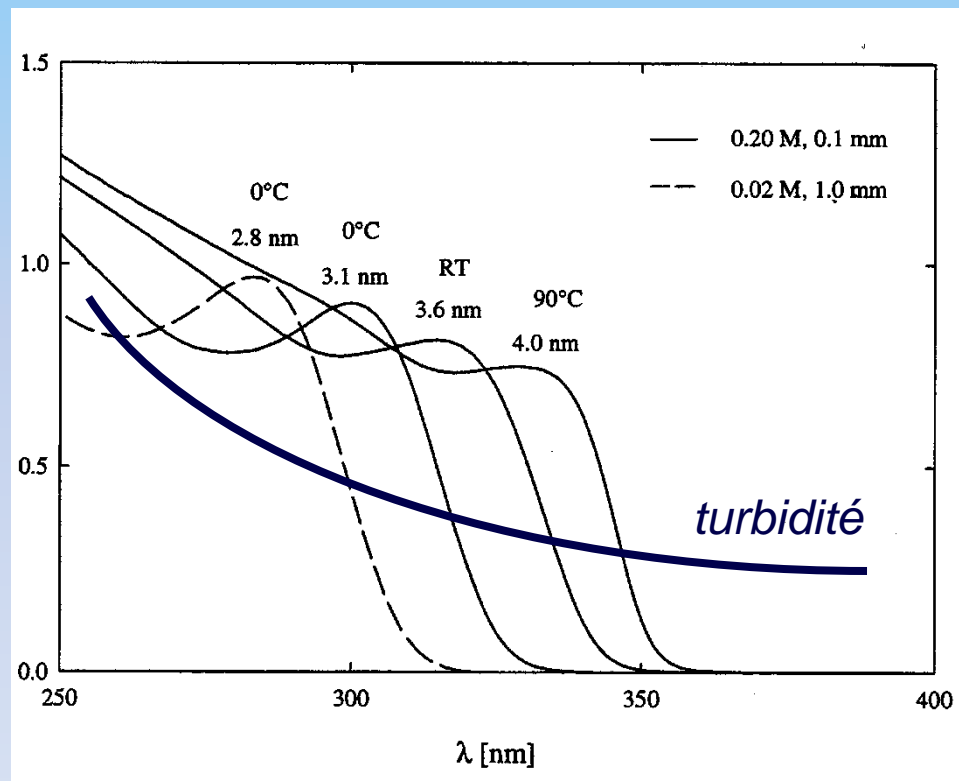
ZnO
size ~ 5 nm

singles



TiO₂
size ~ 5 nm

Aggregation



Size dependent spectral shift for $R(\text{particle}) < R(\text{exciton})$

“Gap-Size” correlation function

L. Brus
1983

$$E_{nano}[eV] = E_g^{bulk}[eV] + \frac{h^2}{8\mu_{eff}R_p^2} - \frac{1.8e}{4\pi\epsilon_r\epsilon_0R_p}$$

ZnO:

$$E_{nano}[eV] = 3,37 - \frac{1.35}{D_p} + \frac{8.47}{D_p^2}$$

E = gap energy (eV)

μ_{eff} = effective exciton mass

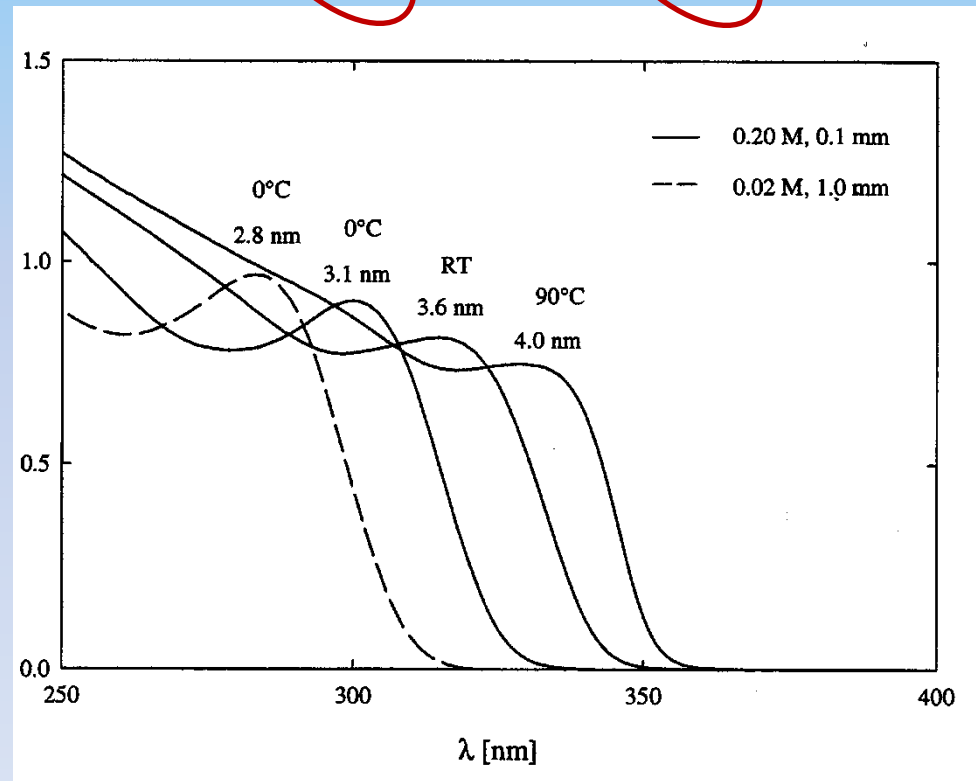
ϵ_r = dielectric constant

ϵ_0 = vacuum permittivity = $8,854 \cdot 10^{-12} \text{ Fm}^{-1}$

D_p, R_p = particle diameter, radius (m)

e = elementary charge = $1,602 \cdot 10^{-19} \text{ As}$

h = Planck constant = $6,626 \cdot 10^{-34} \text{ J s}$



Now even more general



L. Spanhel

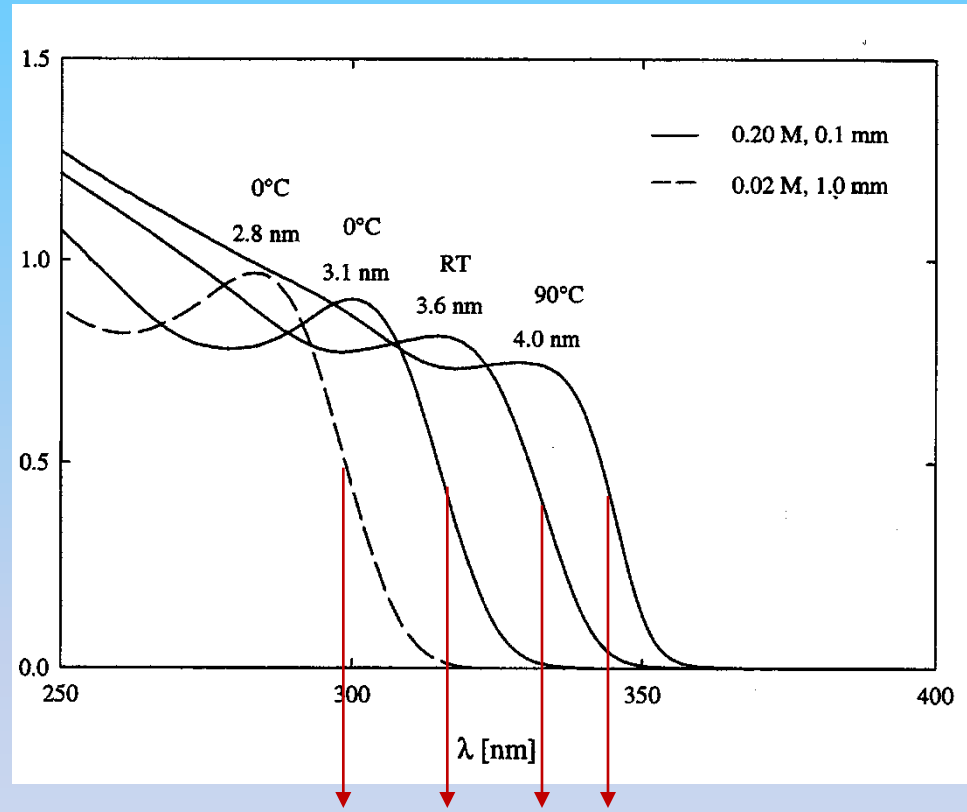
A,B,C: coefficients to be determined via linear regression

ZnO:

$$E_{nano}[eV] = A - \frac{B}{D_p} + \frac{C}{D_p^2}$$

Optical absorption spectrum

XRD/HRTEM



Meulenkamp's finding, JPC B, 1998

ZnO: **1.37** **8.47**

$$E_{nano}[eV] = 3.3 - \frac{1.09}{D_p} + \frac{294}{D_p^2}$$

$$E_{nano}[eV] = \frac{1240}{\lambda(nm)}$$

Joshua Jortner, 1991:

$$P_{\text{nano}}(N) = P_{\text{makro}} + \alpha N^{-\beta}$$

P = property

N = atomic number in cluster

α, β = empirical coefficients

Power law relationship

Number of molecules per particle

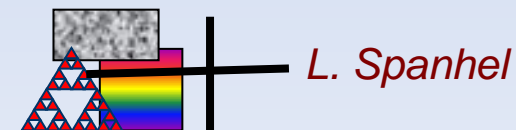
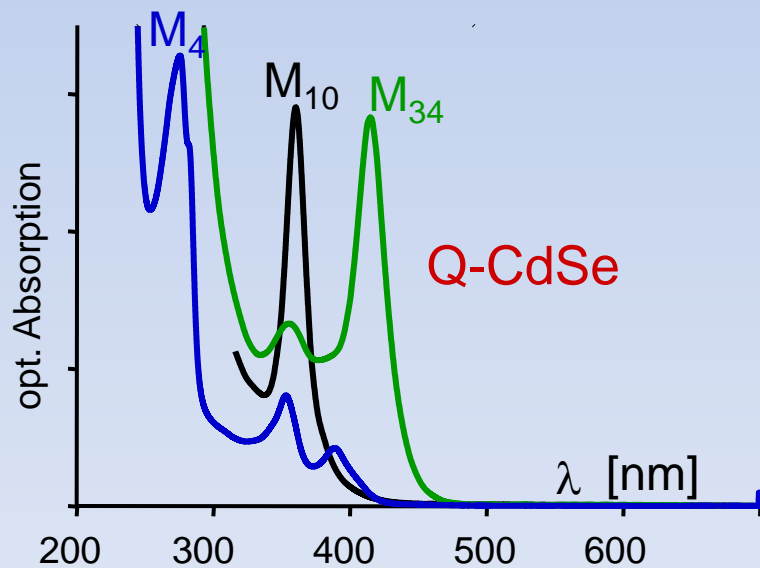
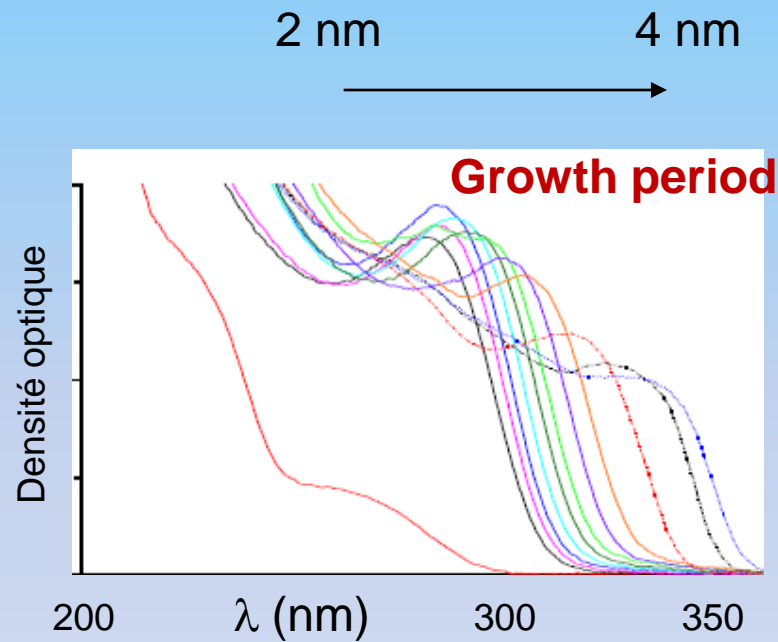
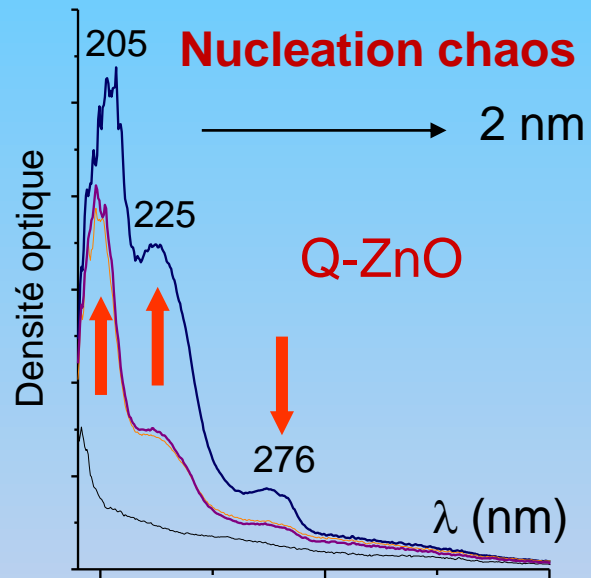
$$N_a = \frac{4\pi R_p^3 M_r N_A}{3\rho_p} = V_p \times N_A \times V_m^{-1}$$

V_p = particle volume

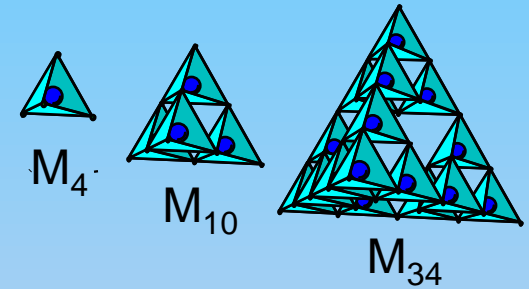
N_A = Avogadro number

V_m = molar volume

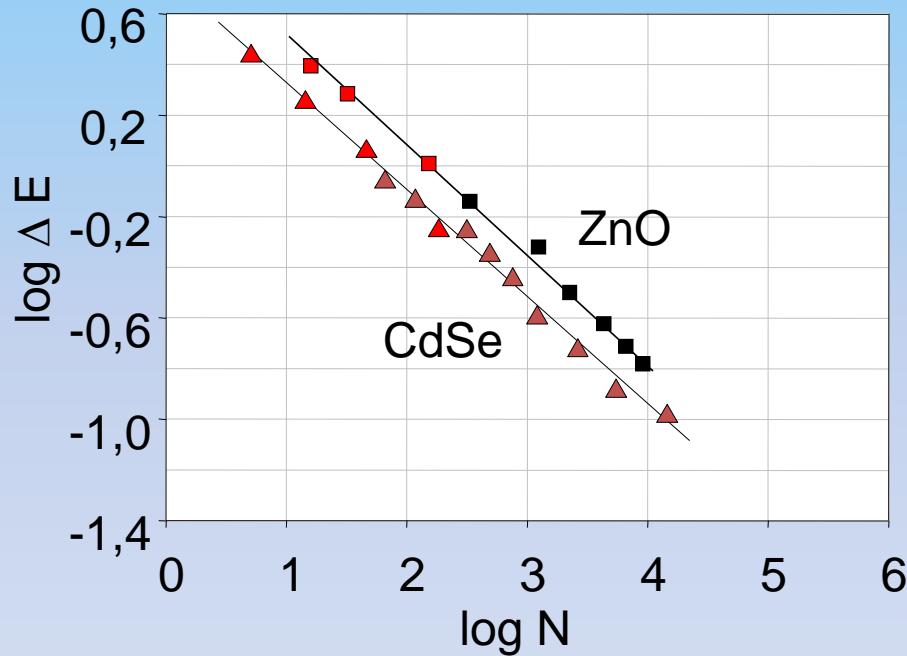




$$\Delta E = \alpha \times N^{-\beta}$$



Chemical elemental analysis, MS, etc..needed to identify the clusters



$\alpha, \beta = ?$

Physical meaning of α, β remains to be searched !!



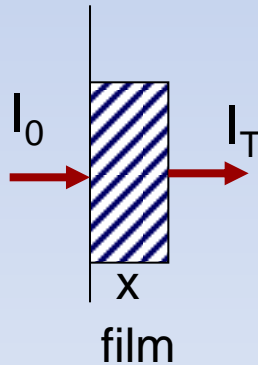
Recall:

Absorption laws

Photophysics

$$I_T / I_0 = T = e^{-\alpha x}$$

α [cm^{-1}] = absorption coefficient
 x = mean light path



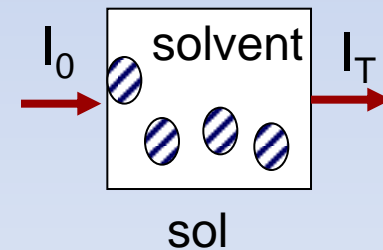
$$\alpha = 2,3 \epsilon / V_m$$

V_m = molar volume

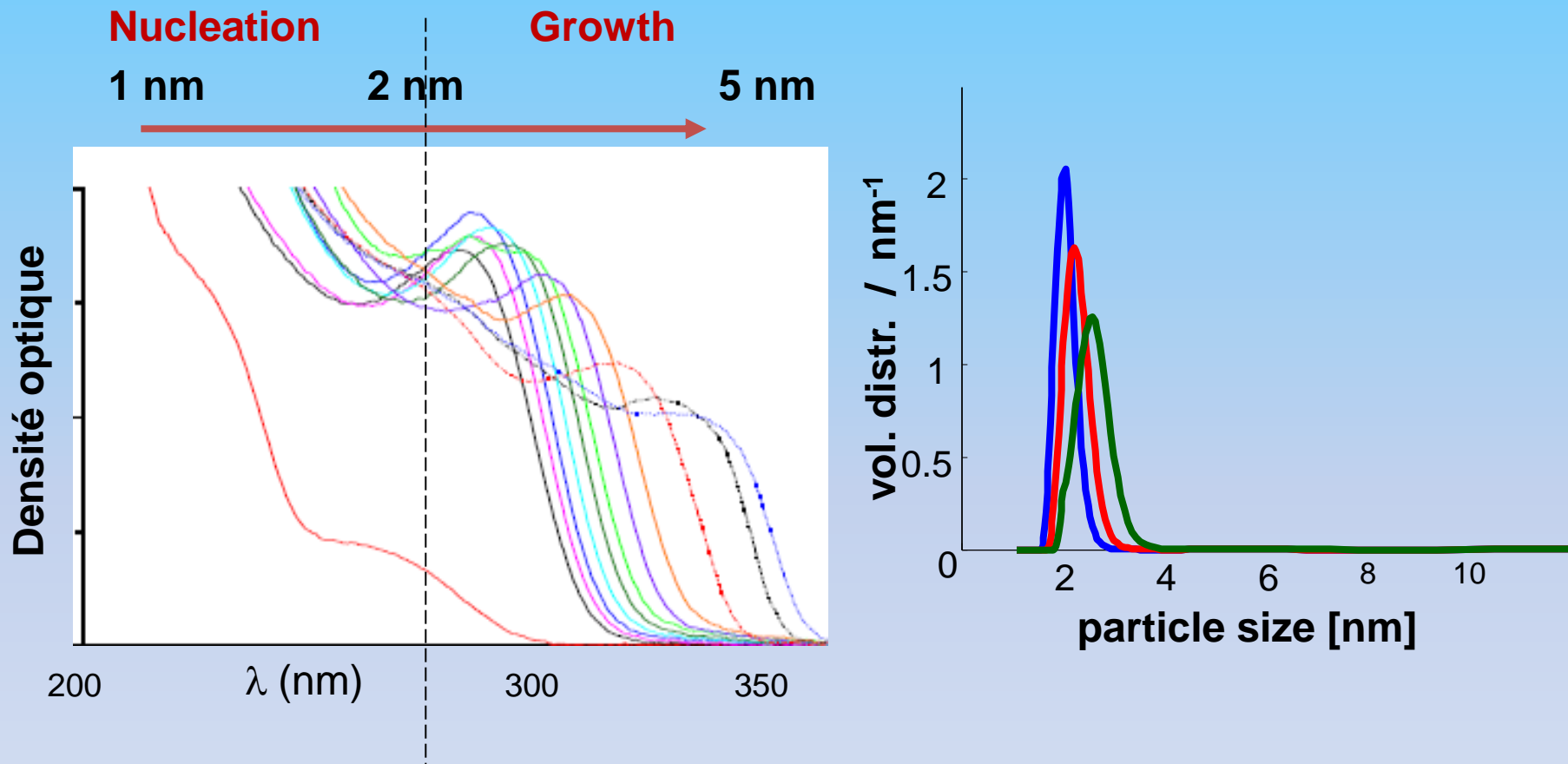
Photochemistry

$$I_T / I_0 = T = 10^{-D.O.}$$

ϵ [$\text{Lmol}^{-1}\text{cm}^{-1}$] = molar extinction
 c [molL^{-1}] = molarity
 d = cell thickness



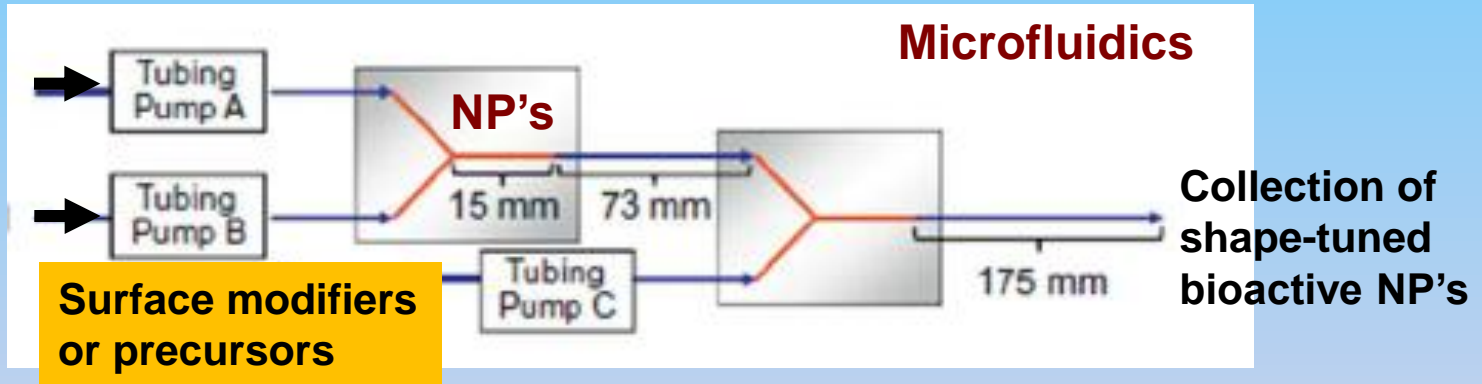
Optical monitoring of the particle size distribution (PDS)



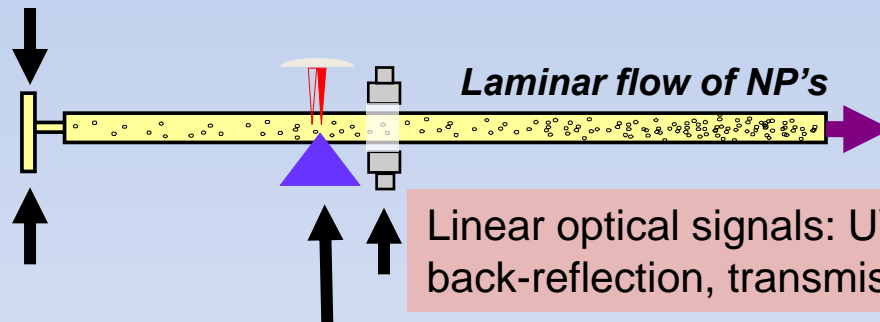
$$E_g \text{ (eV)} = 1240 / \lambda(\text{nm}) \sim f(R^{-2}, R^{-1}, R^{-\beta})$$

Structural/optical monitoring of NP's Up-scaling processes

Precursors
in Y-shaped
micromixer



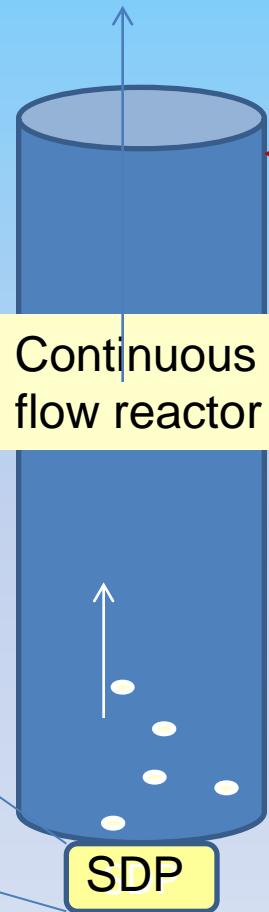
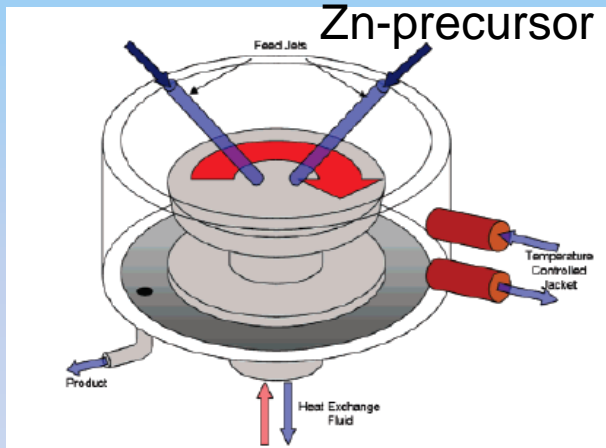
Precursors
in T-shaped
micromixer



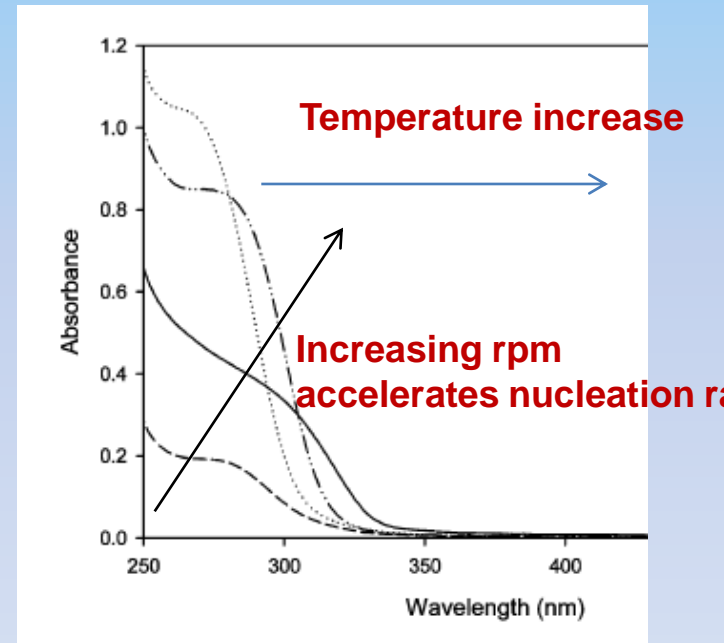
SAXS: small angle X-ray scattering (gyration size, aggregate structures)
Raman analysis of phonons (lattice and superficial molecular vibrations, fs-Laser induced non-linear optical signals)

Spinning disc processor SDP: a way to nano-ZnO Up-scaling

LiOH, NaOH or KOH



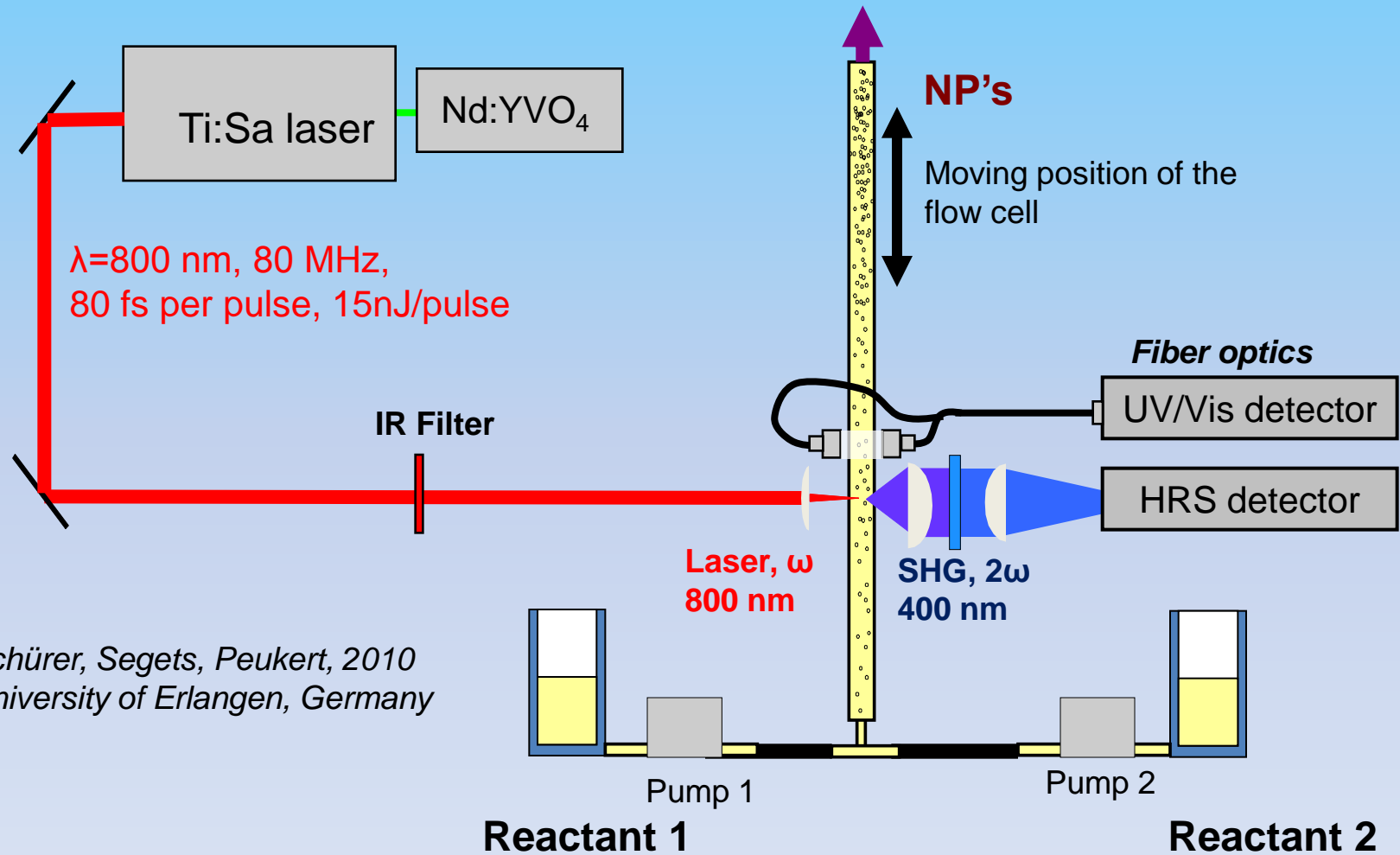
Fiber optical spectrometer



Hartlieb et al, Chem. Mater. 2007

Coupled linear UV-vis and non-linear optical (HRS) nanocolloid growth monitoring

Hyper Rayleigh Scattering



Schürer, Segets, Peukert, 2010
University of Erlangen, Germany

Essentials of non-linear optics

$$P = \epsilon_0 (\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots)$$

Linearity

$$n, \epsilon = c^{te}$$

Non-linearity

$$n, \epsilon \neq c^{te}$$

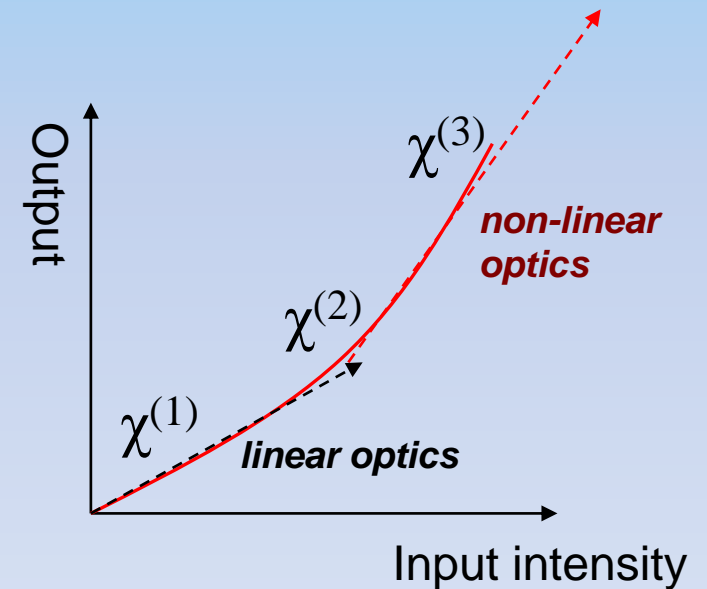
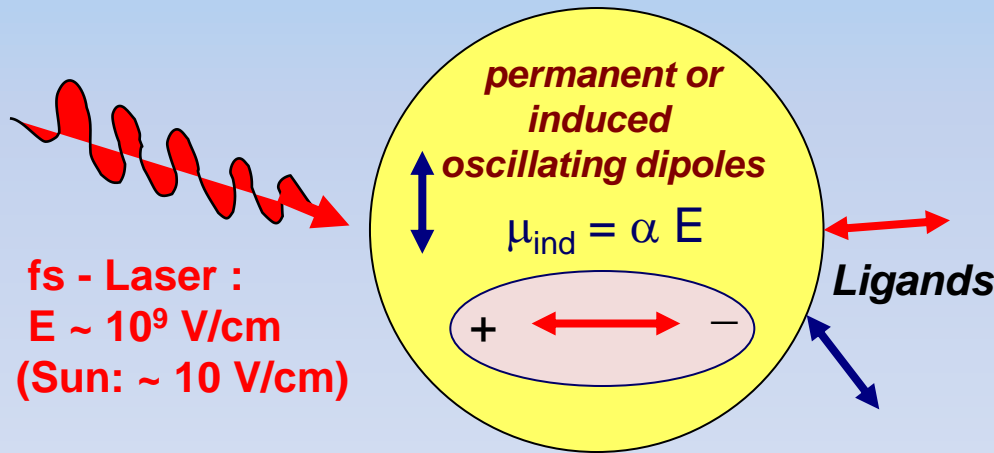
P [C/m²] = Polarisation

$$\chi^{(1)} = F(n, \epsilon_r)$$

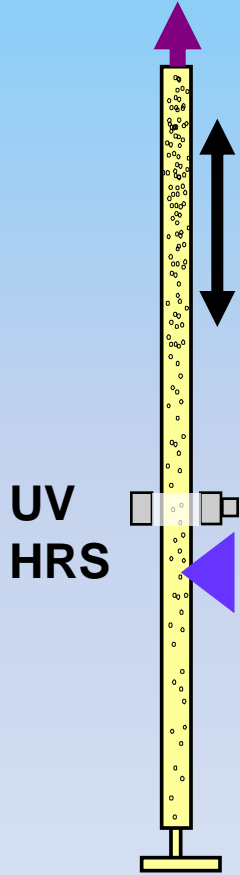
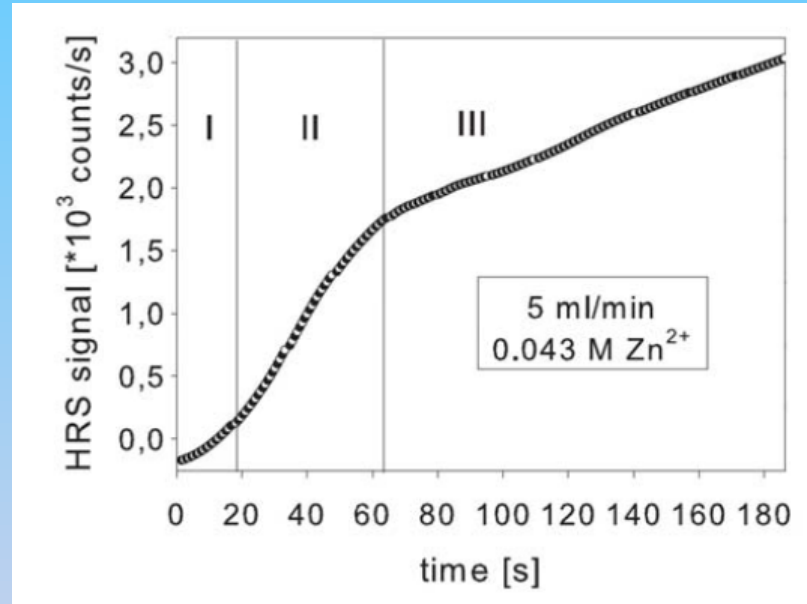
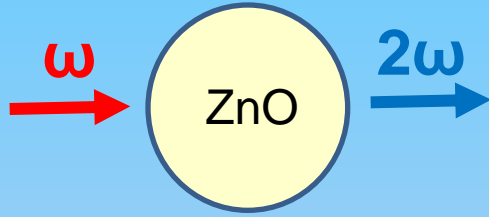
= el. susceptibility

n = refractive index

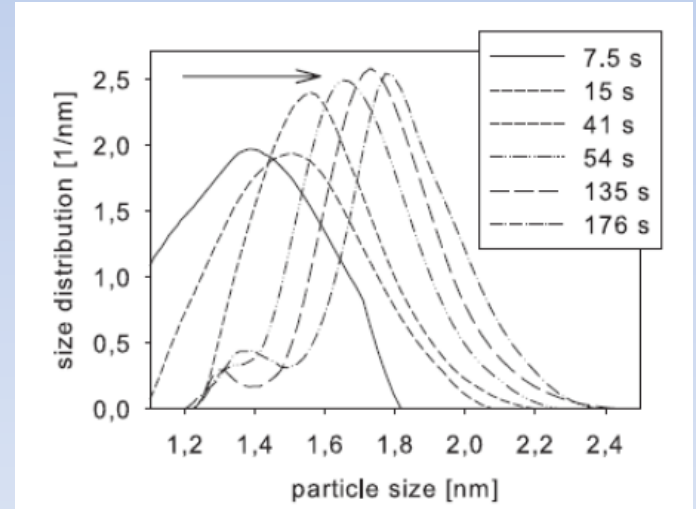
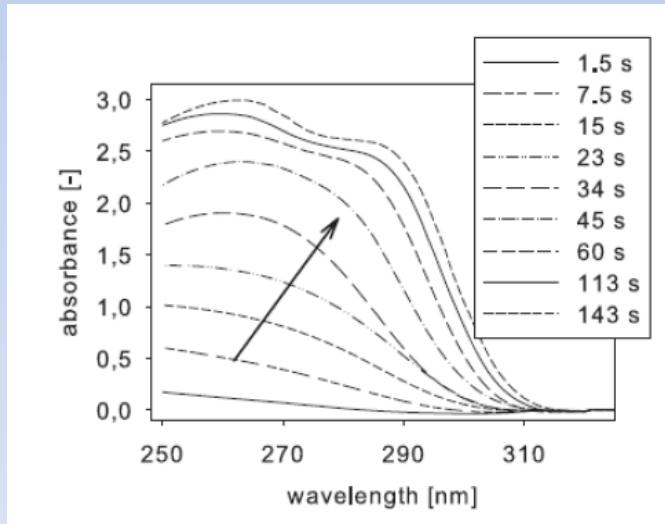
ϵ_r = dielectric coefficient



In our case:

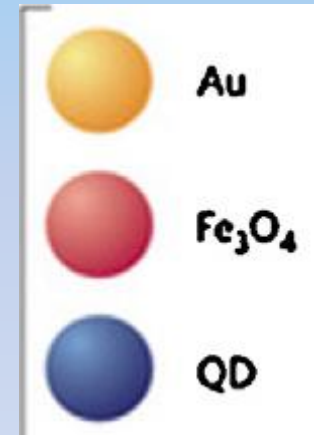
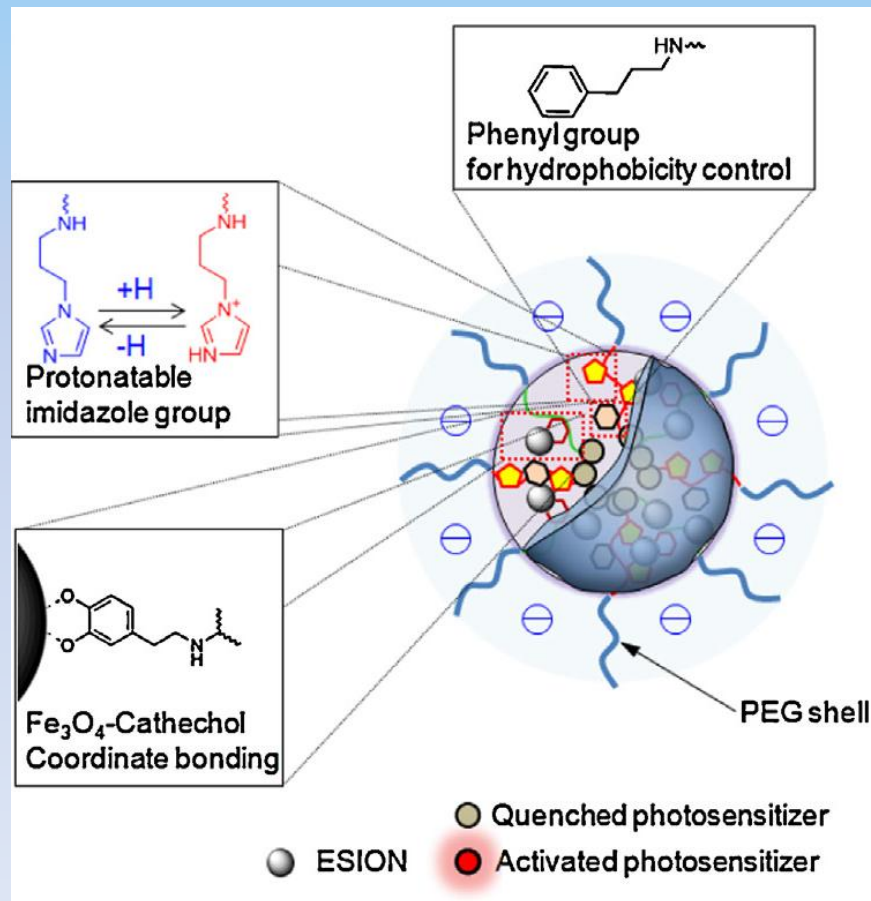


LiOH + Zn-precursor



Isolation and total chemical analysis of monodispersed NP's

Goal: quantification of atoms and molecules inside and in shells
ligand exchange and addition processes
tailoring for biomedicine (theranostics) and standardizations



T. Hyeon et al in Nano Today 2014

Characteristic parameters of spherical nanoparticles

sample	n_A	$(n_s/n_A) \times 100$ [%]	$A = 3/R_p\rho$ [m ² /g]	$V_m = M/\rho$ [cm ³ /mol]
SiO ₂	92 R ³	82	1132	60,08 / 2,648
TiO ₂	99 R ³	81,7	750	101,96 / 4,00
Al ₂ O ₃	126 R ³	78	709	79,86 / 4,23
ZnO	174 R ³	74	535	81,4 / 5,6
Ag	245 R ³	68	285	107,86 / 10,49
Pt	277 R ³	67	139	195,08 / 21,45



$R_p = 1 \text{ nm}$

R_p = radius
 M_r = molar mass
 ρ_p = density
 A = spec. surface area
 V_m = molar volume

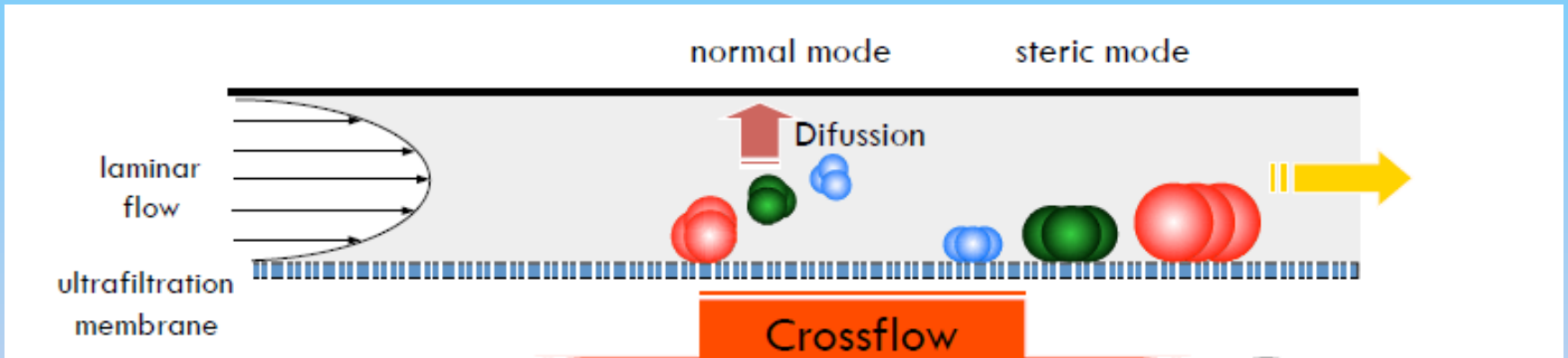
“agglomeration number”
molecules per particle

$$n_A = \frac{4\pi R_p^3 M_r N_L}{3\rho_p}$$

Number of surface molecules

$$n_s \approx (n_A)^{2/3}$$

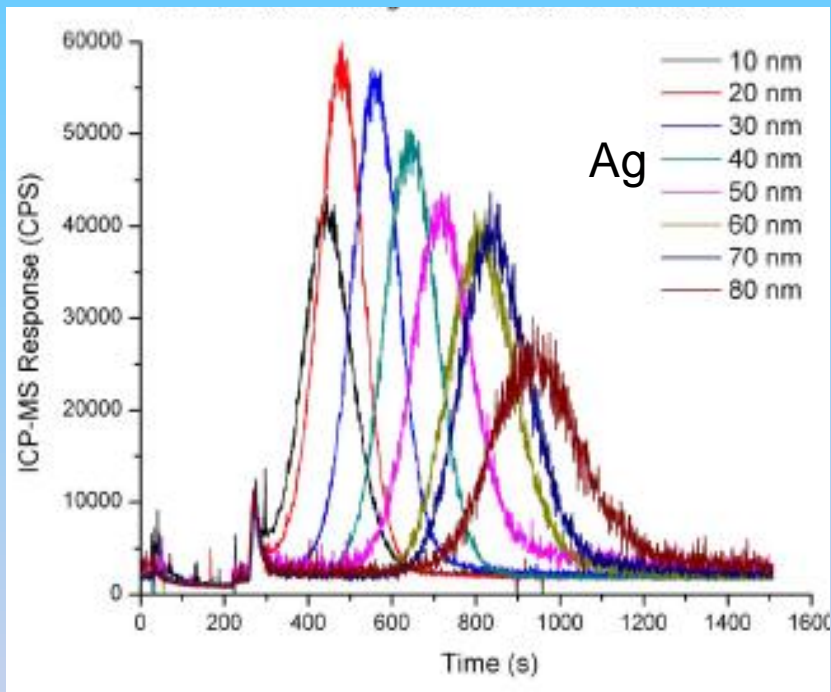
FFF Forced Field Fractionation



ppb-range!



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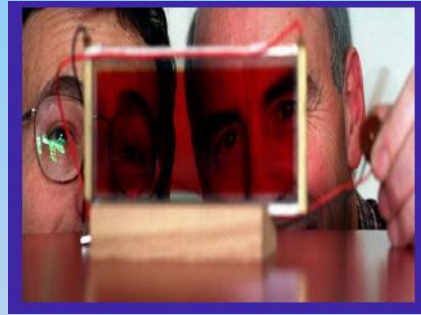
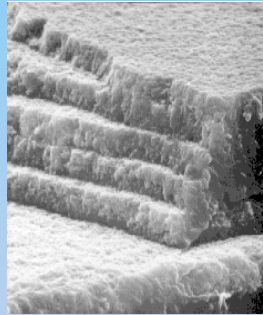
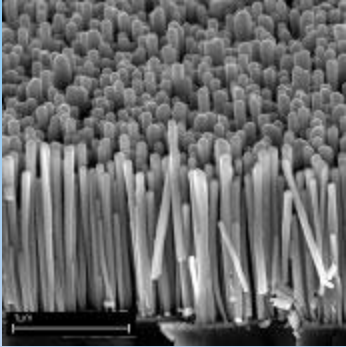


FFF-ICP-MS in comparison with HRTEM and DLS

Note!
FFF-ICP-MS : ~ $\mu\text{g/L}$
HRTEM-DLS : ~ mg/L

Nominal	10nm	20nm	30nm	40nm	50nm	60nm	70nm	80nm
TEM	9 \pm 1	20 \pm 1	32 \pm 4	42 \pm 4	55 \pm 5	67 \pm 4	72 \pm 3	84 \pm 5
DLS	22 (11 - 84)	29 (13 - 90)	41 (15 - 124)	51 (35 - 113)	54 (14 - 121)	67 (32 - 133)	74 (64 - 104)	86 (58 - 142)
FFF-ICP-MS	26	31	40	52	61	75	76	86

Chapter 2 solar sector

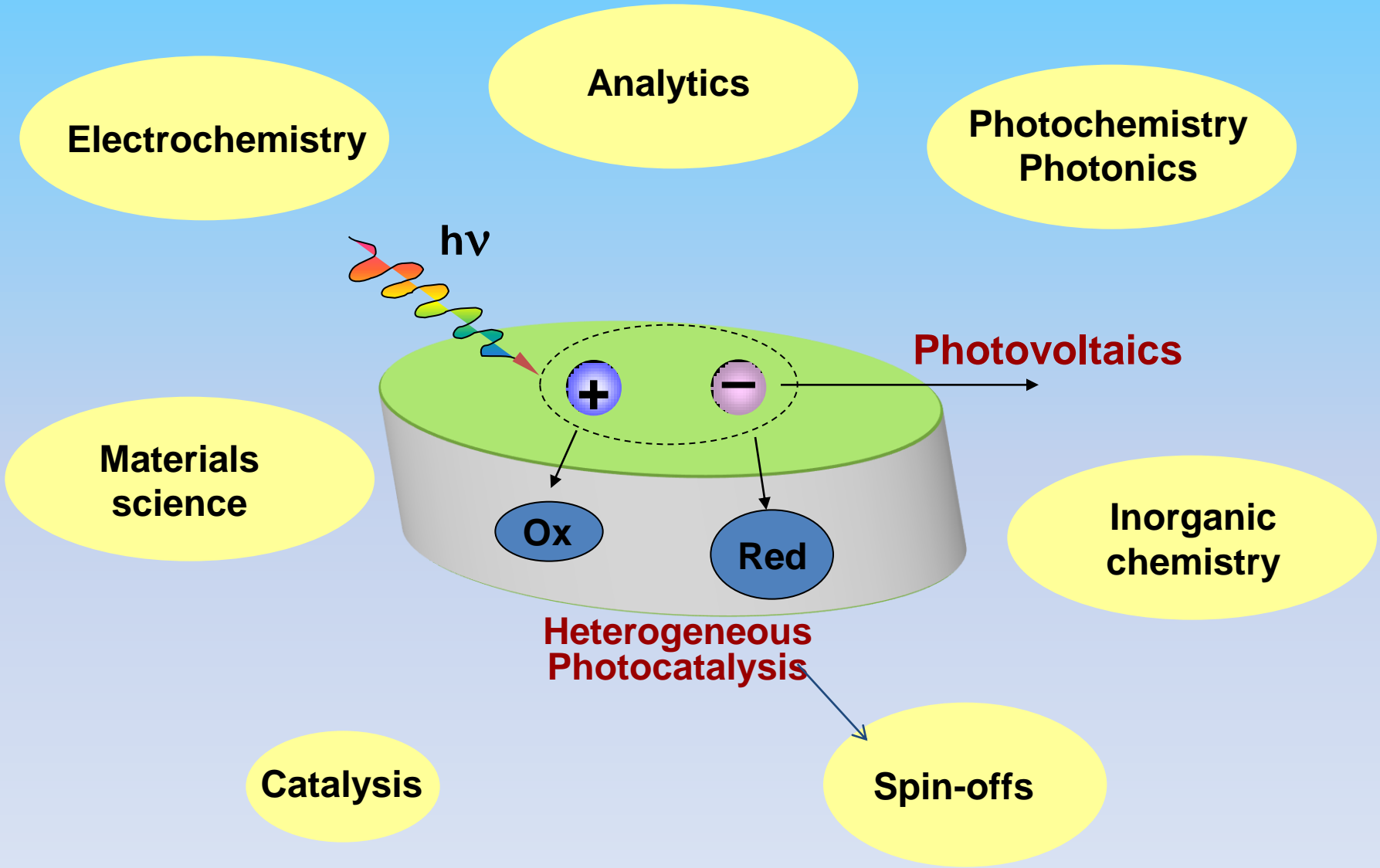


Inorganic nanostructures and Solartech

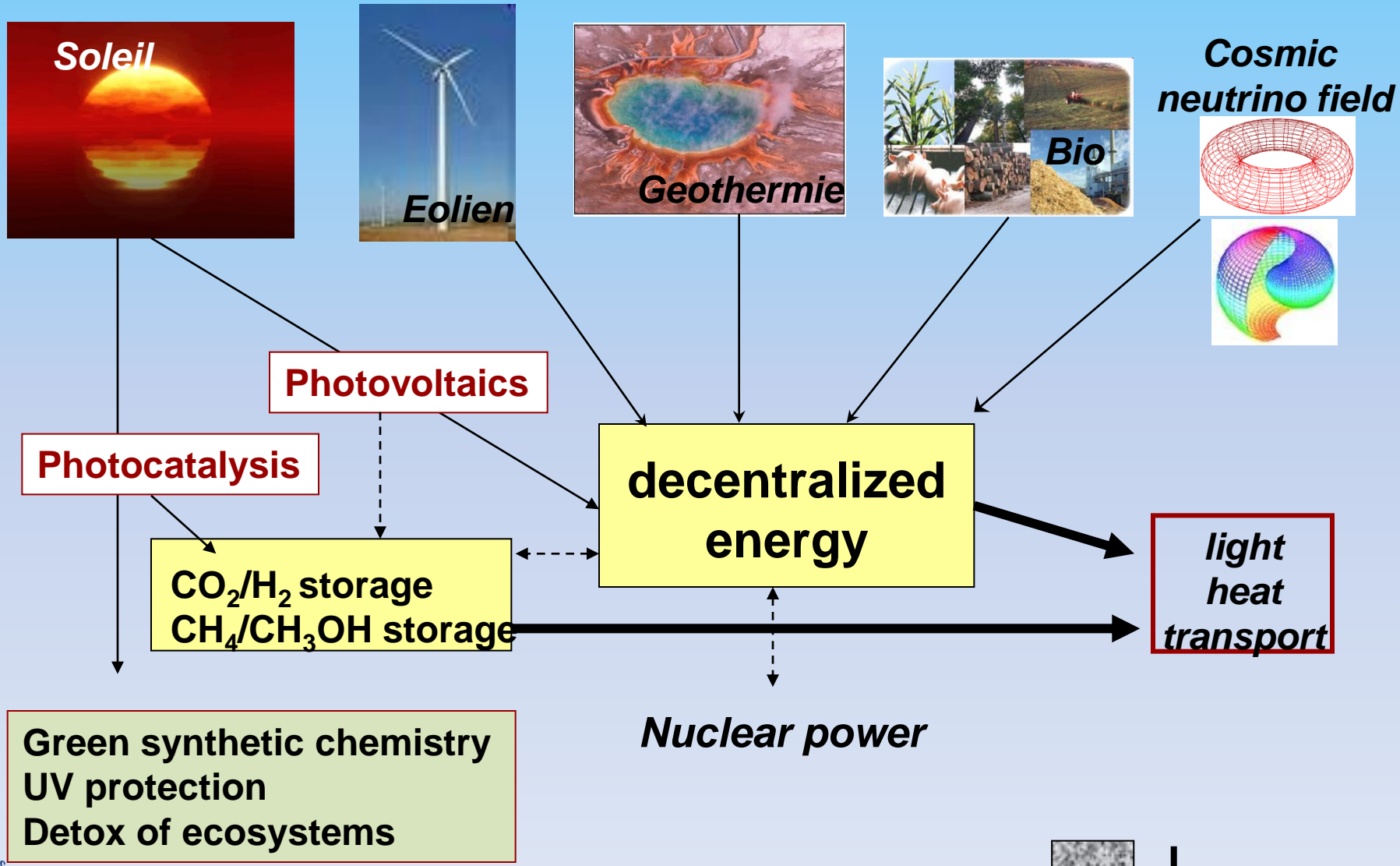
Introduction to renewable energy resources

Theory and applications of nanoscaled photocatalysts

Classical photovoltaics and future solar cells on the nanoscale



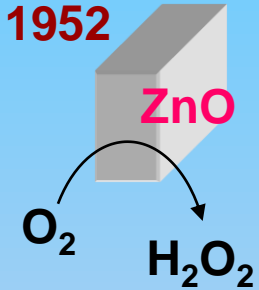
Energy resources of 21 century



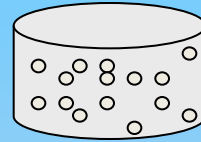
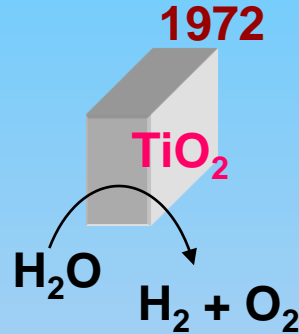
Veselovskii & Shub

Fujishima & Honda

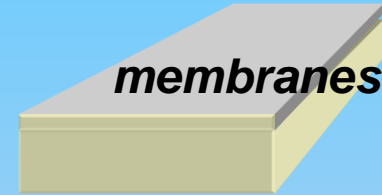
1952



1972



preparative
org. synthesis



environmental
applications

TiO₂, ZnO, Fe₂O₃, CdS, ZnS, ...

1839

1954

1980

nanotechnology 2010

History of solar technology

Photoelectric
effect

PV 1. generation

mono-Si

A. Becquerel Chapin, Fuller, Pearson

PV 2. generation

a-Si, CdTe,
CuInSe₂

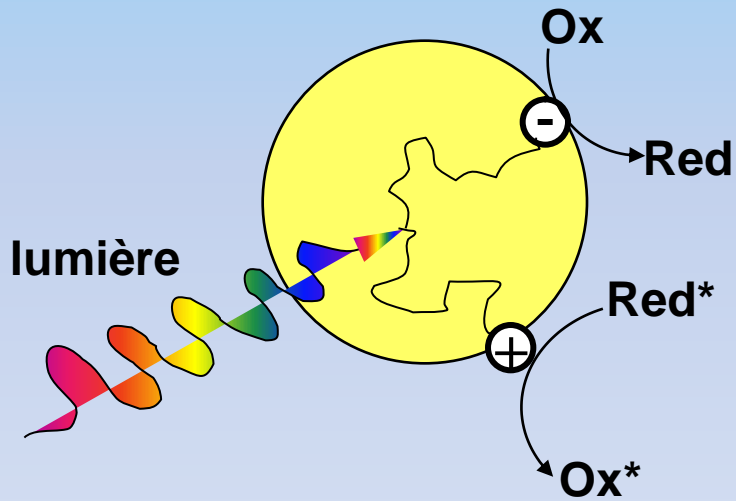
PV 3. generation

nanostructures
metamaterials

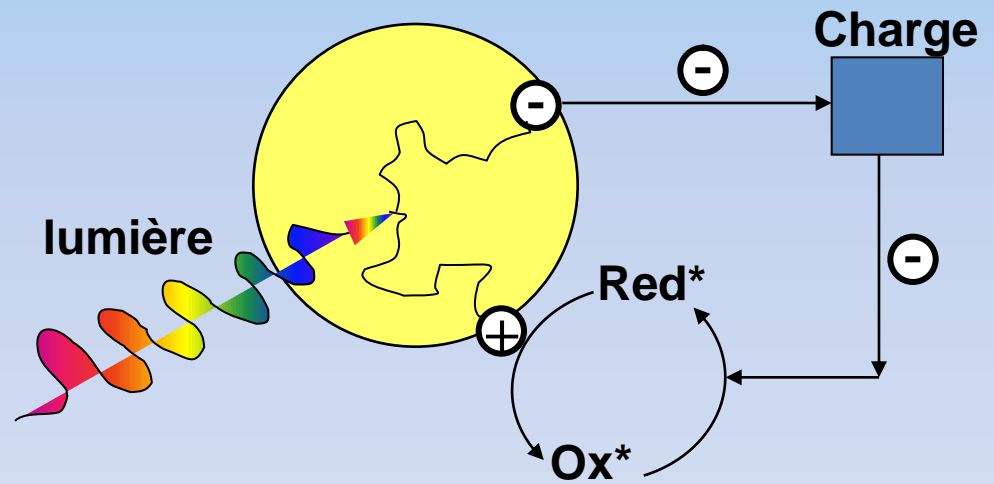


Semiconductor (SC) nanoelectrodes in solar sector

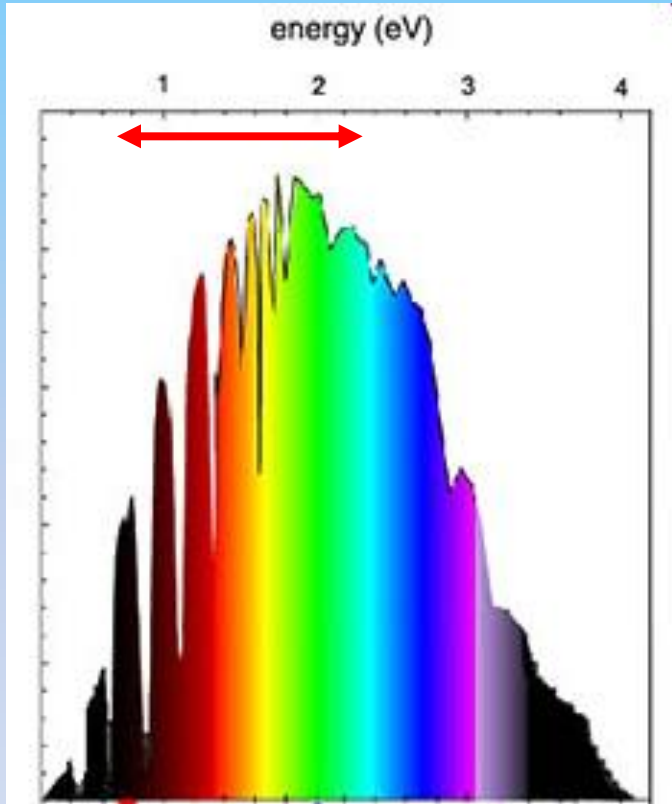
Photocatalysis
Open circuit



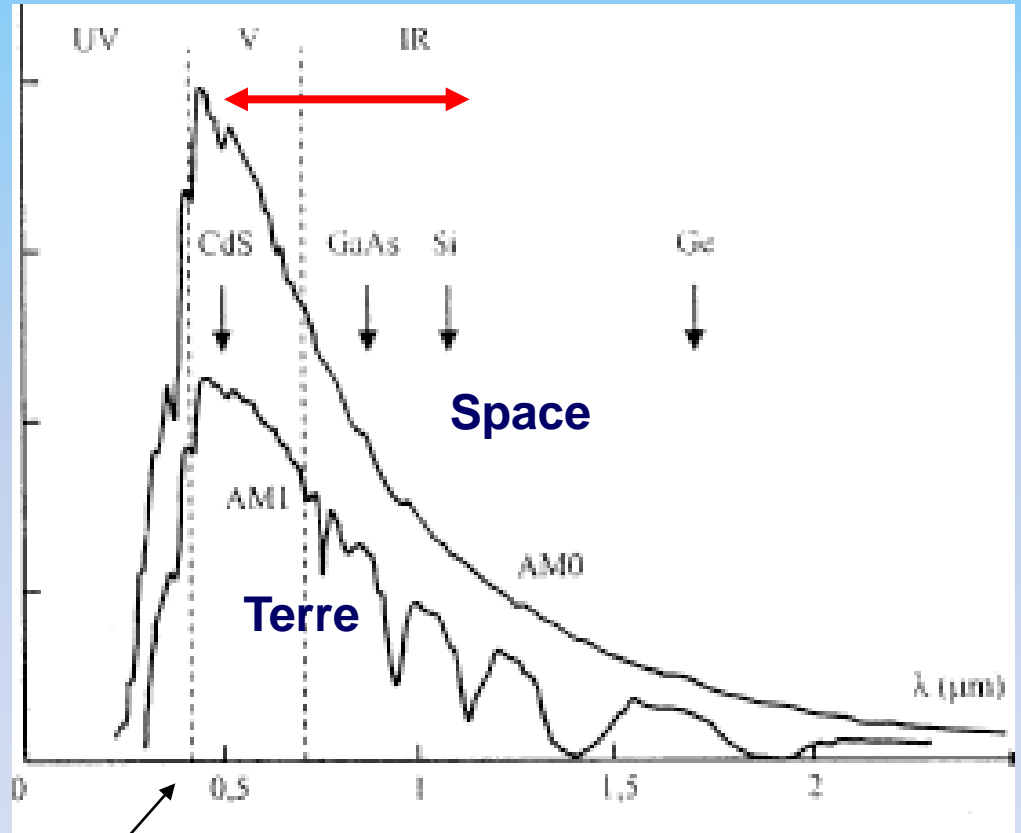
Solar cells
Closed circuit



Emission spectrum of our sun

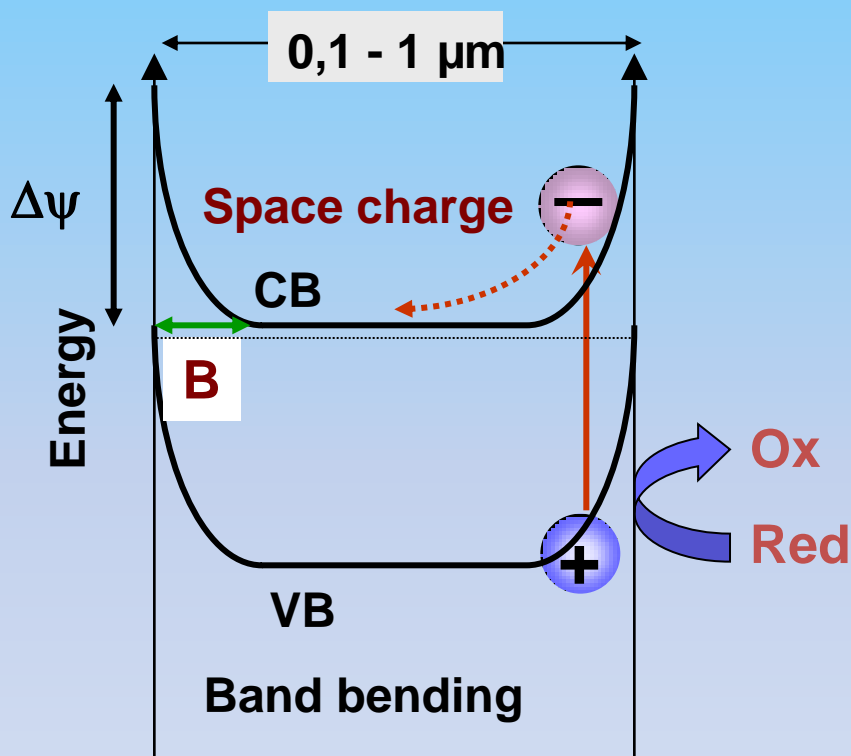


Sun spectrum

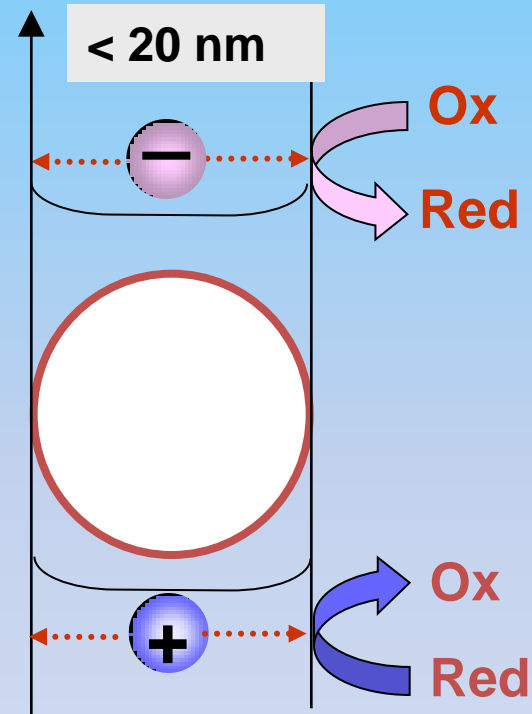


$$E = hc/\lambda$$

SC - Electrochemistry: from micro to nano scale

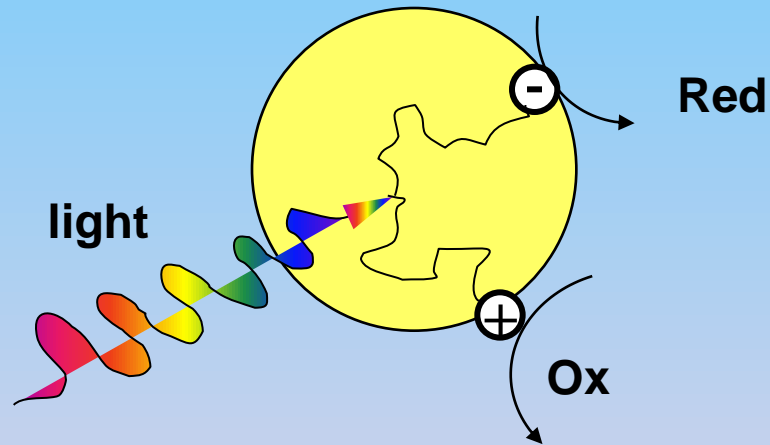


$$\Delta\psi = \frac{kT}{2e} \cdot \left(\frac{B}{1/\kappa} \right)^2$$



$$\Delta\psi = \frac{kT}{6e} \cdot \left(\frac{R_p}{1/\kappa} \right)^2$$

Thermodynamics and kinetics of semiconductor photocatalysis

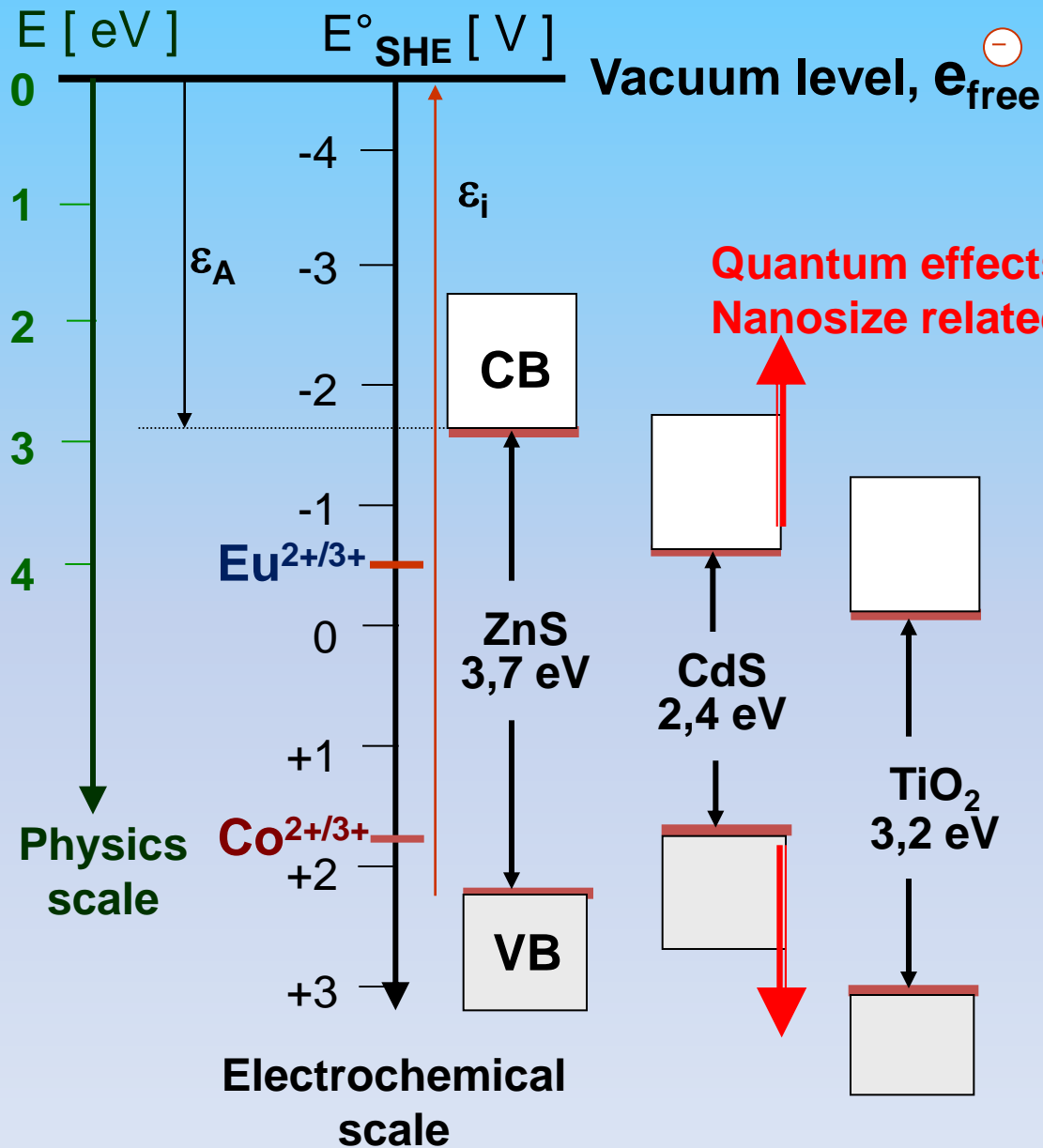


1. Driving force of interfacial red ox processes

$E_{CB,VB}$, E° (red ox)

2. Elementary processes in photoexcited nanoparticles:

diffusion, recombination, transfer, reaction



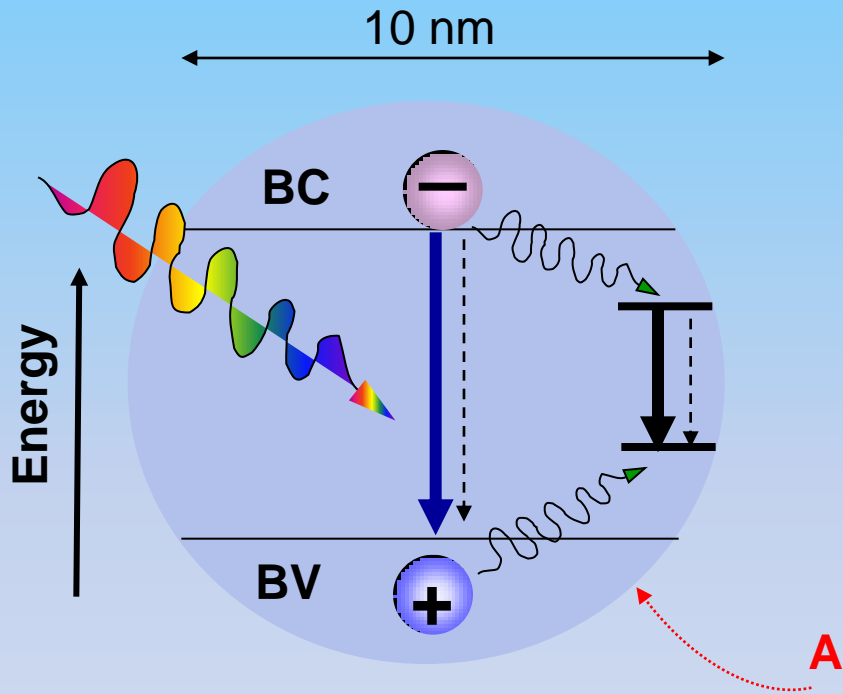
Note:
 $E_{BC} = E^\circ + 0,059 \text{ pH}$

Photoreduction:
 $E_{BC} < E^\circ(A/A^-) !$

Photooxidation:
 $E_{BV} > E^\circ(D/D^+) !$



Kinetics and photocatalysis



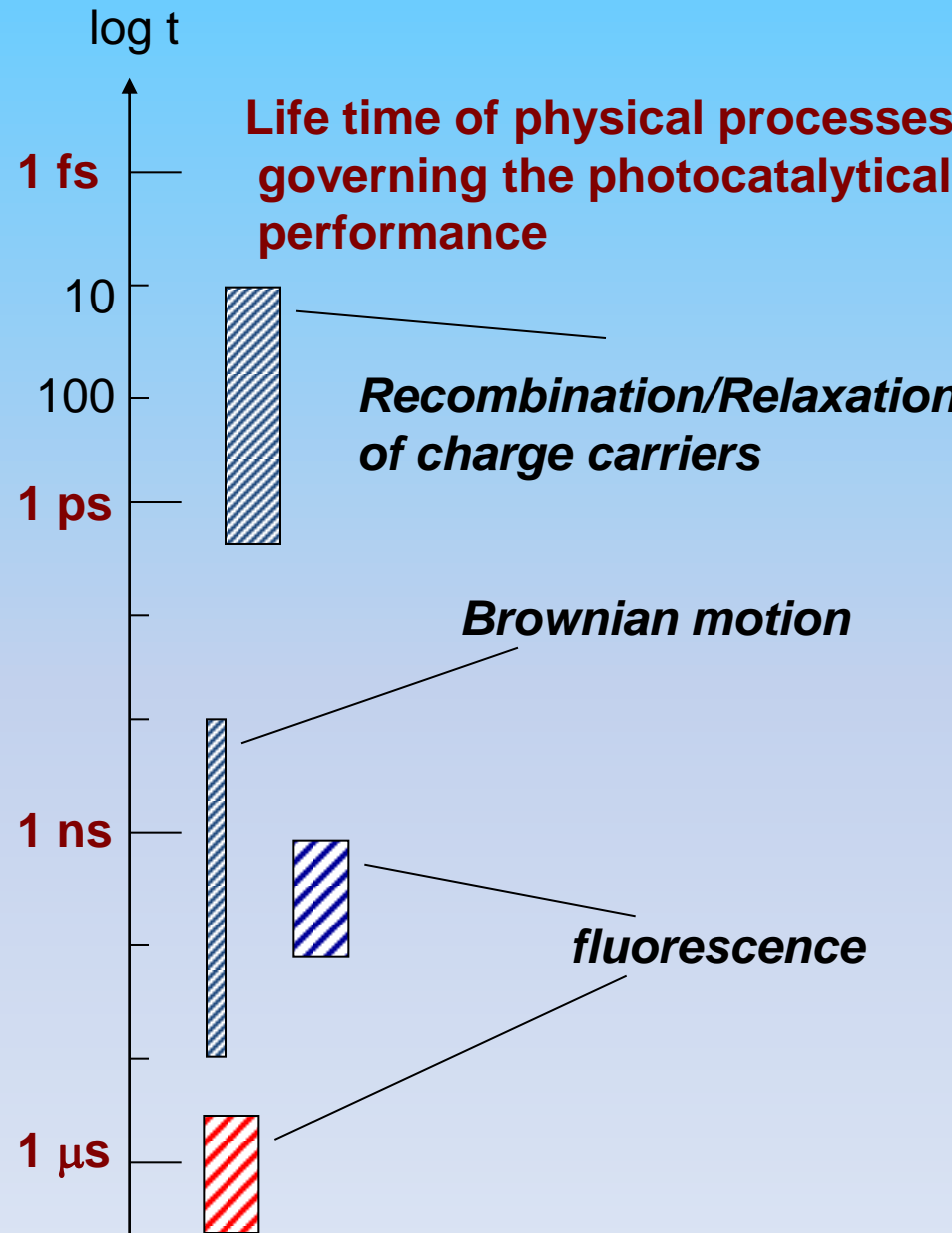
$$\tau_D = \frac{R_p^2}{\pi^2 \cdot D_{e,h}}$$

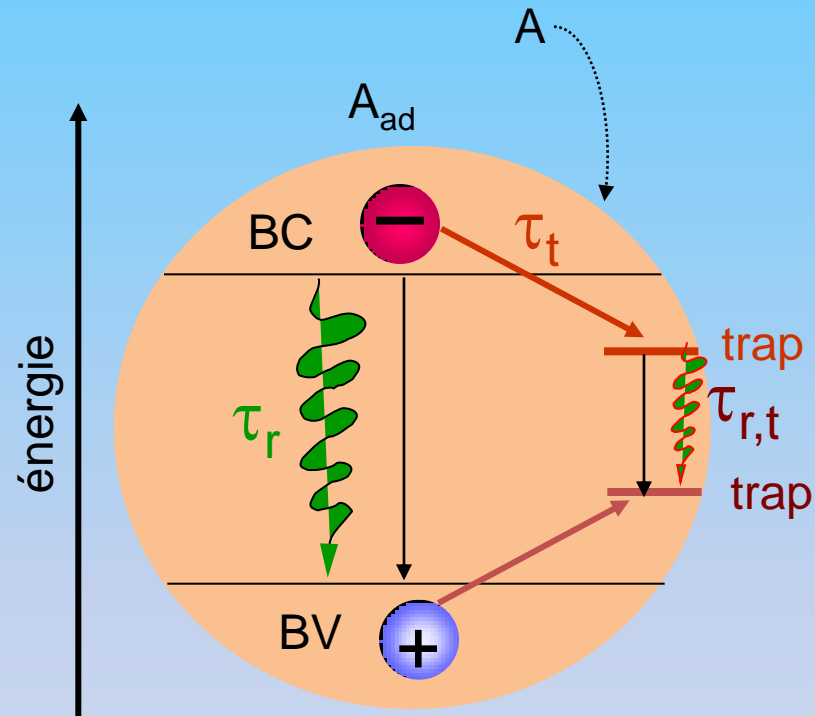
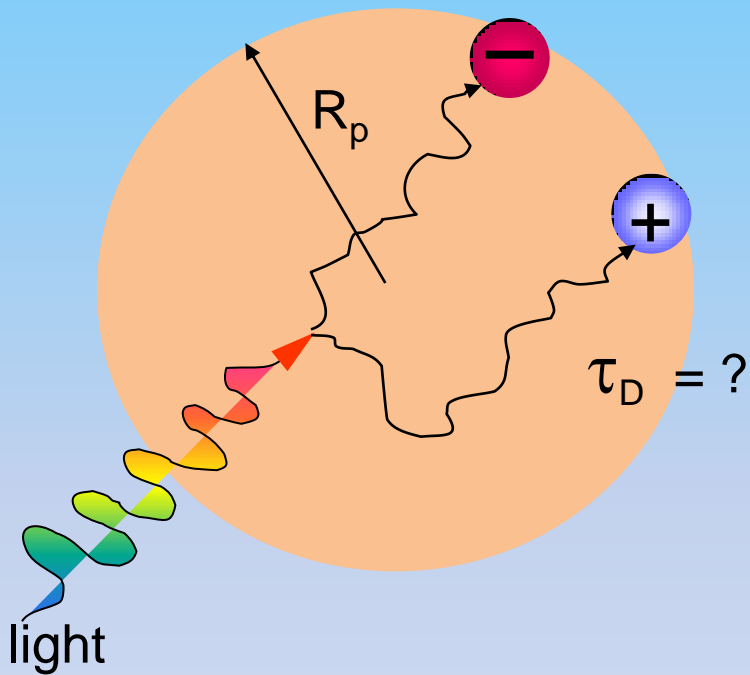
$$D_{e,h} \sim 10^{-5} \text{ m}^2/\text{s}$$

$$\langle x^2 \rangle = 2 D t$$

$$D_{10\text{nm}} = 10^{-9} \text{ m}^2/\text{s}$$

$$D_A = 10^{-7} \text{ m}^2/\text{s}$$





$$\tau_D = \frac{R_p^2}{\pi^2 \cdot D_{e,h}}$$

$D \sim 10^{-5} \text{ m}^2/\text{s}$:

R_p : 5 nm τ_D : 250 fs
 20 nm 4 ps

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

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

Nanophotocatalyst optimization strategies

▶ **spectral profile**

visible light active nano's are needed (400 – 600 nm)

▶ **longe distance charge separation**

heterostructures, dopings and surface modifications

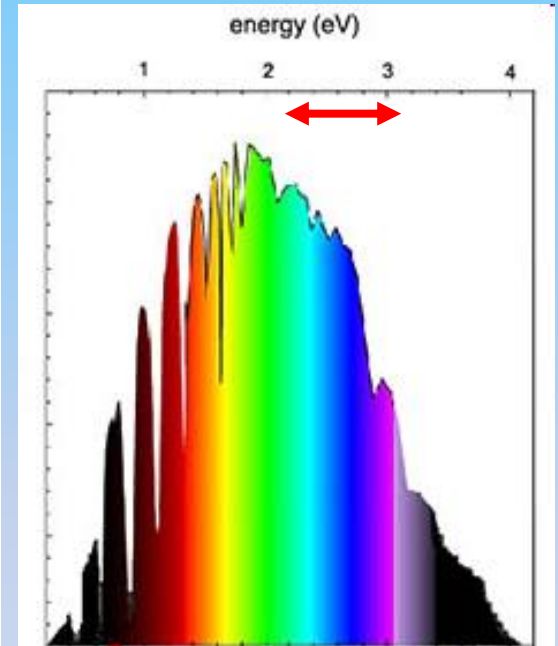
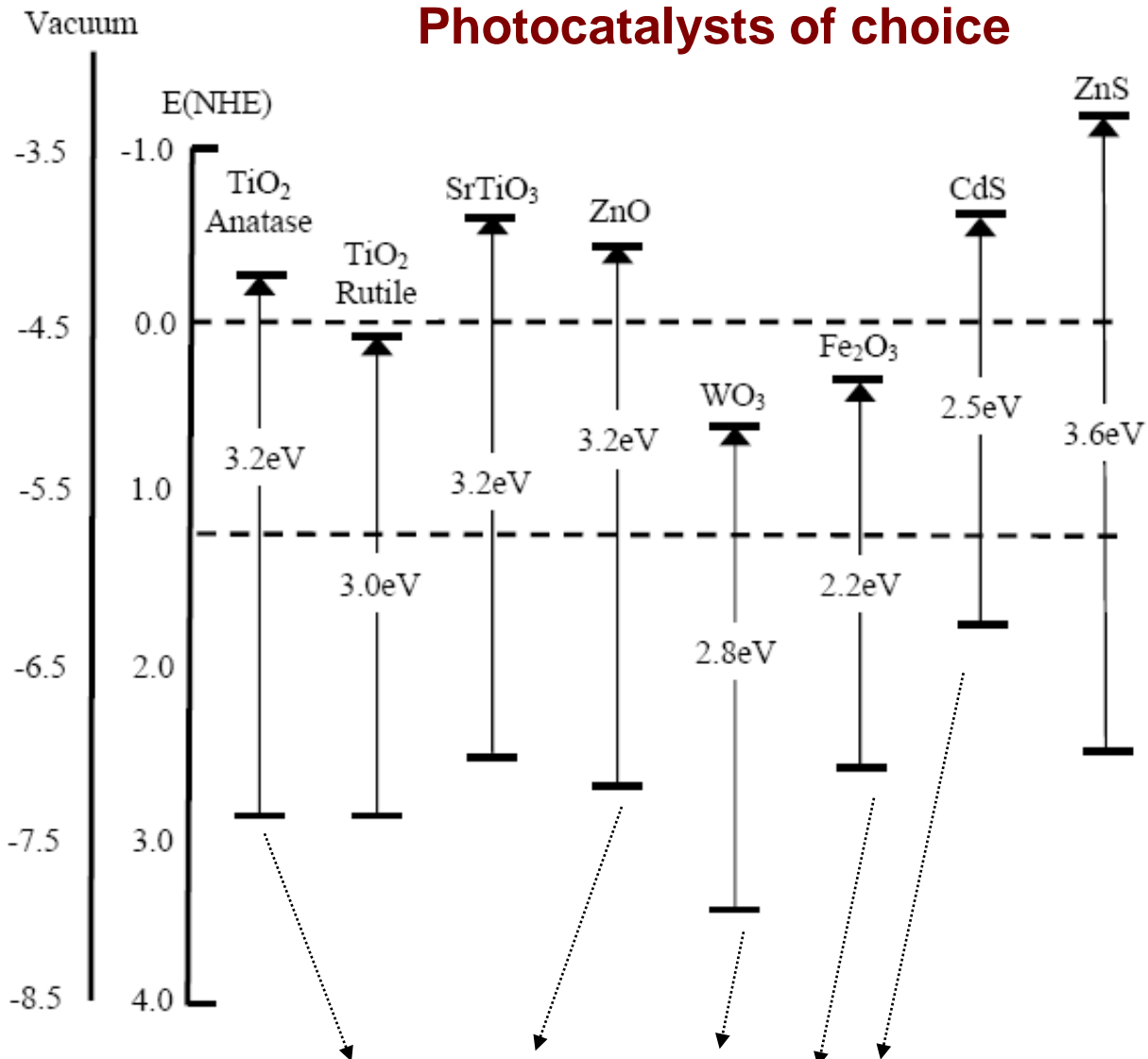
▶ **morphology of immobilized nanostructures**

particle shapes, aggregate architectures and mesoporosity

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

nanocolloids, powders, thin coatings, photoreactor design

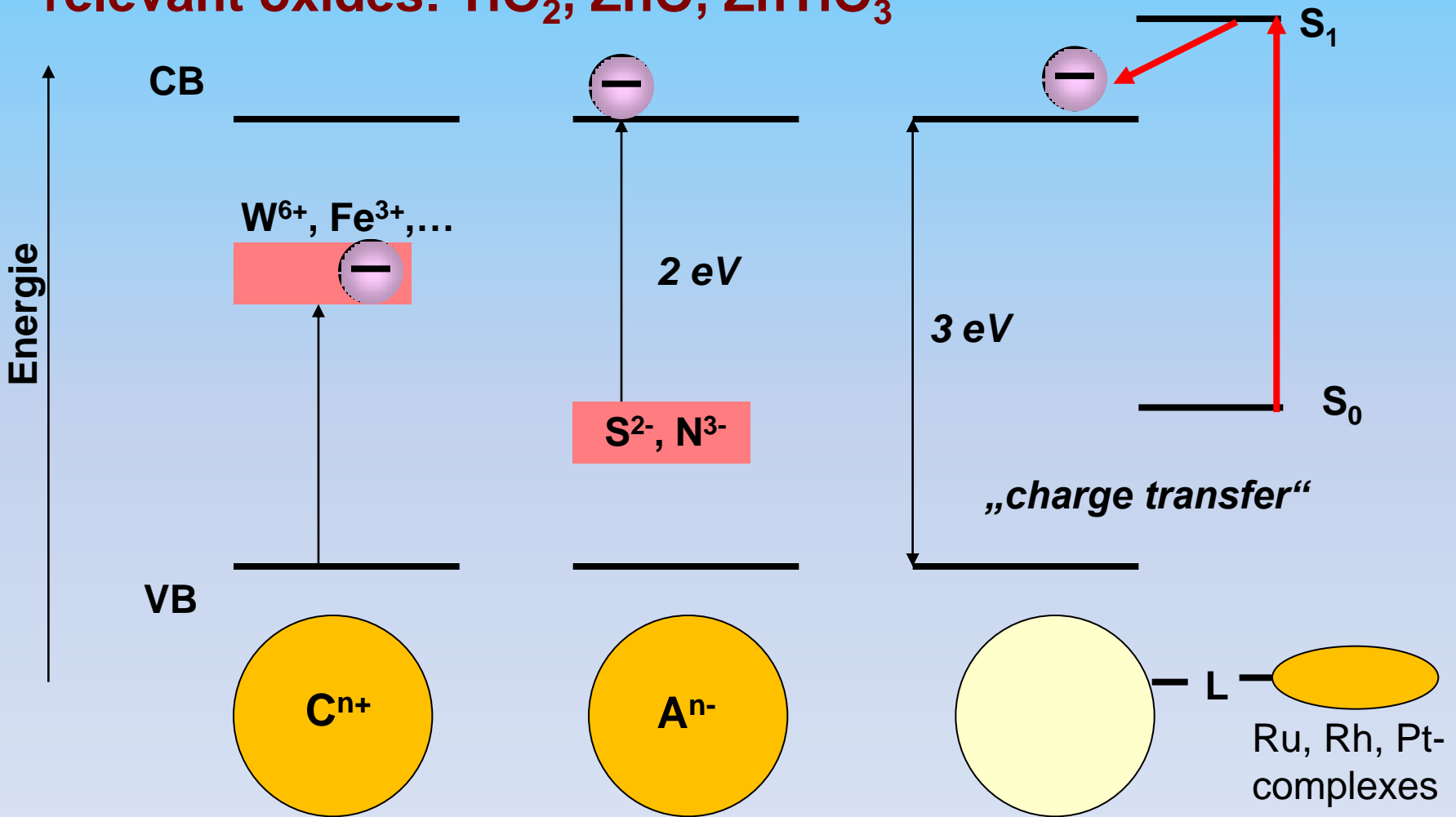
Photocatalysts of choice



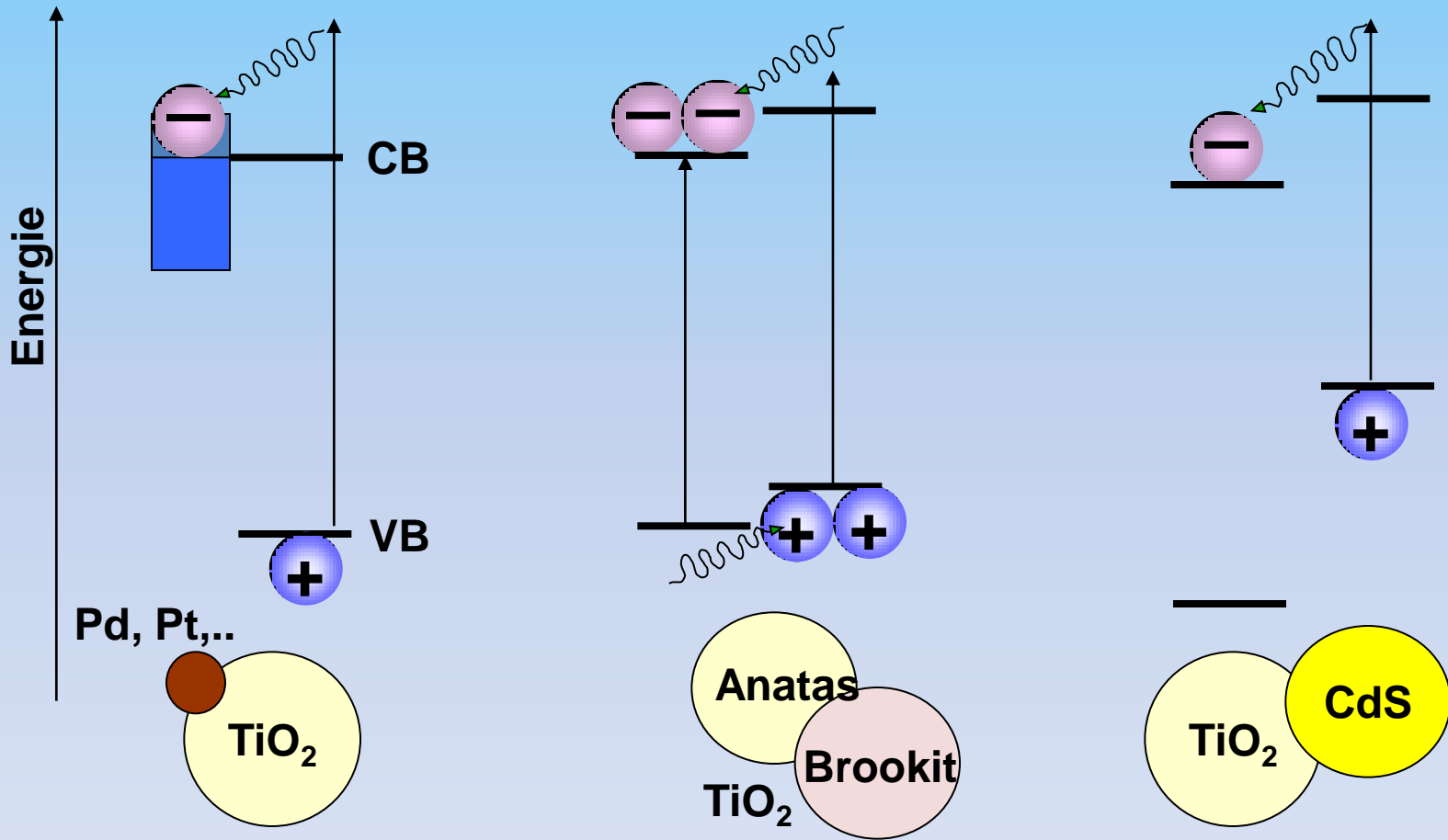
Note:
 Avoid photo-corrosions
 CdS, ZnS, Fe₂O₃

Doping delivers better charge separation

relevant oxides: TiO_2 , ZnO , ZnTiO_3

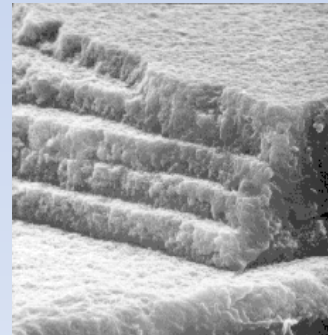
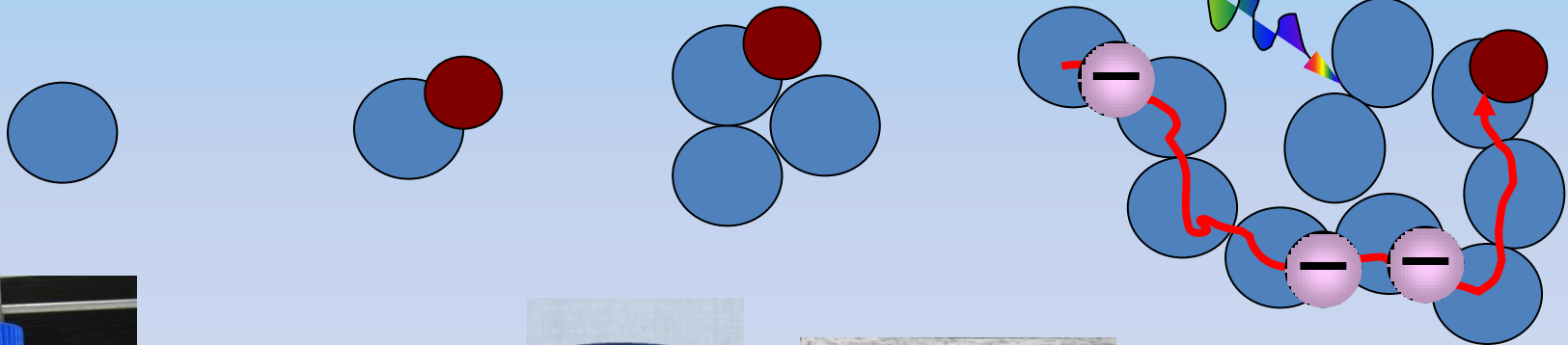


Rapid separation of electron-hole pairs blocks their thermal deactivation (nr, e-h recombination)

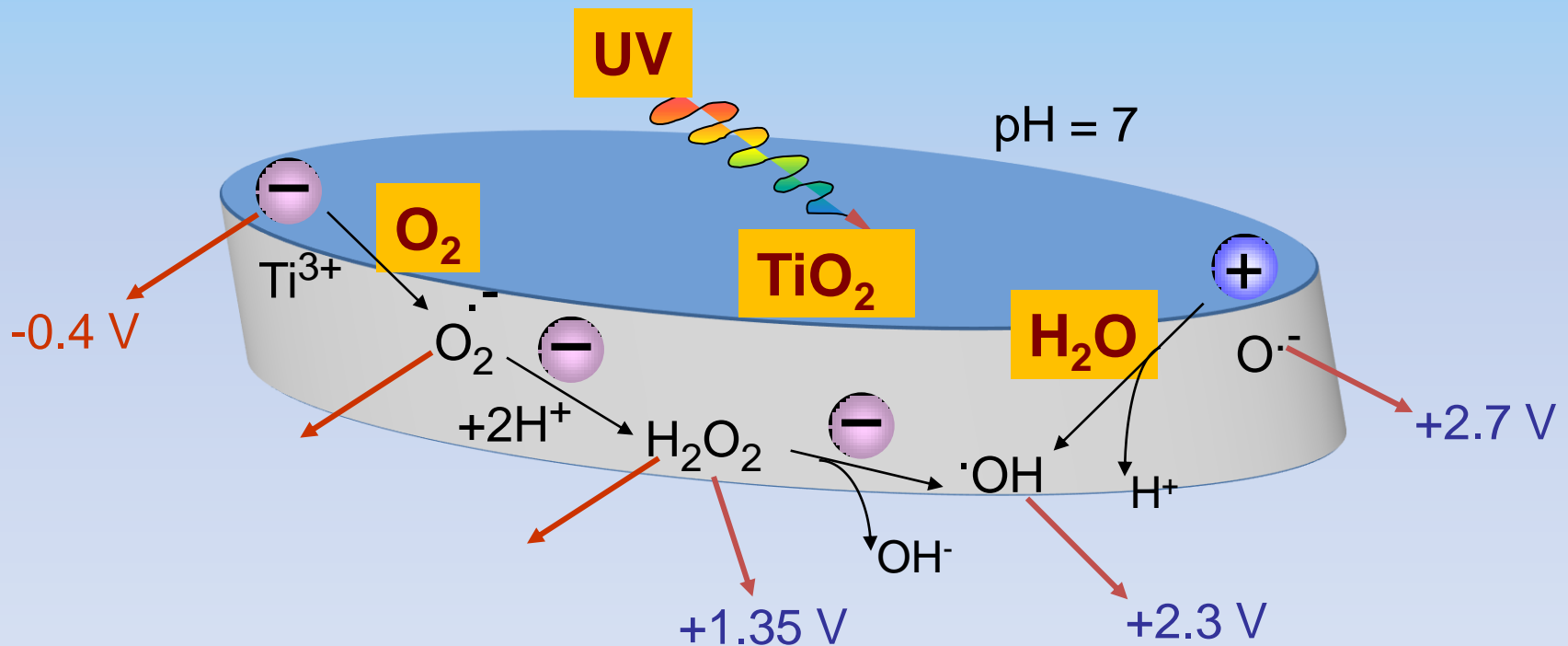
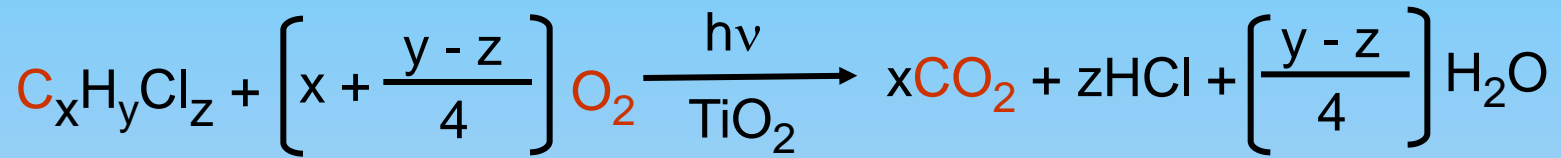


Photocatalysis applications

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



Photomineralisation of organic pollutants



Solar decontamination of industrial waters in the VW company in Taubate (Brasil) since 1999



Total surface: 50 m²

Turnover : 1 m³/jour

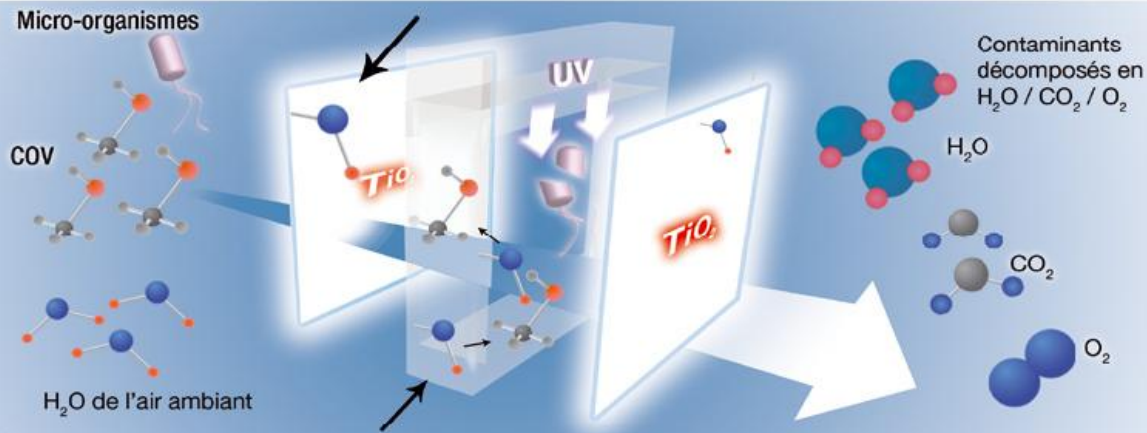
CATA: Hombikat-TiO₂ (Anatase)

Groupe OH° formé par l'action de TiO₂ +UV

Micro-organismes

COV

H₂O de l'air ambiant



Contaminants
décomposés en
H₂O / CO₂ / O₂

H₂O

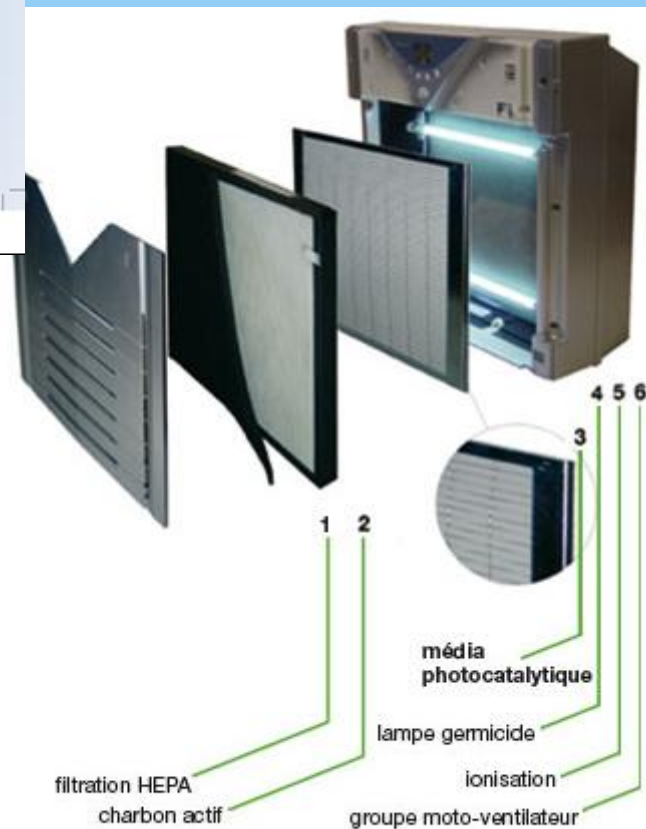
CO₂

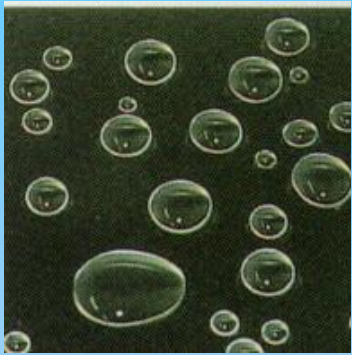
O₂

Groupe OH° détruisant les contaminants

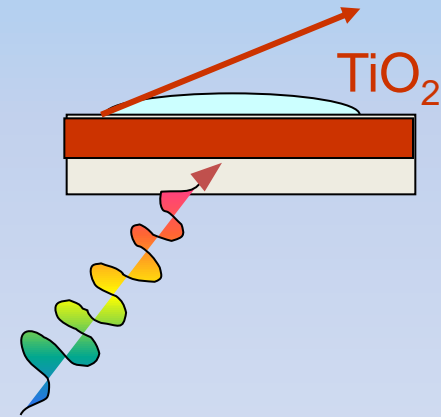
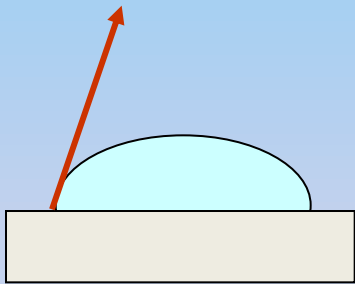
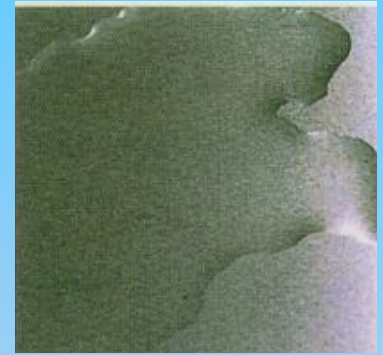


Florence Benoit, Toulouse



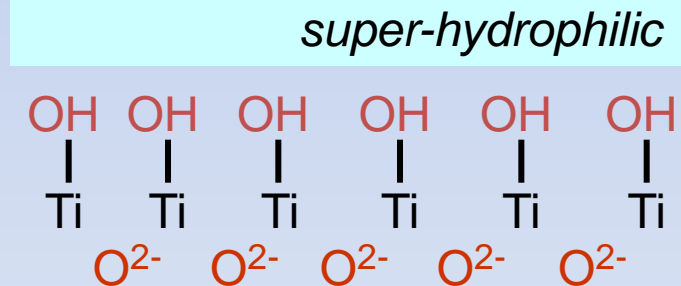
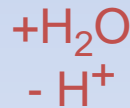
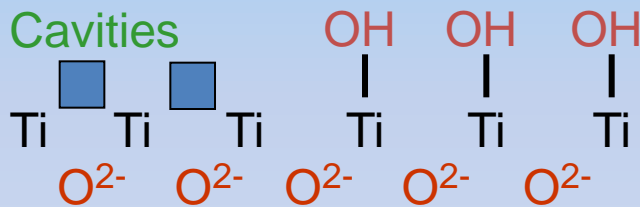
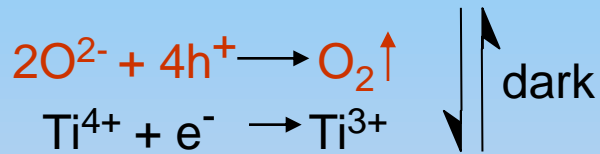
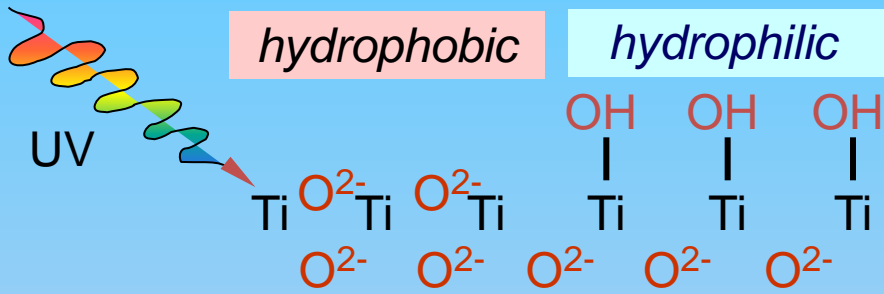


Super-Hydrophilicity via photocatalysis



Asahi
 Pilkington
 St. Gobain
 PPG



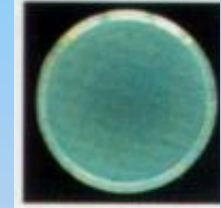
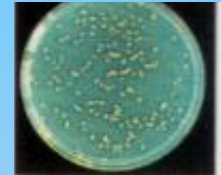


Mechanistic view
of the formation of
Super-Hydrophilicity

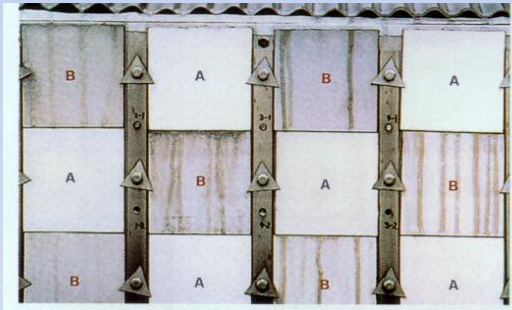
Super-Hydrophilicity in the car industry



Bacteria killing



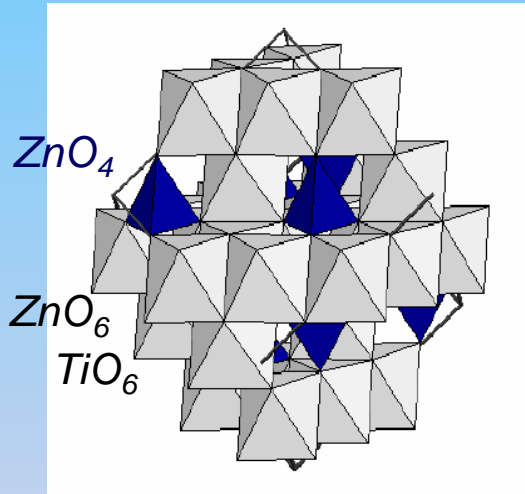
Super-Hydrophilicity in building constructions



Self-cleaning and sterilisation of textiles

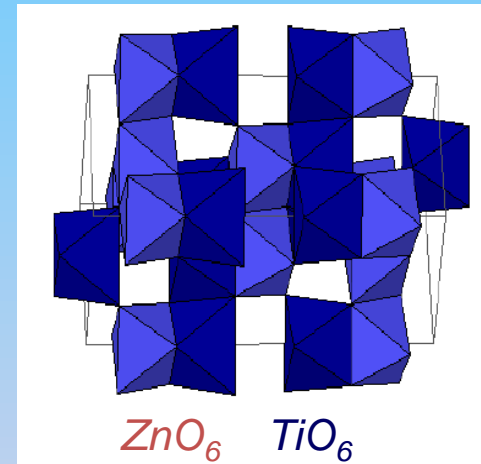


$Zn_xTi_yO_z$ Spinel-Nanostructures

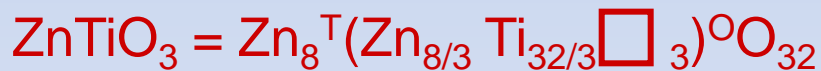


$Fd3m$
 $a = 840 - 844 \text{ pm}$

Cubic inverse spinels

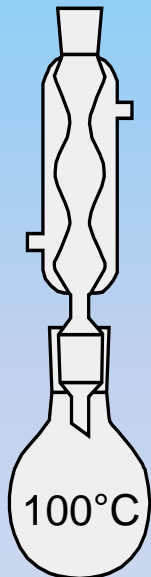
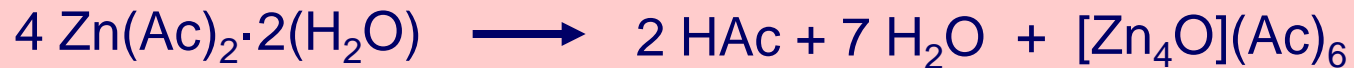


Ilmenite $R3$
 $h\text{-ZnTiO}_3$ $a = 549 \text{ pm}$



Recall normal spinel:
 $AB_2O_4 = A_8^T B_{16}^O O_{32}$

Synthesis of 2 M “polymeric” $Zn_xTi_yO_z$ Sols



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



Complexation

Esterification

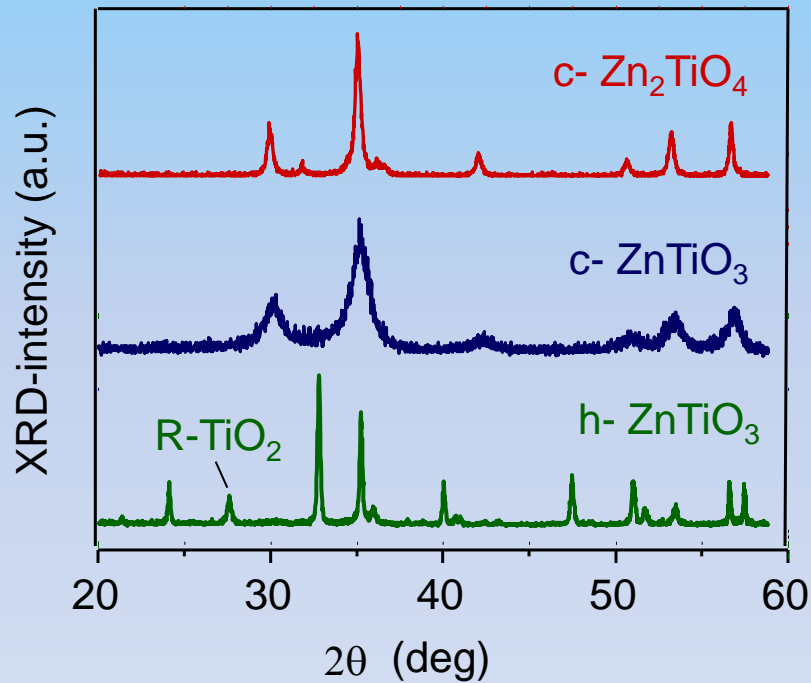
Hydrolysis

Condensation

„Ti-O-Ti“
„Ti-O-Zn-O-Zn“

Z. Phys. Chem. 2007
G. Starukh et al.
Adv. Mater. 2006
F. Grasset et al.

Thermal growth of $\text{Zn}_x\text{Ti}_y\text{O}_z$ nanocrystals > 350°C



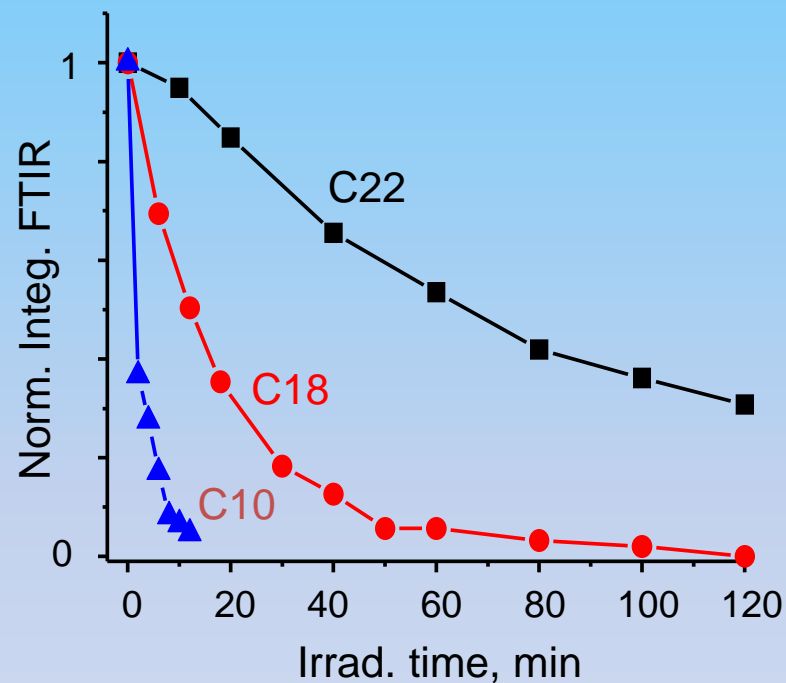
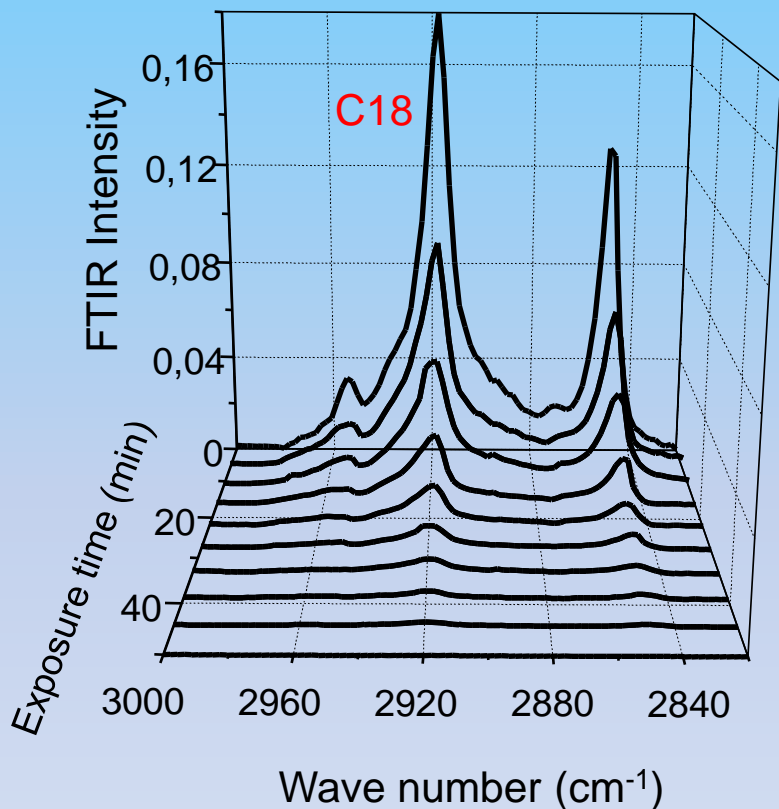
Zn/Ti = 2

Zn/Ti = 1

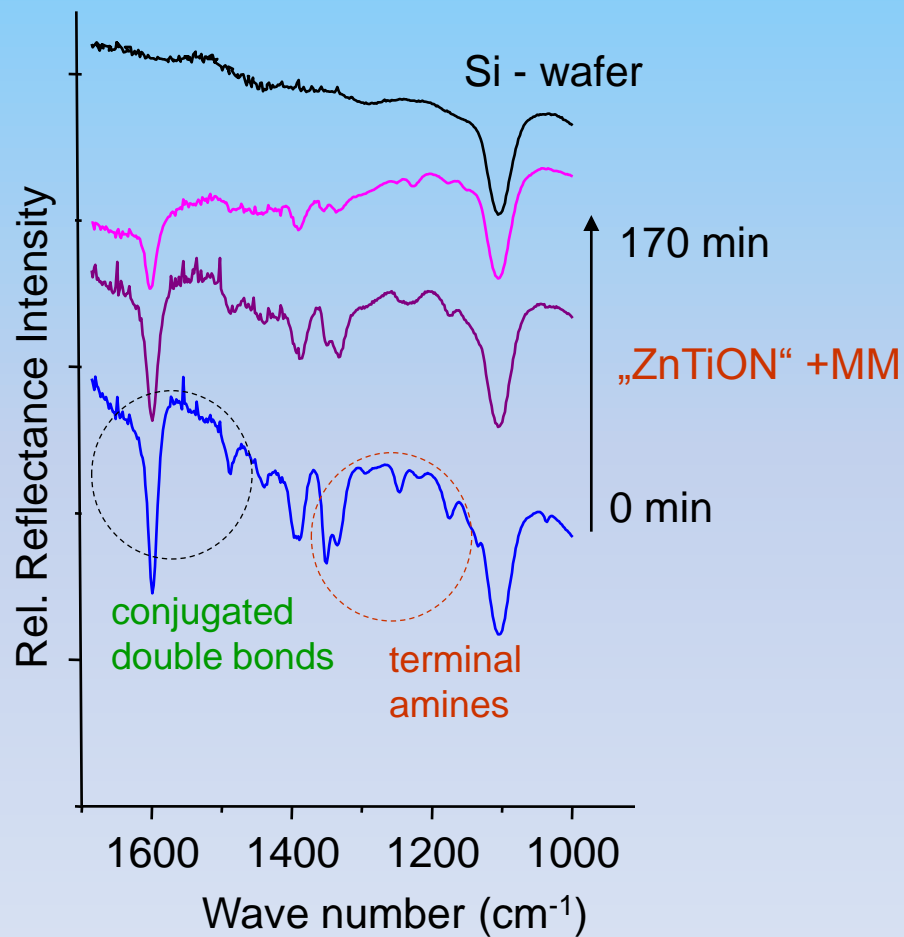
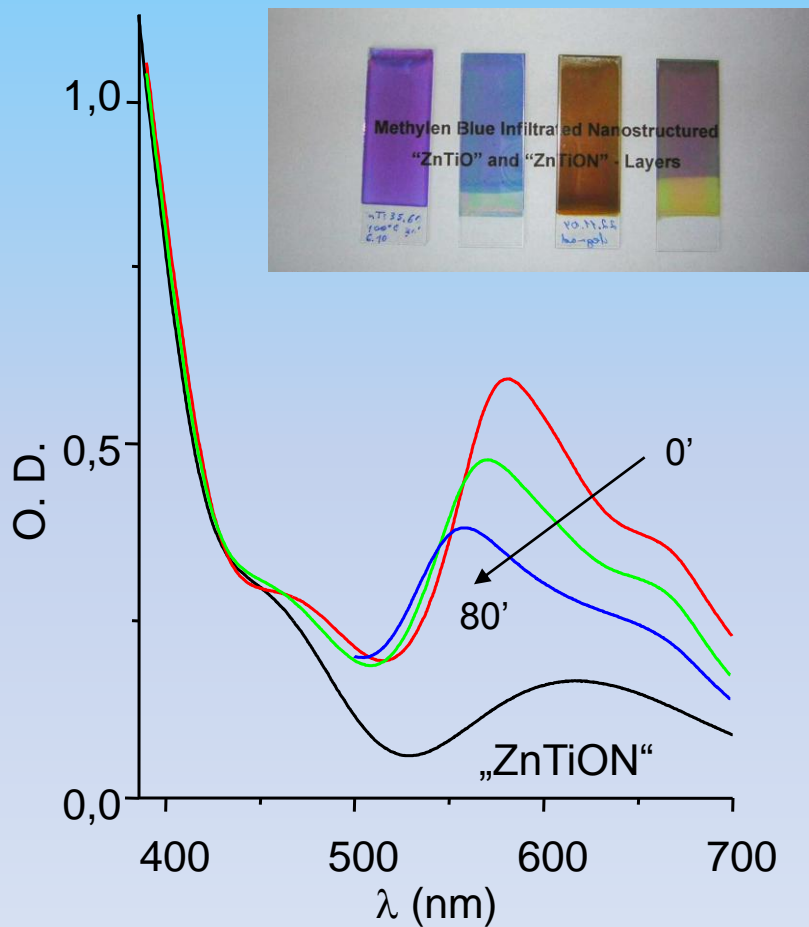
Zn/Ti = 2/3, 3/5

h-ZnTiO₃/r-TiO₂ films in Photocatalysis

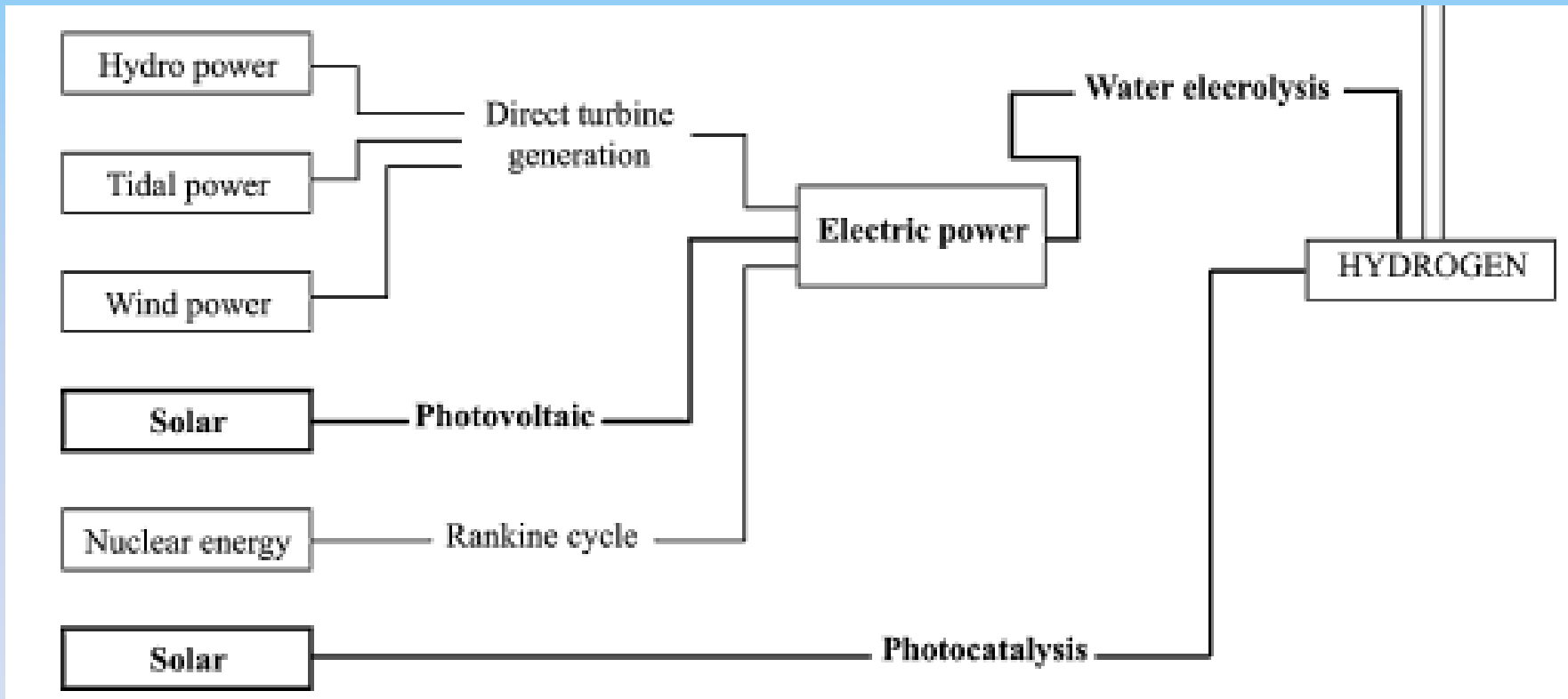
Photodegradation of Fatty Acids, Xe-lamp, air, rel. humidity: 80%



Methylene Blue photodegradation on "ZnTiON"-Spinel layers ($\lambda_{\text{ex}} > 430 \text{ nm}$, Xe – Lamp, humid air)

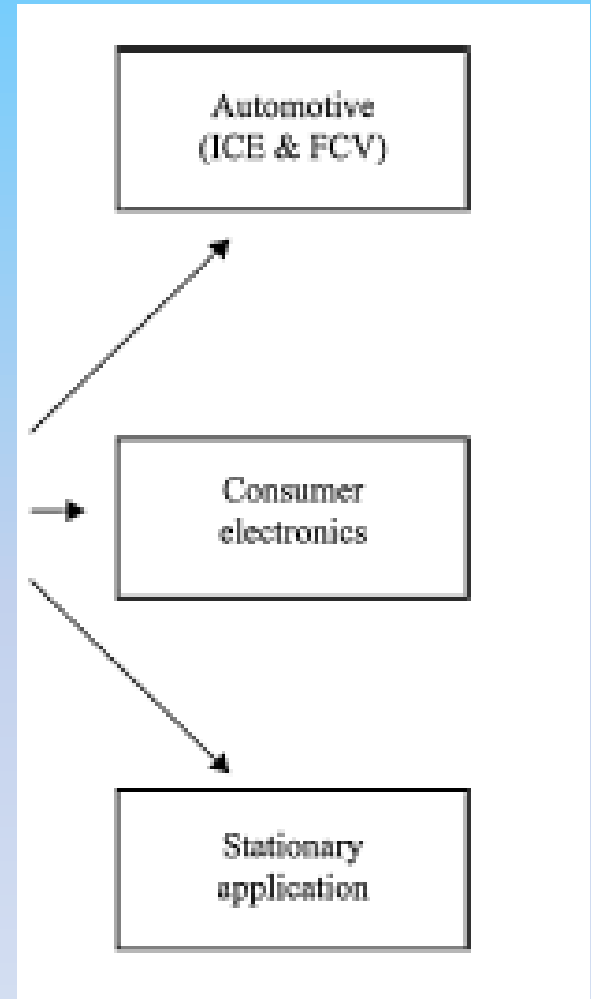
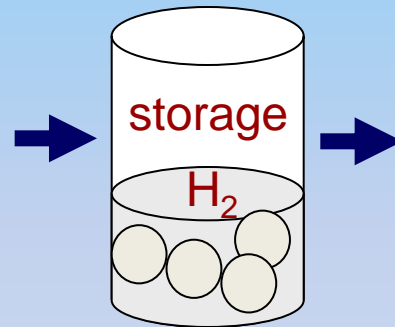
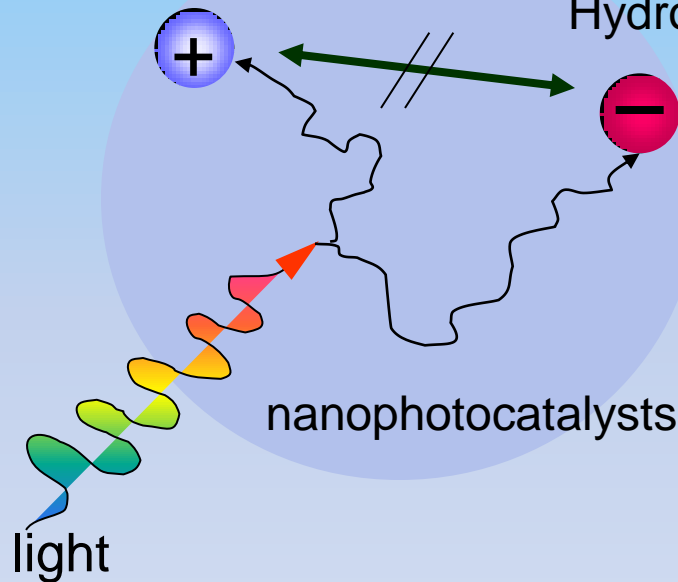


« Nanotechnology for hydrogen industries »



Oxygen evolution

Hydrogen evolution

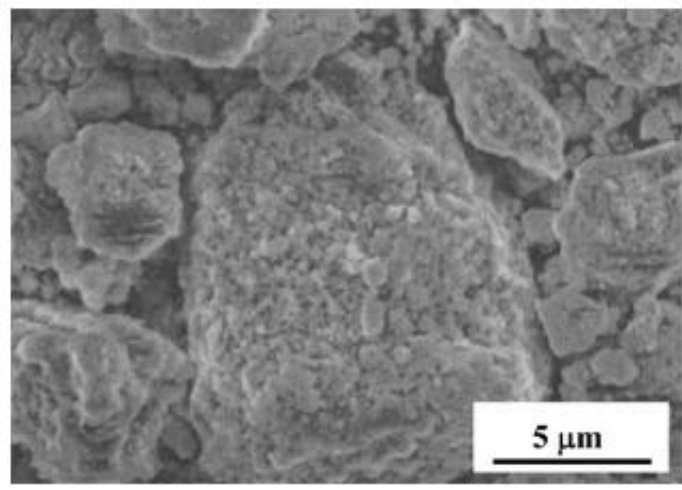
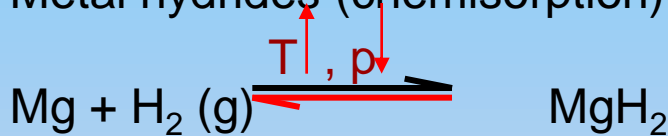


Required photocatalytic efficiency: 10%

Hydrogen storage

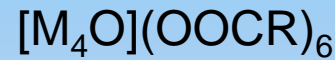
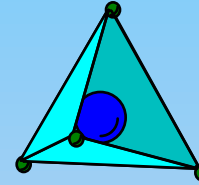
In the car industry:
5-13 kg, ~ 500 km

1. Metal hydrides (chemisorption)



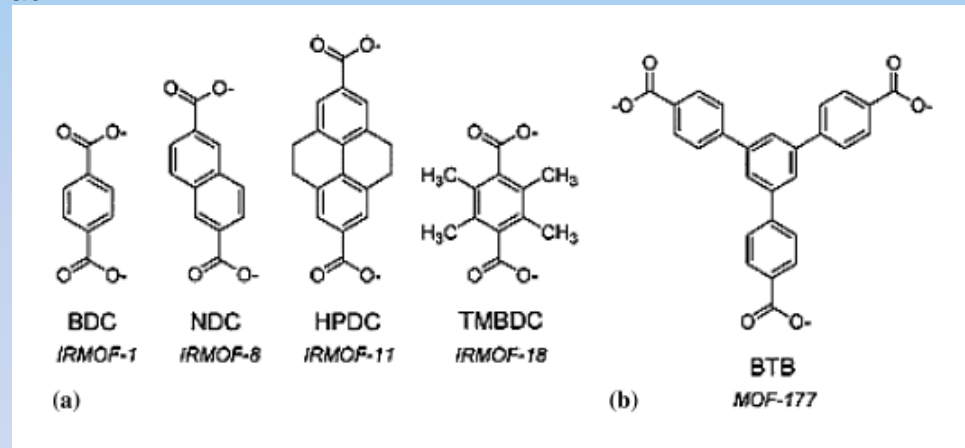
Capacity: 0,076 kg/kg (0,101 kg/L)
with nano-Pd

2. Physisorption on MOF metal organic frameworks



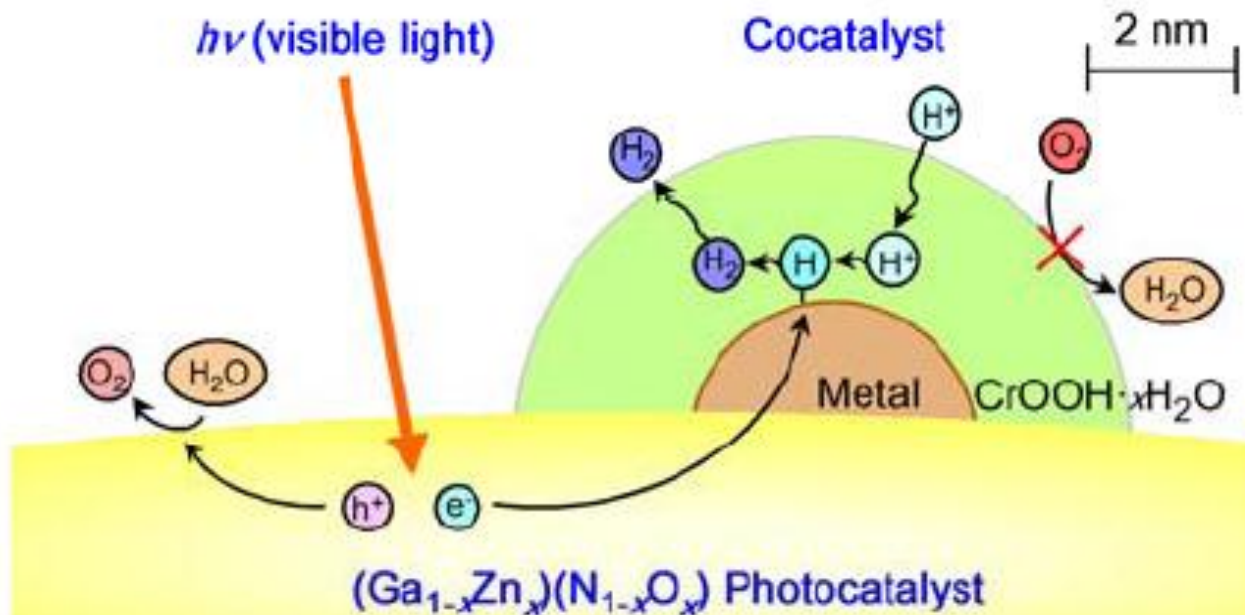
M: Mg, Zn, Be

$$\Delta_{\text{ad}}H < 0$$



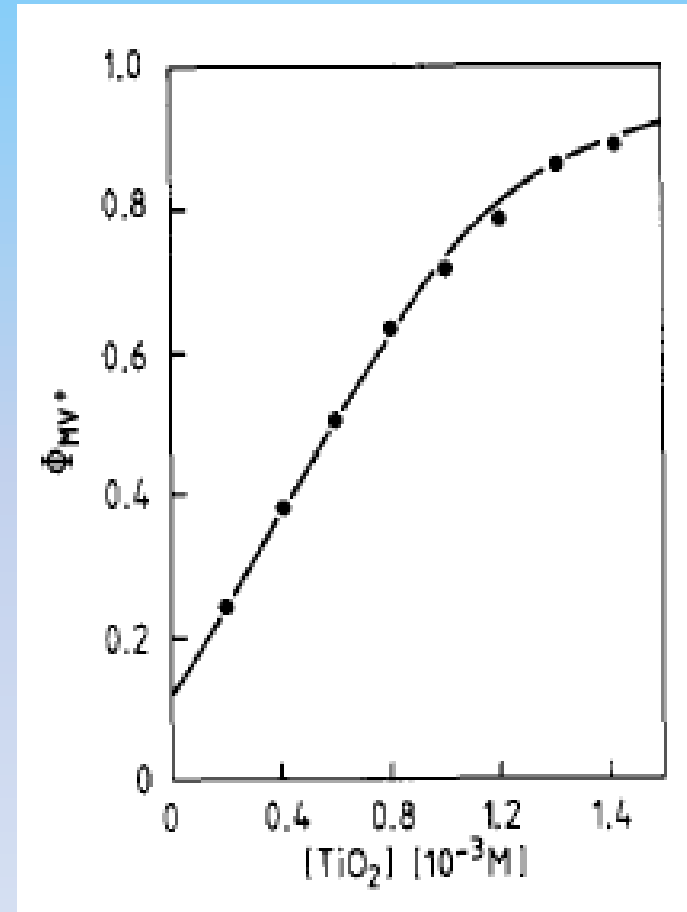
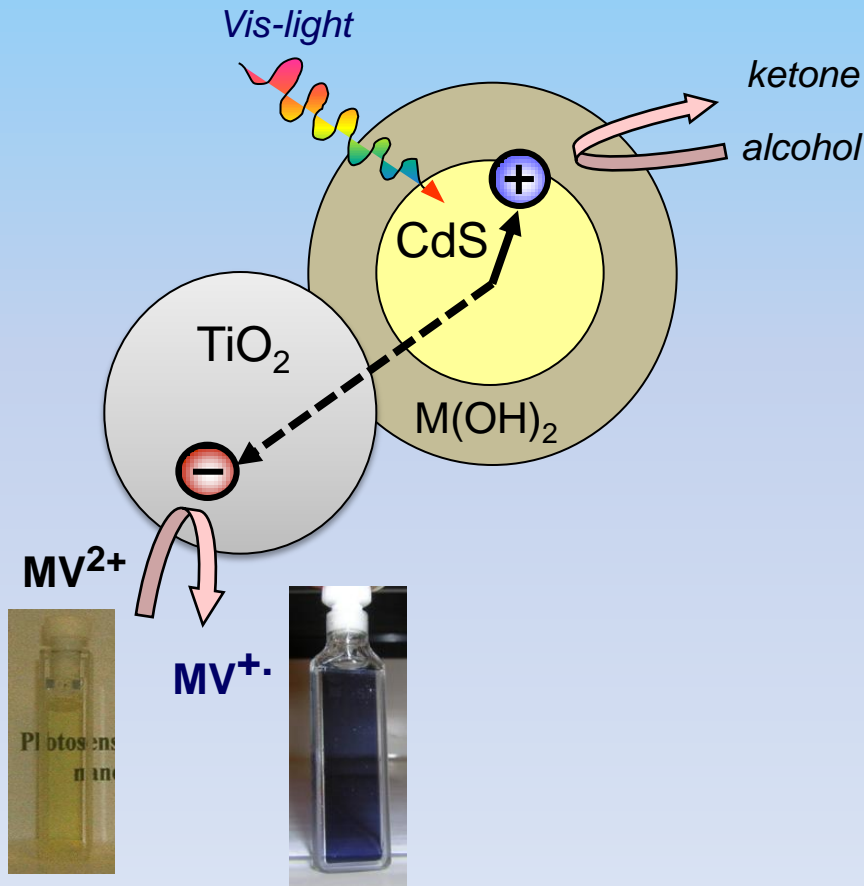
Capacity: 5-10 % w.

Best result on solar water splitting so far ($\phi \sim 5\%$)

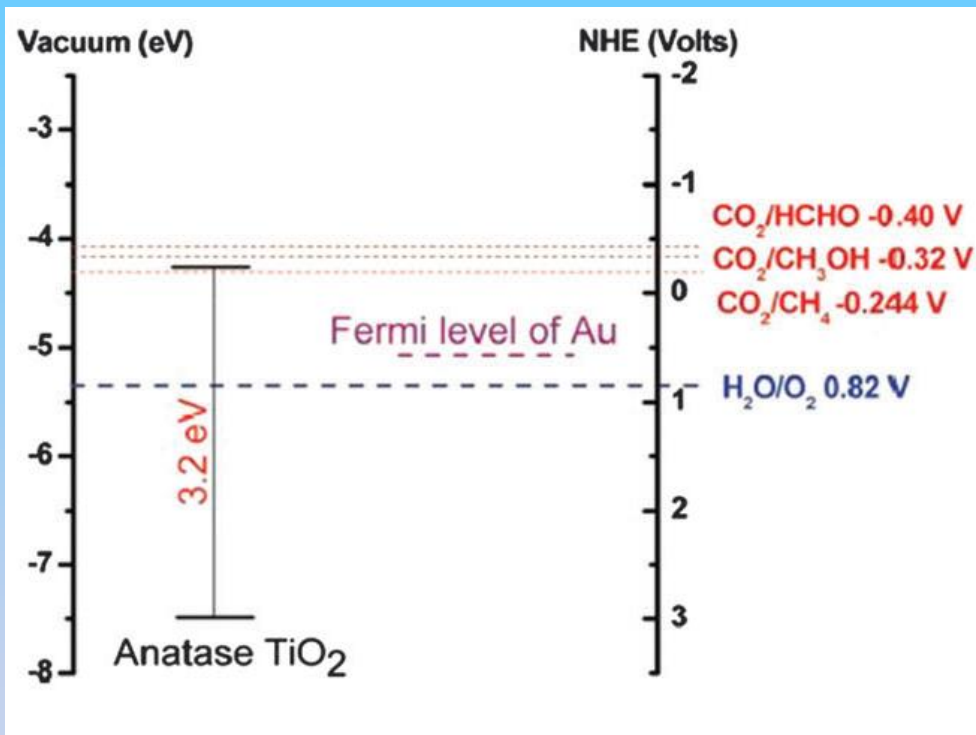
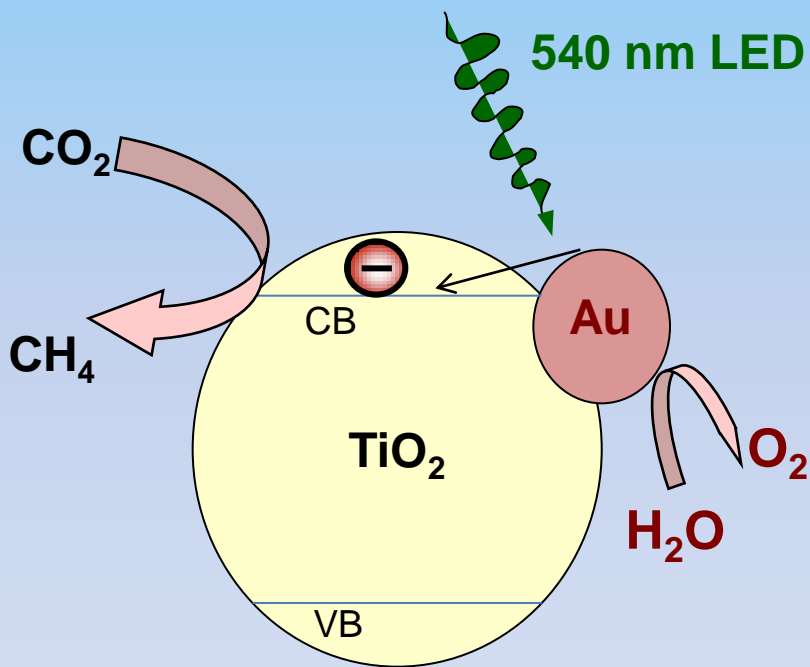


K. Maeda et al, Nature 2006

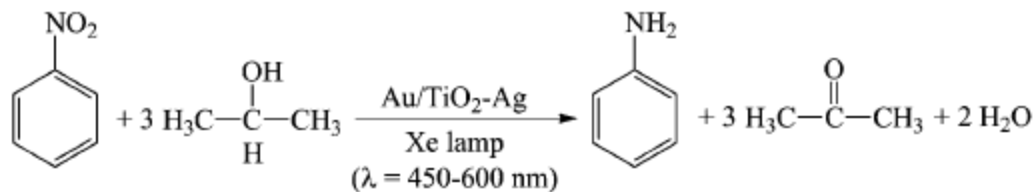
Other Photoreduction processes on combined SC-M hereterojunctions



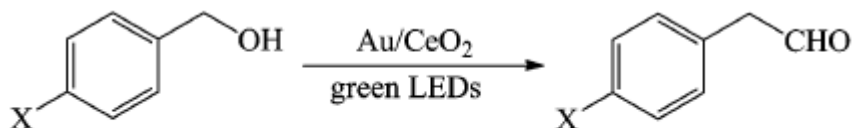
CO₂ photo-transformations via surface plasmons



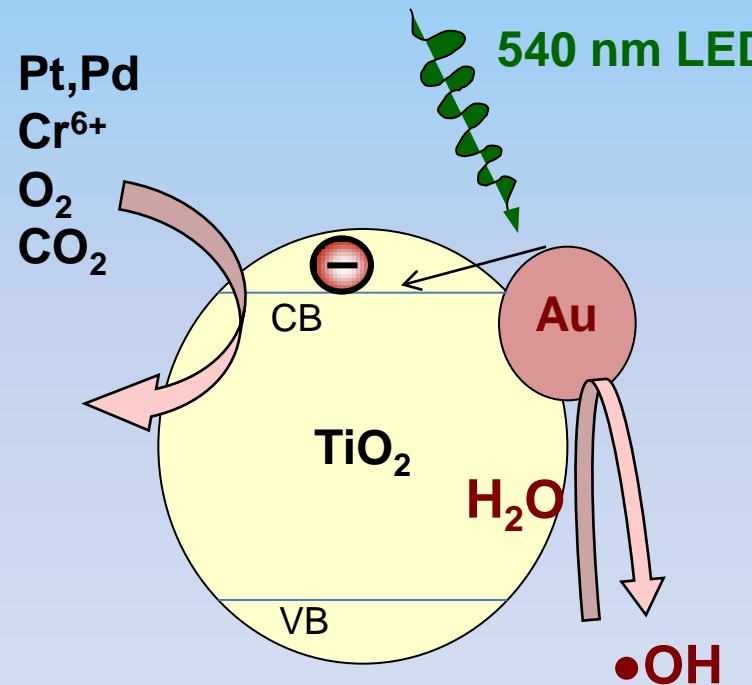
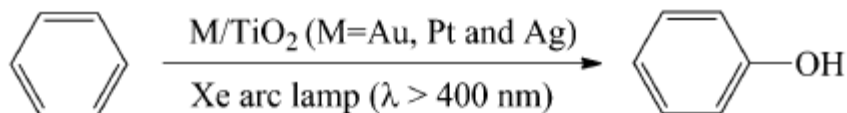
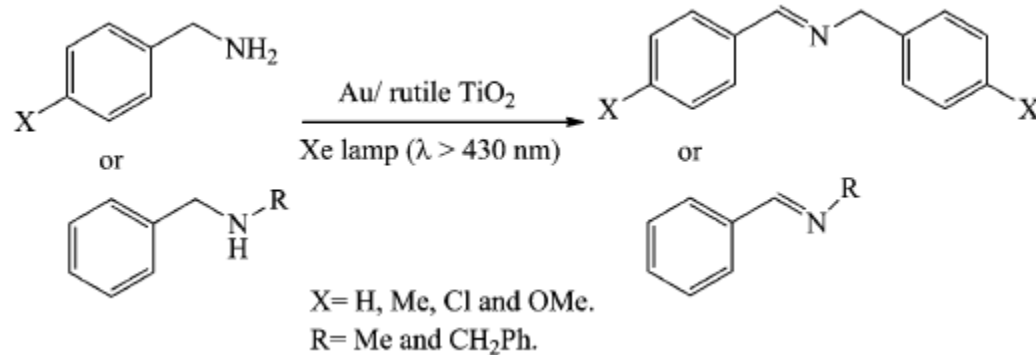
reaction	E° (V) vs SCE at pH = 7
CO ₂ + 2H ⁺ + 2e ⁻ → CO + H ₂ O	-0.77
CO ₂ + 2H ⁺ + 2e ⁻ → HCOOH	-0.85
CO ₂ + 4H ⁺ + 4e ⁻ → HCHO	-0.72
CO ₂ + 6H ⁺ + 6e ⁻ → CH ₃ OH	-0.62
CO ₂ + 8H ⁺ + 8e ⁻ → CH ₄	-0.48



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

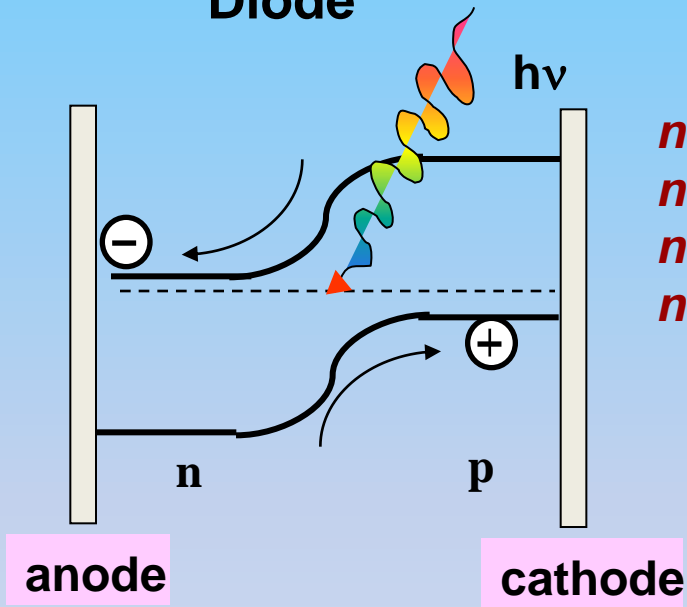


X=NO₂, Cl, CH₃, OCH₃ and NH₂.

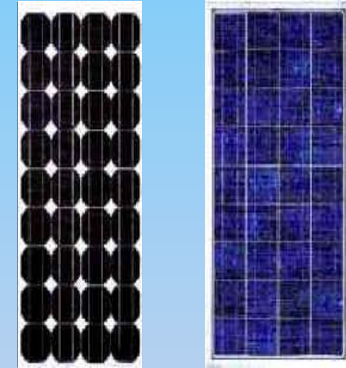


Theory of Solar Cells of the 1. and 2. generation

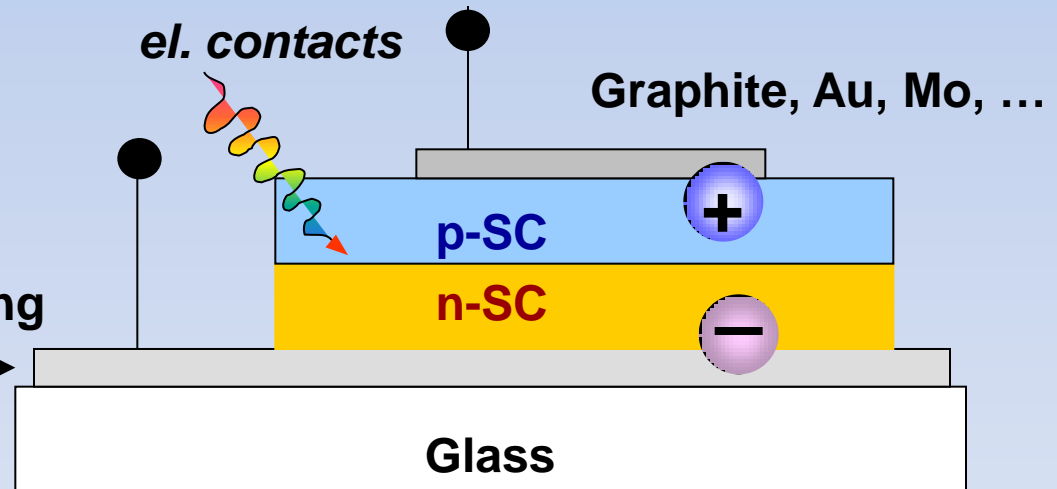
Diode

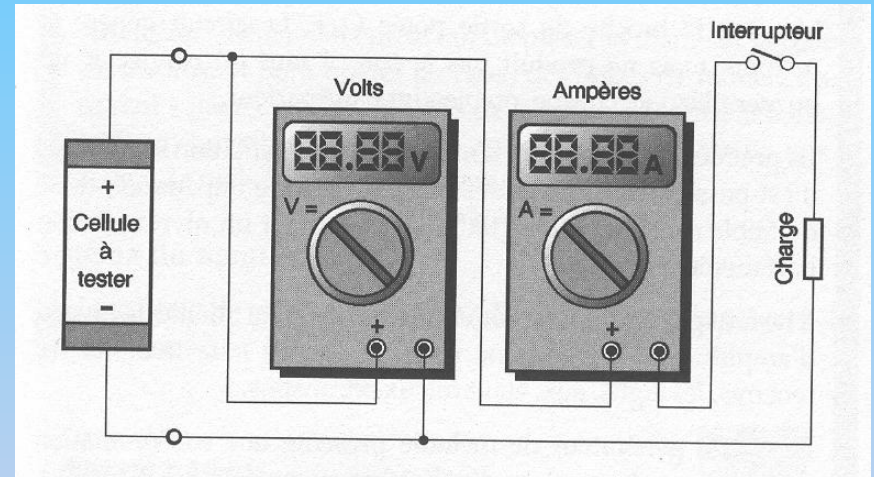
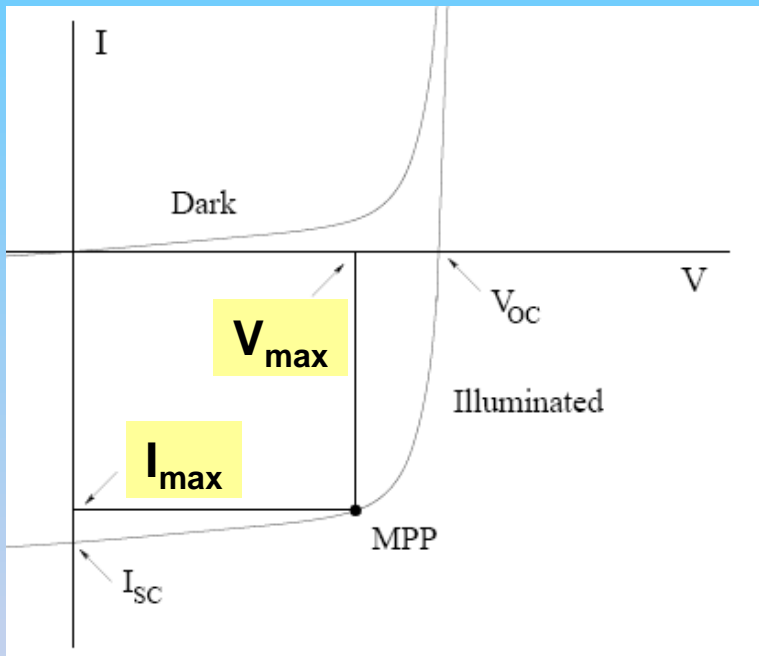


- n-Si/p-Si*
- n-GaAs/p-GaAs (InP)*
- n-CdS/p-CdTe*
- n-CdS/p-CuInSe₂*



Transparent conducting electrode
 $Al@ZnO, F@SnO_2$

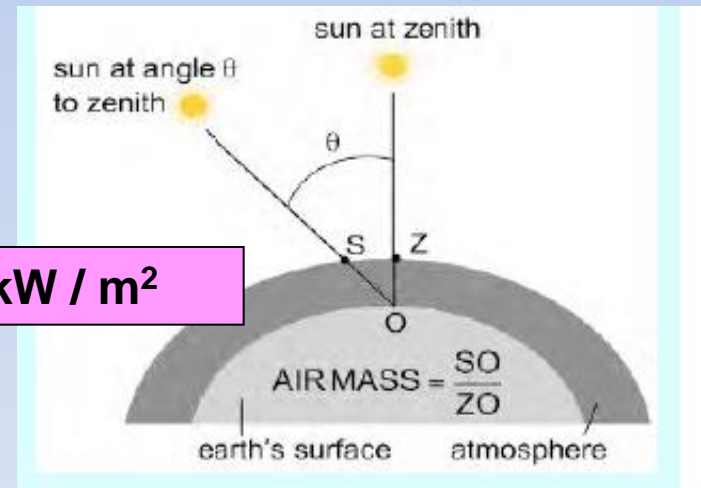




$$\eta = FF \frac{V_{oc} I_{sc}}{P_{in}} = \frac{V_{max} I_{max}}{P_{in}}$$

- 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)

$$P_{in} = 1 \text{ kW} / \text{m}^2$$



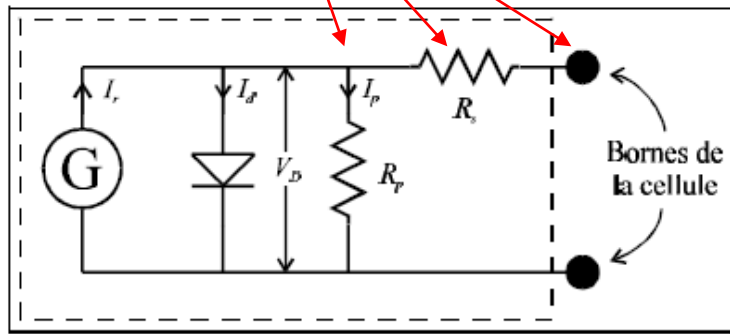
Polycrystalline Thin Film Cells

Cell Type	η (%)	Area cm ²	V _{oc} mV	J _{sc} mA/cm ²	FF %	Lab / Company	Date
CdTe (cell) 3.5 mm CSS	16	1.0	840	26.1	73.1	Matsushita	1997
CIGS submodule	14.2	51.7	6808	3.1	68.3	Showa Shell	1996
GaInP/GaAs monolithic	30.3	4.0	2488	14.22	85.6	Japan Energy	1996
Si (large thin film)	16	95.8	589	35.6	76.3	Mitsubishi (77μm on SiO ₂)	1997
a-Si (submodule) non stabilised	12	100	1250	1.3	73.5	Sanyo	1992

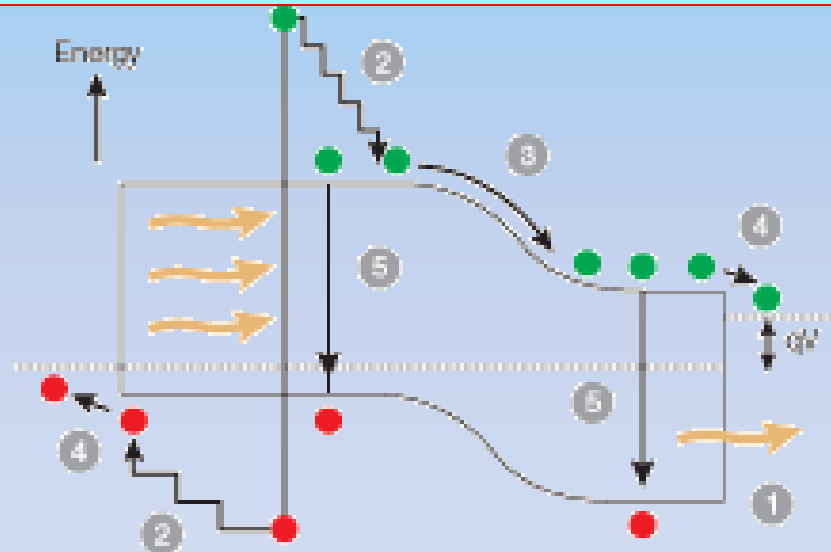
$$\eta = FF \frac{V_{oc} I_{sc}}{P_{in}} = \frac{V_{max} I_{max}}{P_{in}}$$

Origin of losses in solar cells

losses



1. Dissipation de la lumière limitée
2. Relaxation thermique
3. Perte lors de la séparation de charges
4. Contacts électriques non-idéales
5. Désactivation thermique (recombinaison)



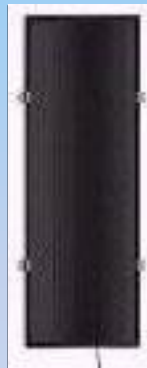
Cellules à base de Si



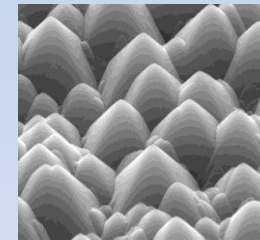
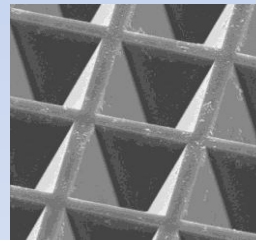
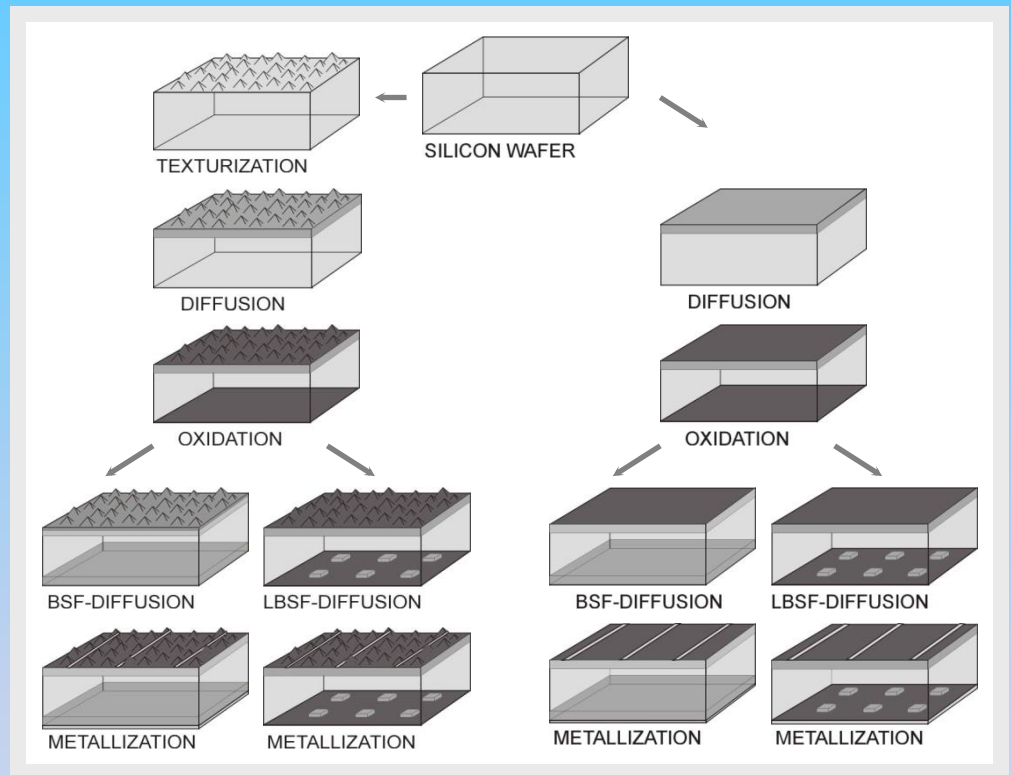
Mono-Si
12-16%



poly-Si
11-13%



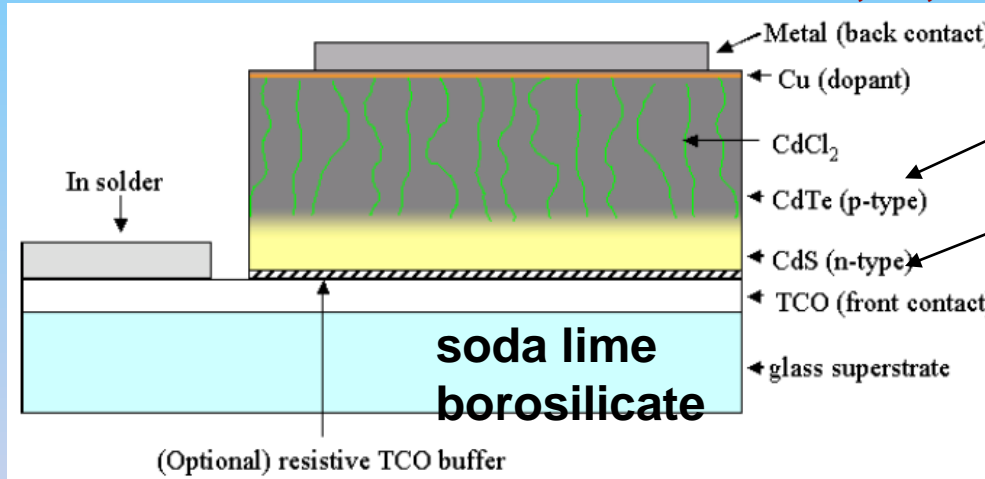
amorphe Si
6-10%



p-CdTe/n-CdS heterojunction

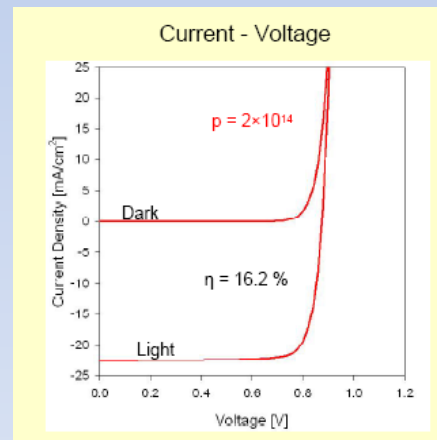
Conversion efficiency > 21%

Au, Ti, Ag-graphite

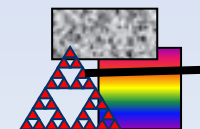


(Optional) resistive TCO buffer

ZnO:Al SnO₂:F



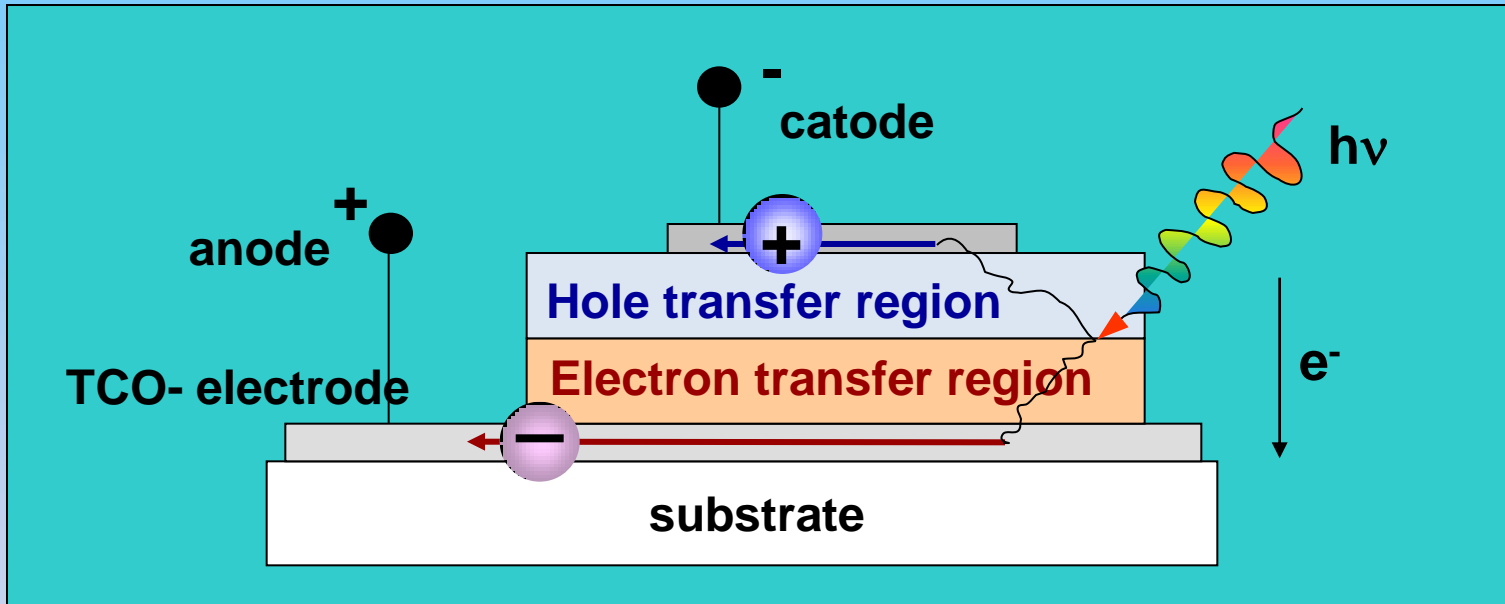
CdTe module



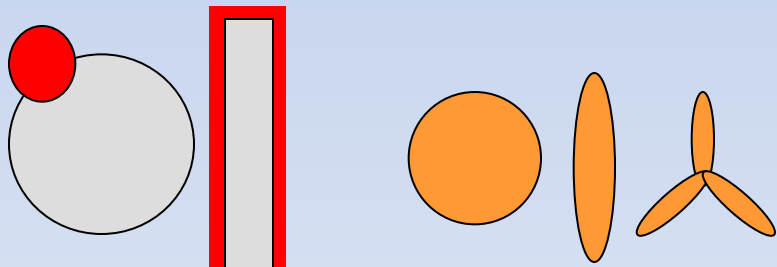
L. Spanhel

Solar Cells of the 3. generation

Nanostructured solar cells – 3. generation cells



solar nano-antenna design



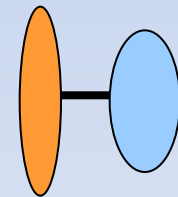
Oxides, M-Chal., fullerenes, dyes

org. polymers

PPV, PEDOT-PSS

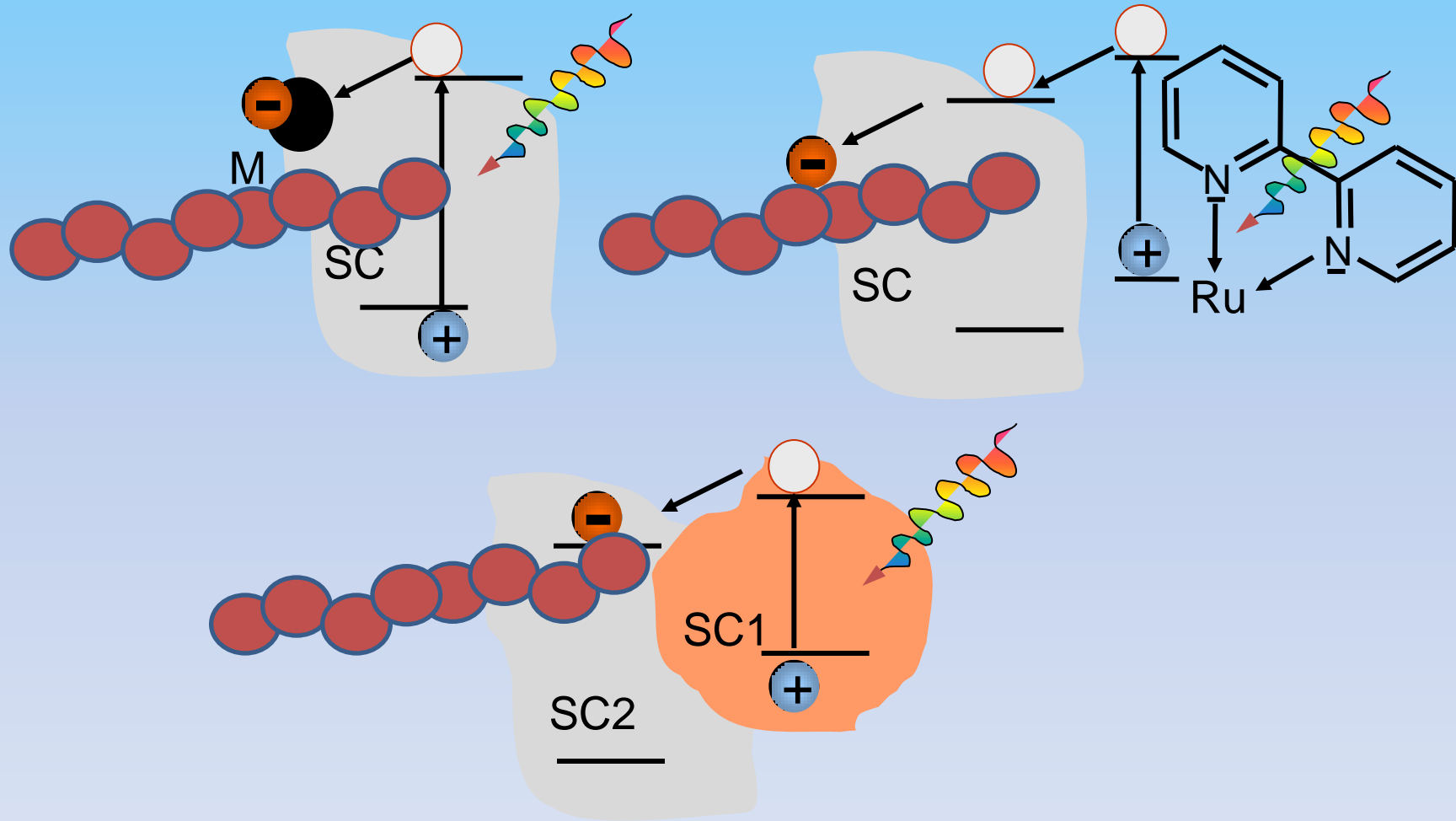


nano-composites

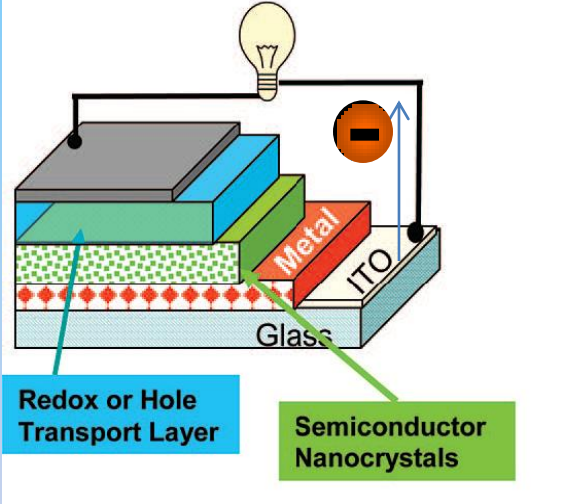


„Man-made“ micro-électrodes selon le principe de la nature

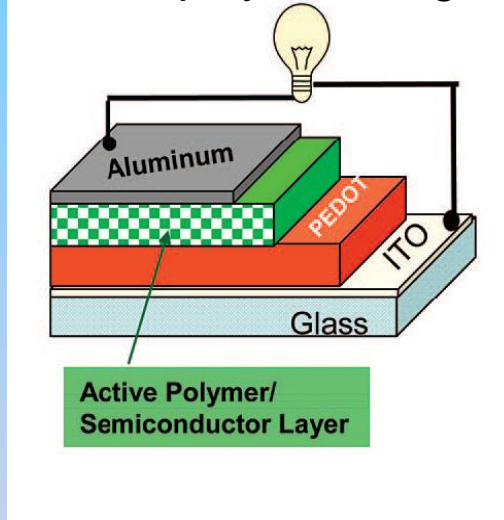
Same approach to nanostructured solar cell and photocatalysts



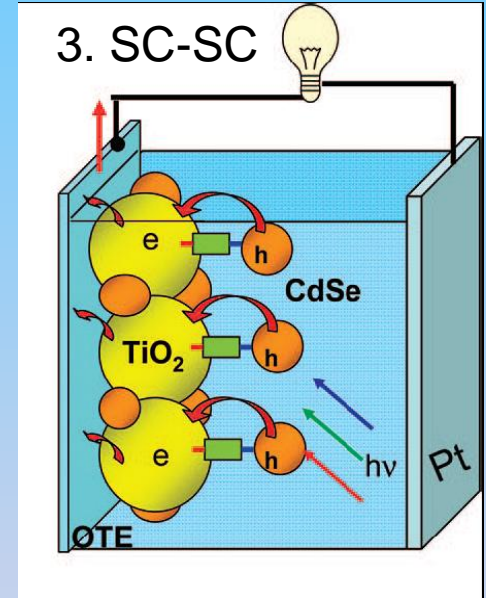
1. Jonction SC-métal



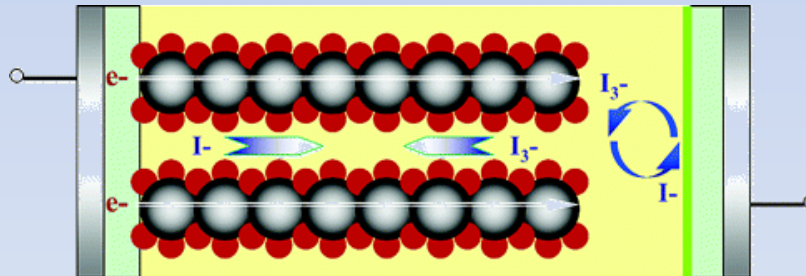
2. SC-polymère org.



3. SC-SC



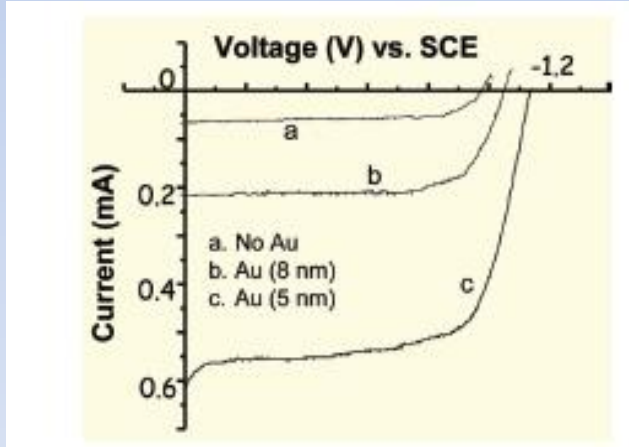
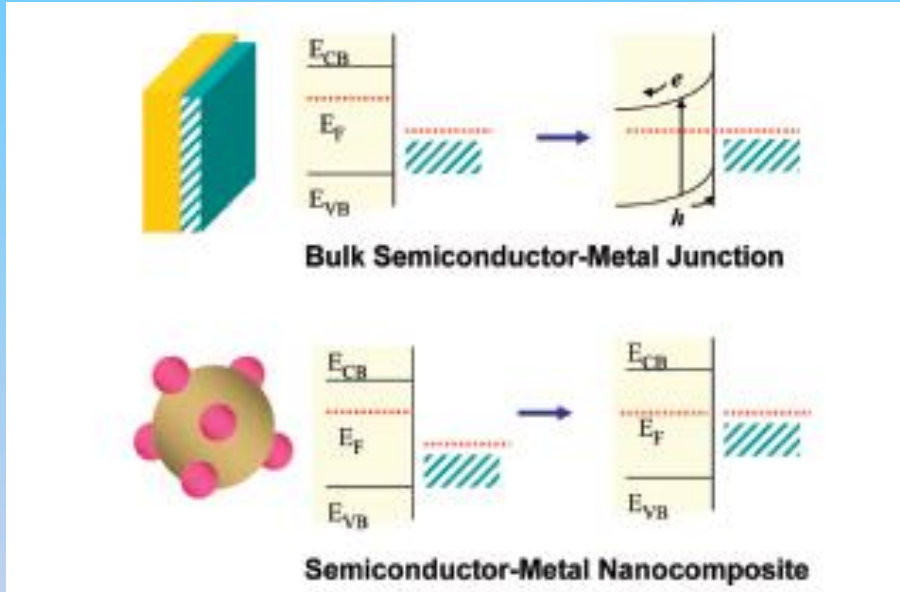
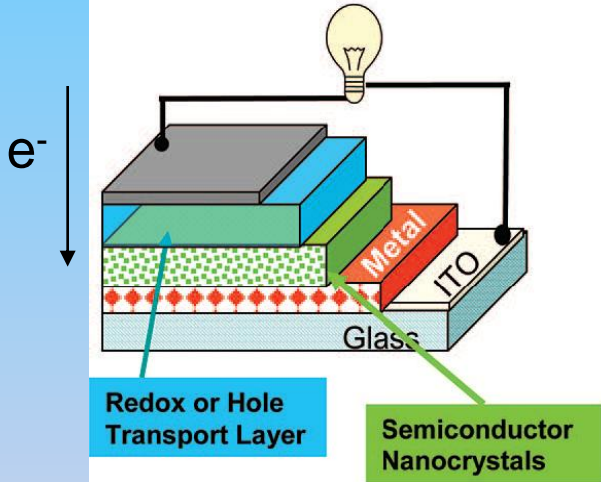
4. Cellule de Grätzel



Adopted from P. Kamat et al
ND National Lab, USA



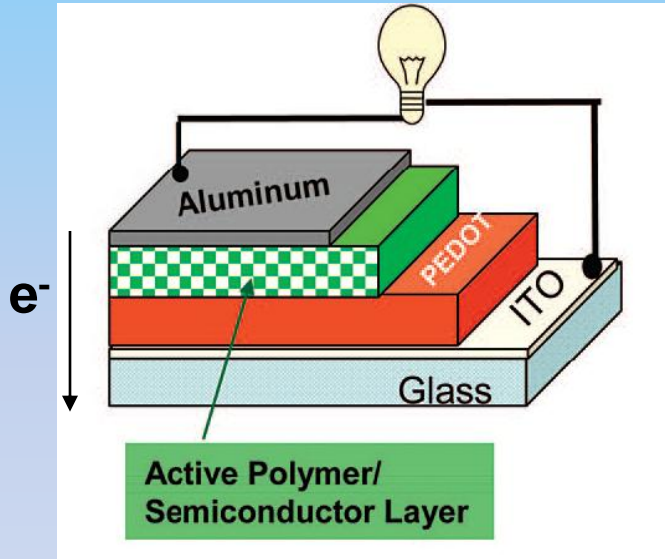
1. Jonction SC-métal



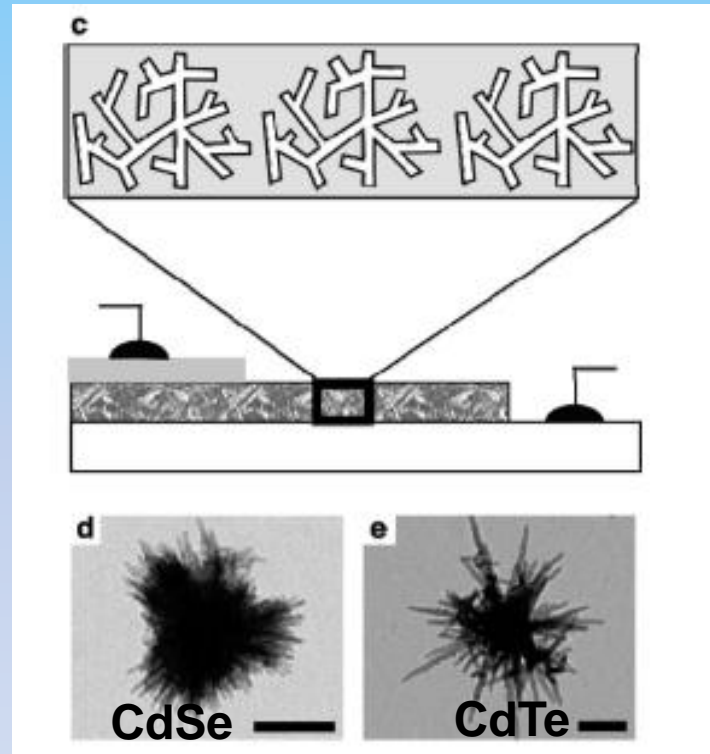
Rendement : 1 - 4%

Kamat et al,
Notre Dame National Lab

Nanocomposites based on Q-CdSe, CdTe (antenna) and organic Poly(3-hexylthiophene) (hole conductor)

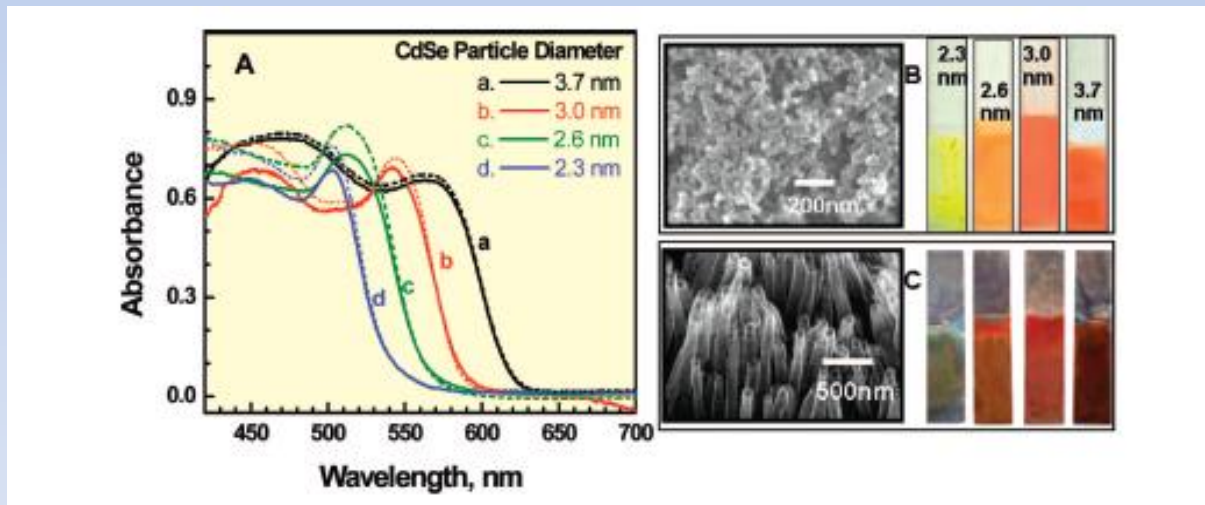
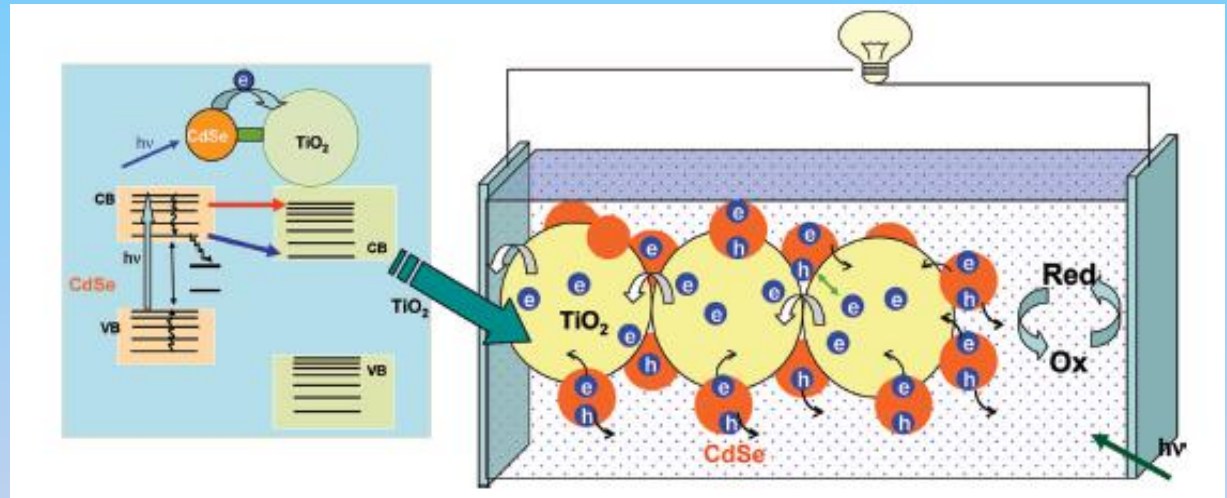
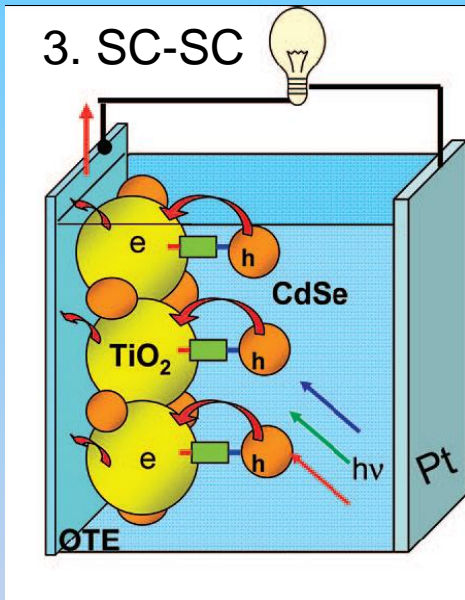


$\eta \sim 5\%$



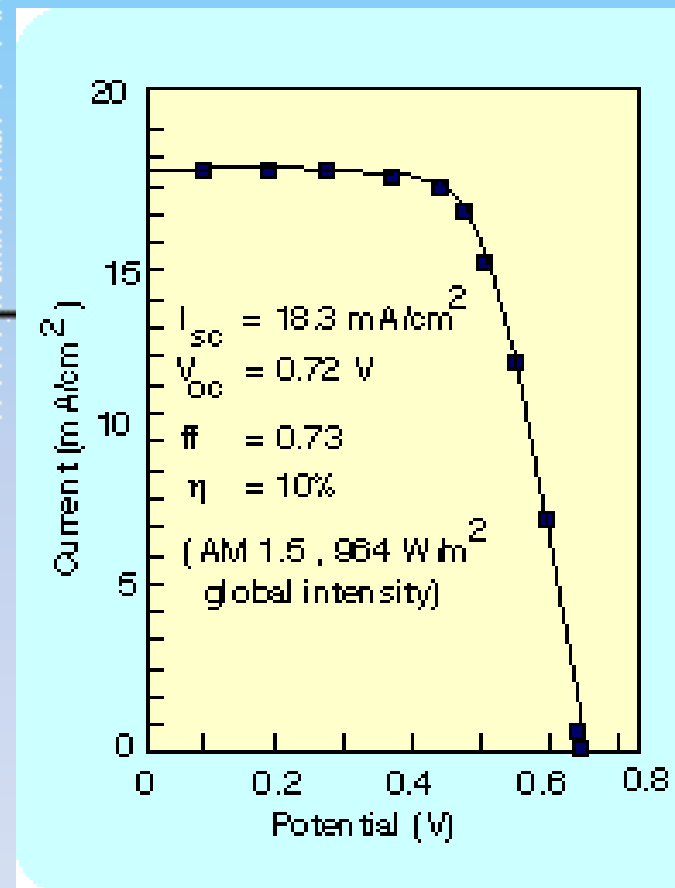
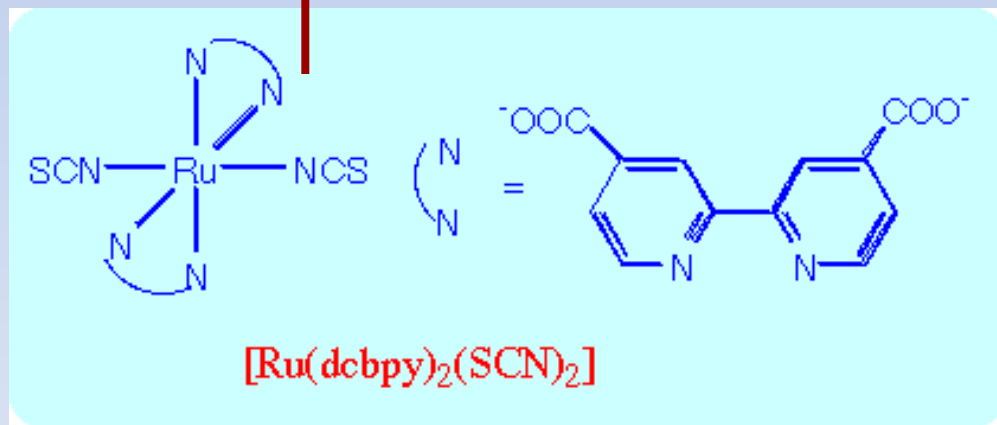
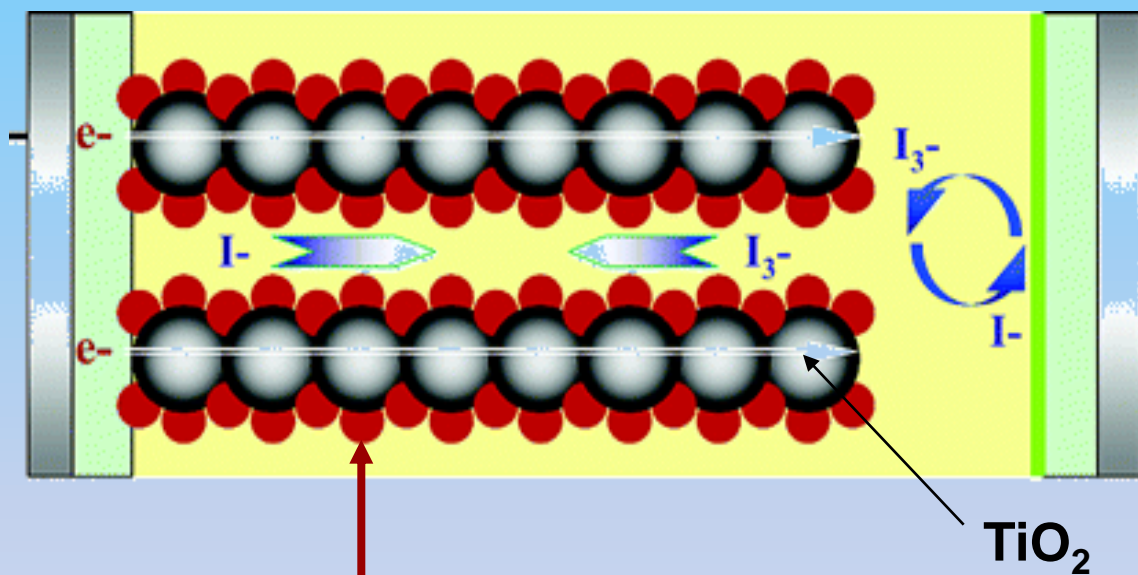
Alivisatos et al, Berkeley

Rendement ~ 8 %



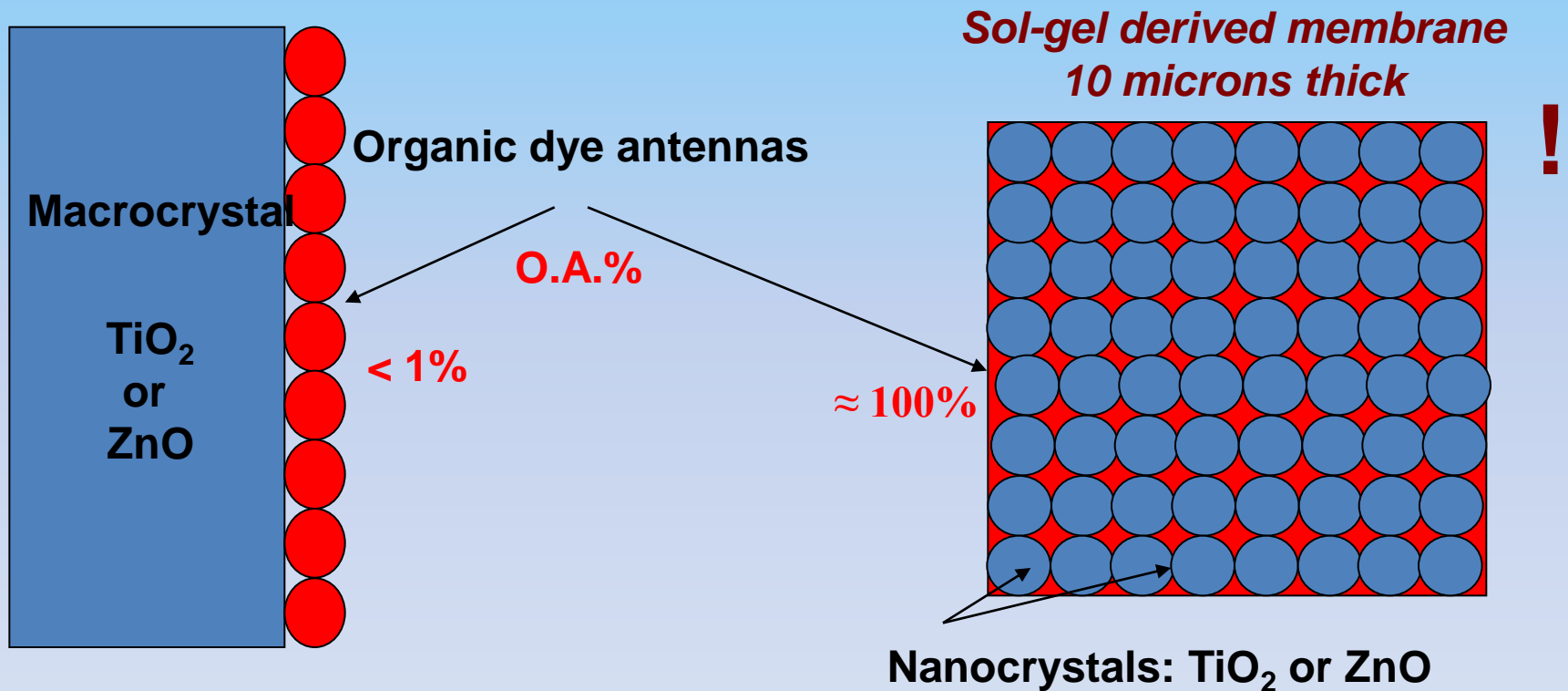
Cellule de Grätzel (1988)

$\eta \sim 10-12\%$

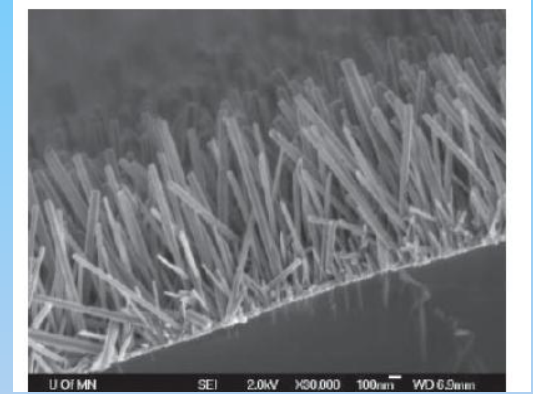
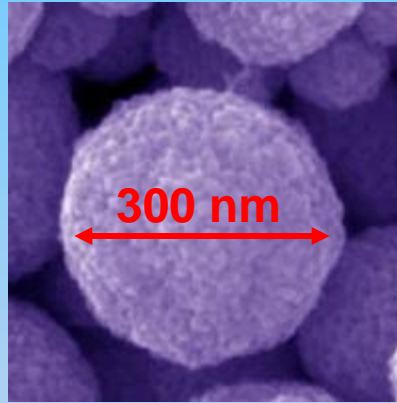
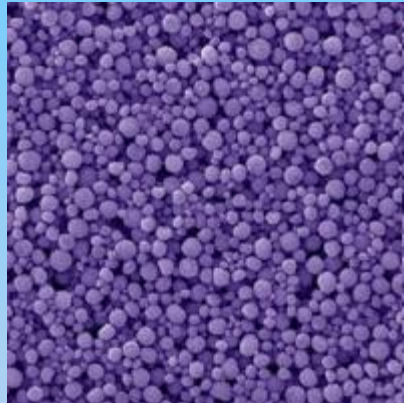
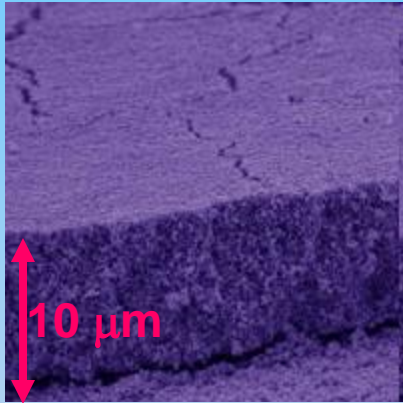


Why and how actually is Grätzel cell functioning?

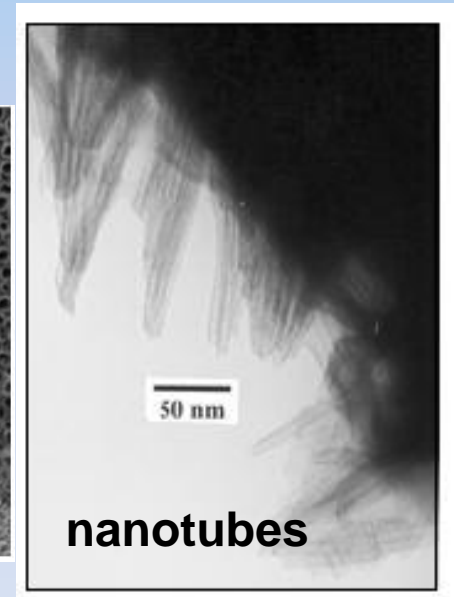
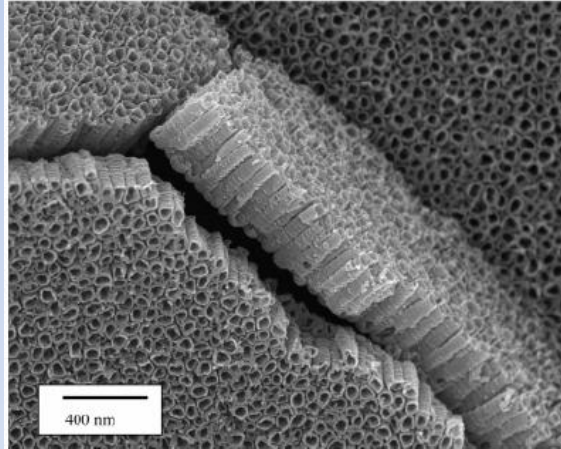
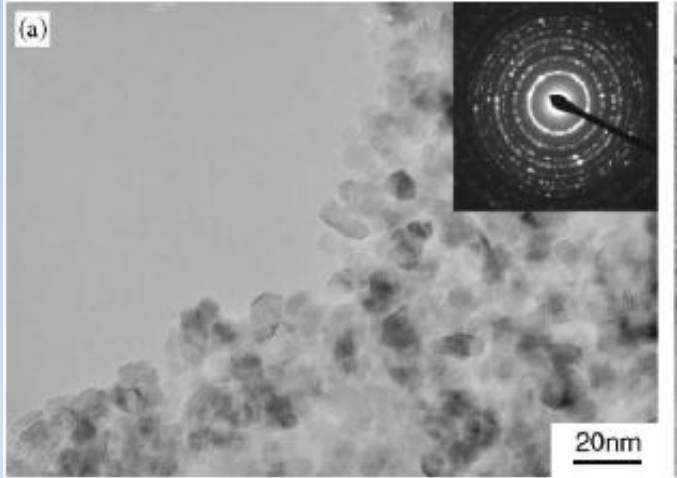
1. Morphology !



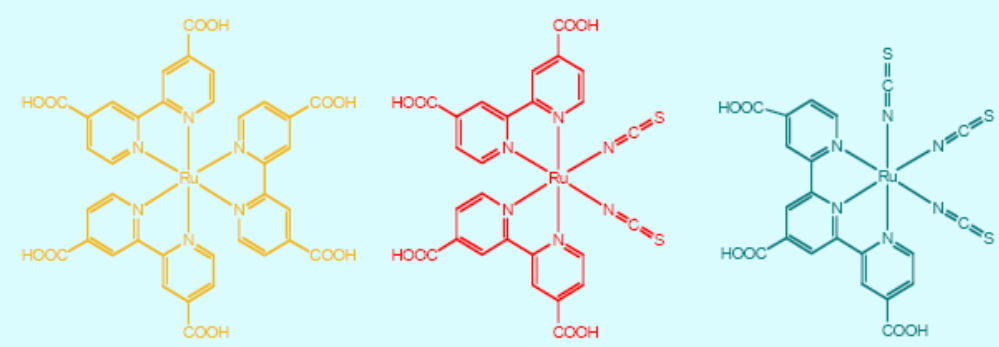
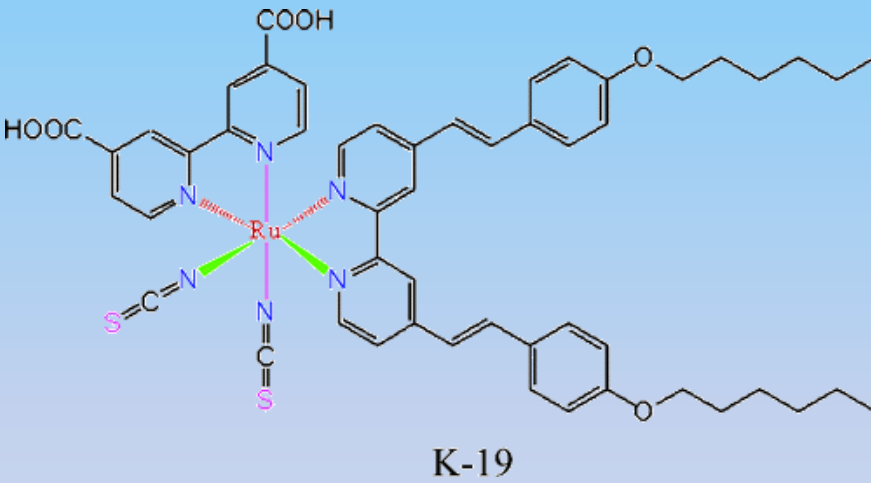
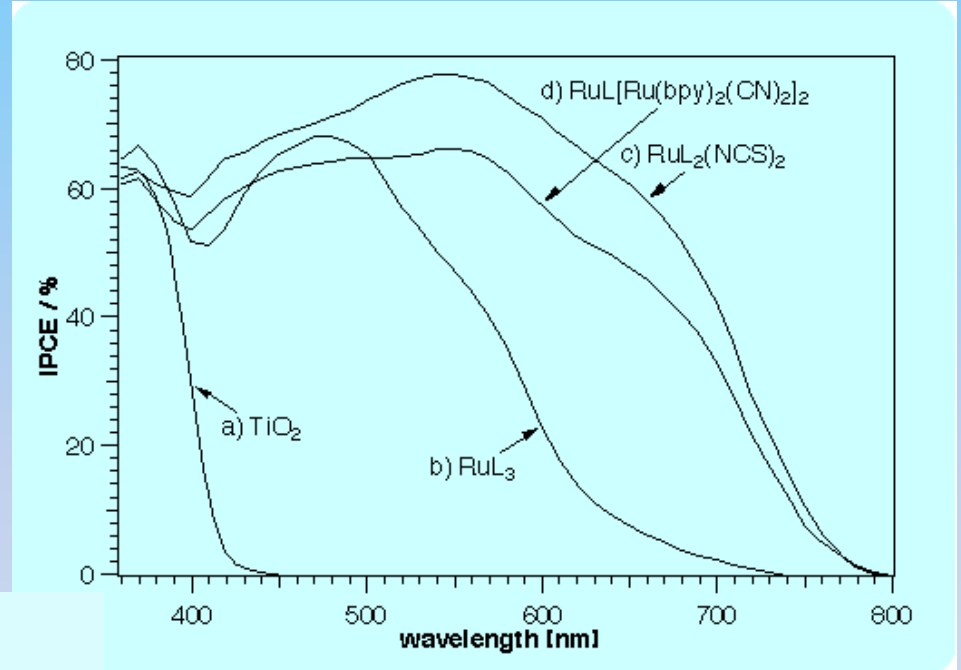
ZnO



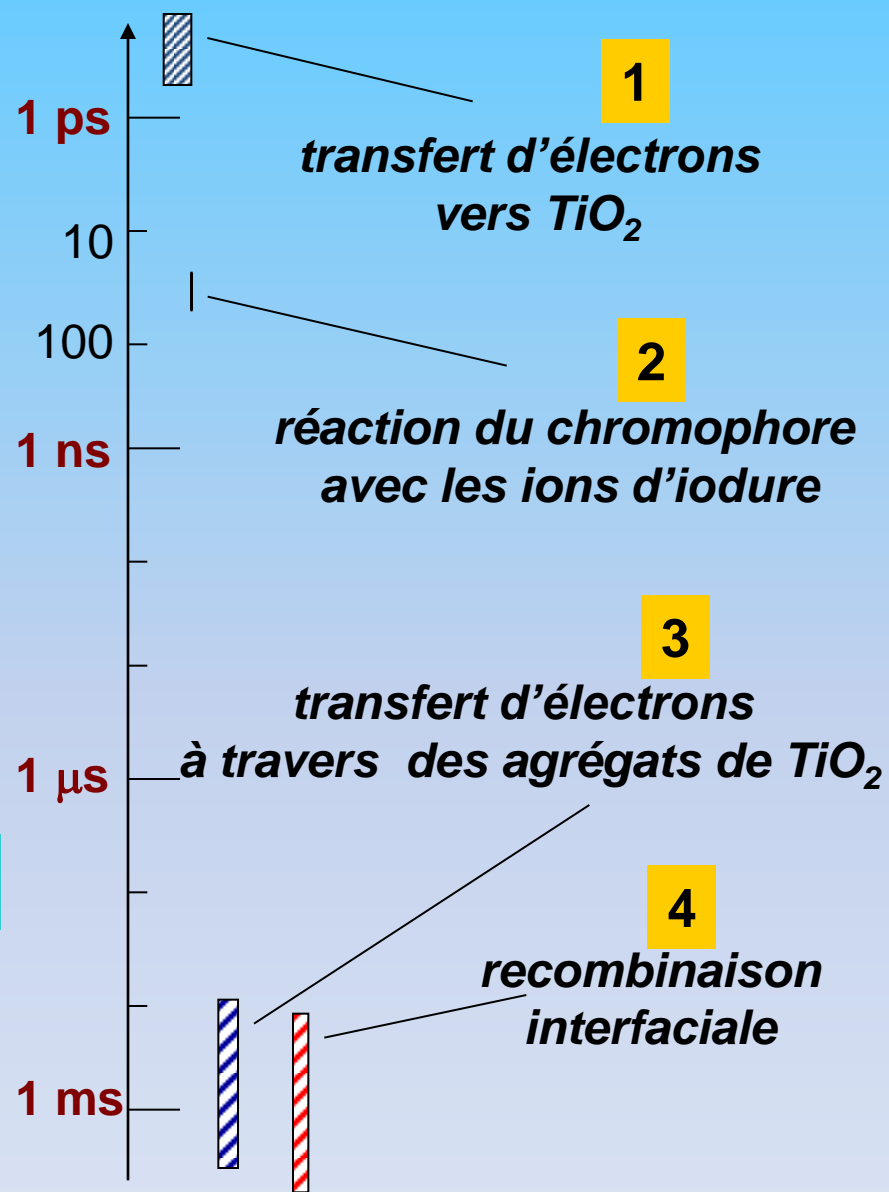
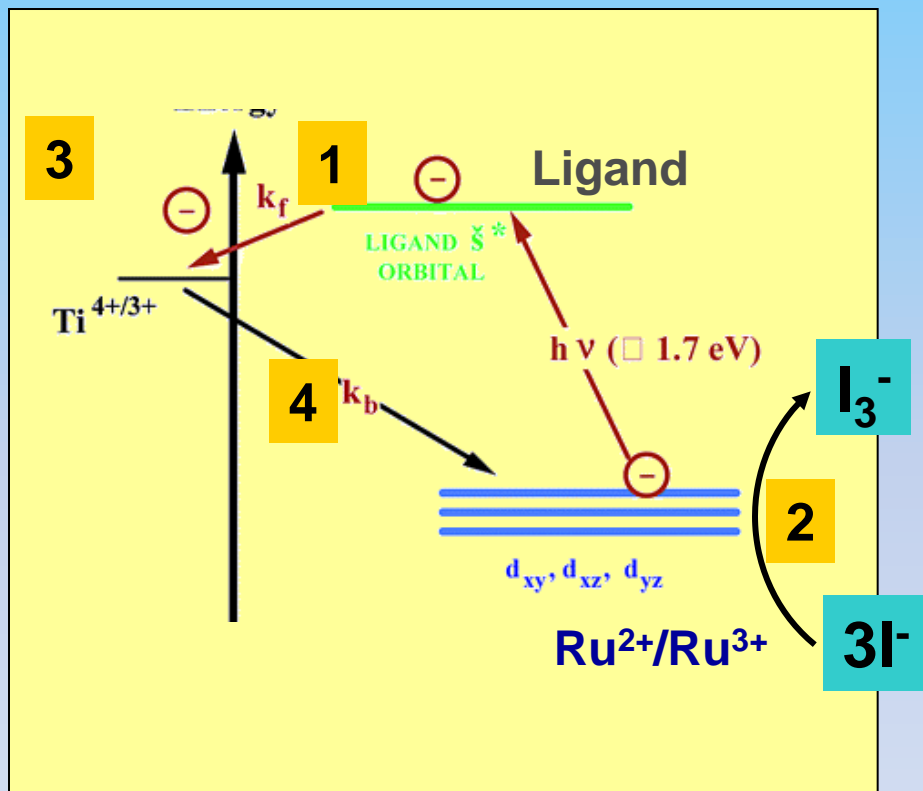
TiO₂



2. Antenna !



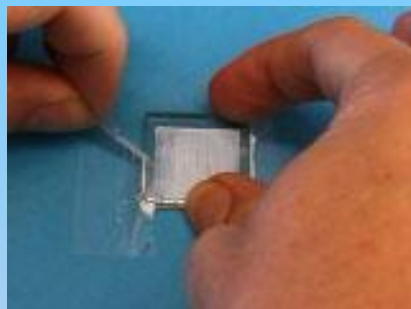
3. Cell kinetics !



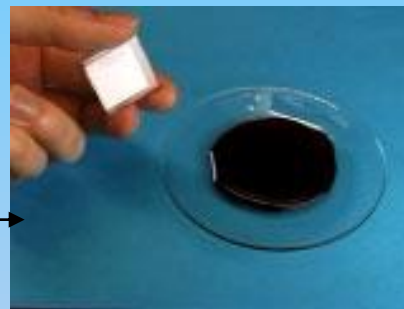
Construction d'une cellule d'après Grätzel



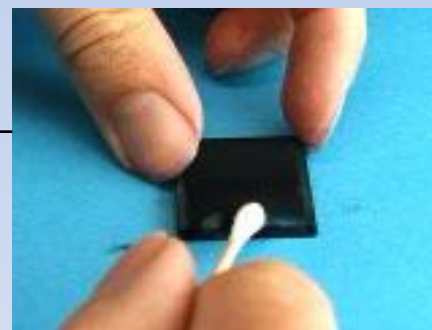
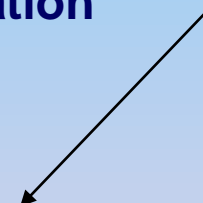
Degussa P 25 TiO₂



Verre avec FTO



Dye infiltration



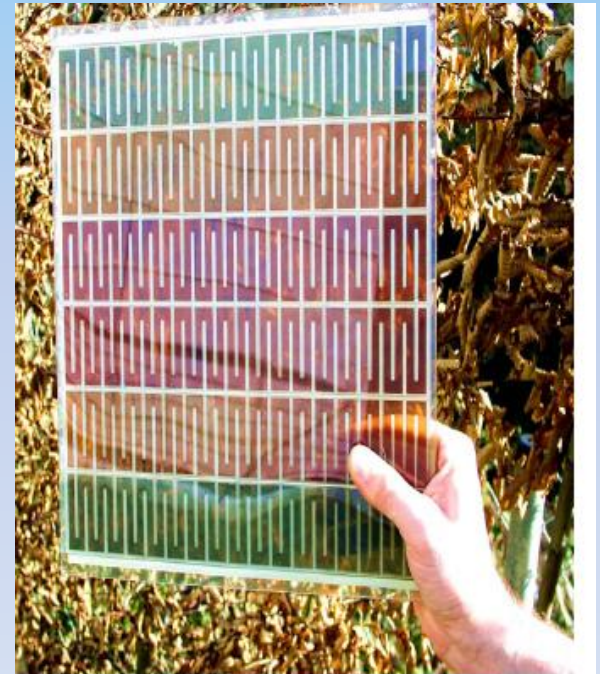
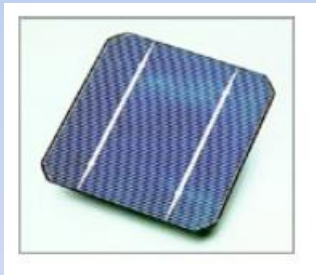
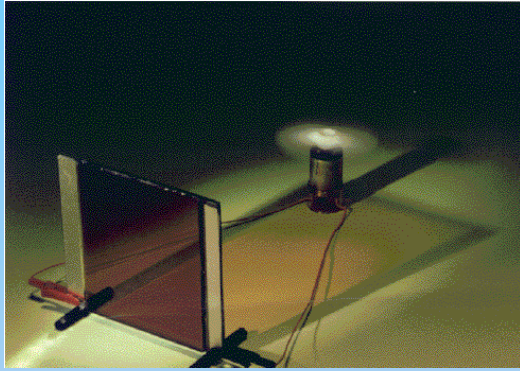
Carbone electrode



Infiltration du KI₃



Mesure photoélectrique



Dr. Andreas Hinsch, FHI, ISE Freiburg Germany

Courtesy Dr. Nam Gyu Park KIST

transparent, colorful, beautiful



Transparency: due to nano-sized (~ 20 nm) TiO_2 particle film

Color: due to visible light absorption by dye

* DSC costs lower than Si solar cell; 1/4 -1/5 of Si solar cell



The Toyota Dream House



DSC
made by
AISIN -SEIKI



ply for mobile



Kariya City at lat. $35^{\circ}10'N$,
Asimuthal angle: 0°
Facing due south, Tilted at 30°

10:00 – 11:45,

14:00 – 16:00H

2015	Dny v týdnu							Týden		Číslo týdne	Pracovních dnů
	Po	Út	St	Čt	Pá	So	Ne				
Březen							1	9	0		
	2	3	4	5	6	7	8	10	5		
	9	10	11	12	13	14	15	11	5		
	16	17	18	19	20	21	22	12	5		
	23	24	25	26	27	28	29	13	5		
	30	31						14	2		
Duben			1	2	3	4	5	14	3		
	6	7	8	9	10	11	12	15	4		
	13	14	15	16	17	18	19	16	5		
	20	21	22	23	24	25	26	17	5		
	27	28	29	30				18	4		
Květen					1	2	3	18	0		
	4	5	6	7	8	9	10	19	4		
	11	12	13	14	15	16	17	20	5		
	18	19	20	21	22	23	24	21	5		
	25	26	27	28	29	30	31	22	5		
Červen	1	2	3	4	5	6	7	23	5		
	8	9	10	11	12	13	14	24	5		
	15	16	17	18	19	20	21	25	5		
	22	23	24	25	26	27	28	26	5		
	29	30						27	2		