Materials for photovoltaic: the revival of sensitization of large bandgap semi-conductors

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Place of renewable energy in the new energetic mix

Worldwide consumption (2010): 1.10^{14} kWh

Biomass

10^{14} kWh

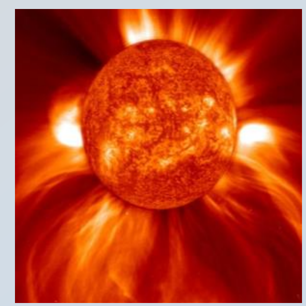
Wind

6.10^{14} kWh

(2011: 5.10^{11} kWh)

Hydro-electricity

10^{13} kWh

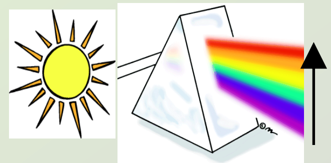


Solar

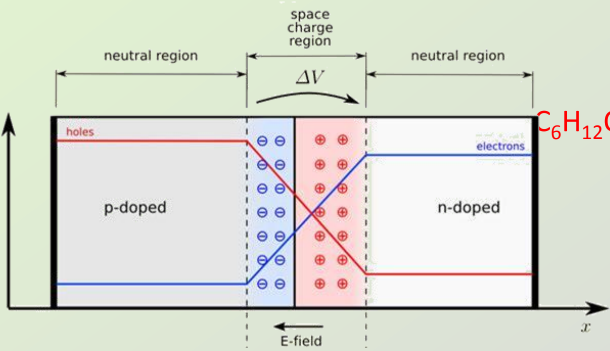
10^{18} kWh

We are receiving in one hour the equivalent of 1yr energy consumption

Sun utilization for energy powering

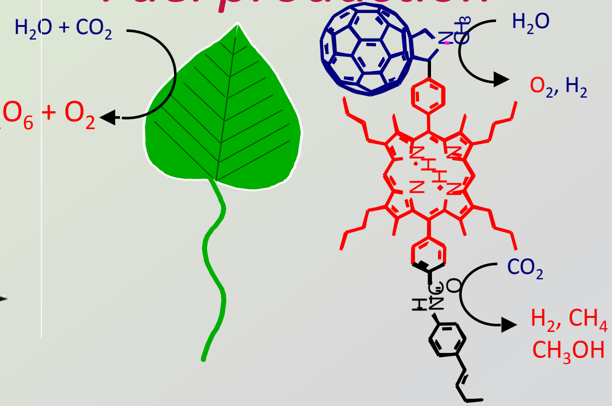


Electricity production



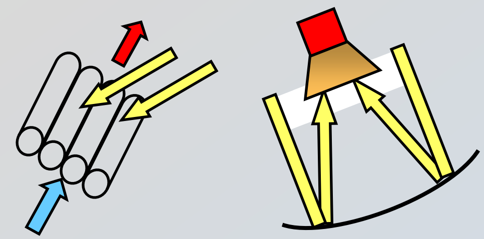
p-n junction solar cells

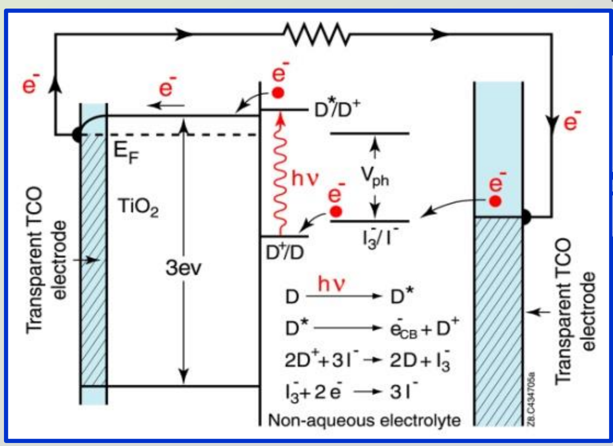
Fuel production



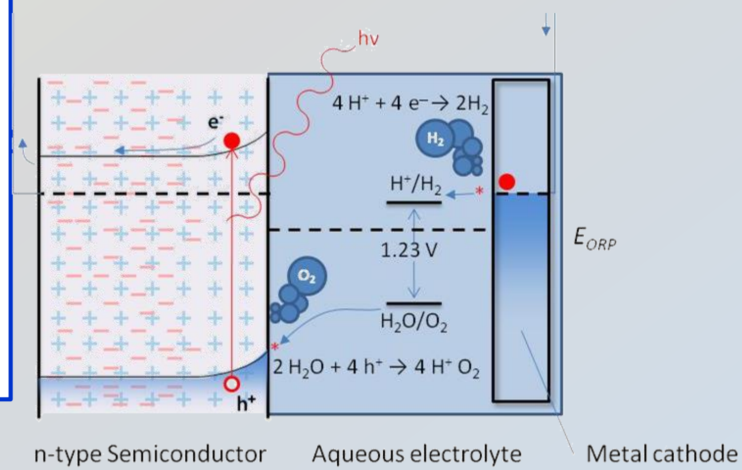
Natural photosynthesis → artificial

Heat production

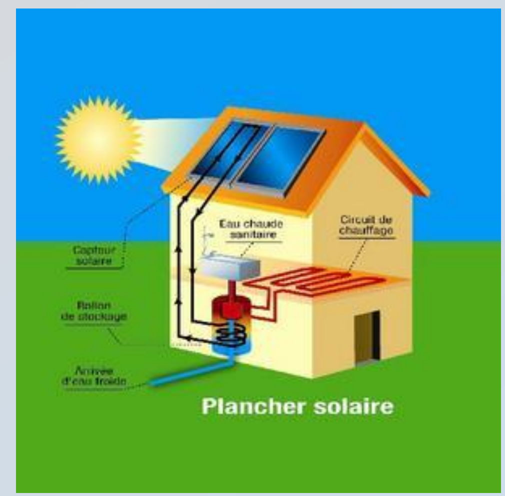




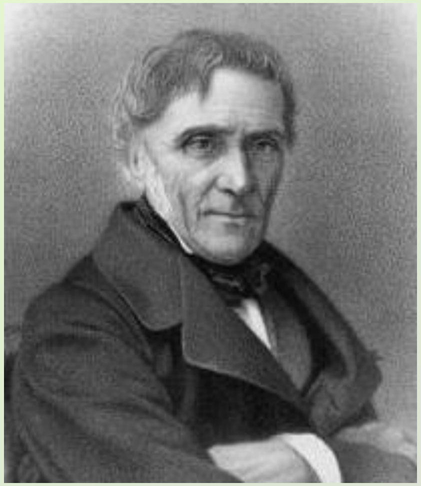
Organic or PV hybrid materials



Water splitting for hydrogen production

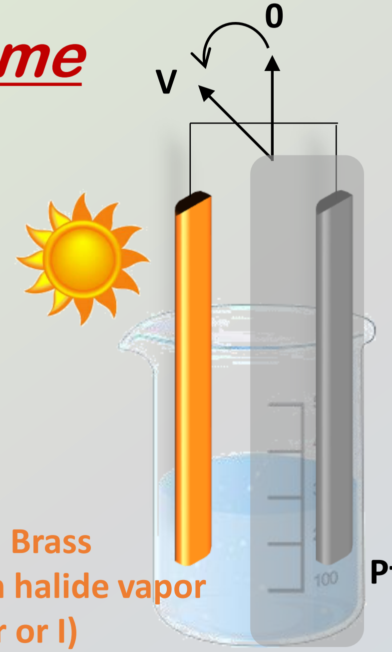


Photovoltaic history: a question of name



Antoine Cesar Becquerel
(1788-1878)

Alexandre Edmond Becquerel
(1820-1890)



Pt, Ag, Brass
Modified with halide vapor
(Cl, Br or I)

Pt CE in darkness

Acid or alkaline aqueous electrolyte

MÉMOIRES LUS.

Mémoire sur les effets électriques produits sous l'influence des rayons solaires; par M. EDMOND BECQUEREL.

§ 1er. *Action de la radiation sur les lames métalliques.*

« Dans le dernier Mémoire que j'ai eu l'honneur de présenter à l'Académie, dans sa séance du lundi 29 juillet 1839, je me suis attaché à mettre en évidence, à l'aide des courants électriques, les réactions chimiques qui ont lieu au contact de deux liquides, sous l'influence de la lumière solaire. Le procédé que j'ai employé nécessitait l'emploi de deux lames de platine, en relation avec les deux extrémités du fil d'un multiplicateur très sensible et qui plongeaient chacune dans une des dissolutions superposées. Or comme ces deux lames éprouvaient elles-mêmes les effets de la radiation, il a dû en résulter des phénomènes composés, dont je vais m'occuper dans ce nouveau Mémoire. On sera à même ensuite de faire la part de chacun des effets produits.

» *Lames d'argent.* — Des lames d'argent parfaitement décapées ont été mises dans l'appareil à compartiment rempli d'eau acidulée par l'acide sulfurique; exposées successivement à la radiation solaire, elles ont donné un courant de 1 à 2 degrés; la lame exposée était négative par rapport au liquide : en opérant avec les mêmes lames qui avaient servi d'électrodes et exposant à la radiation solaire la lame positive ou oxidée, le courant n'a pas été plus intense.

» Cette faible action pouvant être négligée, j'ai déposé sur les lames d'argent des vapeurs de brome, d'iode et du chlore. Avec une couche épaisse de vapeur d'iode, répandu sur la lame, on a obtenu un courant assez intense, dirigé dans un sens tel, que la lame exposée au soleil prenait au liquide l'électricité négative, résultat qui annonçait l'action de l'iode sur l'argent; quand la couche d'iode était très mince, on avait un courant électrique allant en sens inverse, ce qui indiquait une action chimique inverse de la précédente; par première impulsion à la lumière diffuse, le courant obtenu, dans une expérience, produisait une déviation de 45 degrés.

» Quand on emploie du brome au lieu d'iode, le courant qui est assez fort a toujours lieu de manière que la lame exposée est négative par rapport au liquide.

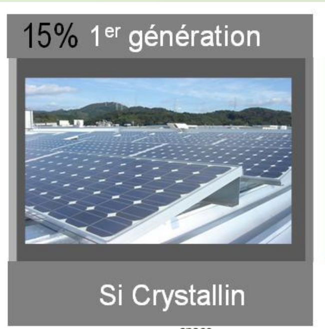
» Ces courants n'ont que peu de durée, car une exposition de quelques instants à la radiation atmosphérique suffit pour effectuer complétement la réaction du brome et de l'iode sur l'argent.

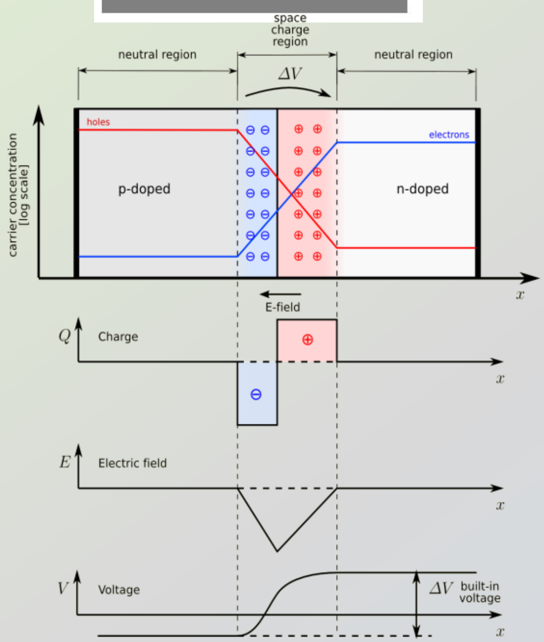
Towards applications

1st generation (1954)

p-n junction made of Si

(Bell-labs: Chapin Pearson Prince)

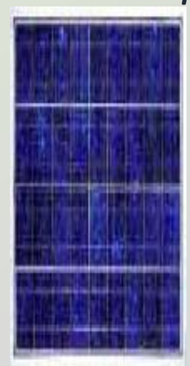




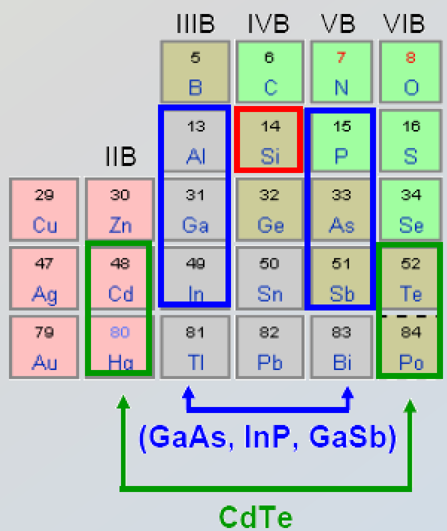
2nd generation (1983)

p-n junction

Polycristalline or amorphous Si

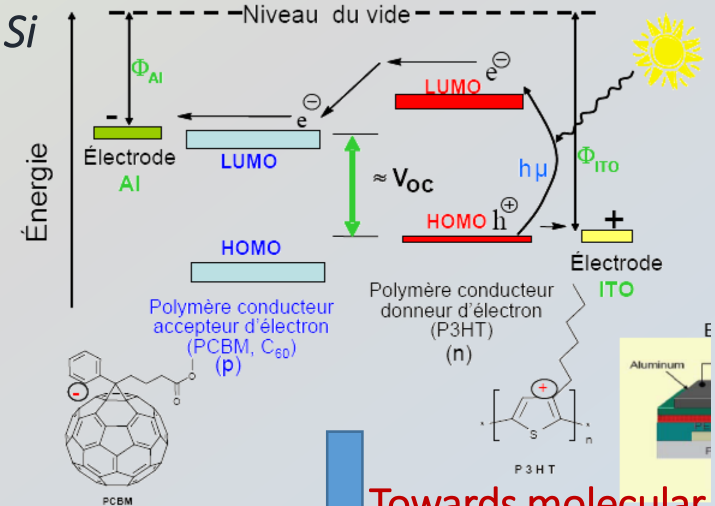


III – V or II – VI junction

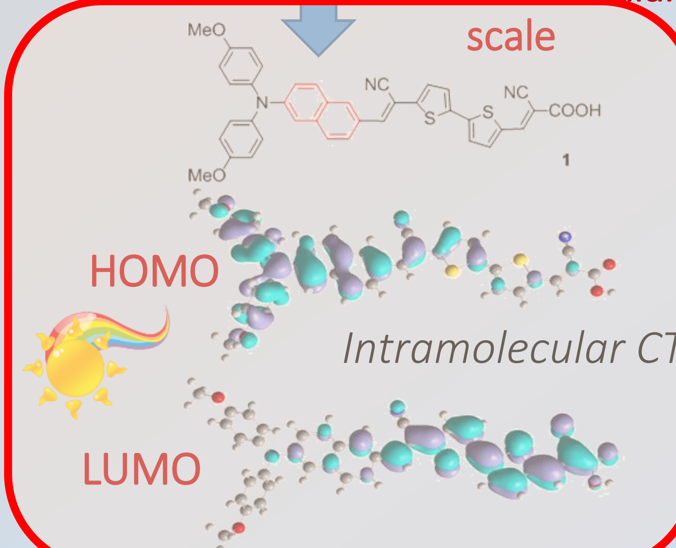


3rd generation (1990's)

Donor / Acceptor systems



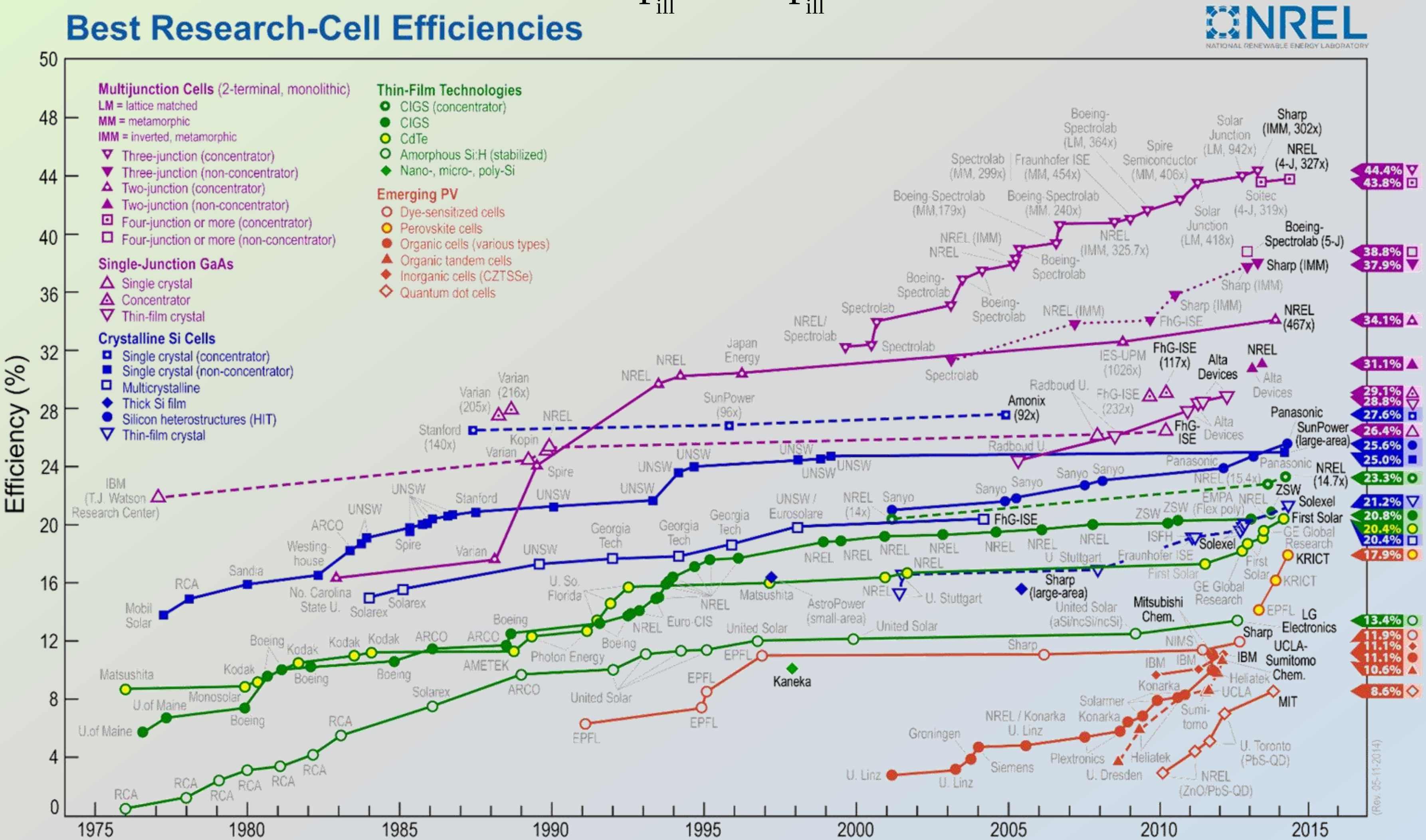
Towards molecular scale



↘ Cost, Energy payback but also power conversion efficiency

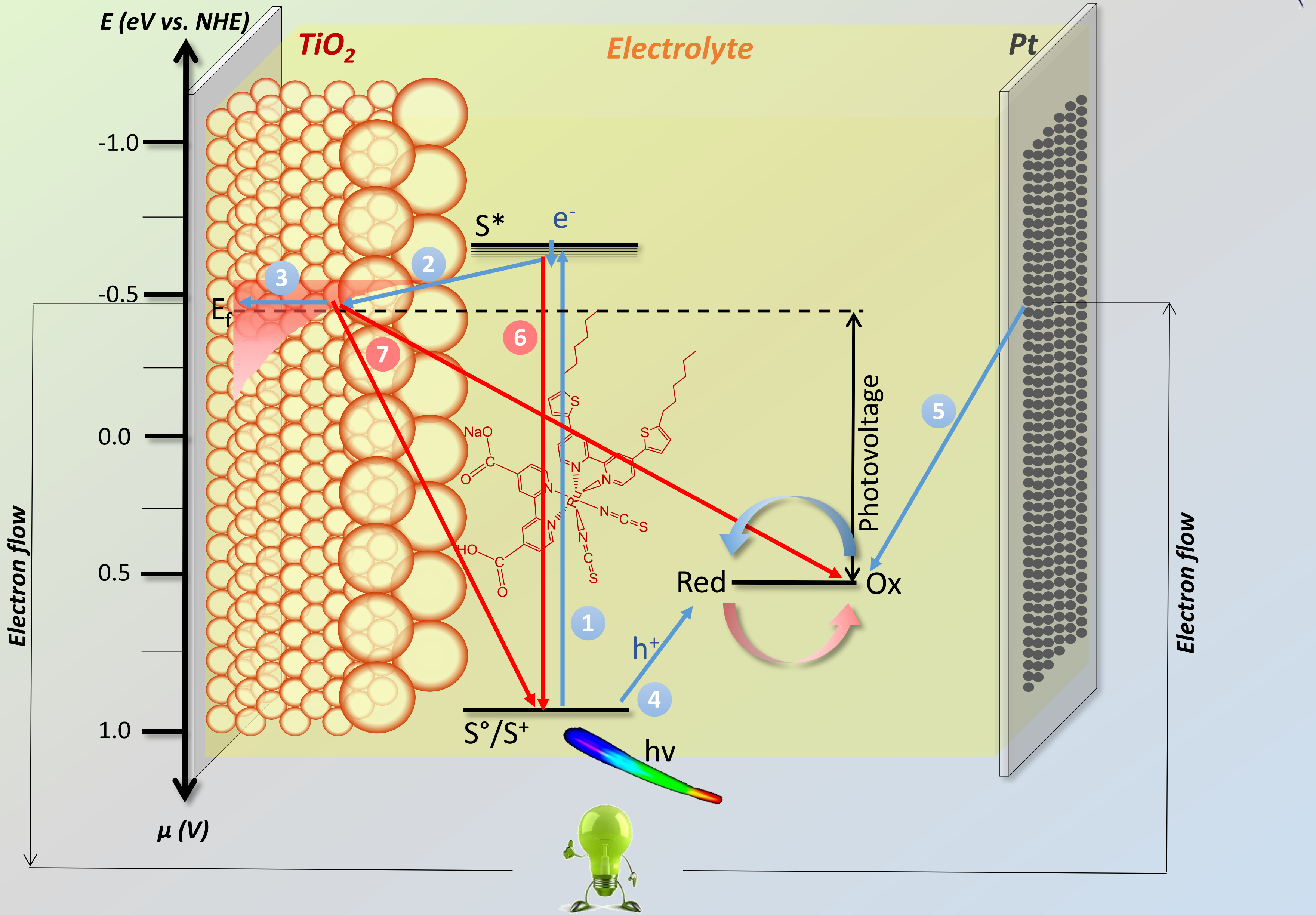
Last update about PV records

$$\eta = \frac{P_{max}}{P_{ill}} = \frac{J_{SC}.V_{OC}.ff}{P_{ill}}$$



1st and 2nd generation stagnation or incremental progress
3rd generation continues substantial improvement

Dye-sensitized solar cells principle

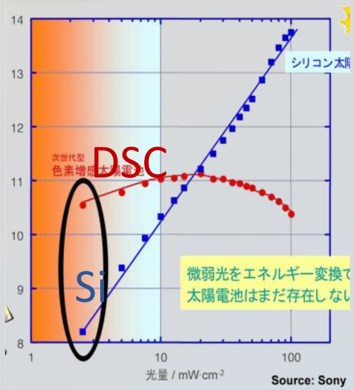


Dye-sensitized solar cells

Set of advantages over Si

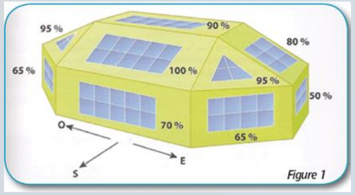
Low cost (0.5 $/W$_p$)

Sensitiveness to diffuse light



Power conversion efficiency independent to light intensity or temperature

Transparent cell (BIPV) and bifacial

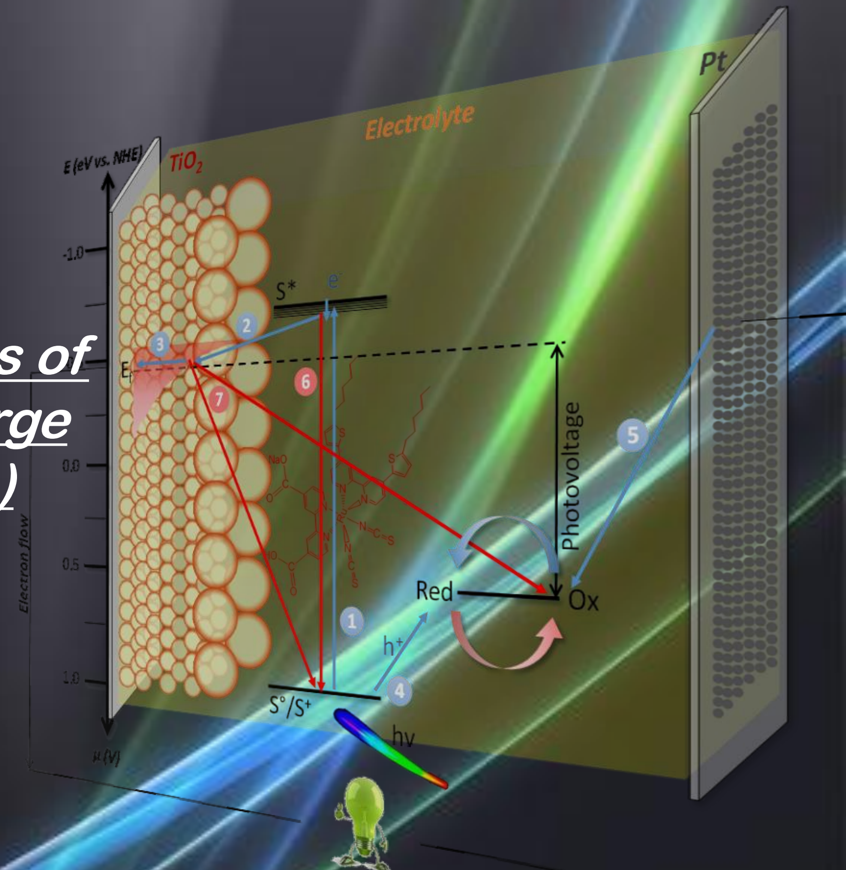


Can be made flexible

Lower environmental footprint

Approach to improve efficiency and stability / Outline

$$\eta = J_{sc}\, V_{oc}\, ff \,/\, \Phi_{ph}$$



Outline

1/ Approaches to increase PCE by means of light confinement enhancement and charge collection efficiency (beads and 1D nano)

2/ Understanding of the degradation mechanisms in dye-sensitized solar cells

$$J_{sc} = qI_0(1-\eta_{inj}\, e^{-\alpha d}) - q\frac{D^\circ n^\circ d}{L^2}\left(e^{\frac{qU}{kT}}-1\right)$$

$$V_{oc} = \left(\frac{\alpha RT}{F}\right)\mathrm{Ln}\left(\frac{k\phi}{k_1[S+]+k_2[I_3-]}\right)$$

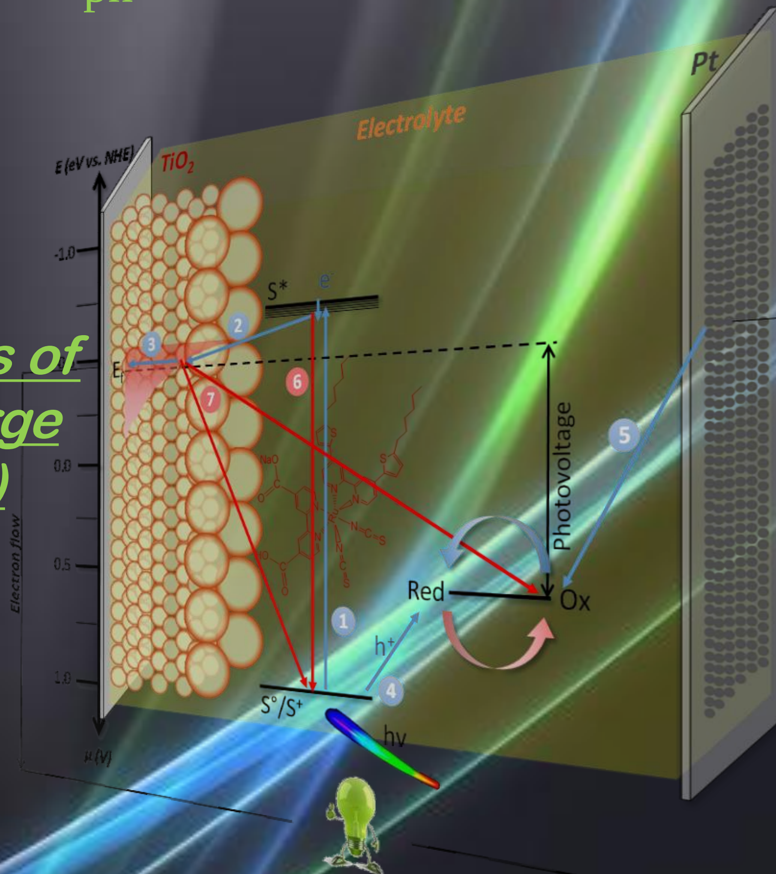
Approach to improve efficiency and stability / Outline

$$\eta = J_{sc}\, V_{oc}\, ff \,/\, \Phi_{ph}$$

Outline

1/ Approaches to increase PCE by means of light confinement enhancement and charge collection efficiency (beads and 1D nano)

2/ Understanding of the degradation mechanisms in dye-sensitized solar cells



$$J_{sc} = qI_0(1-\eta_{inj}\, e^{-\alpha d}) - q\frac{D^\circ n^\circ d}{L^2}\left(e^{\frac{qU}{kT}}-1\right)$$

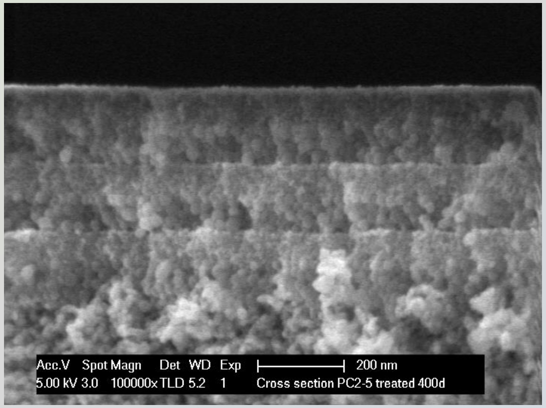
$$V_{oc} = \left(\frac{\alpha RT}{F}\right) \mathrm{Ln}\left(\frac{k\phi}{k_1[S+]+k_2[I_3-]}\right)$$

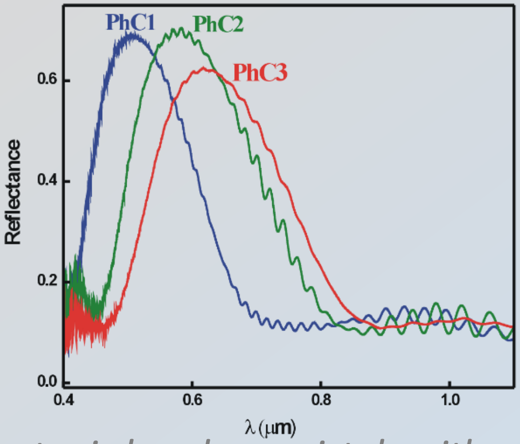
Why improving light confinement and cc efficiency ?

$$\eta = J_{sc}\, V_{oc}\, ff \,/\, \Phi_{ph}$$

$$J_{sc} = qI_0(1-\eta_{inj}\, e^{-\alpha d}) - q\frac{D°n°d}{L^2}\left(e^{\frac{qU}{kT}}-1\right) \qquad V_{oc} = \left(\frac{\alpha RT}{F}\right) \mathrm{Ln}\left(\frac{k\phi}{k_1[S+]+k_2[I_3-]}\right)$$

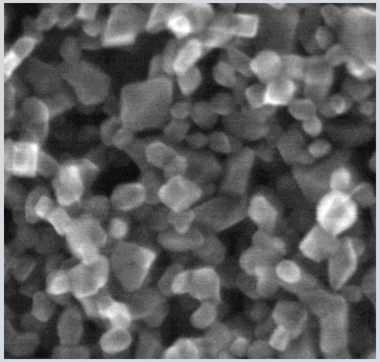
Increase of both J_{sc} and V_{oc} are expected !

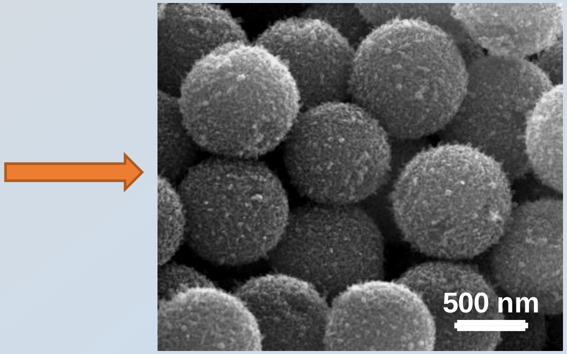




Sheltering the photo-anode by photonic bandgap cristals with controlled periodicity

Approaches to improve light confinement



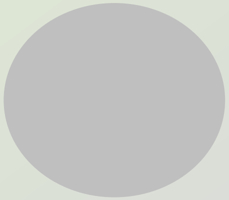


Synthesis of bifunctional beads of TiO_2

Synthesis of beads of anatase TiO_2

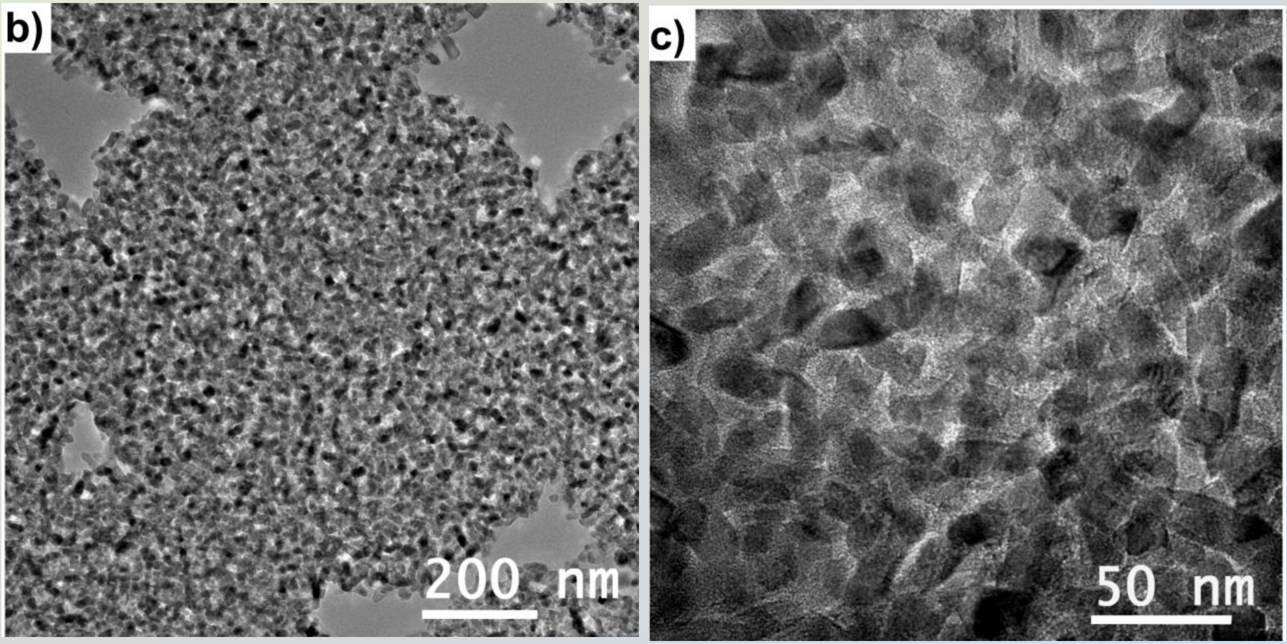
1st step: Synthesis by sol-gel of the spheres

Addition of Ti(iOPr) into a solution of hexadecylamine in ethanol (0.1M KCl)



Monodisperse spheres of amorphous $Ti(OH)_4$ (ca. 1µm)

2nd step: Hydrothermal treatment in 25% NH_4OH in ethanol at 160°C for 16 hrs



Porous spheres

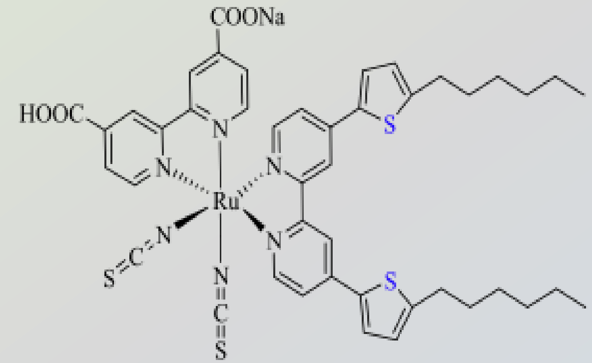
S_{BET} = 87 m^2/g with bimodal distribution meso-macro

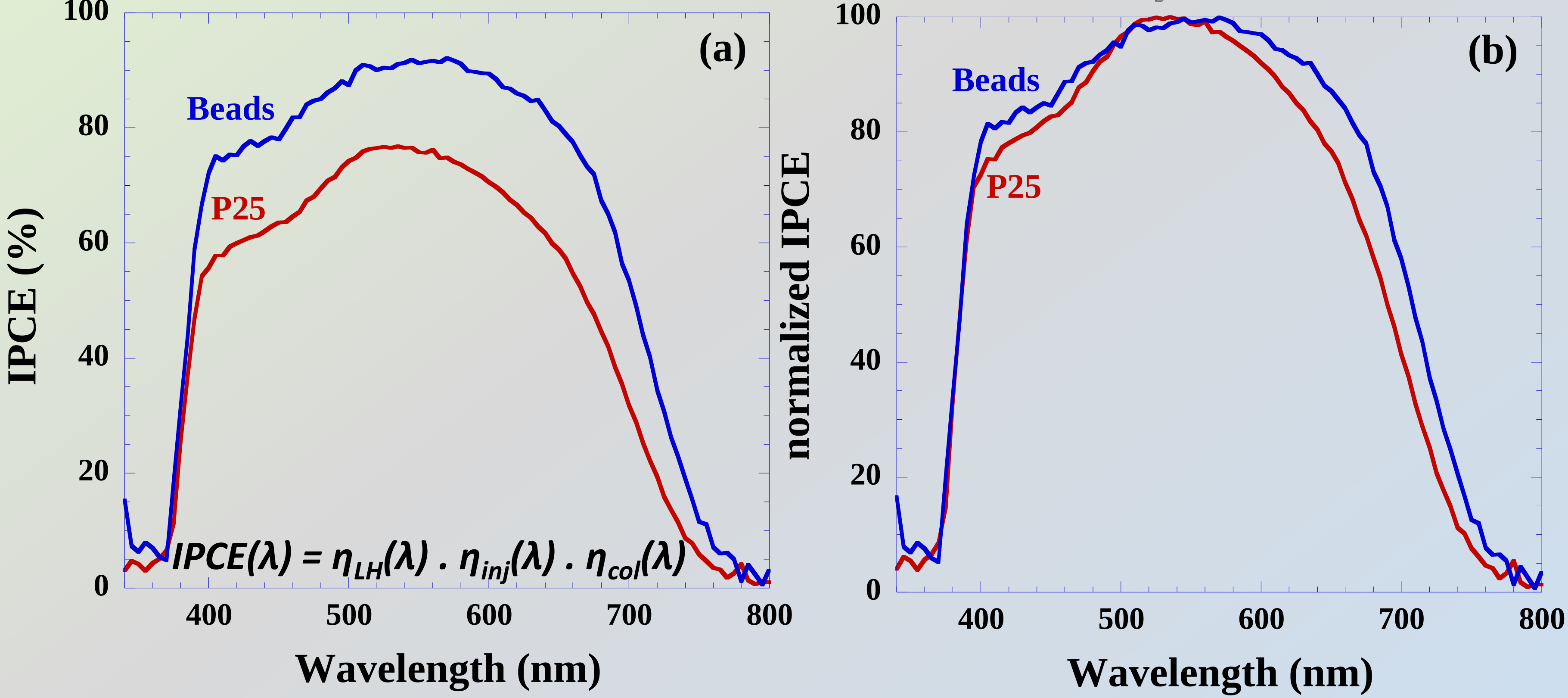
Beads morphology exhibits dual functionality: high surface area and scatter light according to Mie-theory

F. Sauvage et al., ACS nano 2010, 4(8), 4420

Beads performances vs. P25

Comparaison of quantum efficiency using C101 dye

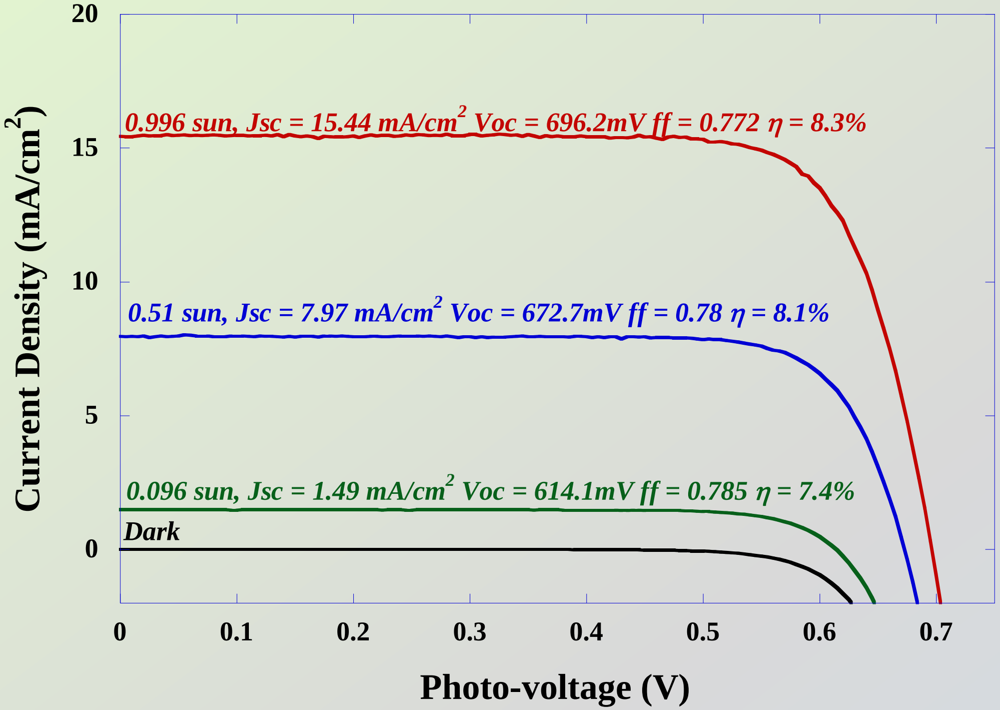




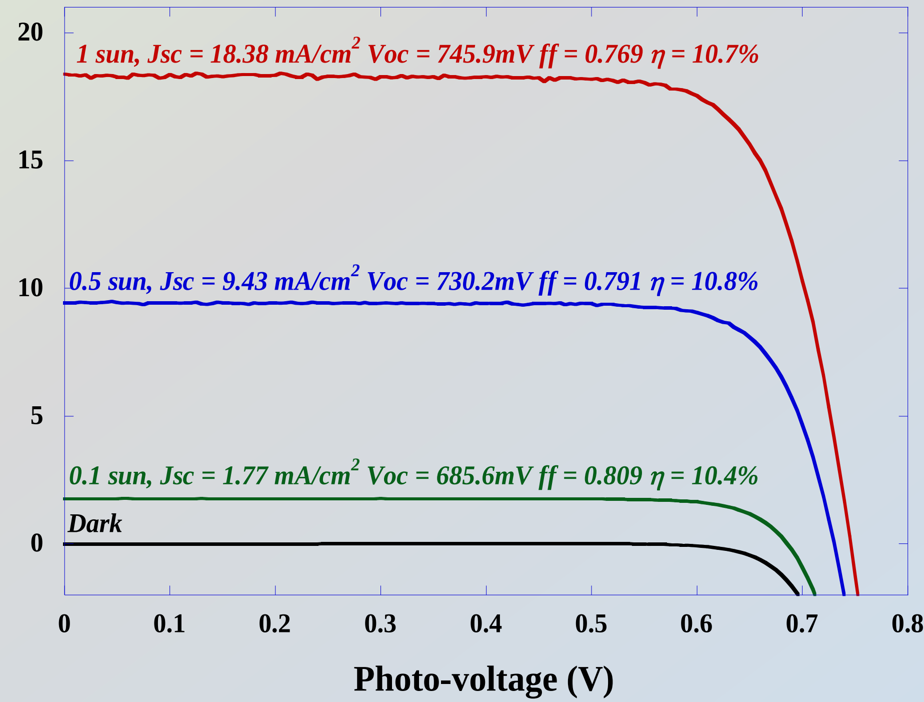
Enhancement of light conversion in the whole absorption spectrum of the dye

Beads performances vs. P25

Single layer of 8 µm thick of P25



Single layer of 8 µm thick of Beads



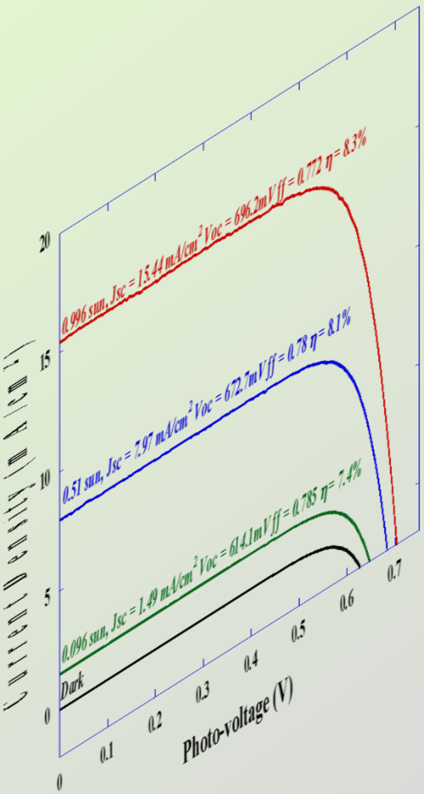
Significative improvement of power conversion efficiency when using the beads (gain in Jsc and Voc)

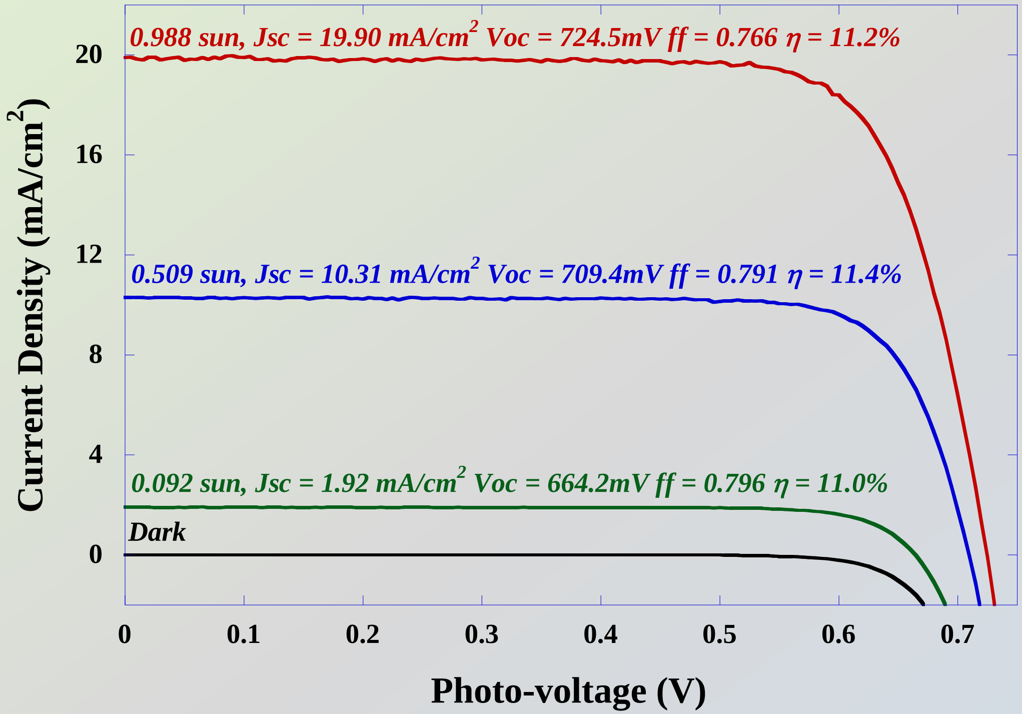
$$J_{sc} = qI_0(1-\eta_{inj}\, e^{-\alpha d}) - q\frac{D^\circ n^\circ d}{L^2}\left(e^{\frac{qU}{kT}}-1\right) \qquad V_{oc} = \left(\frac{\alpha RT}{F}\right)\mathrm{Ln}\left(\frac{k\phi}{k_1[S+]+k_2[I_3-]}\right)$$

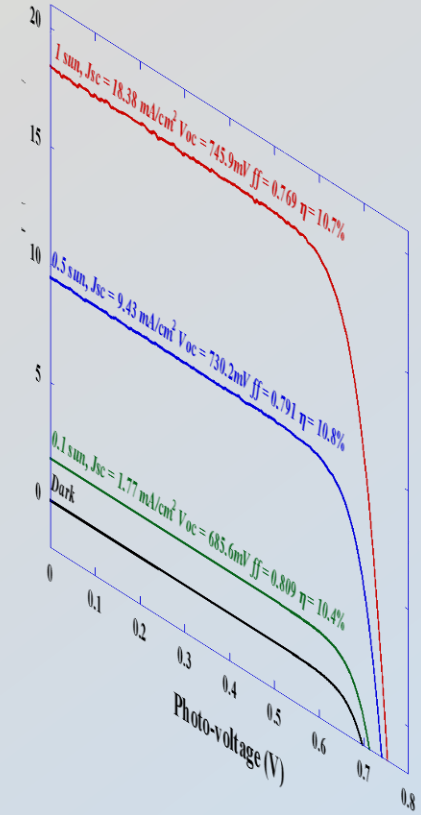
Beads performances vs. P25

LRCS

Three layer configuration 20nm + beads + 400nm (C101)





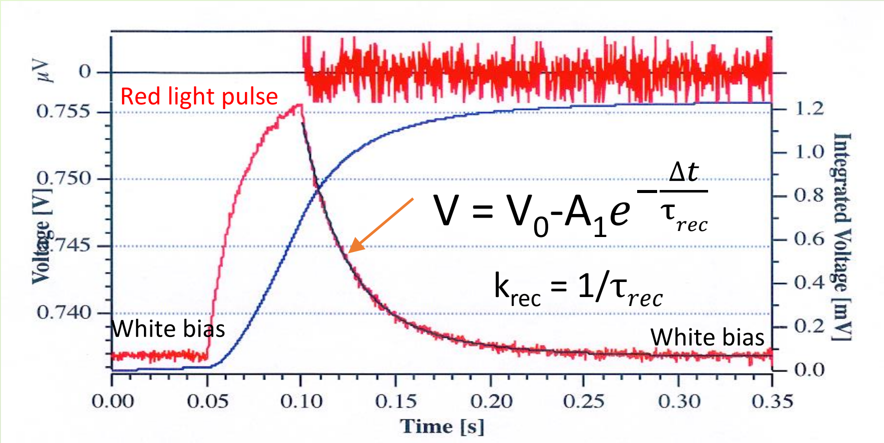


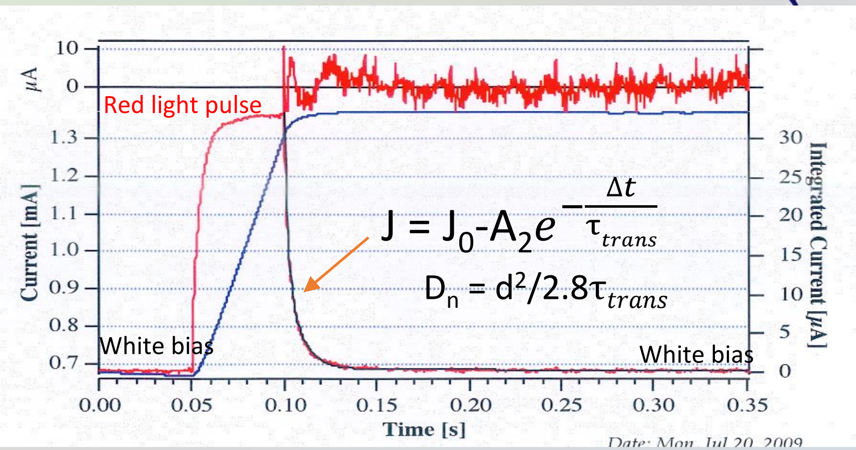
Highest PCE reported with C101 and close to record

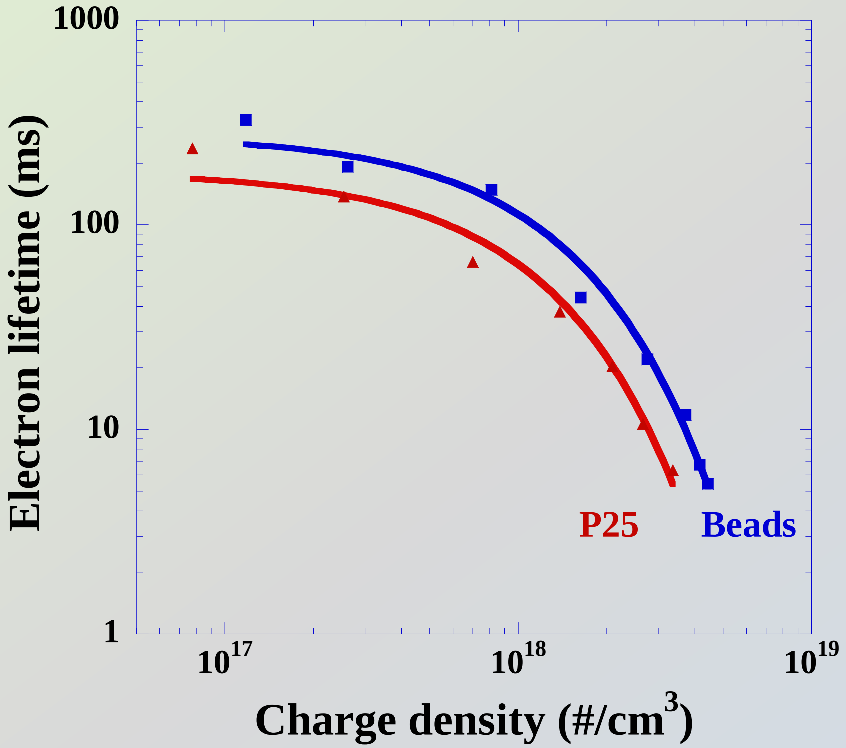
$$J_{sc} = qI_0(1-\eta_{inj}\, e^{-\alpha d}) - q\frac{D^\circ n^\circ d}{L^2}\left(e^{\frac{qU}{kT}}-1\right) \quad ?$$

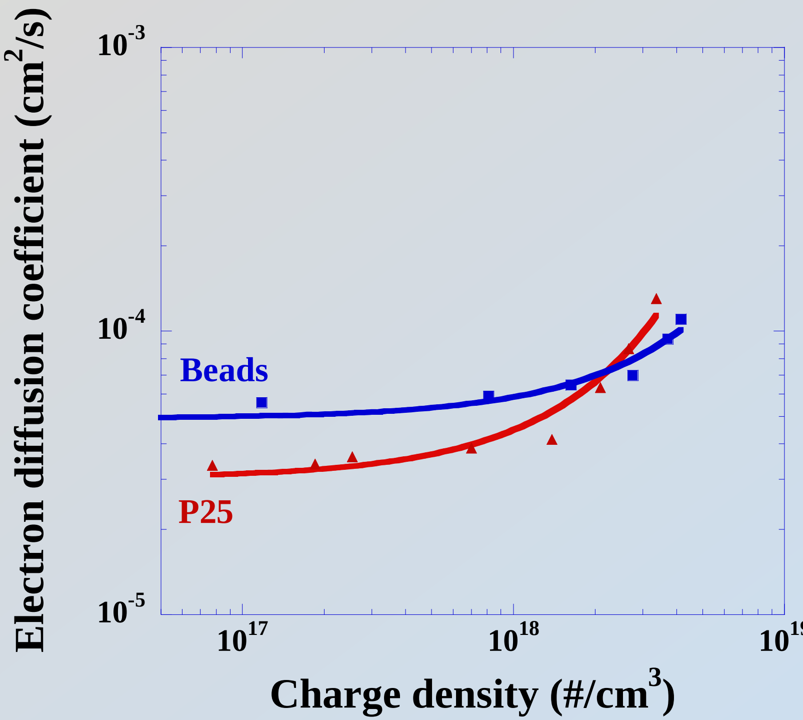
$$V_{oc} = \left(\frac{\alpha RT}{F}\right)\mathrm{Ln}\left(\frac{k\phi}{k_1[S+]+k_2[I_3-]}\right) \quad ?$$

μs/ms photocurrent and photovoltage transient decay



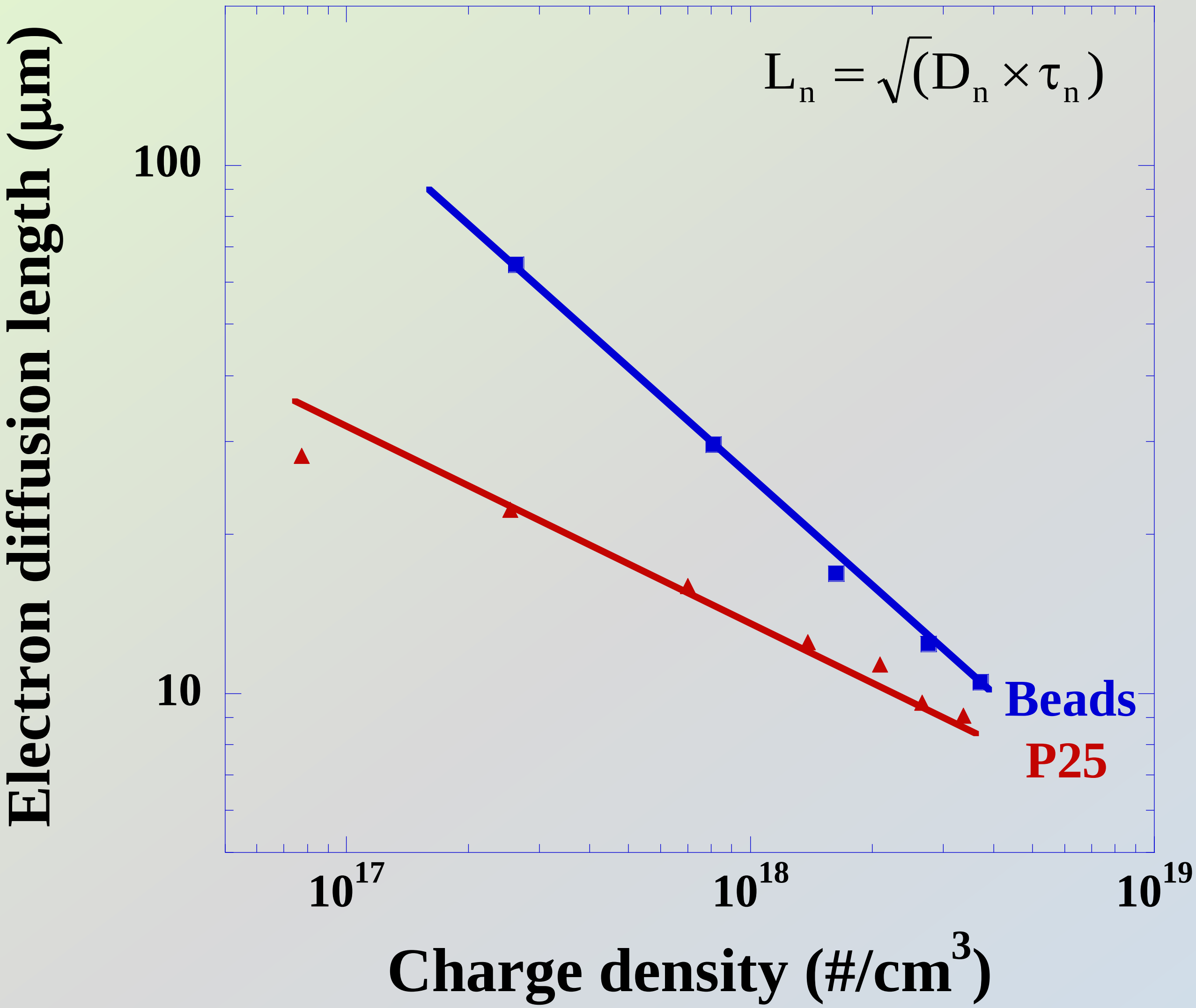






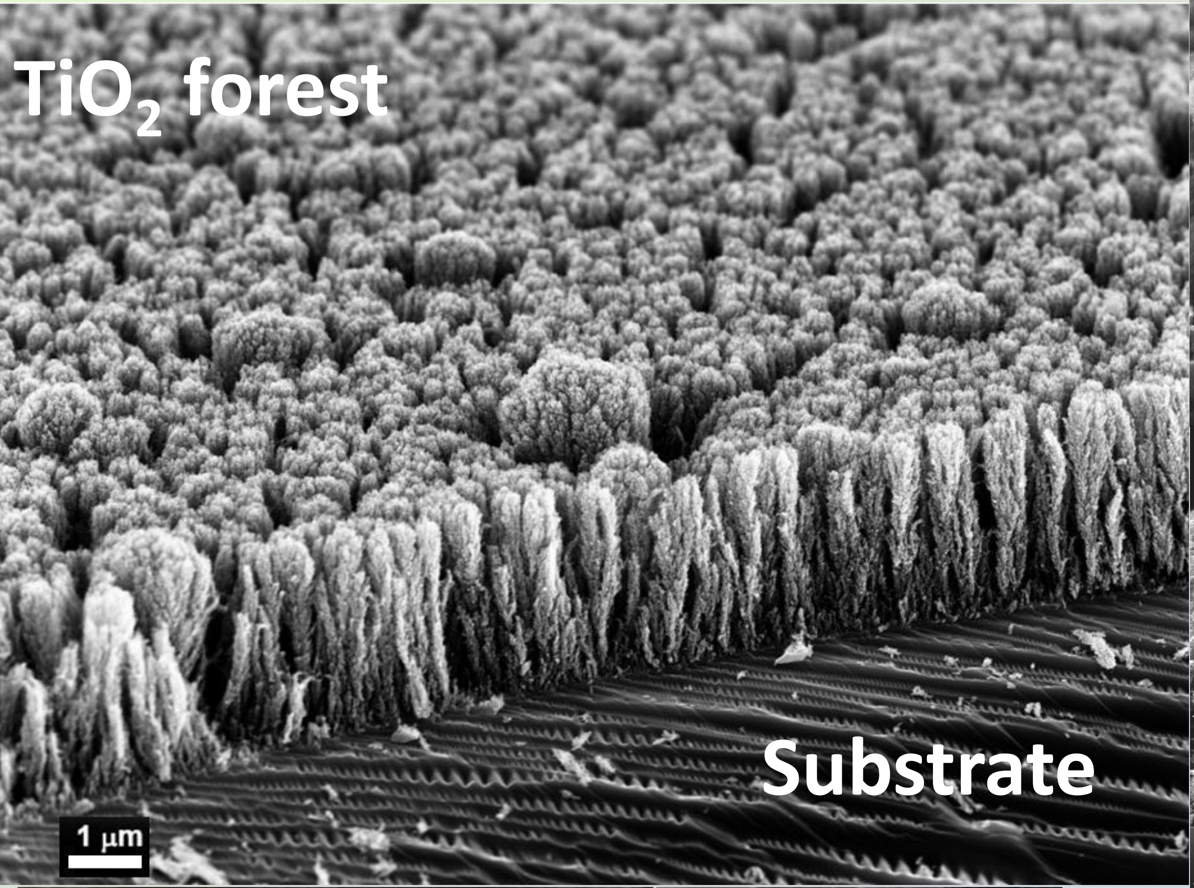
Greater electron lifetime and enhanced charge transport in beads

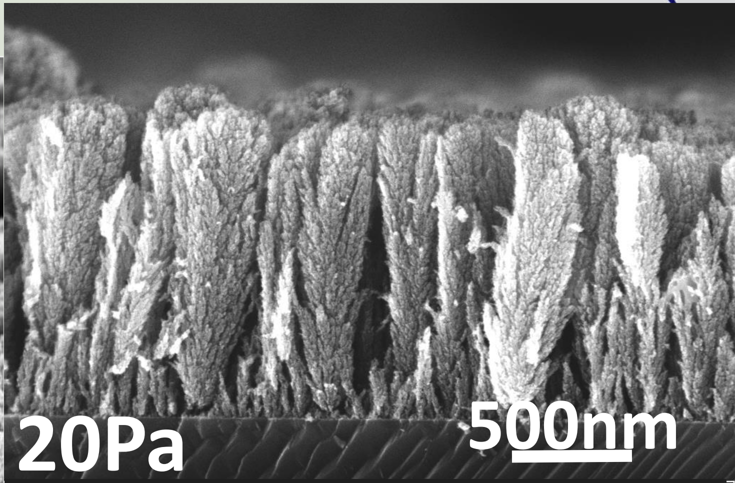
μs/ms photocurrent and photovoltage transient decay

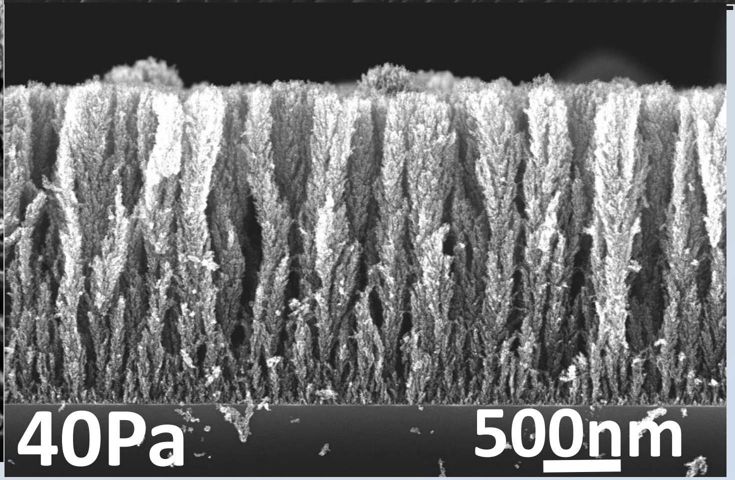


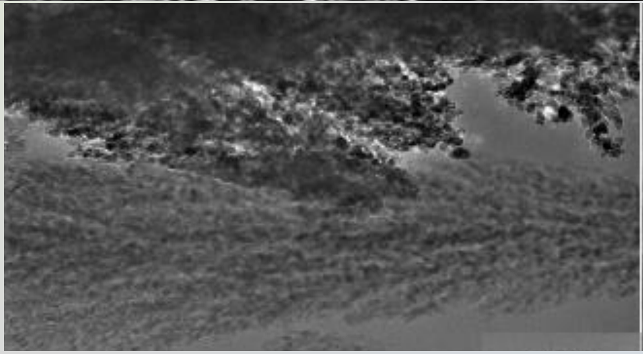
$$J_{sc} = qI_0(1-\eta_{inj}\, e^{-\alpha d}) - q\frac{D^\circ n^\circ d}{L^2}\left(e^{\frac{qU}{kT}}-1\right) \qquad V_{oc} = \left(\frac{\alpha RT}{F}\right)\mathrm{Ln}\left(\frac{k\phi}{k_1[S+]+k_2[I_3-]}\right)$$

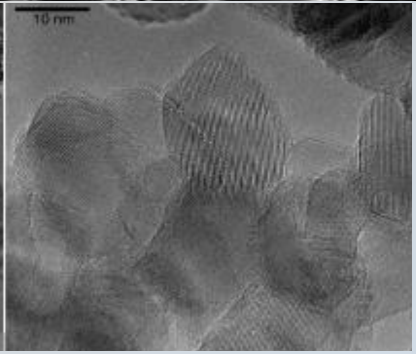
1D nanostructuration of photoanode by PLD











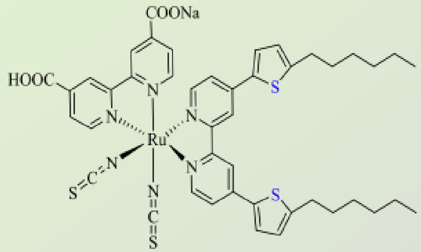
Highly porous (80%) hierarchical nanostructure

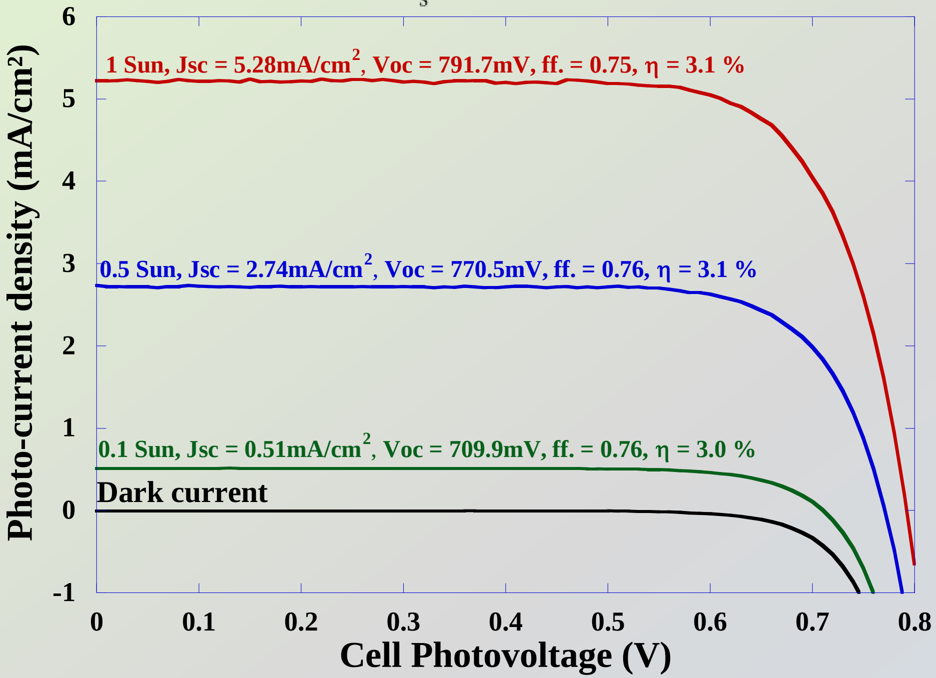
Anatase TiO_2 crystals of ca. 15 nm

F. Sauvage et al., Nano Lett. 2010, 10, 2562-2567

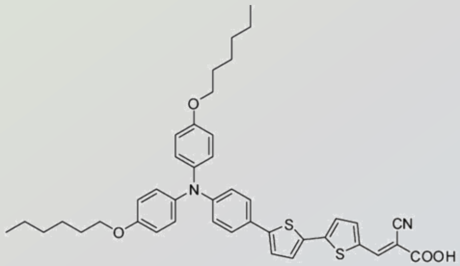
1D nanostructure TiO_2

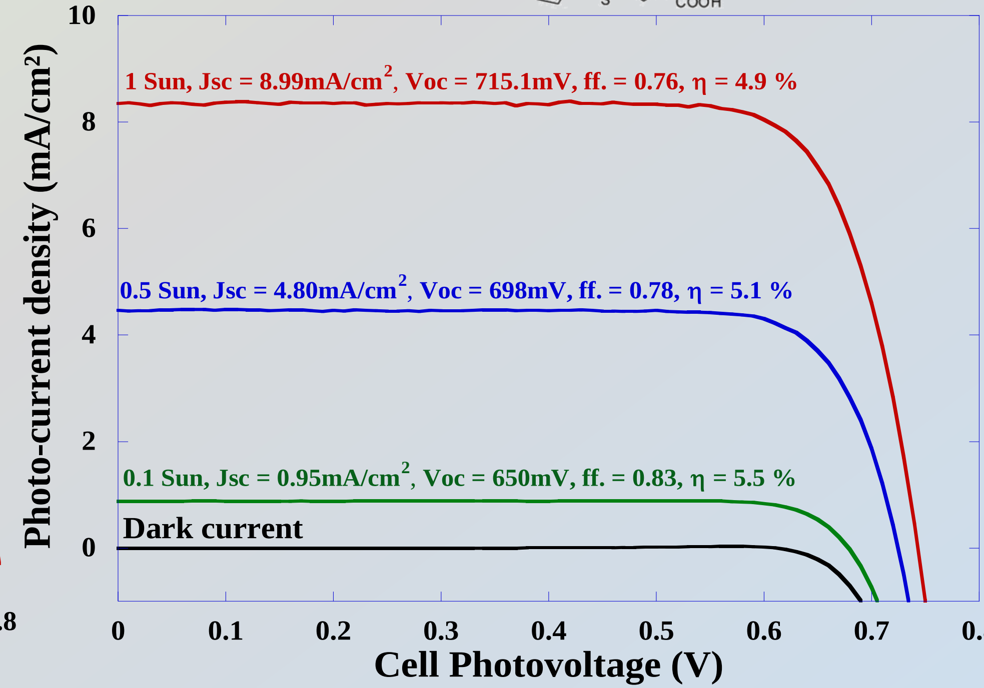
C101 dye





D21L6 dye

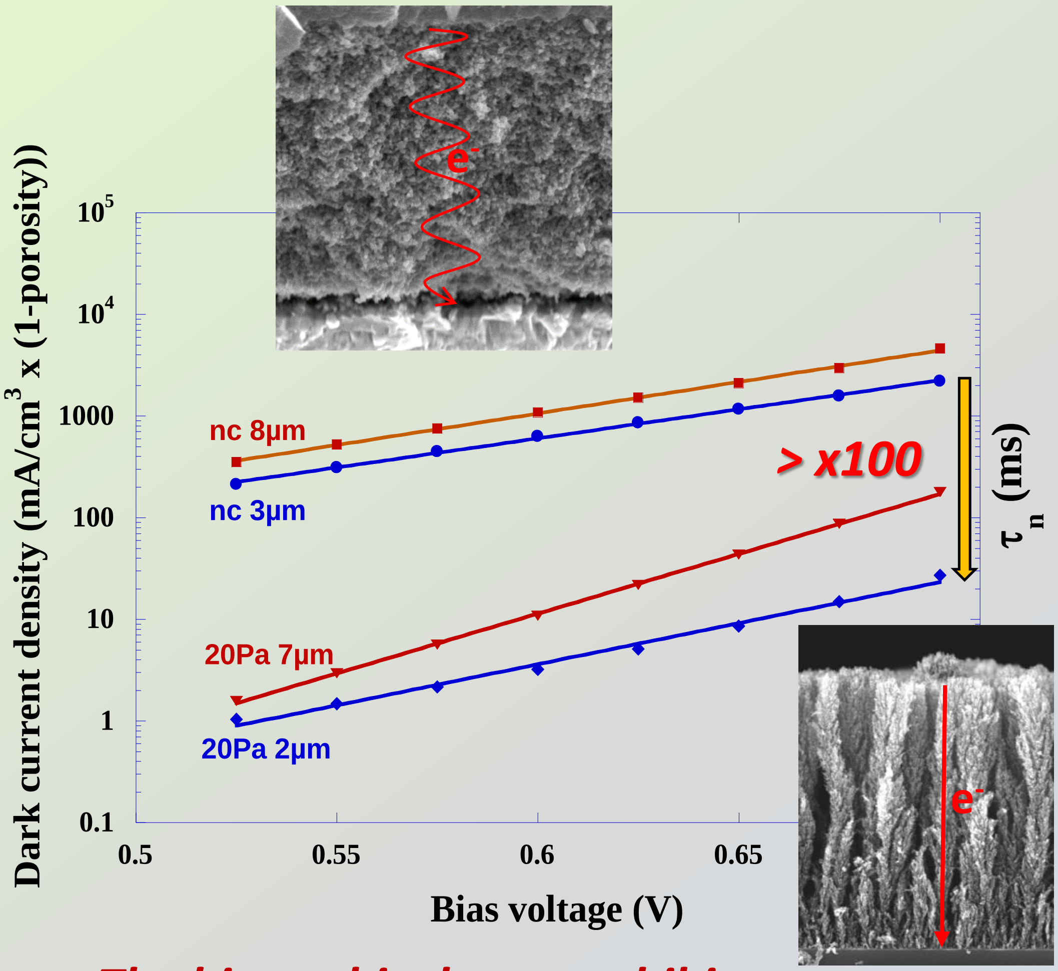


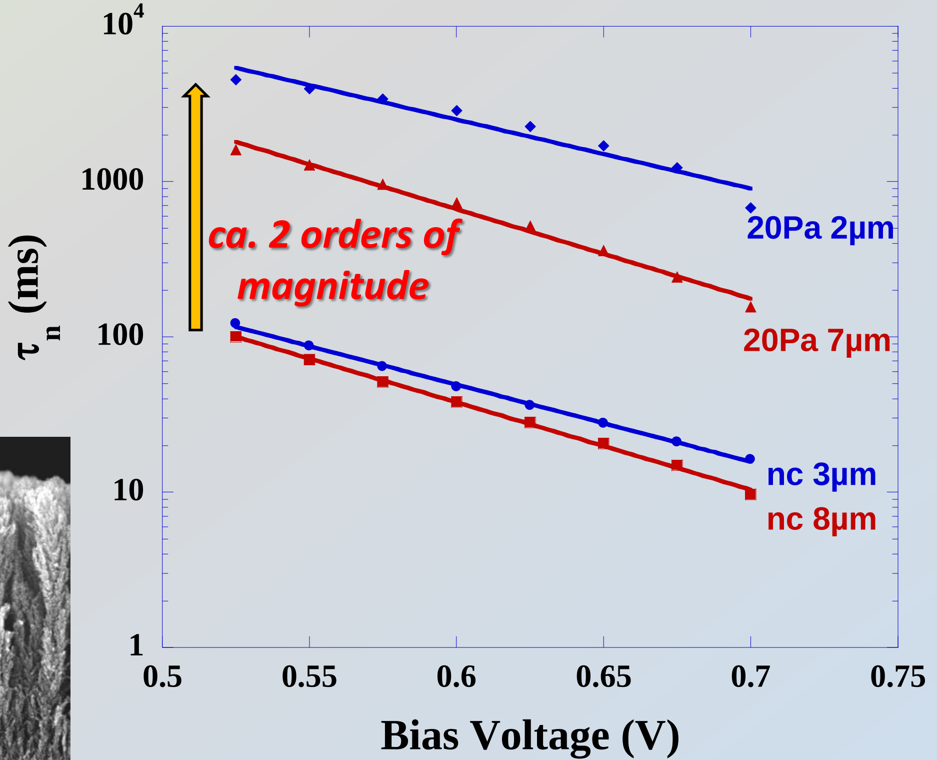


Low efficiencies owing to thinner films…

…very high Voc !

1D nanostructured TiO_2



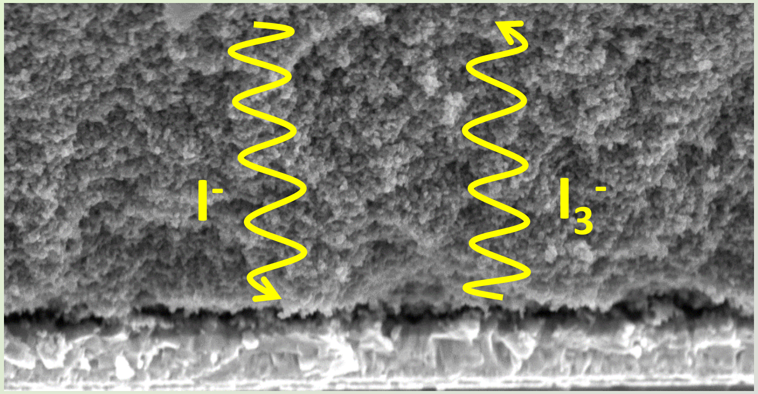


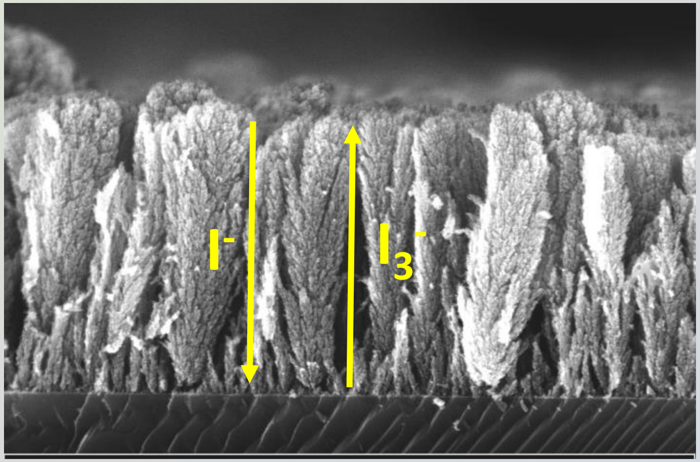
The hierarchical trees exhibit more than 100 times lower dark current

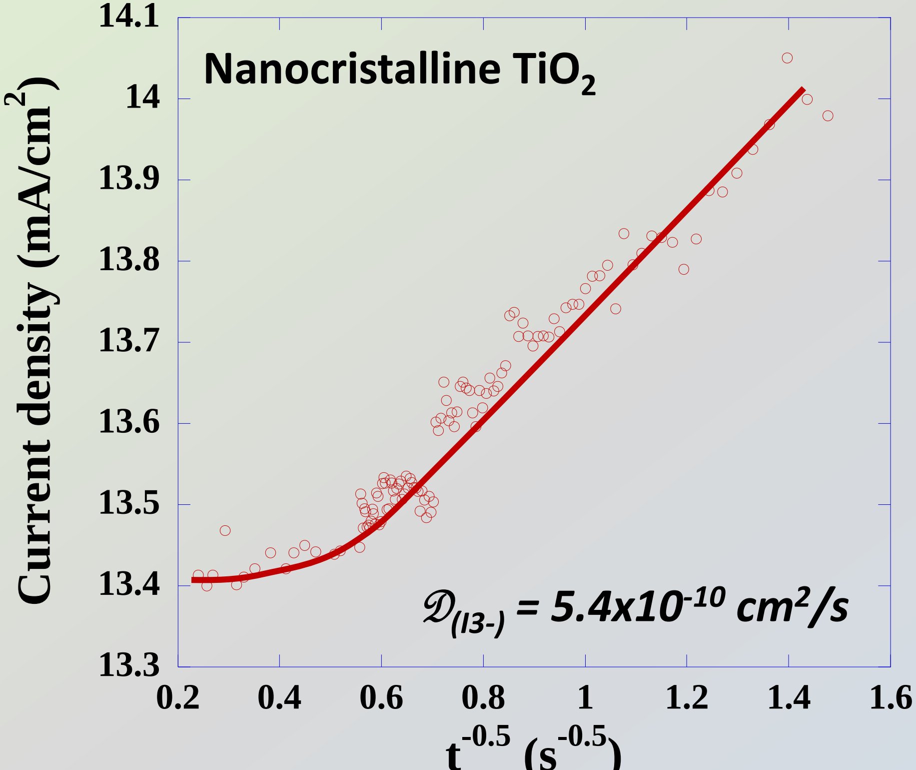
2 orders of magnitude greater electron lifetime

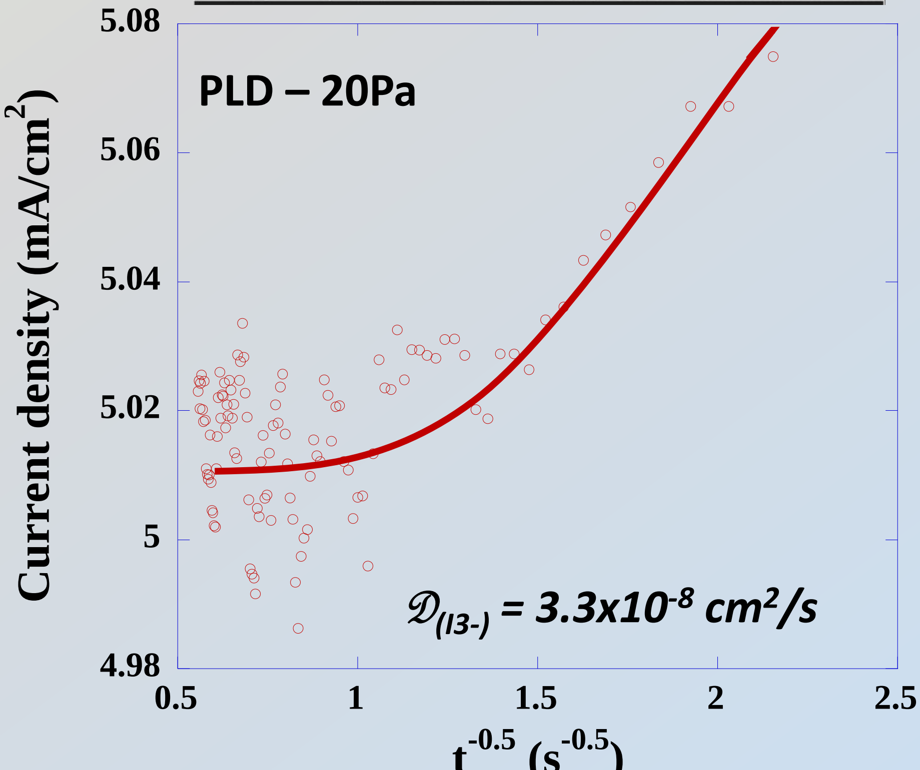
F. Sauvage et al., Nano Lett. 2010, 10, 2562-2567

Advantage of 1D structure for mass transport in pure ILs









Alleviation of the mass transport limitation in the mesopores

Approach to improve efficiency and stability / Outline

$$\eta = J_{sc}\, V_{oc}\, ff \,/\, \Phi_{ph}$$

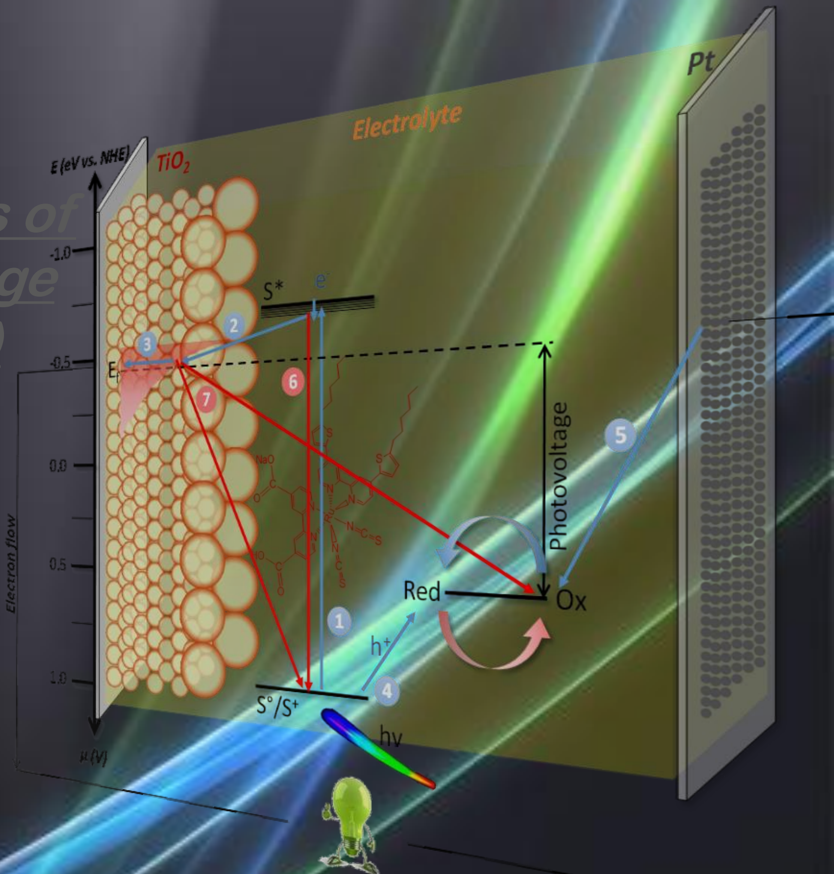
Outline

1/ Approaches to increase PCE by means of light confinement enhancement and charge collection efficiency (beads and 1D nano)

$$J_{sc} = qI_0(1-\eta_{inj}\, e^{-\alpha d}) - q\frac{D°n°d}{L^2}\left(e^{\frac{qU}{kT}}-1\right)$$

$$V_{oc} = \left(\frac{\alpha RT}{F}\right)\mathrm{Ln}\left(\frac{k\phi}{k_1[S+]+k_2[I_3-]}\right)$$

2/ Understanding of the degradation mechanisms in dye-sensitized solar cells



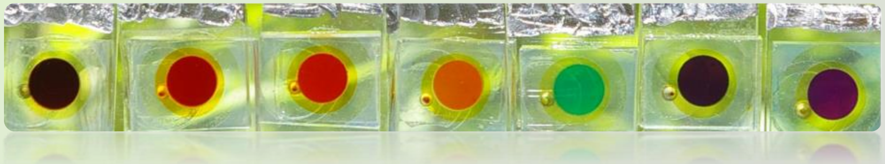
Ce projet est cofinancé par l'Union européenne L'Europe s'engage en Picardie avec le Fond européen de développement régional

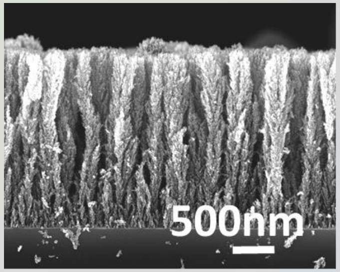
l'Europe s'engage en Picardie avec le FEDER

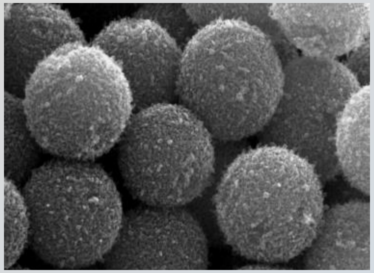
PICARDIE LA RÉGION

Research overview

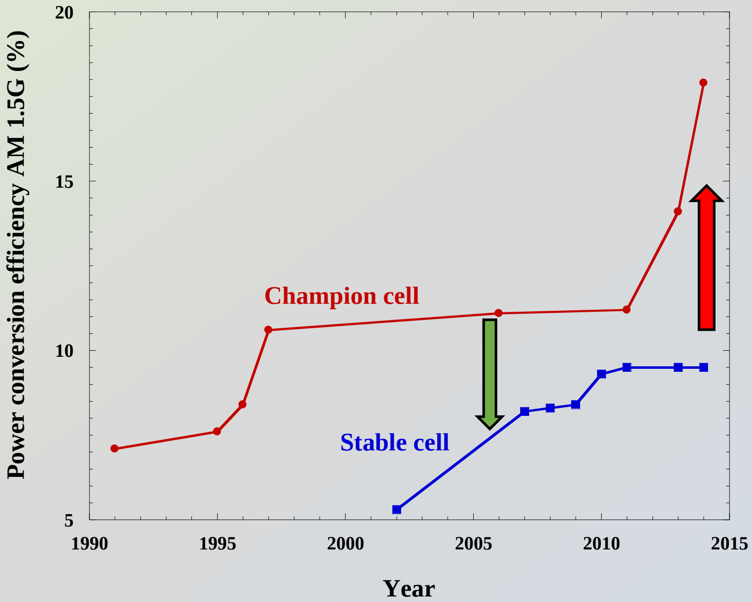
Research activity in DSSC is dominated by dye engineering for maximum light harvesting and mesostructured TiO_2 for improving light confinement and fast charge collection







Much less in electrolyte development for high stability (Polymers, Ionogels, IL, alternate low-volatile solvents) → with slower success of improvements and still difficulties to meet IEC61646 protocol

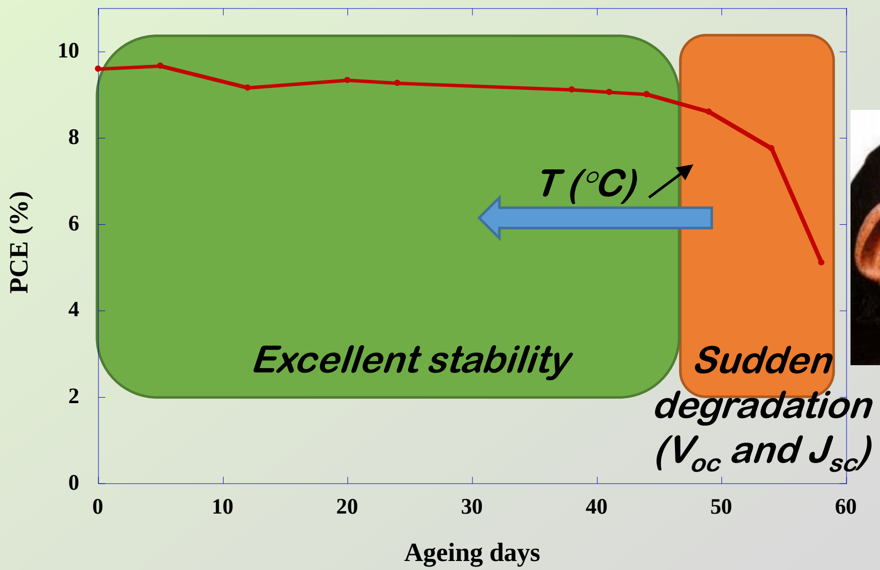


Our approach

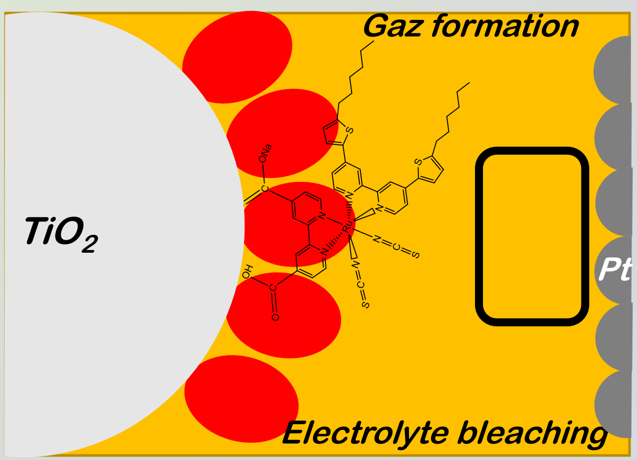
Improving fundamental knowledge on cell component interactions and to better understand the mechanisms of degradation:
TiO_2, dye, electrolyte?
Light, temperature or both actions ?
Why 85°C stability so difficult to pass?

State of the art

MPN-based electrolyte – C106 dye
Ageing at 60°C/100 mW.cm^{-2}



Evolution of cell ageing unusual for an electrochemical device with sudden breaking down



Electrolyte bleaching *upon ageing resulting from iodine consumption* [1]*:*

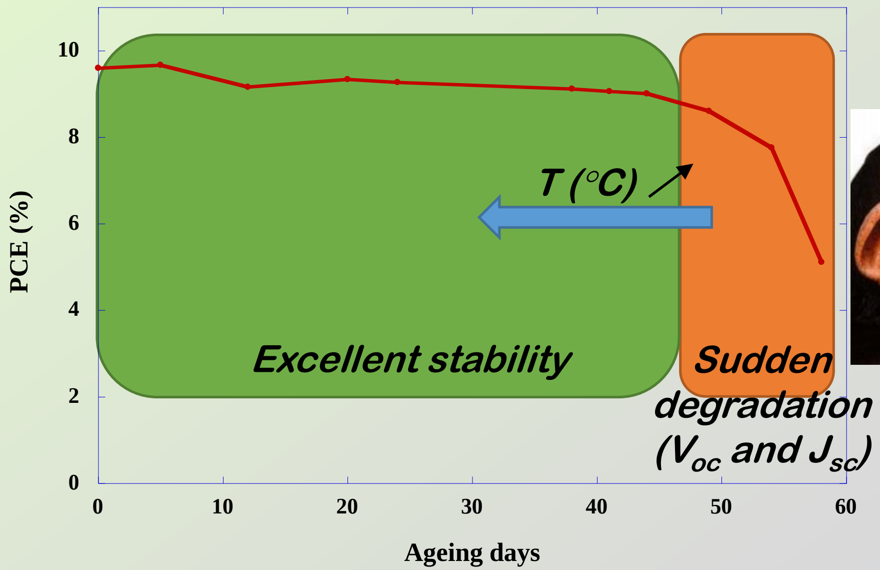
- *Formation of IO_3^- induced by water traces* [2,3]
- *Glass frit reaction with iodine* [4]
- *Iodine "sublimation"* [5]
- *TiO_2 bandgap excitation* [6]
- *Iodine reaction with TBP and NCS* [7]
- *Solvent dependent* [8]

Gas formation *under reverse biased* [3]

[1] M.I. Asghar et al., *Solar Energy* **2012**. 86(1), 331
[2] B. Macht et al., *Sol. Energy Mater. Sol. Cells* **2013**, 119, 36-50
[3] S. Mastroianni et al., *ChemPhysChem* **2012**. 13(12), 2964
[4] K.F. Jensen et al., *Proceeding 27th Eu-PVSEC* **2012**, Germany
[5] M. Gorlov et al., *Dalton Trans.* **2008**, 2655-2666
[6] A. Hinsch et al., *Prog. Photovoltaics* **2001**, 9, 425-438
[7] H. Greijer et al., *J. Phys. Chem. B* **2001**, 105, 6314-6320
[8] A.G. Kontos et al., *J. Phys. Chem. C* **2013**, 117, 8636-8646

State of the art

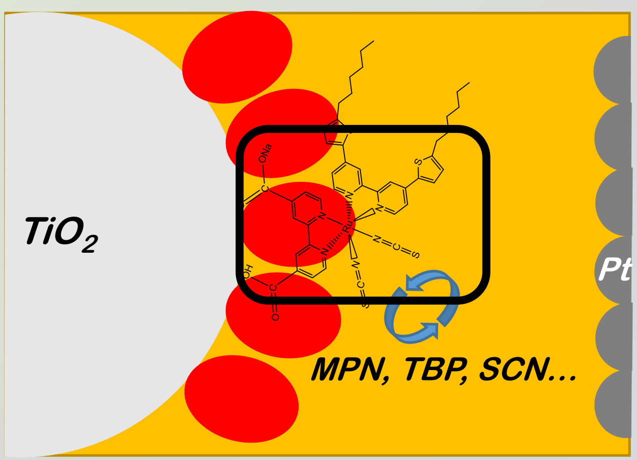
MPN-based electrolyte – C106 dye
Ageing at 60°C/100 mW.cm^{-2}

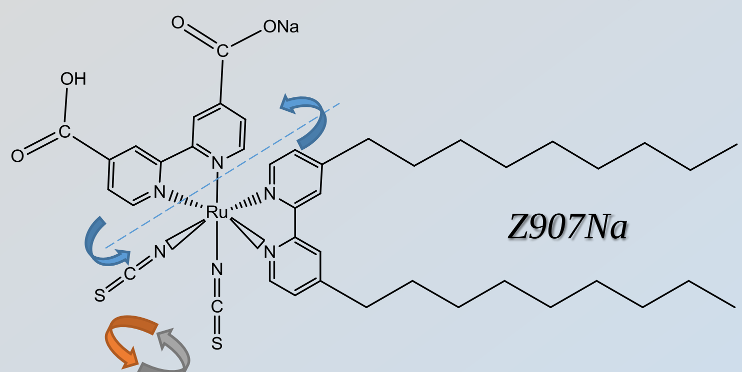


Evolution of cell ageing unusual for an electrochemical device with sudden breaking down

***Ligand exchange** reaction and complex **rupture** [9]:*

- *btw NCS$^-$ and TBP, H_2O, CN from solvent at RT/hυ [10]*
- *btw NCS$^-$ and MPN; Reaction faster when anchored on TiO_2 [11]*



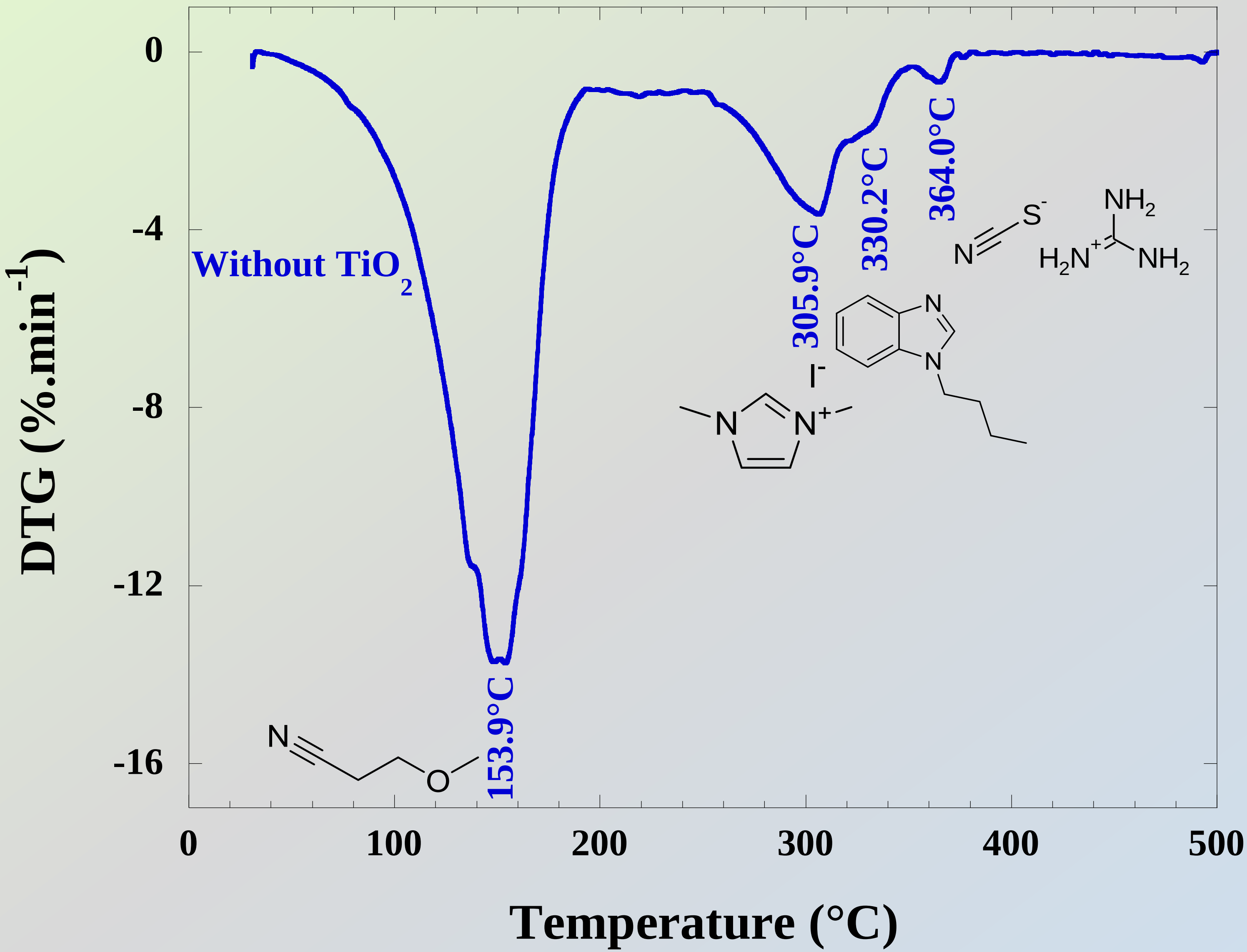


Z907Na

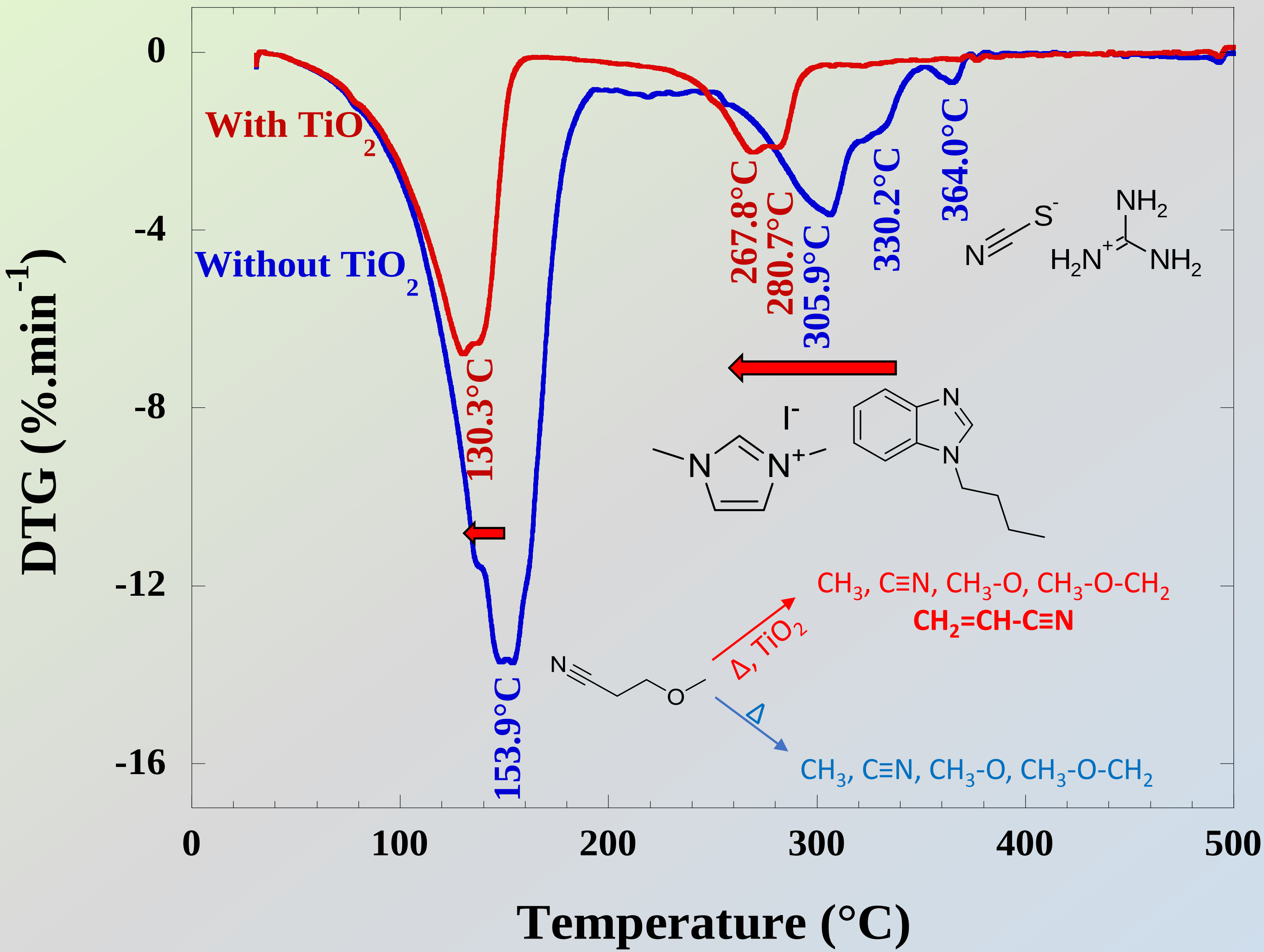
TBP, H_2O, MPN, SCN, CN

[9] R. Grünwald et al., *J. Phys. Chem. B* **1997**, 101, 2564-2575
[10] F.N. Mohammadi et al., *J. Photochem. Photobiol. A: Chem*, **2007**, 187, 348-355
[11] P.T. Nguyen et al., *Solar Ener. Mater.& Solar Cells*, **2009**, 93, 1939-1945

Effect of TiO_2 on thermal stability of MPN-electrolyte



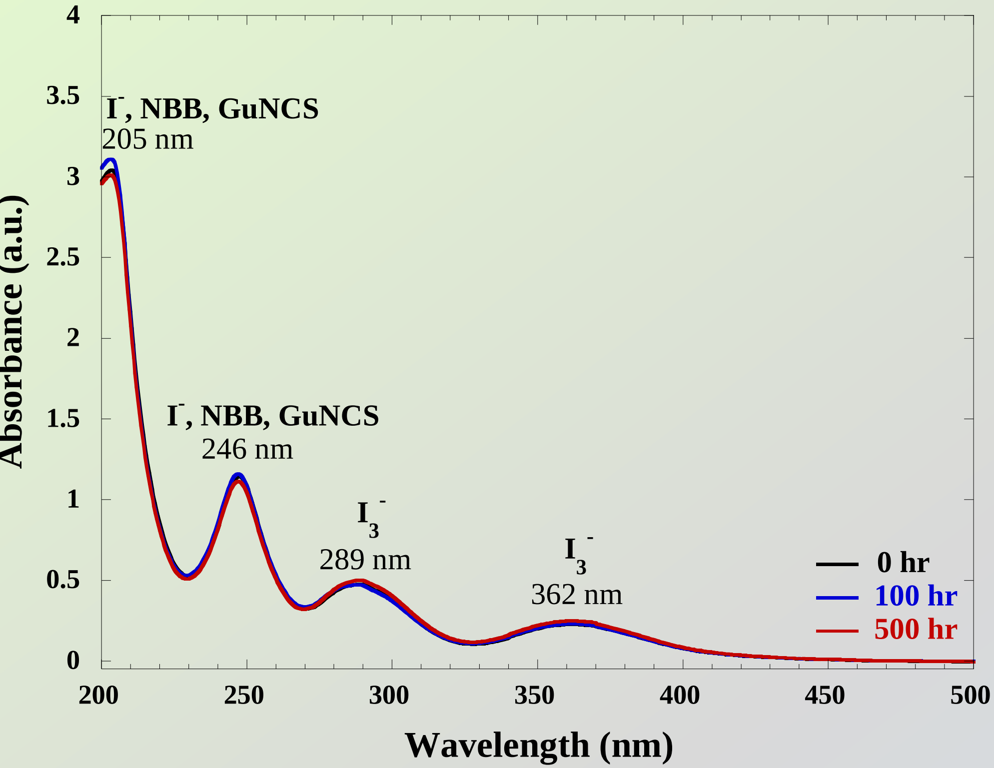
Effect of TiO_2 on thermal stability of MPN-electrolyte

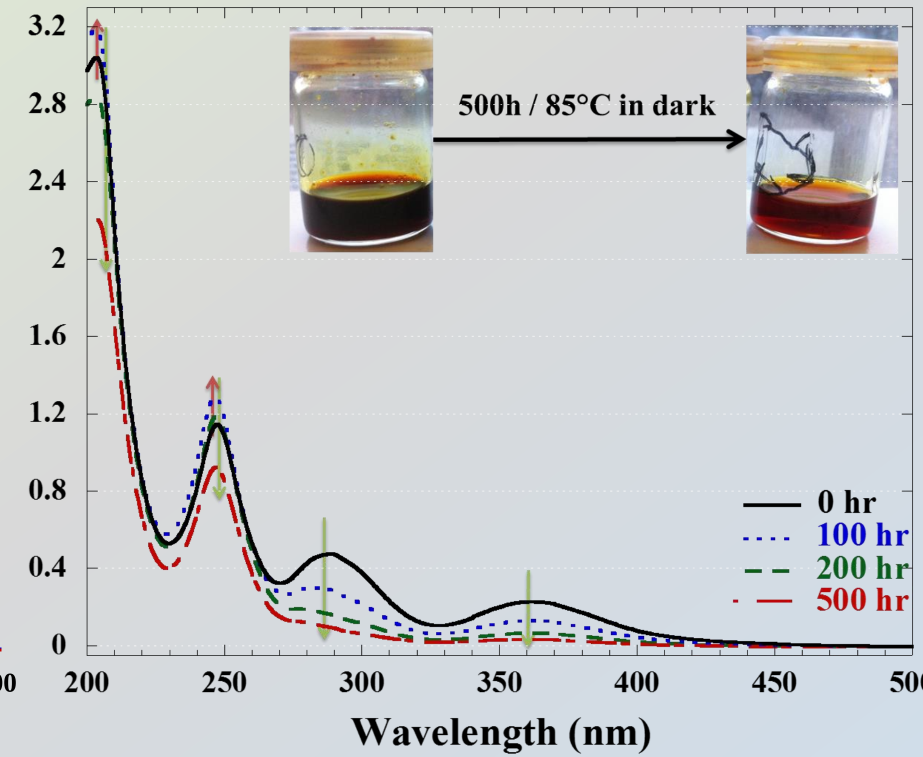


The surface of TiO_2 catalysis the thermal degradation of MPN electrolyte components and induces AN formation as an intermediate degradation product

Effect of TiO_2 on electrolyte ageing

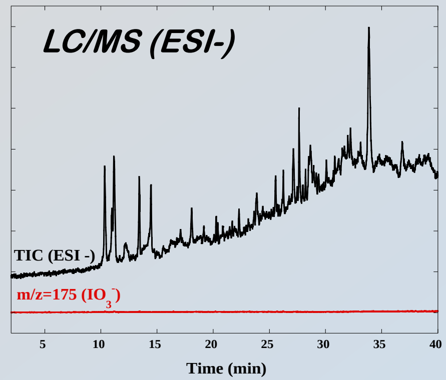
85°C/dark ageing





The well-known *iodine depletion stems from the surface of TiO_2* (activated by temperature and no light action)

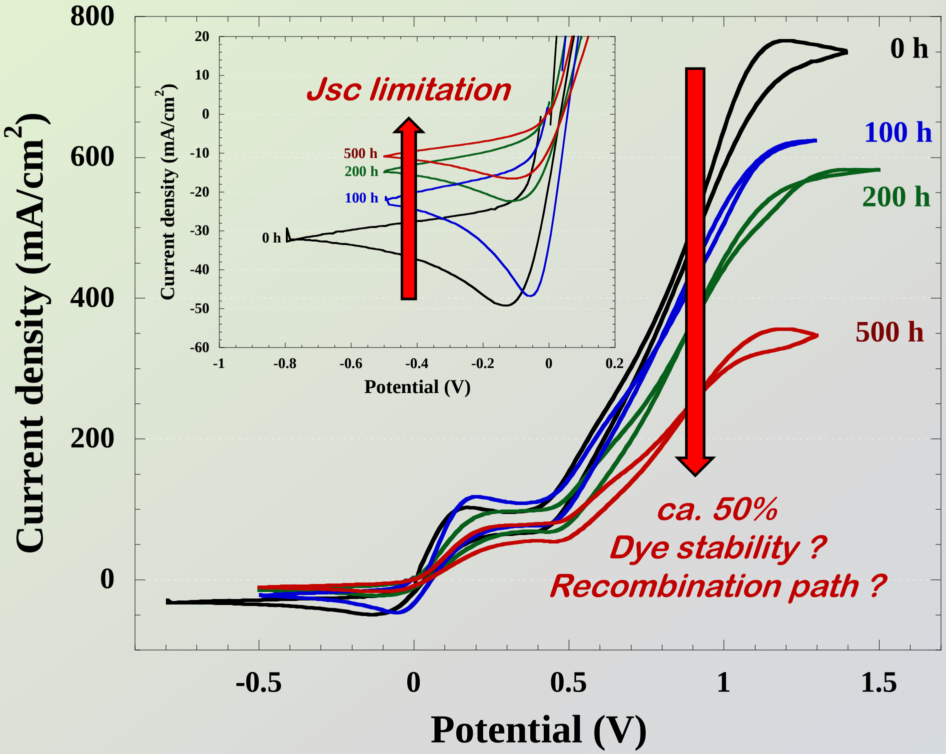
- ~~*Formation of IO_3^- induced by water traces* [2,3]~~
- ~~*Glass frit reaction with iodine* [4]~~
- ~~*Iodine "sublimation"* [5]~~
- ~~*TiO_2 bandgap excitation* [6]~~
- *Iodine reaction with TBP and NCS* [7]
- *Solvent dependent* [8]

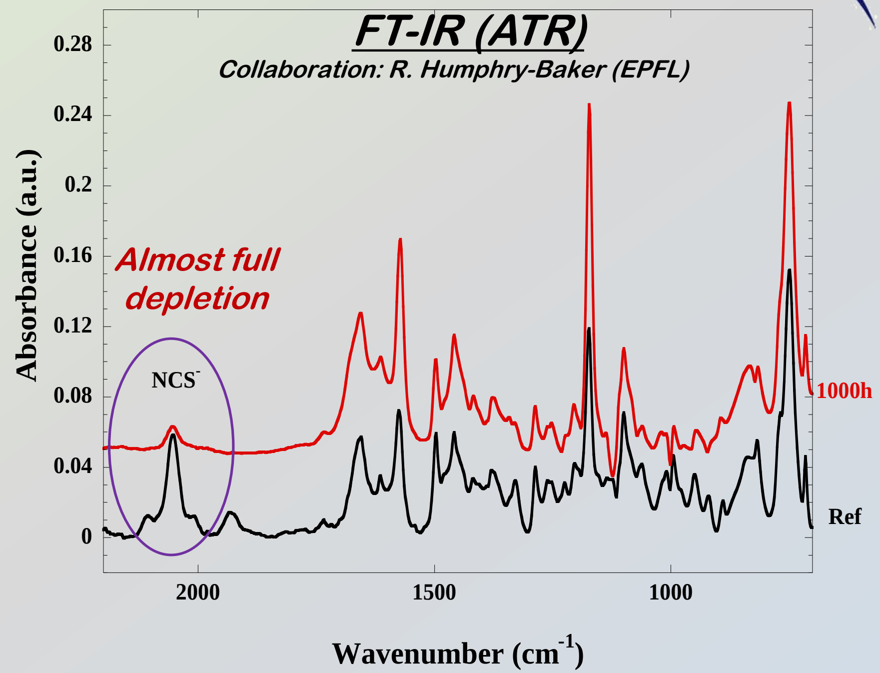


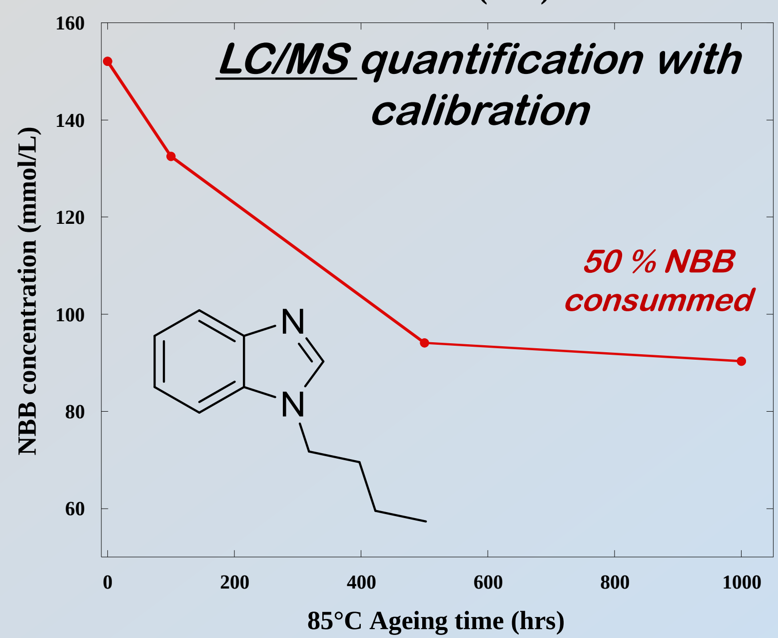
[1] M.I. Asghar et al., *Solar Energy* **2012**. 86(1), 331
[2] B. Macht et al., *Sol. Energy Mater. Sol. Cells* **2013**, 119, 36-50
[3] S. Mastroianni et al., *ChemPhysChem* **2012**. 13(12), 2964
[4] K.F. Jensen et al., *Proceeding 27th Eu-PVSEC* **2012**, Germany
[5] M. Gorlov et al., *Dalton Trans.* **2008**, 2655-2666
[6] A. Hinsch et al., *Prog. Photovoltaics* **2001**, 9, 425-438
[7] H. Greijer et al., *J. Phys. Chem. B* **2001**, 105, 6314-6320
[8] A.G. Kontos et al., *J. Phys. Chem. C* **2013**, 117, 8636-8646

What is really consumed in the electrolyte ?

Cyclic voltamperometry

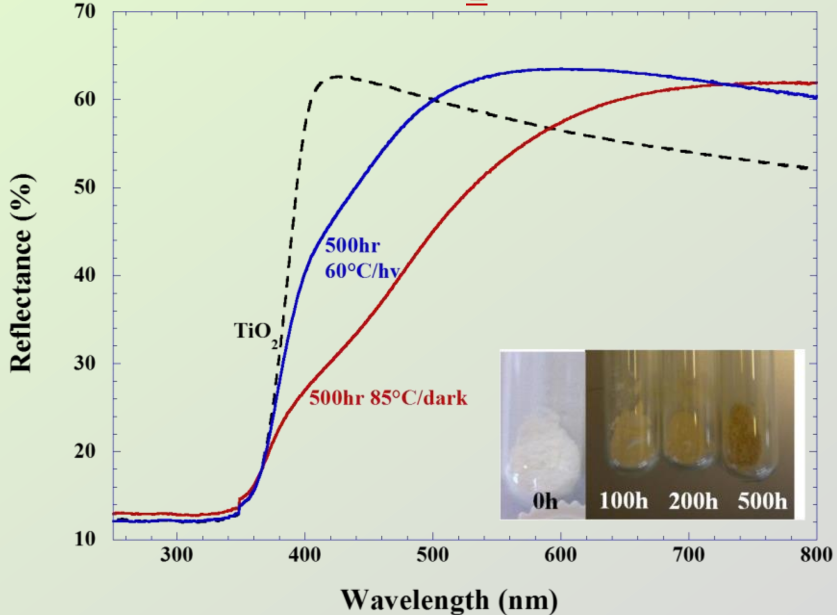




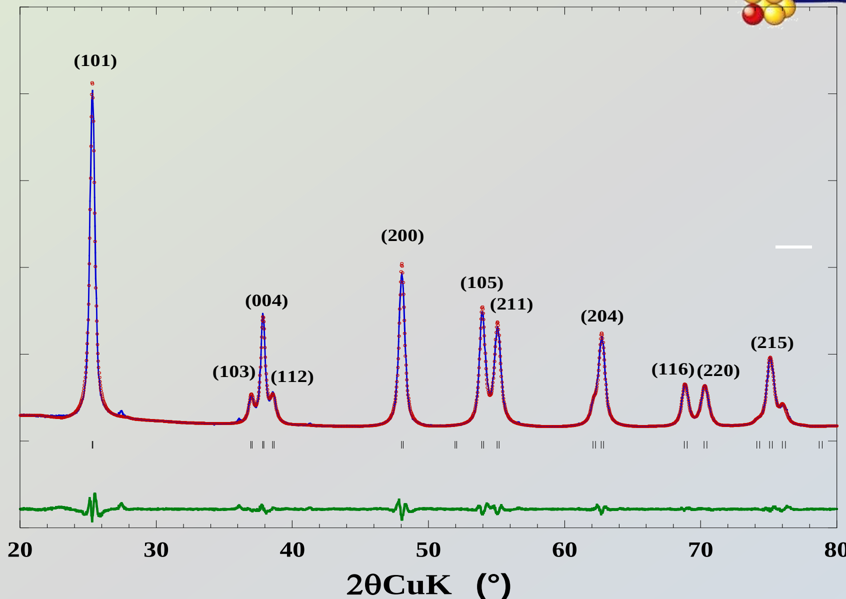


Important reduction of amount of charge species in electrolyte…consequences to mass transport in electrolyte (migration vs. diffusion)

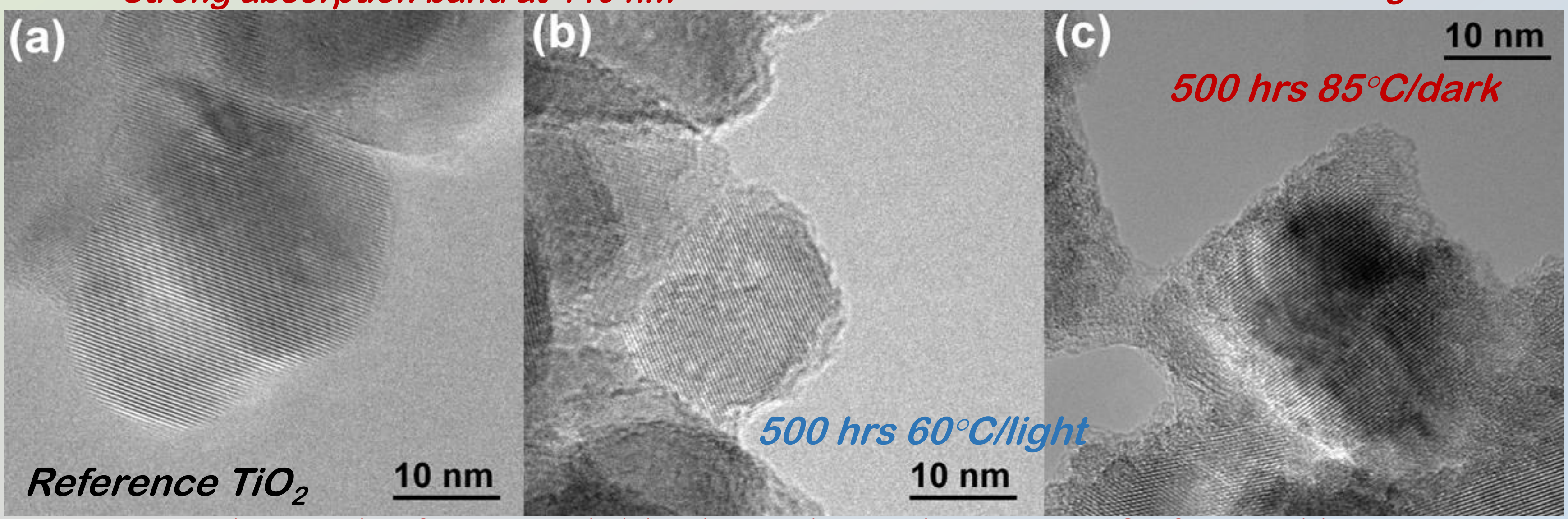
Analysis of aged TiO_2



Strong absorption band at 440 nm



No cristallisation of other things…



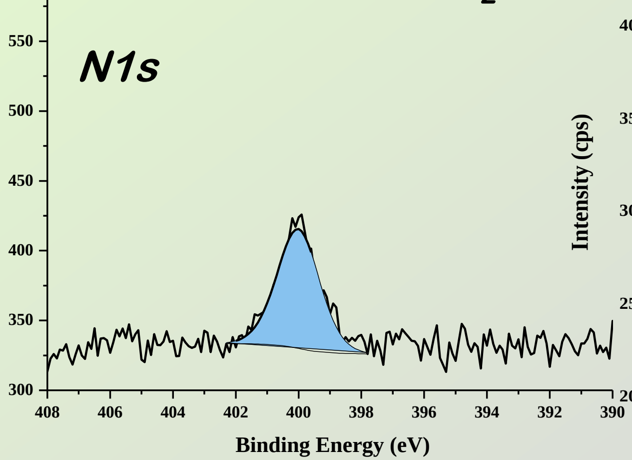
Formation and growth of an unsoluble degradation layer on TiO_2 favored by temperature and ageing time → SEI layer using Pelled nomenclature (Solid Electrolyte Interphase)

M. Flasque et al., ChemPhysChem, 2014, 15(6), 1126-1137

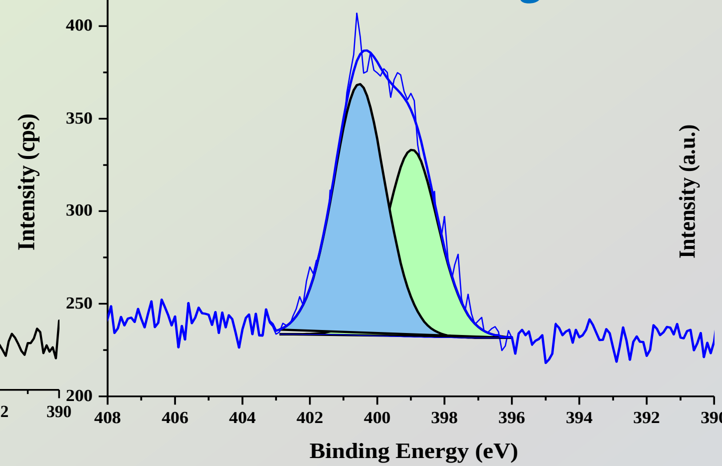
What is this SEI made from ?

XPS analysis (C, N, S, I signals appearing)

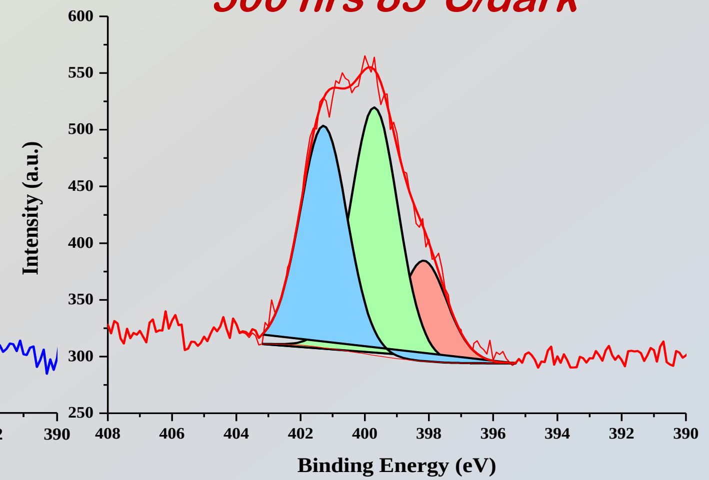
Reference TiO_2

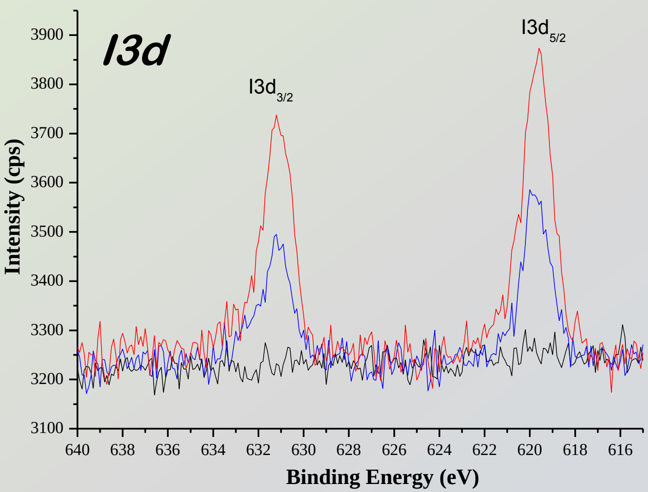


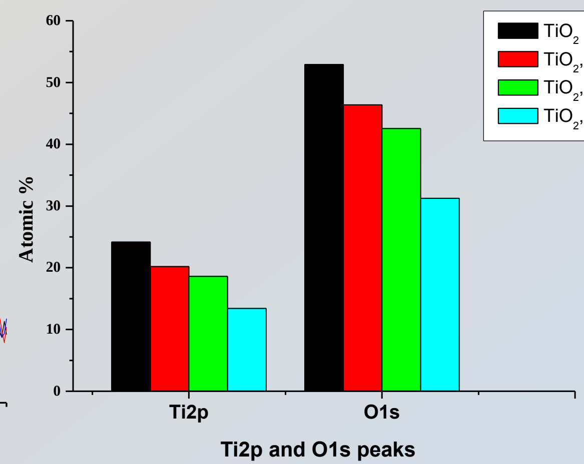
500 hrs 60°C/light

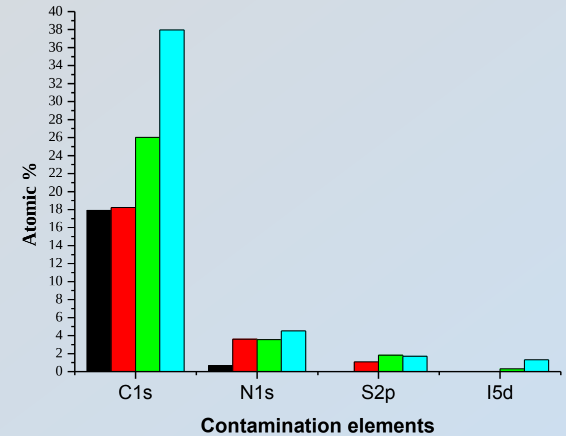


500 hrs 85°C/dark



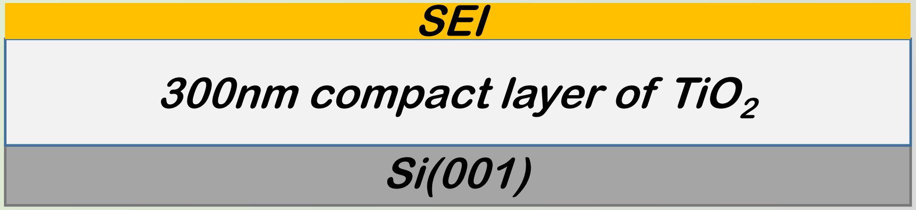




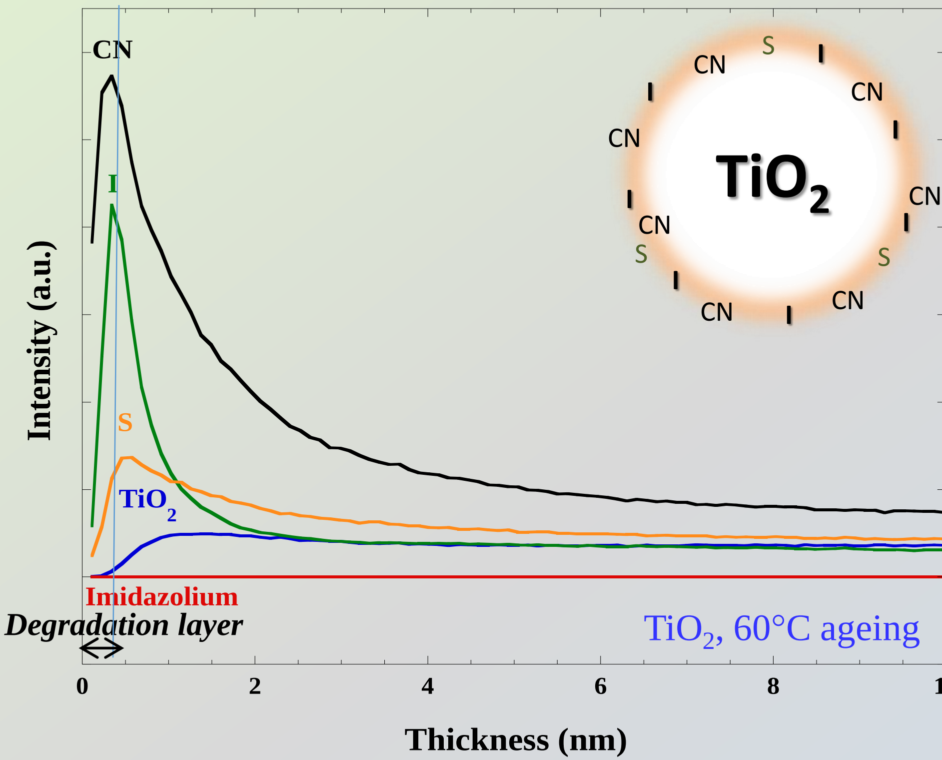


What is this SEI made from ?

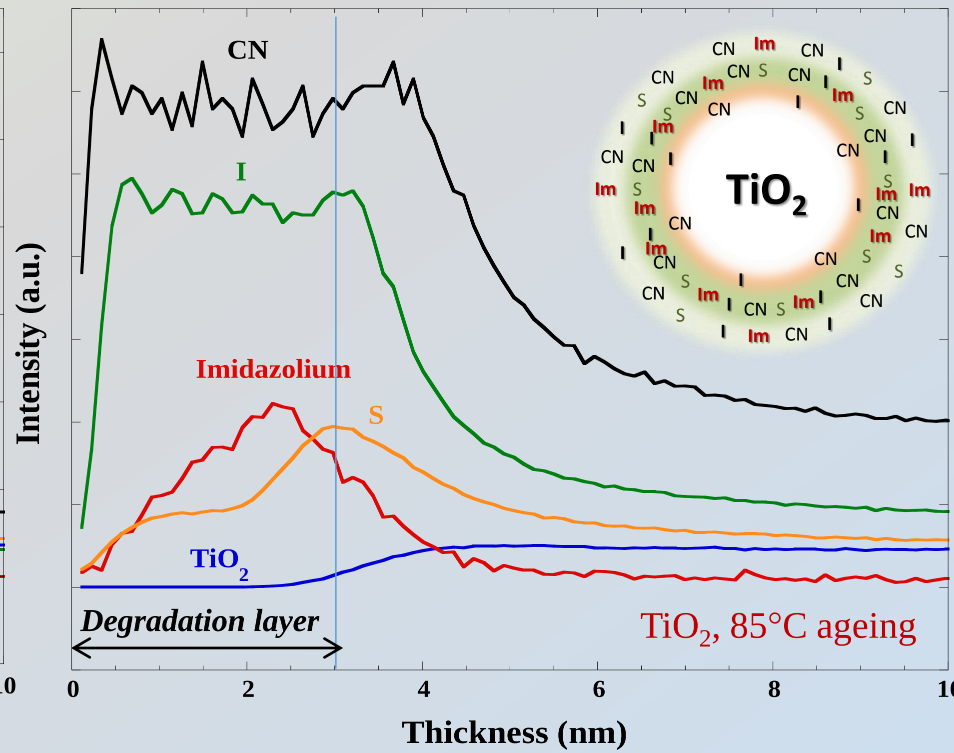
ToF-SIMS



500 hrs 60°C/light

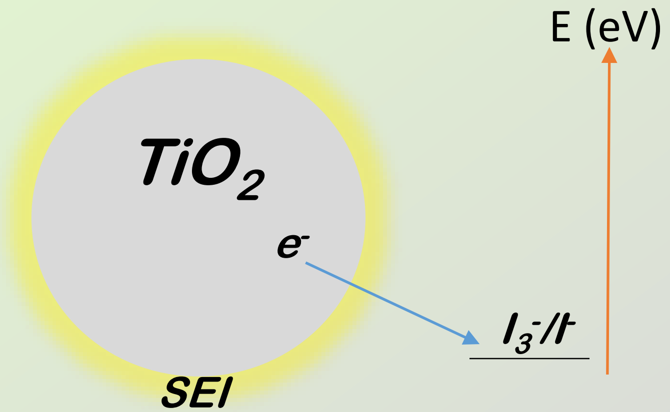


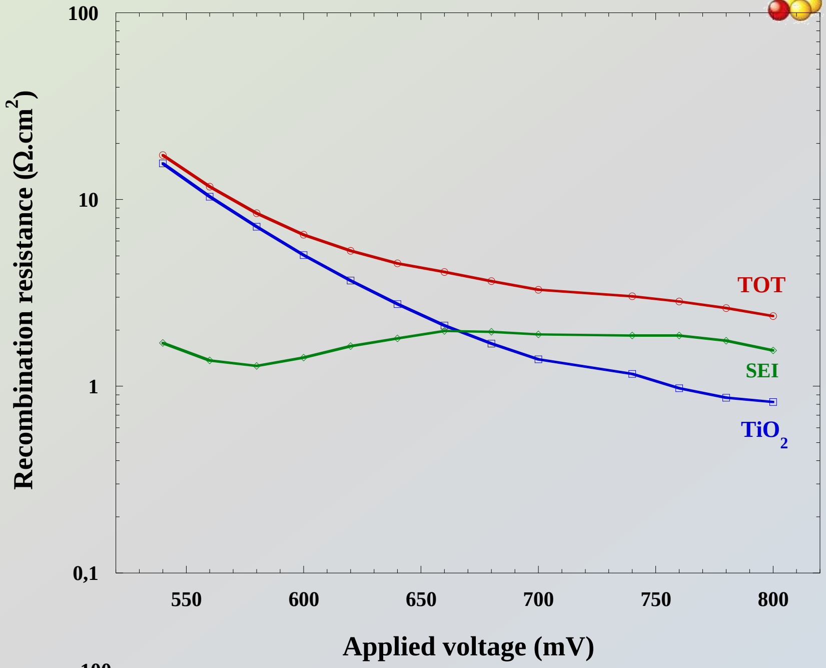
500 hrs 85°C/dark



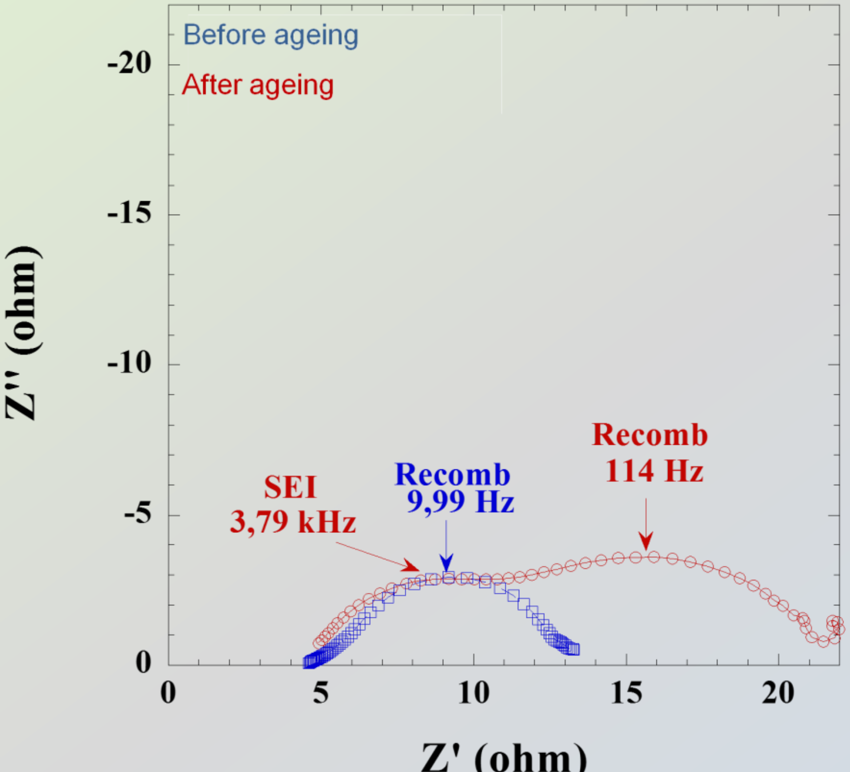
ToF-SIMS consistent with XPS (2 signals from N) and HRTEM

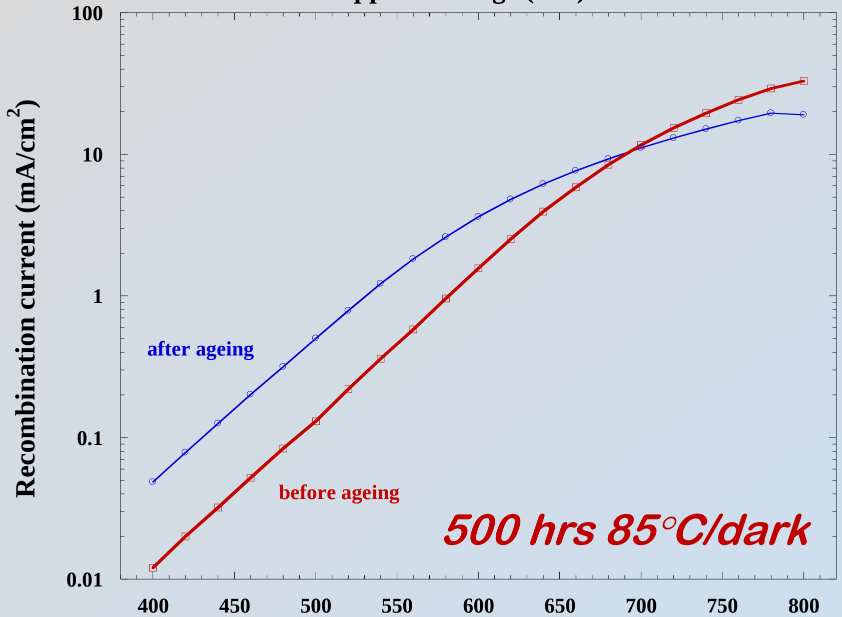
Impact of this SEI on recombination





Electrochemical Impedance Spectroscopy



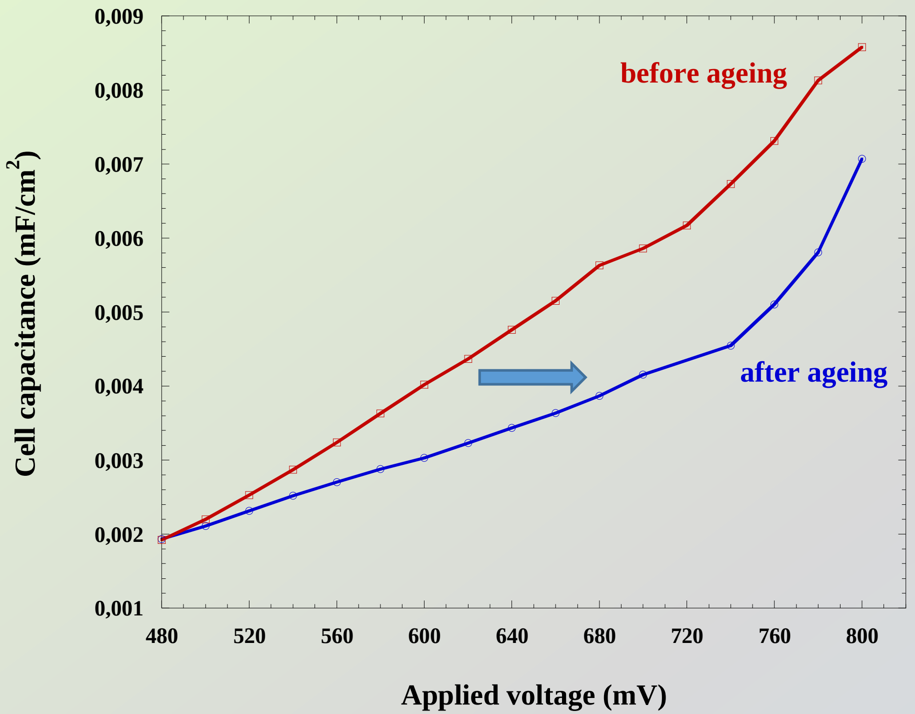


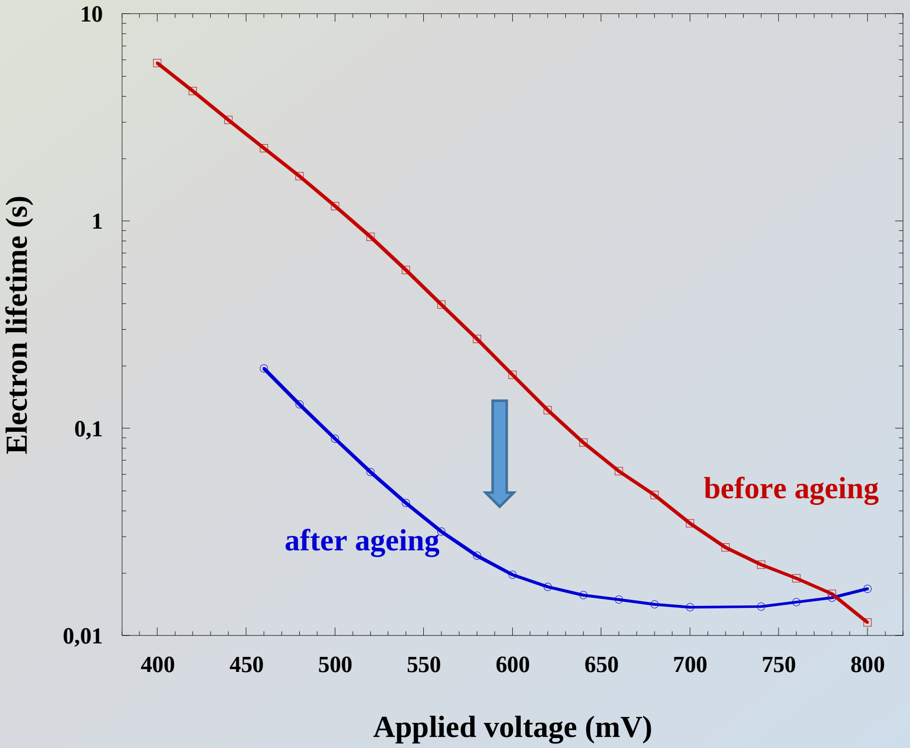
500 hrs 85°C/dark

SEI seems promoting the interfacial recombination btw TiO_2 and I_3^-

Impact of this SEI on recombination

Electrochemical Impedance Spectroscopy

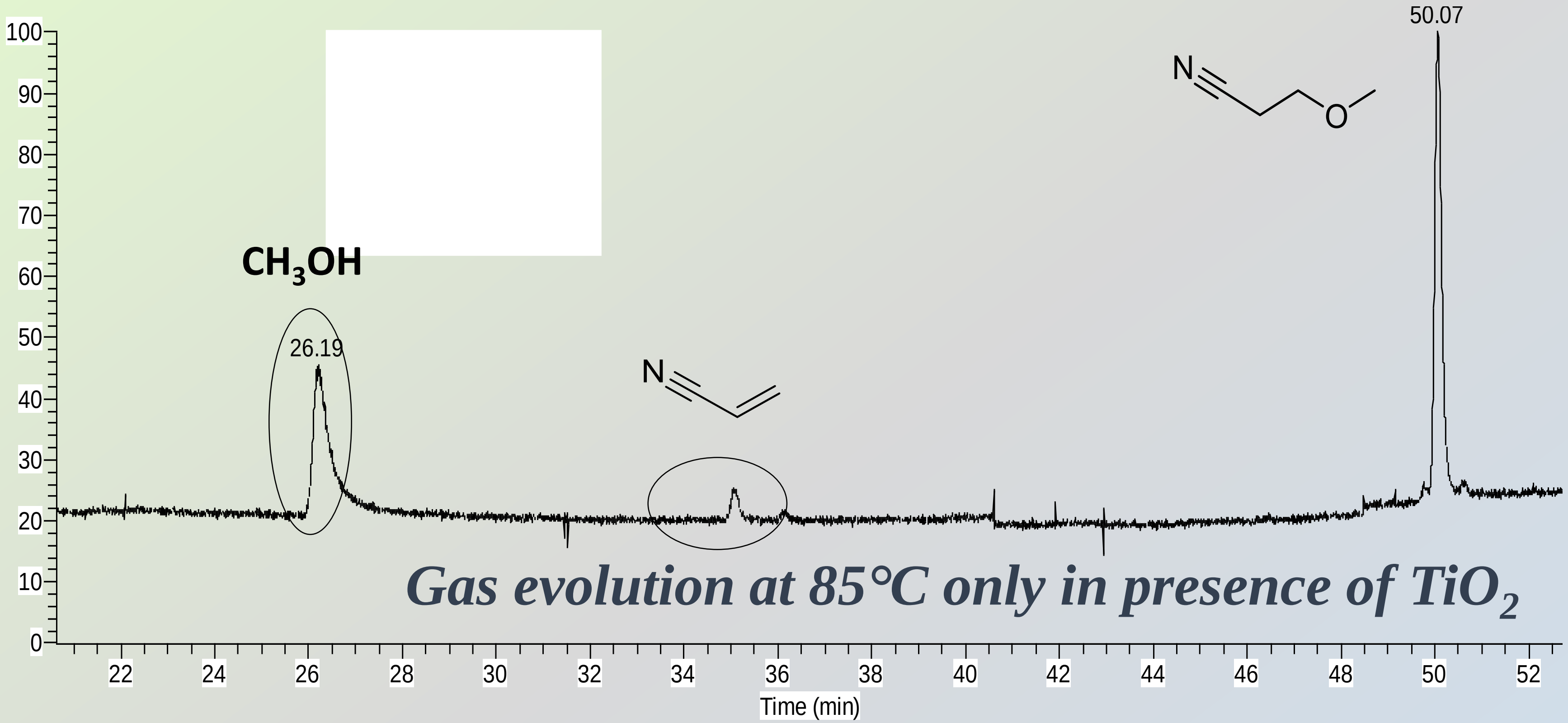




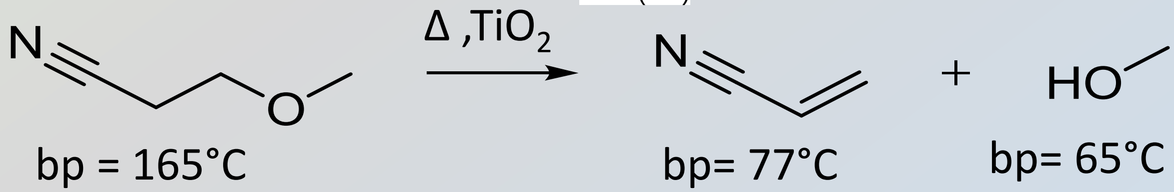
Upshift of the surface trap states contributing to the cell capacitance

Lower electron lifetime → responsible for Voc loss upon ageing

Impact of this SEI on recombination



Gas evolution at 85°C only in presence of TiO_2



Bond breaking of MPN favored by TiO_2 leading to AN and MeOH

SEI likely made of polymeric AN

Conclusions

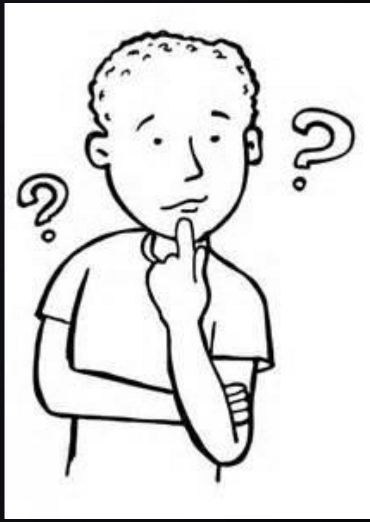
For high efficiencies

Improvement of cell characteristics / efficiency can be obtained by improving light confinement in the photoanode (beads) and high Voc by 1D nanostructuration of TiO_2

11.3 % achieved by using C101 dye combined to beads architecture

For improving stability

Top-down approach to understand the (photo)-chemical reactions inducing stress to the cell (only group following this approach)



TiO_2 surface deserves MPN electrolyte stability and is at origin of not only iodine depletion but also iodide, NCS^- and NBB

Formation of a complex SEI layer on TiO_2 which upshifts traps and activates recombination

SEI layer growth also on Pt with less consequences in electrolyte composition. This SEI has another chemistry and show enhance electrocatalytic properties

Understanding, puzzling and putting the right chemistry in

Acknowledgements

For high efficiencies

Aravind Kumar Chandiran (Ph-D student) – work on doping
Leo-Philip Heiniger (Ph-D student) – work on beads/up-conversion
Dr. Shaik Zakeeruddin (Senior scientist) – C-dyes

For high stability


Miguel Flasque (Ph-D student)
Dr. Nadia Barbero (PostDoc)
Dr. Albert Nguyen VanNhien (LG2A) (Ass. Prof.)
Julien Ridoux (MSc) & Iryna Sagaidak (MSc)
Dr. Gregory Gachot (IR), Dr. Serge Pilard (IR)
Dr. Jolanta Swiatowska (CR) – Dr. Antoine Seyeux (IR) XPS
ToF SIMS @chimieparis-tech)