



**The Abdus Salam
International Centre for Theoretical Physics**



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Winter College on Optics and Energy

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DSC: Production, applications and market opportunity

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DSC: Production, applications and market opportunity

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www.chose.it



EU Renewable Energy Road Map

The European Community has defined (10 Jan 2007) the following equation

$$20+20-20=2020$$

By 2020 EU have to reduce by **20%** the CO₂ emissions
increase by **20%** renewable energy and increase by
20% the energy efficiency

http://ec.europa.eu/energy/index_it.html

Benefits:

- 443 billion euro investment 2001-2020
- 115.8 billion euro gained from fuel reduction
- 130 - 320 billion euro gained from additional costs
- 2 milioni additional jobs

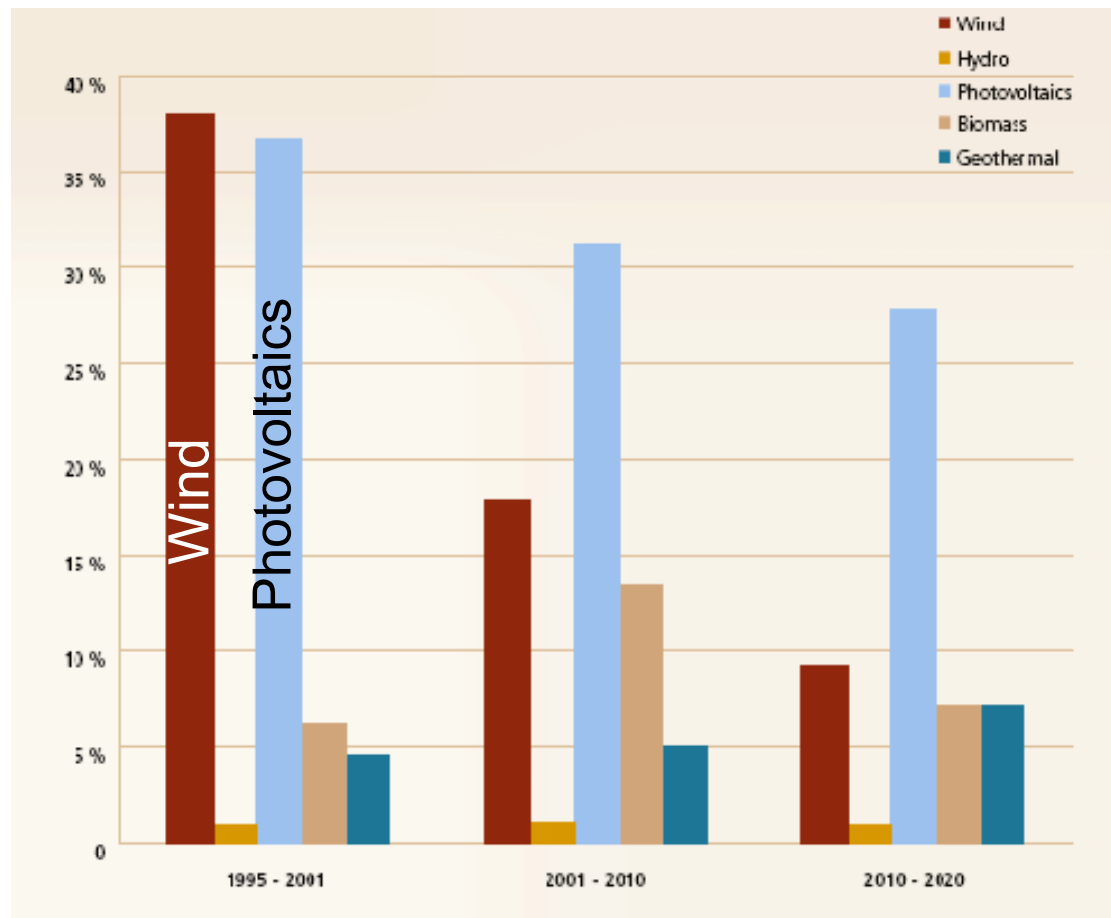


Renewable energy objectives (2020)

Electricity by renewable energies

Type of energy	1995 Eurostat	2001 Eurostat	AGR * 1995-2001	Projection 2010	AGR * 2001-2010	Projection 2020	AGR * 2010-2020
1. Wind	2.5 GW	17.2 GW	37.9 %	75 GW	17.8 %	180 GW	9.1 %
2. Hydro	87.1 GW	91.7 GW	0.9 %	100 GW	1.0 %	109 GW	0.9 %
3. Photovoltaics	0.04 GWp	0.26 GWp	36.6 %	3GWp	31.2 %	35 GWp	27.8 %
4. Biomass	6.1 GWe	8.7 GWe	6.1 %	27 GWe	13.4 %	54 GWe	7.1 %
5. Geothermal	0.5 GW	0.65 GW	4.5 %	1 GW	4.9 %	2 GW	7.1 %

Source EREC



Annual Growth Rate



Investment and jobs

Investment (billion euro)

	2001-2010	2011-2020	2001-2020
Wind	55	101	156
Photovoltaic	10	66	76
Biomass	44	45	89
Hydro	11	9	20
Geothermal	4	7	11
Solar Thermal	16	75	91
TOTAL RES	140	303	443

Jobs

	2010 jobs FTE	2020 Jobs FTE *
Wind	184,000	318,000
Photovoltaic	30,000	245,000
Biomass	338,000	528,000
Biofuels	424,000	614,000
Small Hydro	15,000	28,000
Geothermal	6,000	10,000
Solar Thermal	70,000	280,000
TOTAL RES	1,067,000	2,023,000

Source EREC



EU 2020 - PV technical objectives

Strategies of the European Photovoltaic Industry Association (EPIA)

The European Photovoltaic Industry Association (EPIA) has defined a set of development strategies for achieving the goals of 2020.

Besides increasing the efficiency of silicon modules, EPIA identifies the development of new materials and concepts as a crucial step for achieving these objectives.

Among these new concepts, particular emphasis has been given to organic cells and in particular to Dye Sensitized Solar Cells (DSC).


EPIA considers the DSC as the most mature amongst the OPV technologies and thus pushes for a decisive plan for its research and development that can deliver the first production lines in the near future.



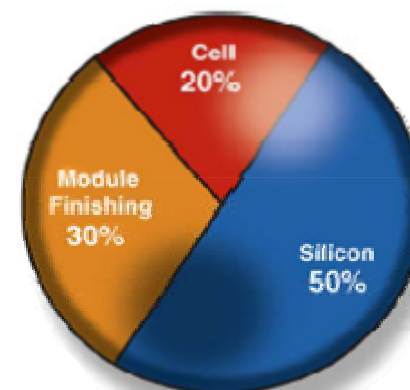
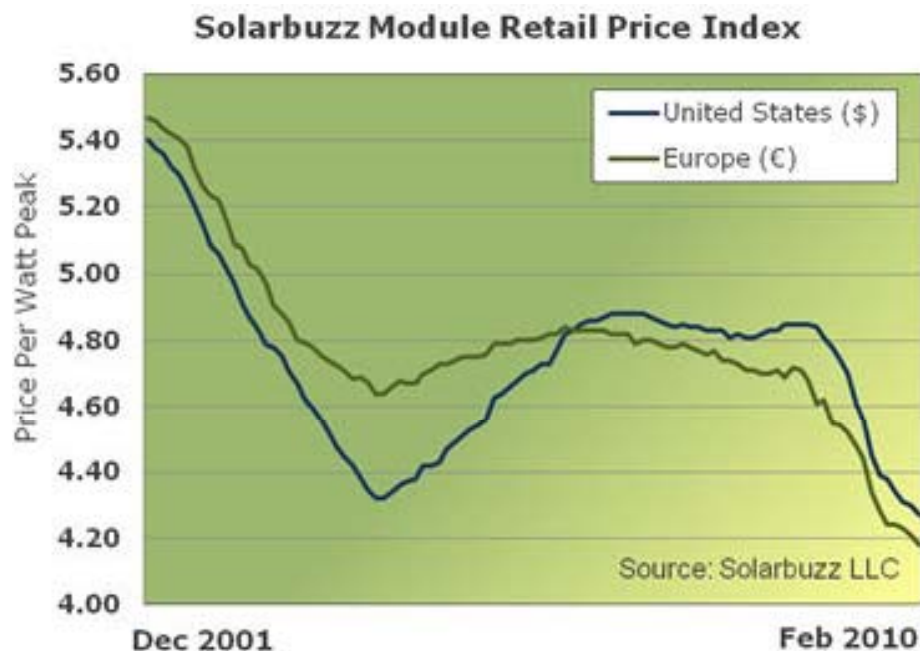
Energy from the sun



To satisfy the electricity needs of a typical family one needs 3kWp PV system, i.e. $\sim 20\text{m}^2$ of photovoltaic surface (assuming system efficiencies of 15%).

COST  20.000 euro

Cost reduction of PV systems per Wp/m² becomes paramount in order to make PV technology an important instrument for energy production.



Could we reduce cell costs ?

Cost of silicon wafers is high (2 euro/ Wp, one doping level)

Production equipments are expensive

- 100 Meuro for 40 MWp/year amorphous silicon
- 15 Meuro for 30 MWp/year bulk silicon

Is it possible to produce photovoltaic cells by reducing production and material costs ?

Moreover, is it possible to create a photovoltaic module suited for Building Integration (control on colour, transparency etc) ?

This is possible but we have to re-invent the cells and the fabrication processes

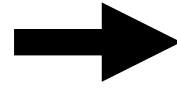


Organic photovoltaics



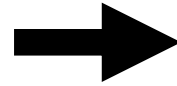
“New” manufacture processes

Conventional Electronics

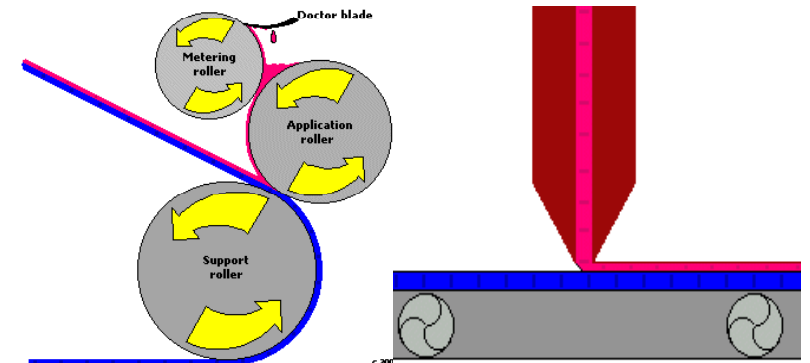
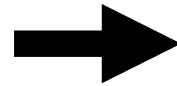


Organic Electronics

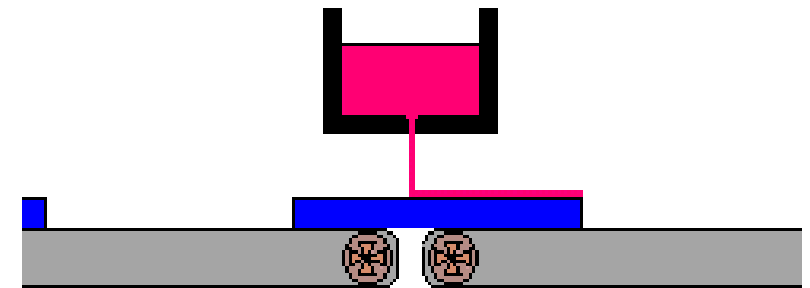
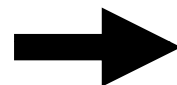
**Conventional
semiconductor industry**



Printing methods



**High temperature, doping,
vacuum**

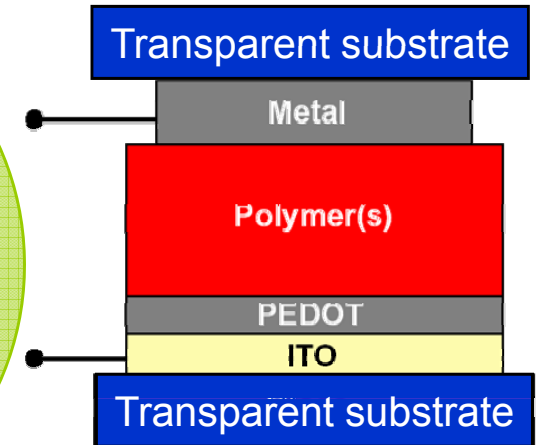
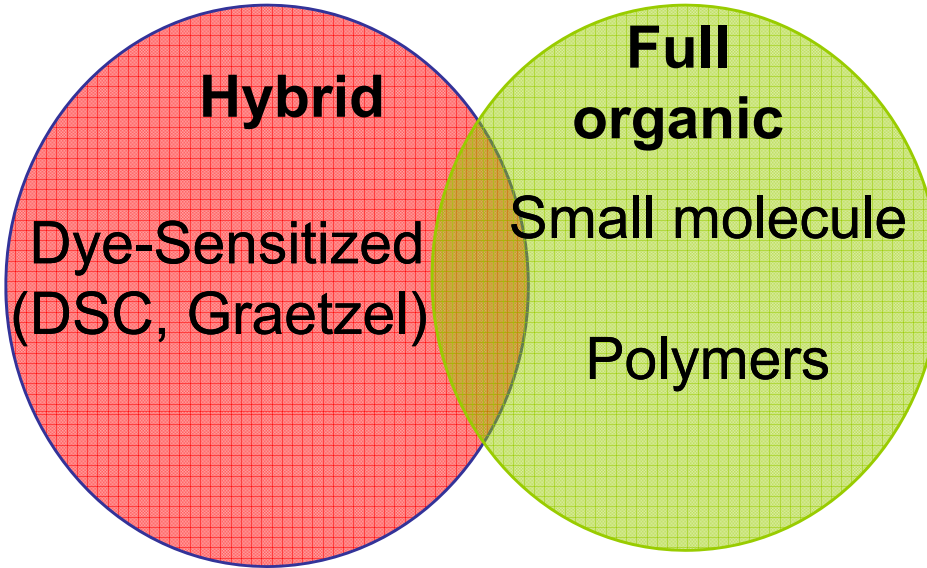
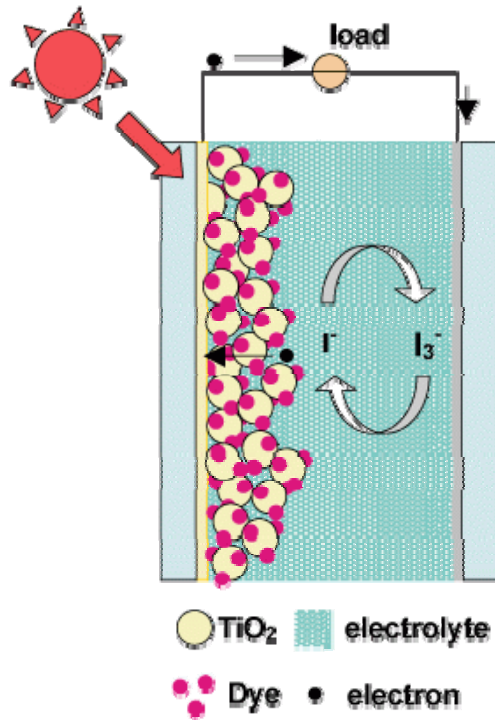


Very Large enterprises

**Liquid deposition
Small Medium
enterprises /
local productions**



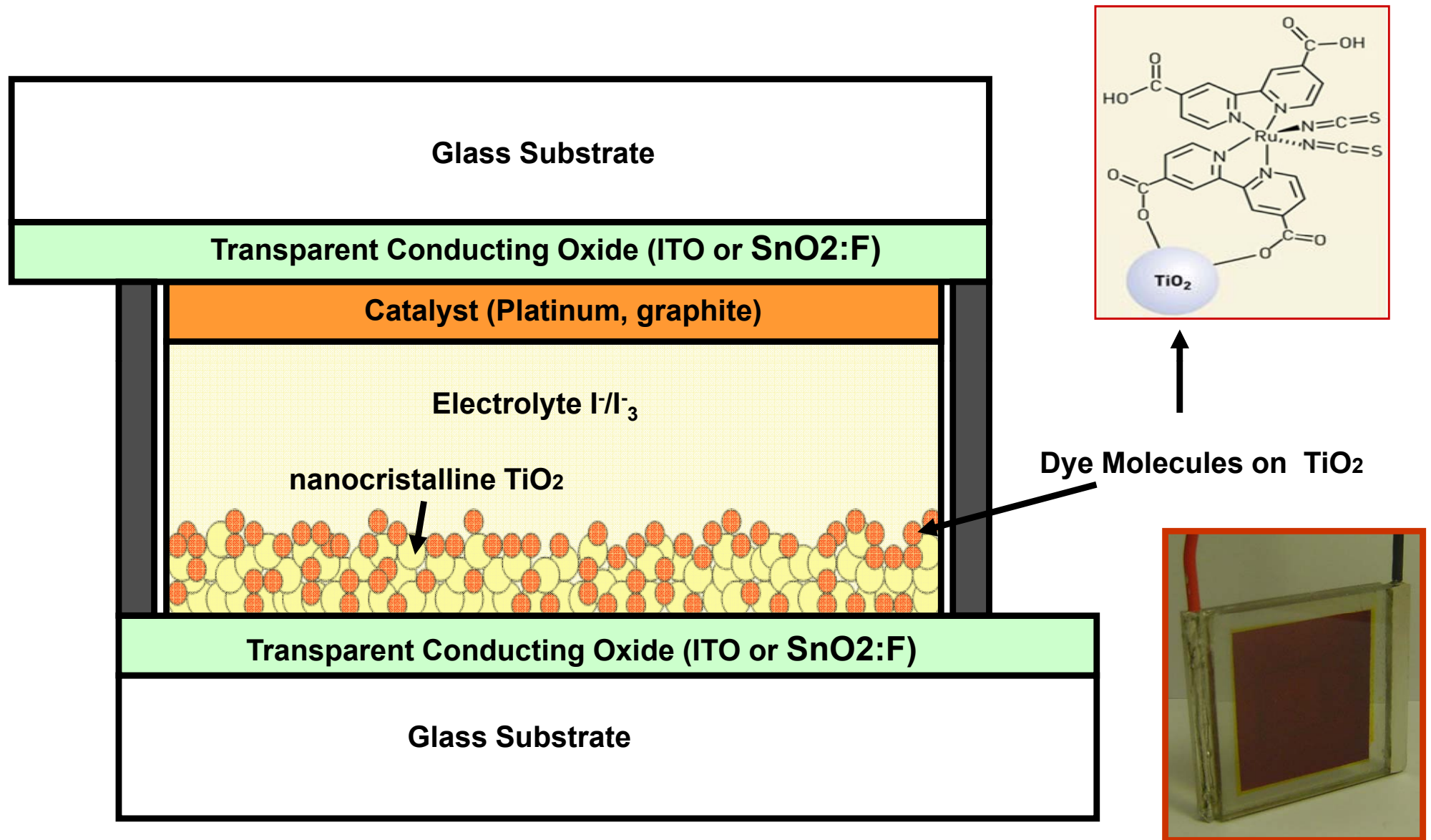
Organic photovoltaics



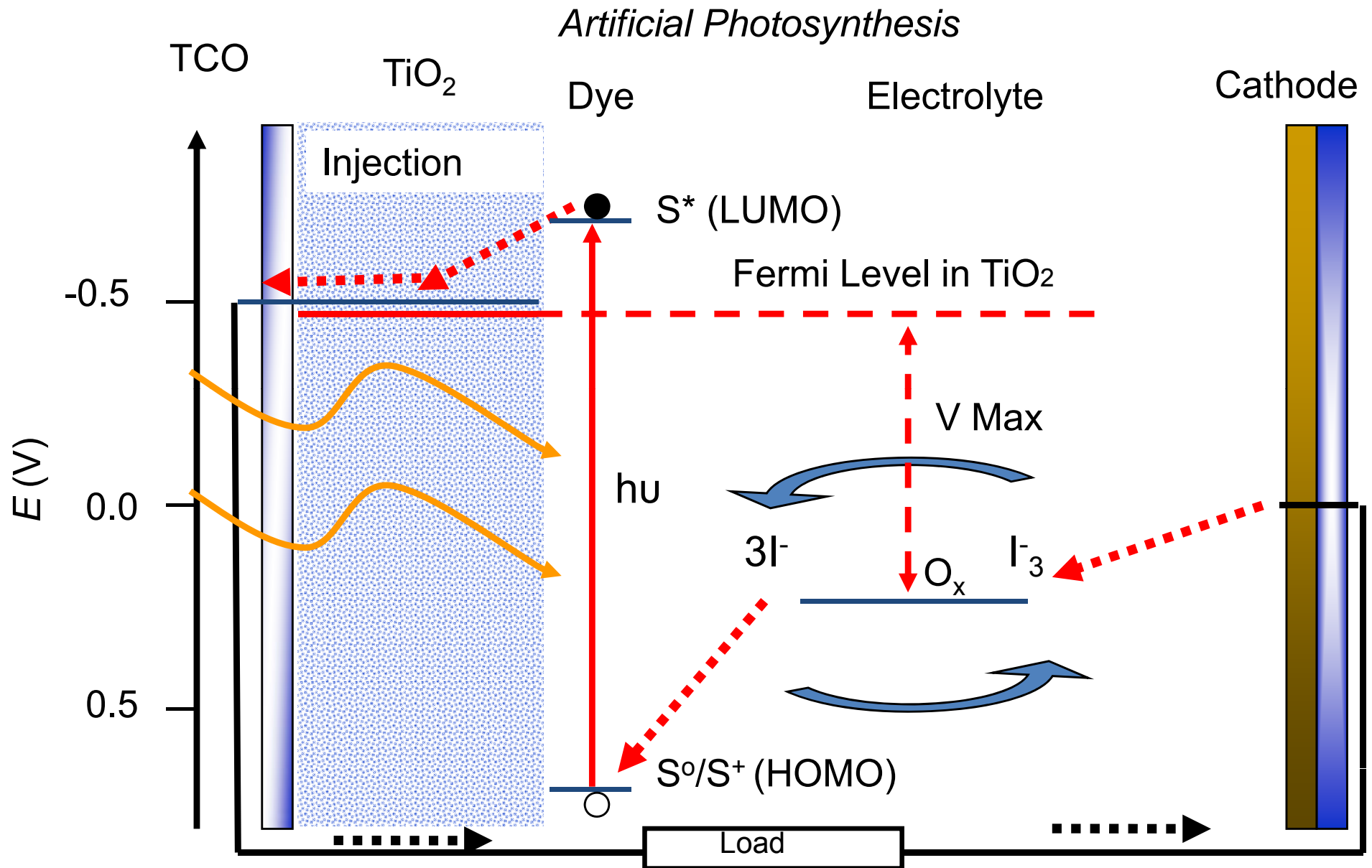
Type	Max lab efficiency	Stability	R&D
Hybrid Dye Sensitized (Graetzel)	~ 11-12%	20 years	University and industry
Full organic solar cells	~ 5%	3 years	University and industry



Structure of Dye Sensitized Cells



Working principle of DSC



No permanent chemical transformation in the materials composing the cell

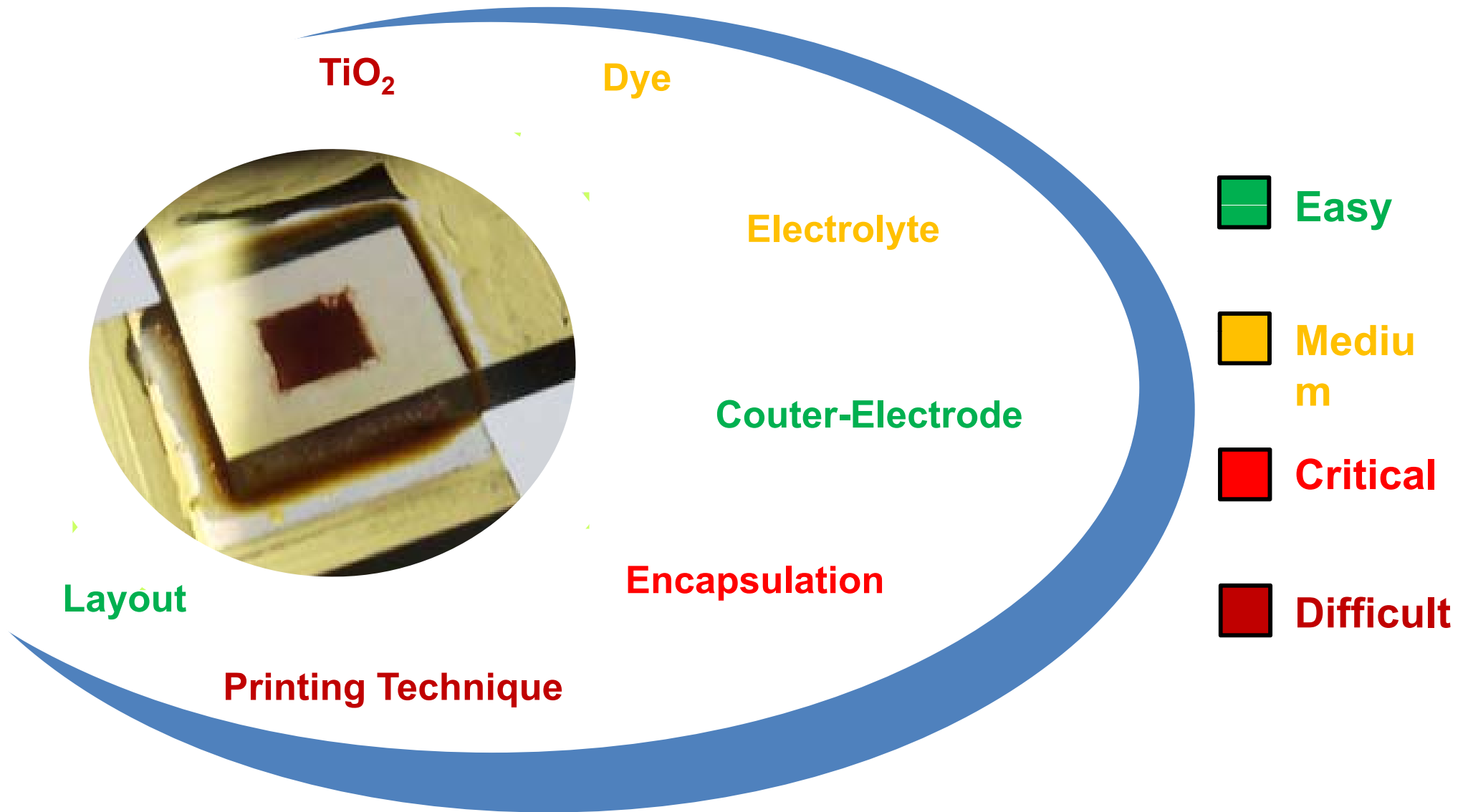


Cell optimization

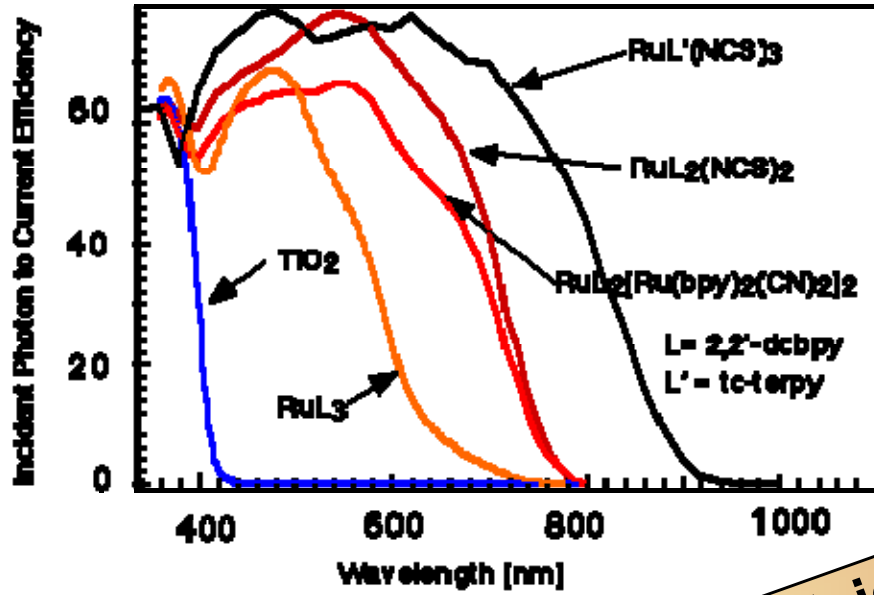


Optimization parameters

(an engineer view)



Dyes



11%

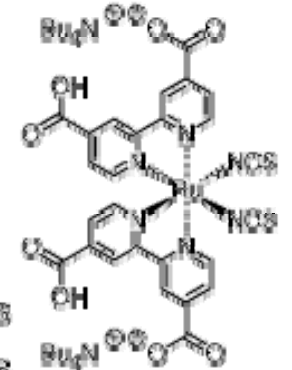
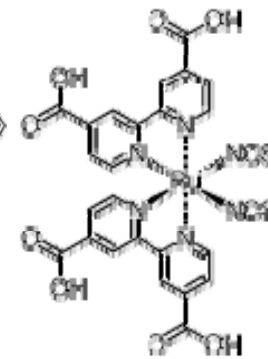
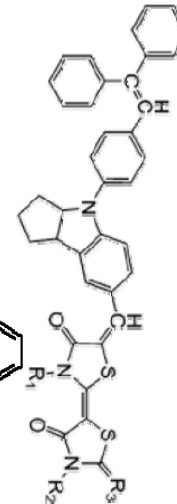
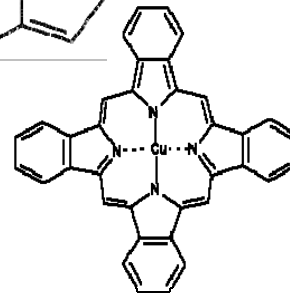
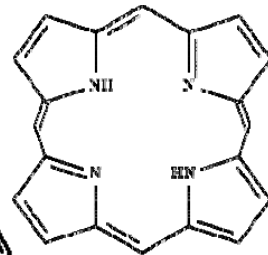
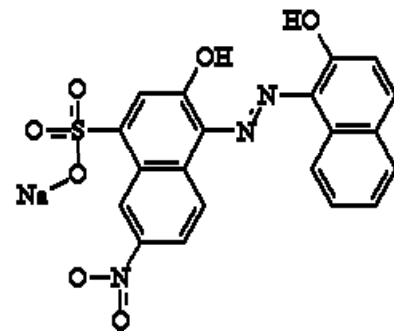
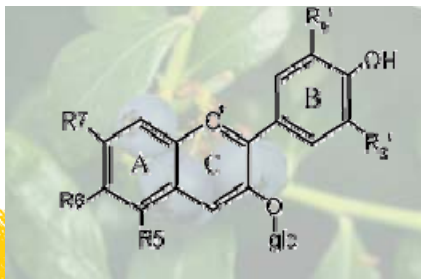
Rutenium-Based Dyes

Organic Dyes

Industrial Dyes

1%

Natural Dyes

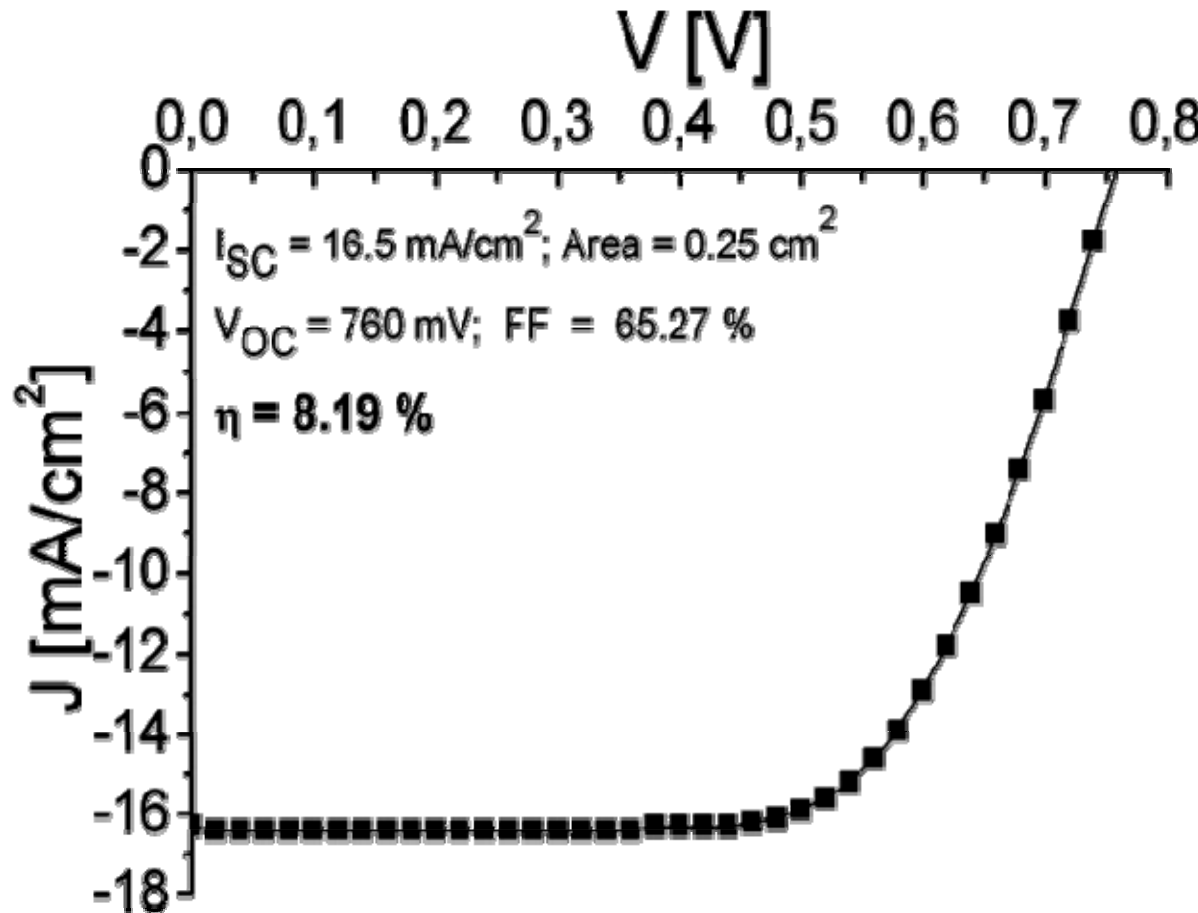


CHOSE

A. Di Carlo



Comercial TiO₂: Standard Characteristics



Fabrication Process:

- ✓ TiO₂ Dyesol Paste 18-NRT
sintered 525°C @ 30'
final thickness 17.5-18.5 μm
- ✓ Dye N719 Solaronix
time dipping 15h
- ✓ CE Platisol Solaronix
fired 400°C @ 5'
- ✓ Spacer Surlyn 60 μm
- ✓ Electrolyte Dyesol HPE

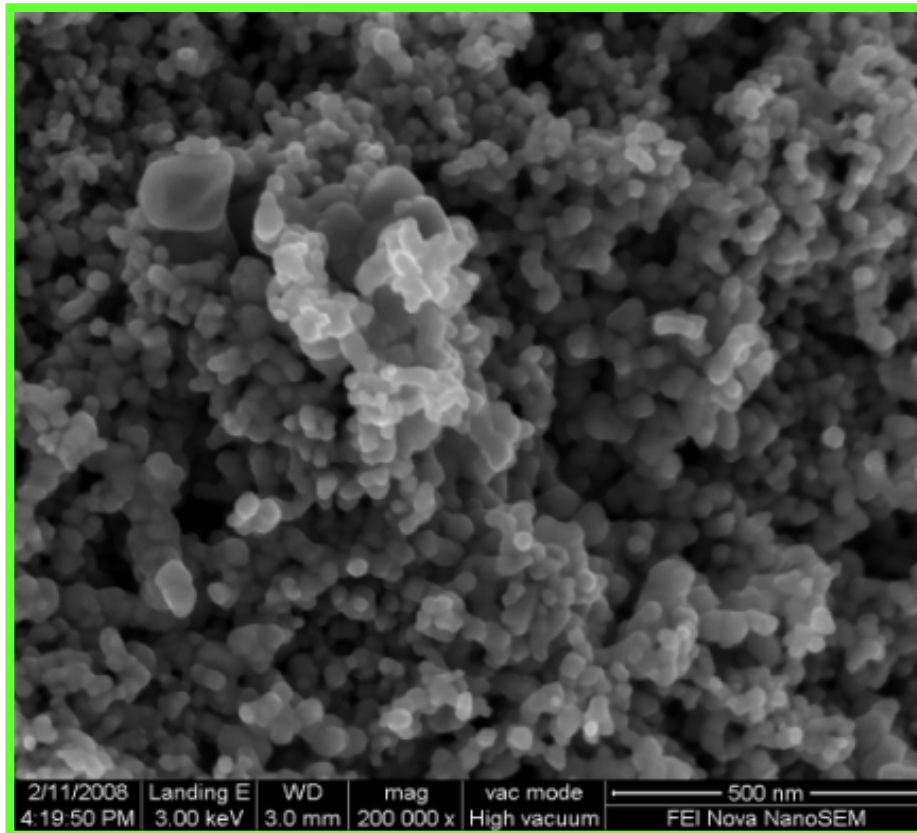


Process Improvements 1/2

Introduction of TiCl_4 treatments

Pre TiO_2 deposition + post sintering treatments

TiCl_4 solution 40mM 30' @ 70°C

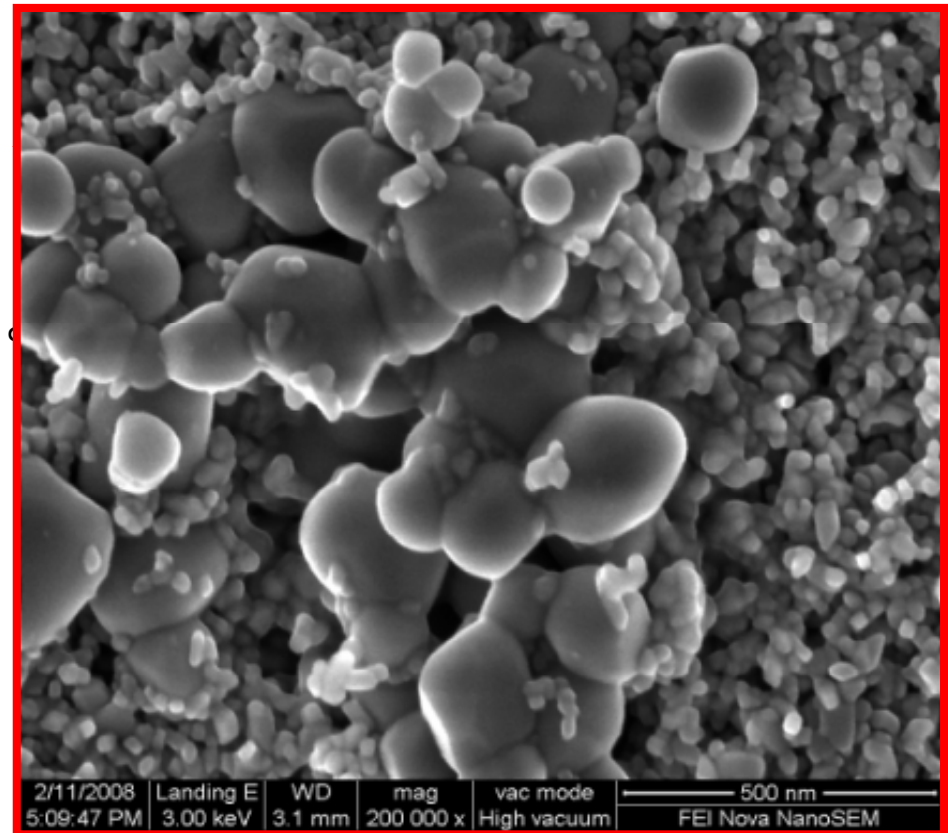


Transparent

Introduction of scattering layer

TiO_2 Dyesol scattering paste WER4-0

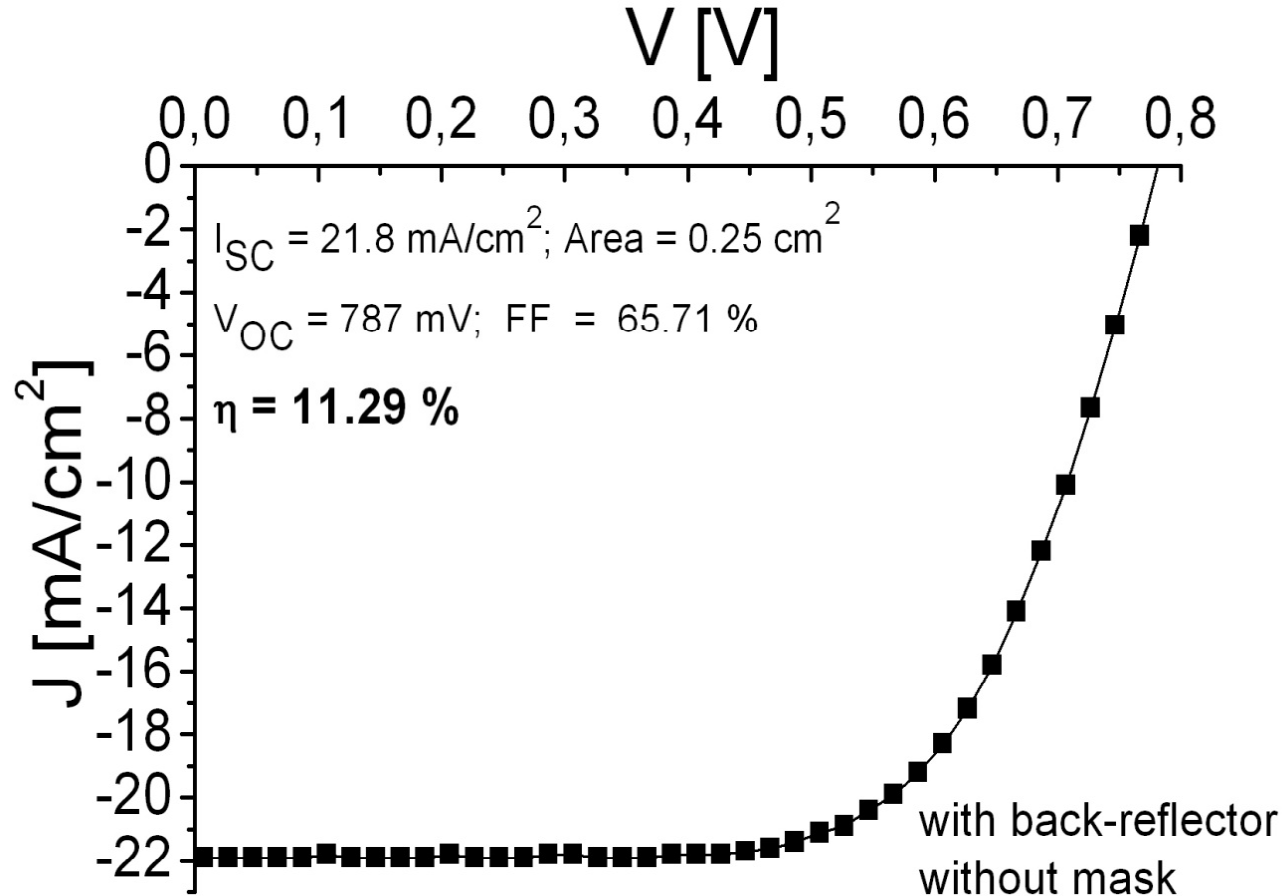
Thickness 8 μm^*



Not Transparent



Process Improvements 2/2



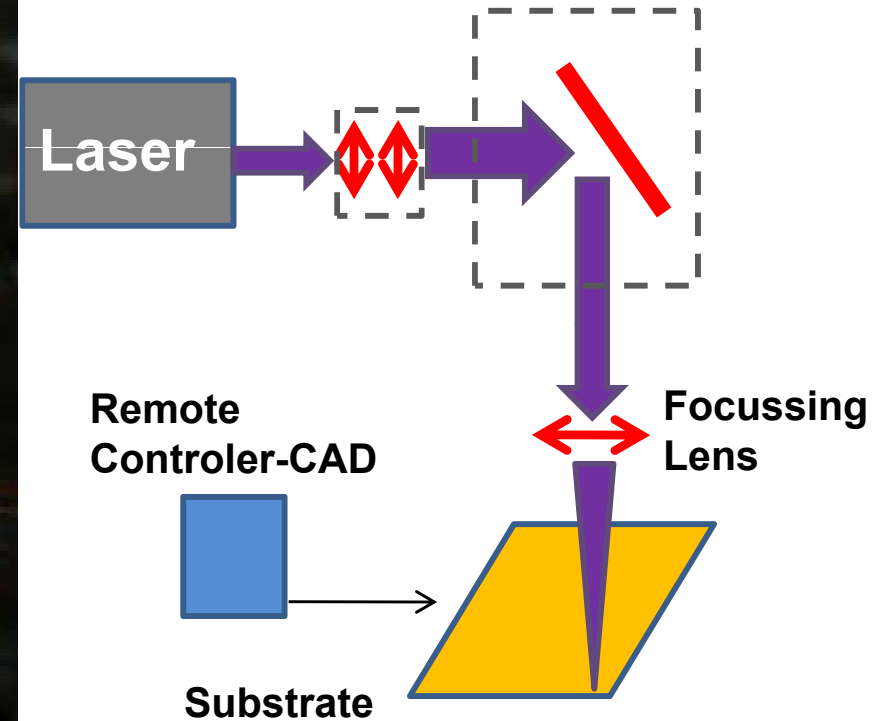
I/V Characteristics of the TiCl_4 treated cell measured with the introduction of back-reflector

Good reproducibility within 2% deviation



Laser sintering of TiO₂ layer

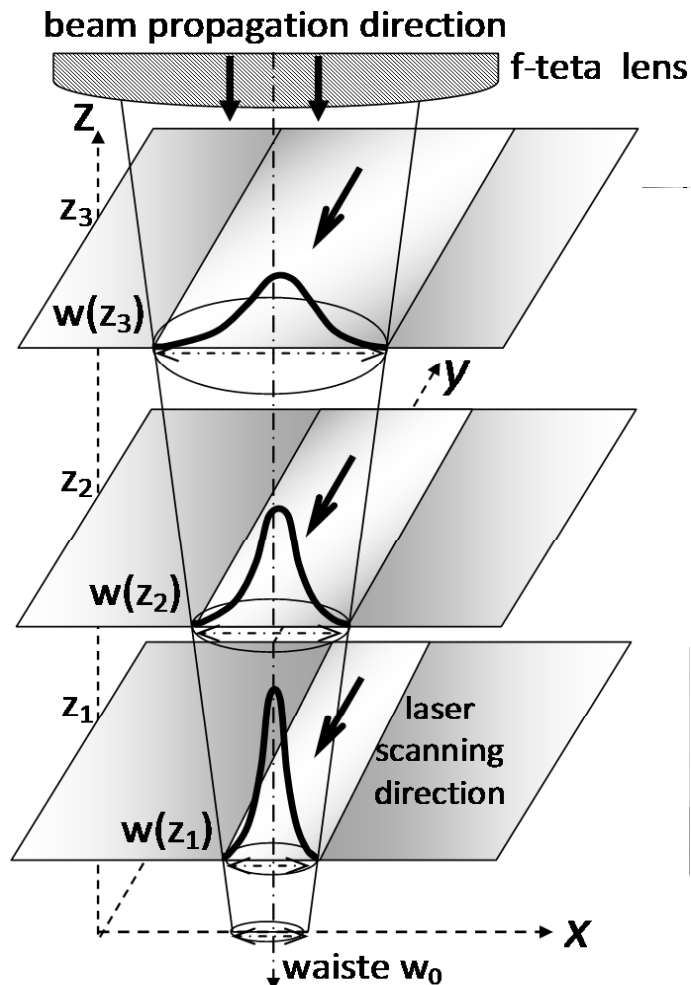
LASER SINTERING of TiO₂
an alternative to oven sintering



TiO2 laser sintering/1

Widely used in the thin film solar cell industry, laser scanning processing could bring about many advantages to DSC industrial production .

(non-contact, local, rapid, selective, scalable processing, low temperature)

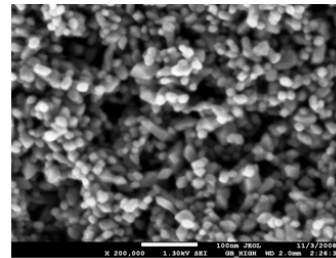
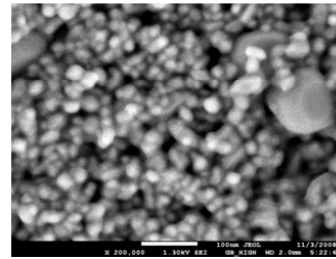


U.V. laser ($\lambda=355\text{nm}$)

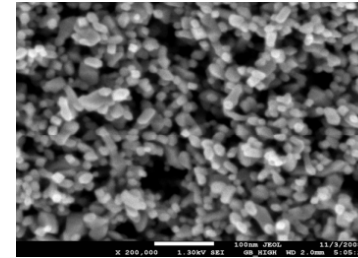
pulsed at 30 kHz

$P_{\text{ave}} = 1\text{W}$

Scan speed $s \sim 0.35 \text{ mm s}^{-1}$



\approx



Optimum laser Sintered

Standard oven sintered

Important parameter for the process is

$$\Phi = P / 2sw(z)$$

laser integrated fluence [J



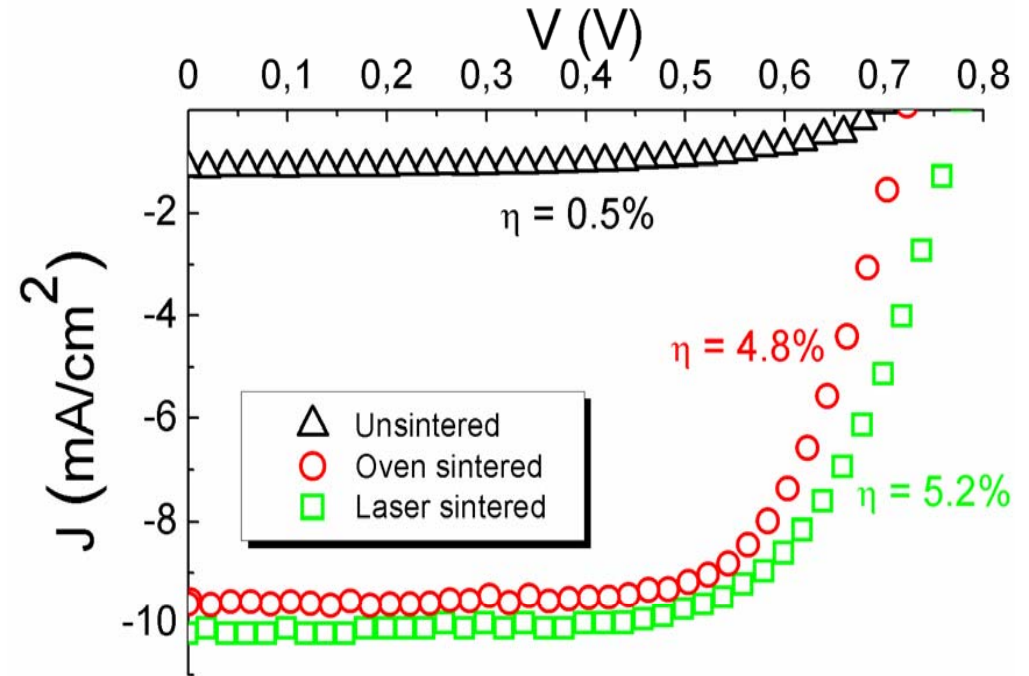
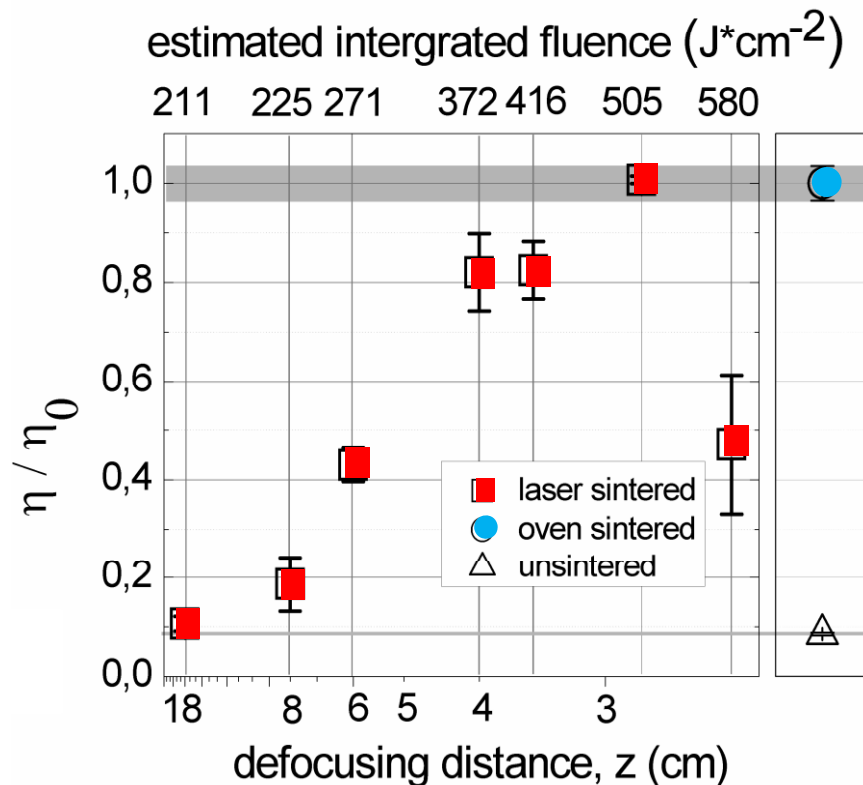
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TiO2 laser sintering/2

Clear trend of power conversion efficiency η vs. Φ



Record performance of DSCs with laser sintered TiO2

G.Mincuzzi, L.Vesce, A. Reale, A. Di Carlo, T.M. Brown, "Laser Sintered Nanocrystalline Titanium Dioxide Films for Efficient Dye Solar Cell Device Fabrication", APL 2009

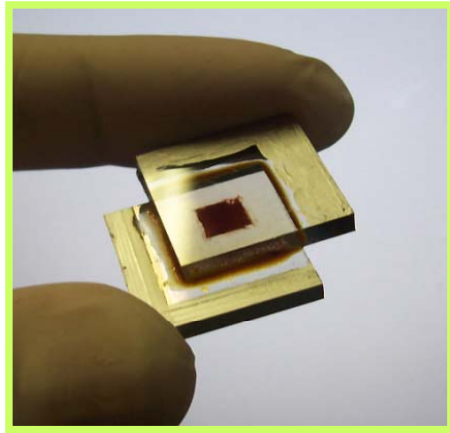


From cells to modules

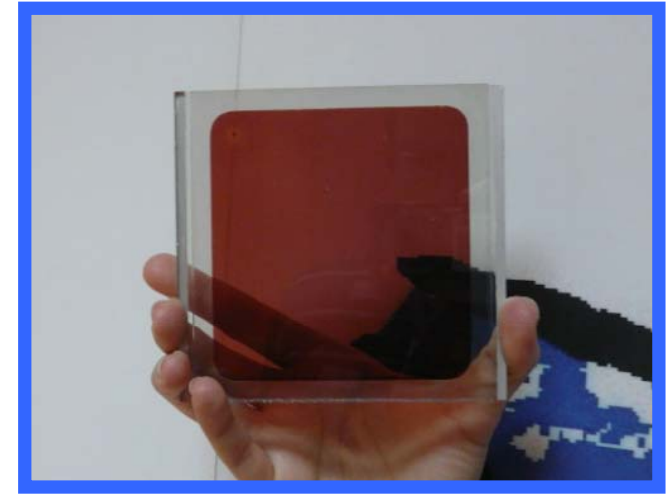
Large Area



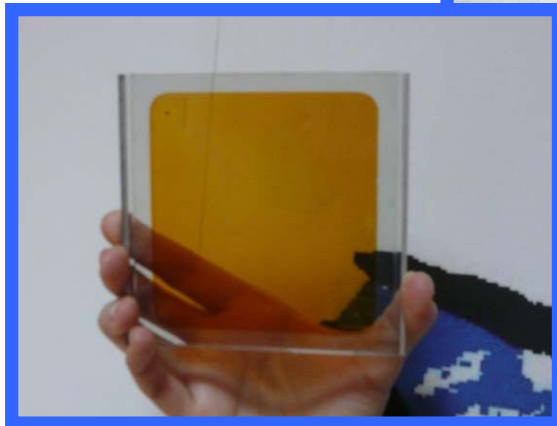
From small cell to (sub)module



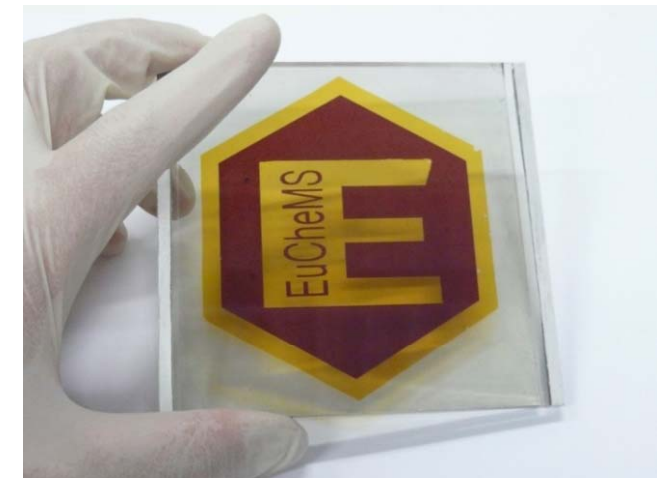
The easiest
(and wrong) way:
simple scale up



Cell scaling up and colours



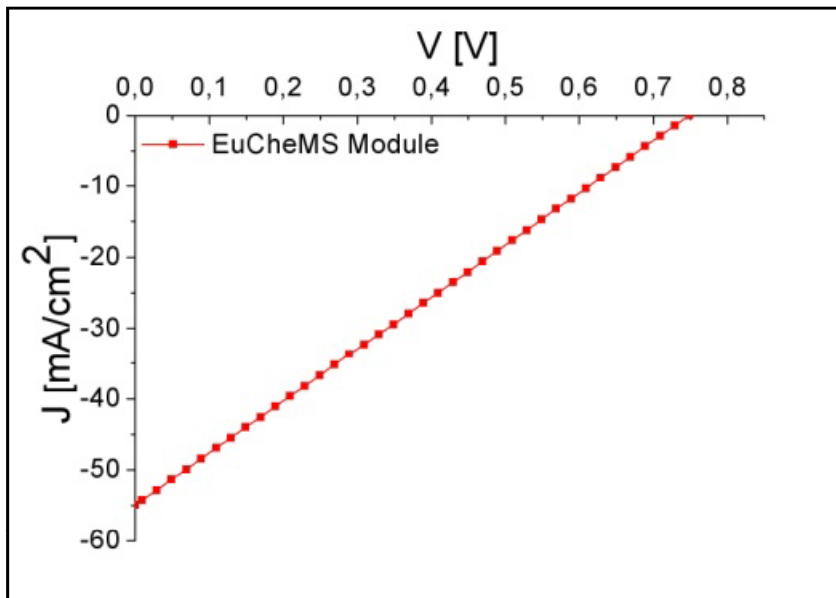
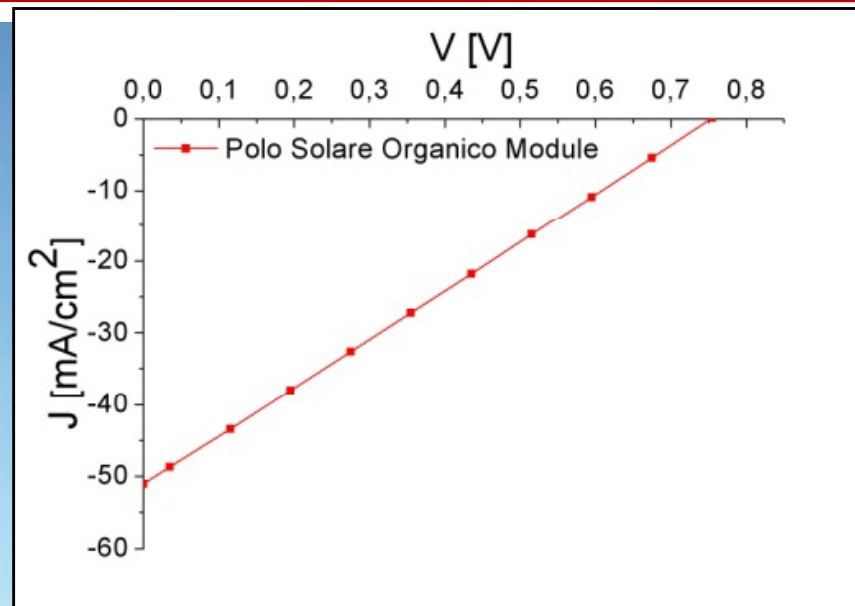
Cells with pattern



Cells with pattern



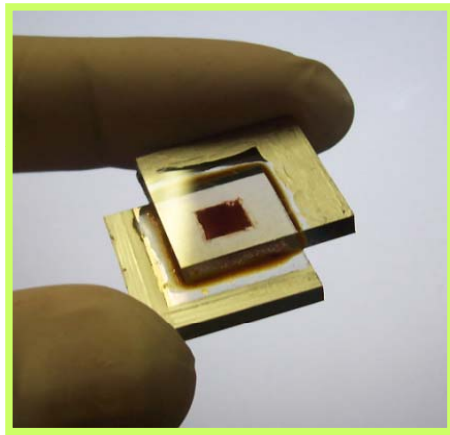
Example of patterned DSC (single cells)



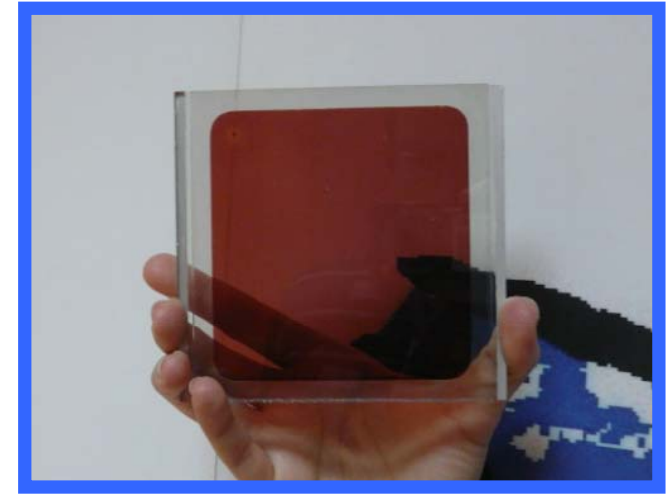
Very Very low efficiency



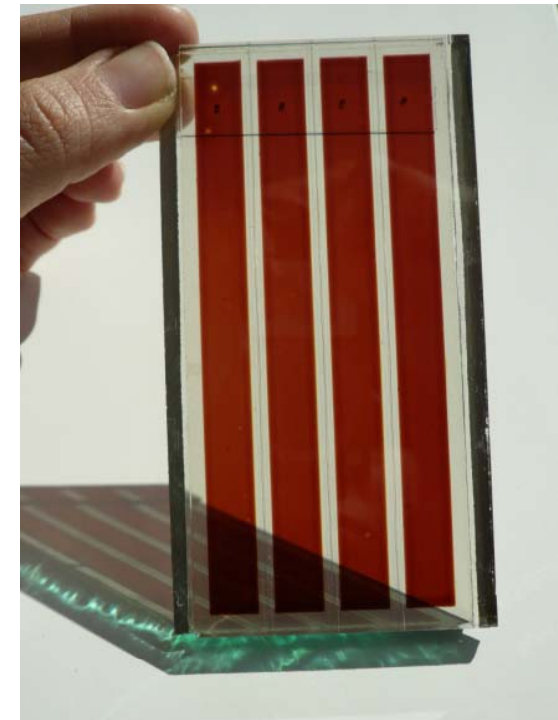
From small cell to (sub)module



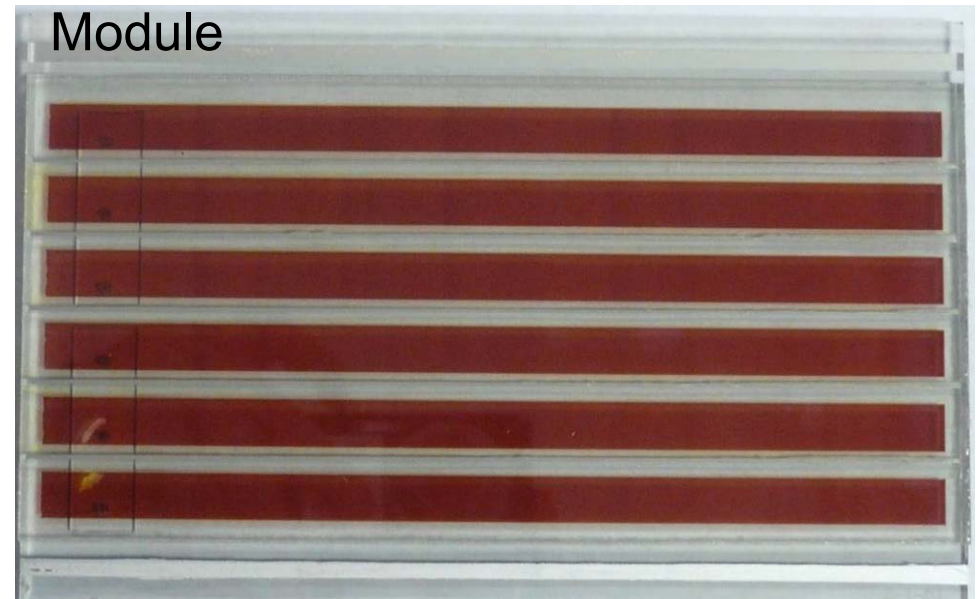
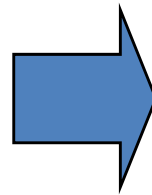
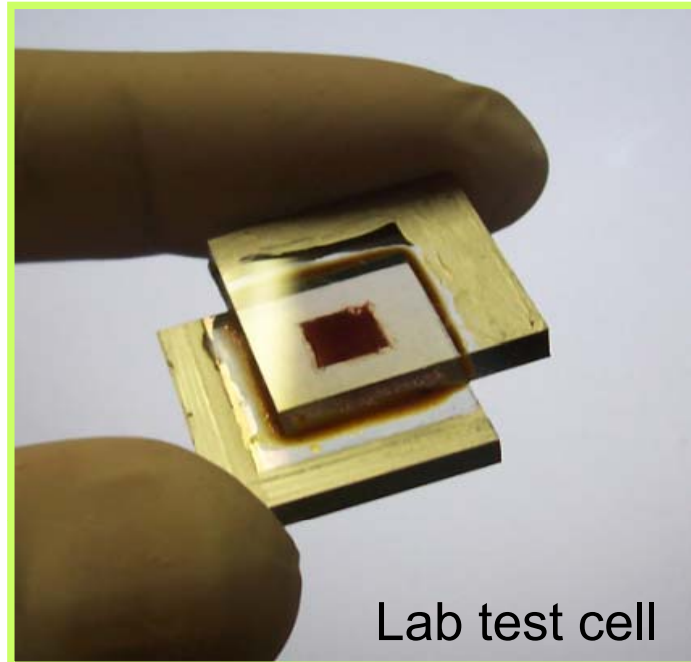
The easiest and
wrong way:
simple scale up



The right way:
proper aspect
ratio



Cells and modules



- Optimization of the materials
- Optimization of the deposition
- Optimization of sealing

Cell optimization +

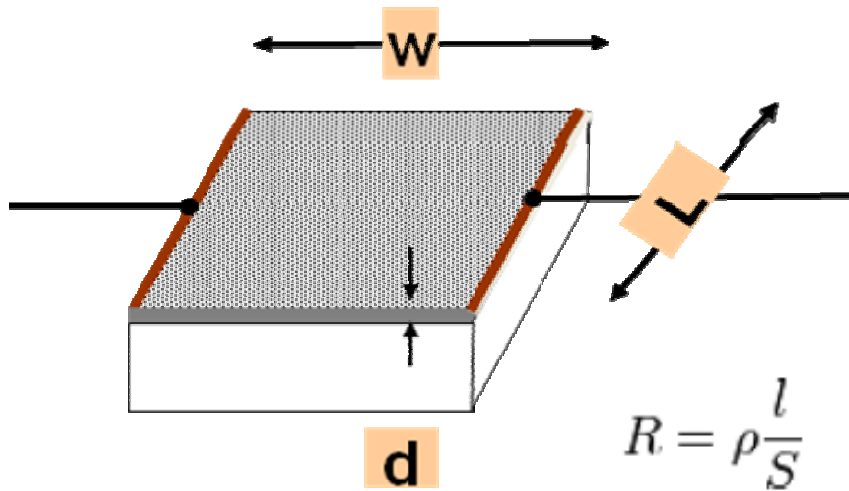
- interconnections
- reduction of series resistance
- balance among cells
- engineering of the module design
- thermal expansion

Scaling up is not trivial and it is one of the major problem !

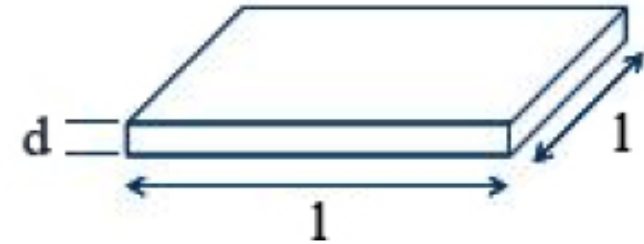


Large area cells: The sheet resistance

Let us consider a substrate ($S=L \times W$) with TCO on top (thickness of TCO = d)



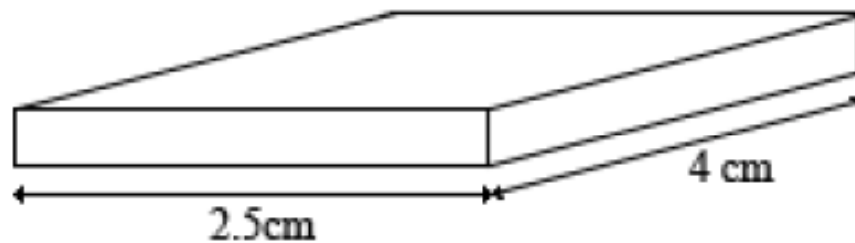
If $L=W$



$$R = \rho \frac{l}{S} = \rho \frac{l}{dl} = \rho \frac{1}{d}$$

$$R_{square} = R[\Omega / \square] = \frac{\rho}{d} \quad \text{characteristic of the TCO}$$

Example

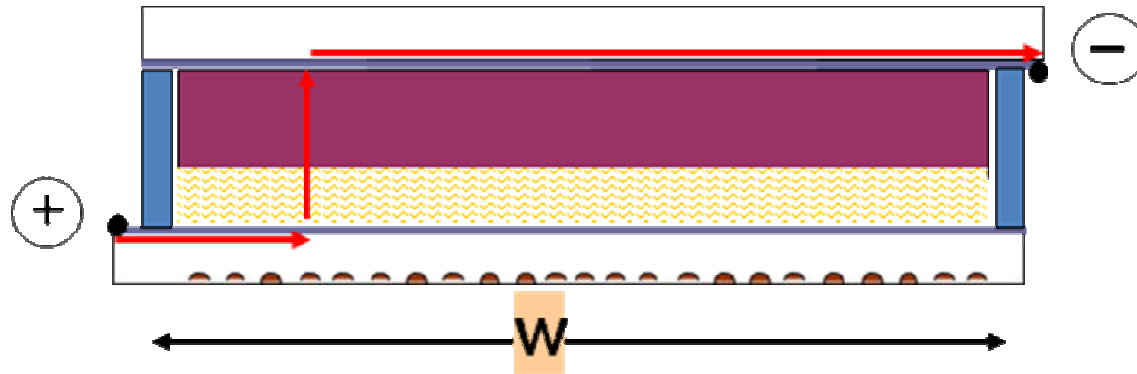


$$R = 8(\Omega / \text{square}) * \frac{2.5(\text{cm})}{4(\text{cm})} = 5(\Omega)$$

$$R = 15(\Omega / \text{square}) * \frac{2.5(\text{cm})}{4(\text{cm})} = 9.375(\Omega)$$



Sheet resistance influence



$$\Delta V = RI = \left[\frac{\rho W}{dL} \right] [J \cdot L \cdot W] = J \cdot W^2 \cdot R_{square}$$

Example ($J=10 \text{ mA/cm}^2$, $R_{square} = 8 \text{ } \Omega/\text{sq}$):

1) Small area cell ($0.5\text{cm} \times 0.5 \text{ cm}$) = $\Delta V=0.02\text{V}$

2) Large area cell ($10 \text{ cm} \times 10 \text{ cm}$) $\Rightarrow \Delta V = 8 \text{ V} \gg V_{oc} !!$



Single Cell - simulated data

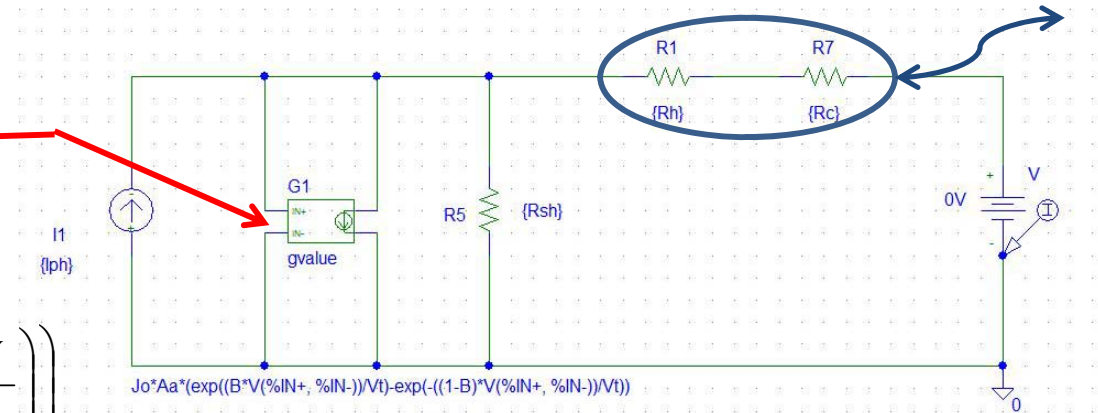
Non Linear Resistance
Butler-Volmer eq.

$$J = J_0 \left(\exp\left(\beta \frac{V}{V_T}\right) - \exp\left(- (1-\beta) \frac{V}{V_T}\right) \right)$$

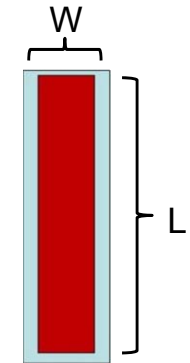
$\beta = 0.35$ $J_0 = 7.5 \times 10^{-7} \text{ A}$ $V_T = 26 \text{ mV @ RT}$

$\frac{\rho}{d} = TCO \text{ sheet resistance} = 8 \Omega / \square$

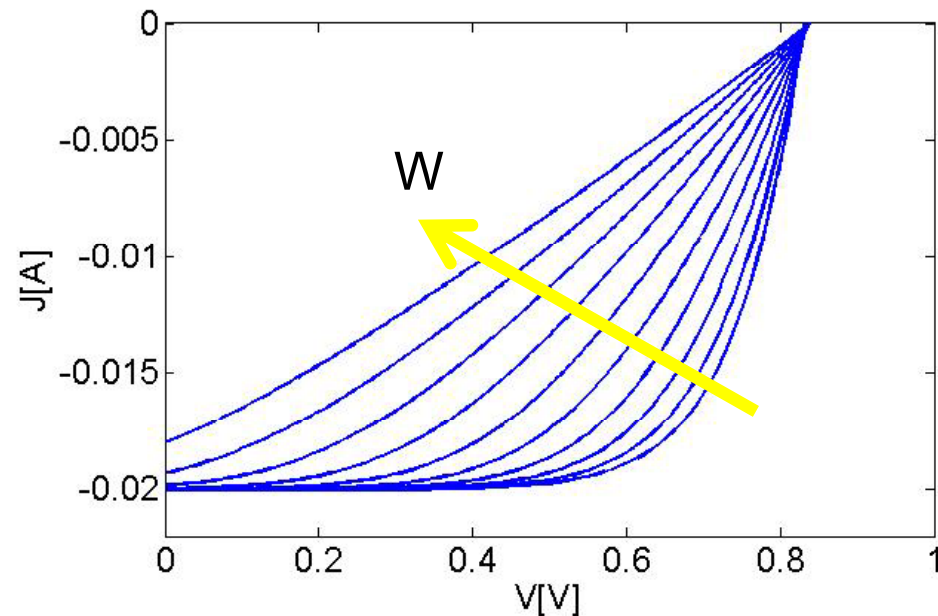
$L = 5 \text{ cm}; W = 1.5 \text{ mm}$



$$R_s = \frac{\rho W}{d L}$$

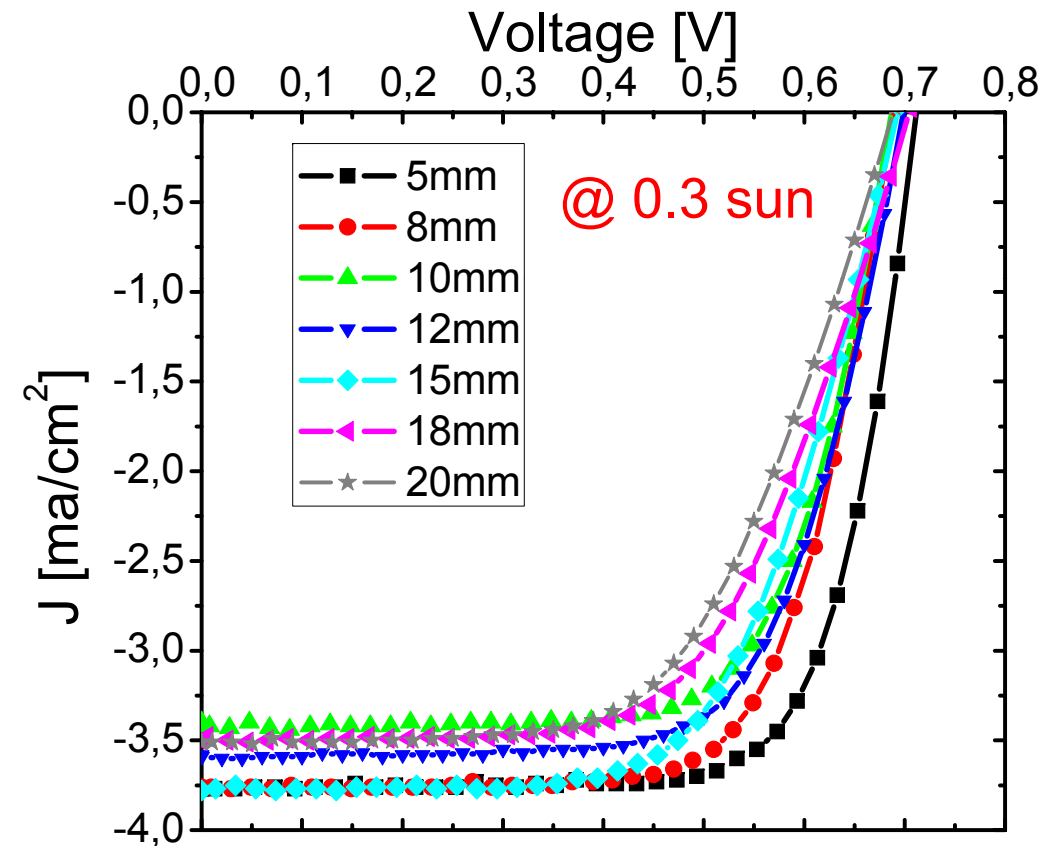
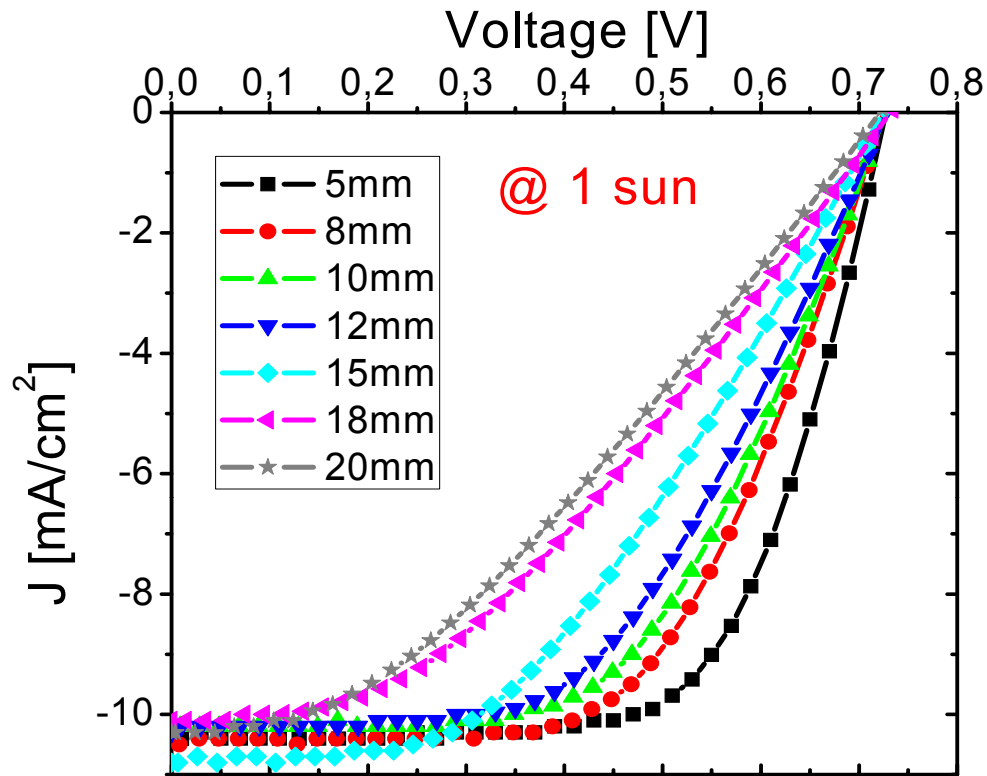


W(mm)	Rs(Ω)	FF	eff
2	0.8	68.9	11.5
4	1.1	66.2	11.1
6	1.4	62.5	10.4
8	1.7	57.7	9.6
10	2.1	52.1	8.7
12	2.4	46.1	7.7
14	2.7	40	6.7



Single Cell - experimental data

F. Giordano et al, HOPV conference 2009

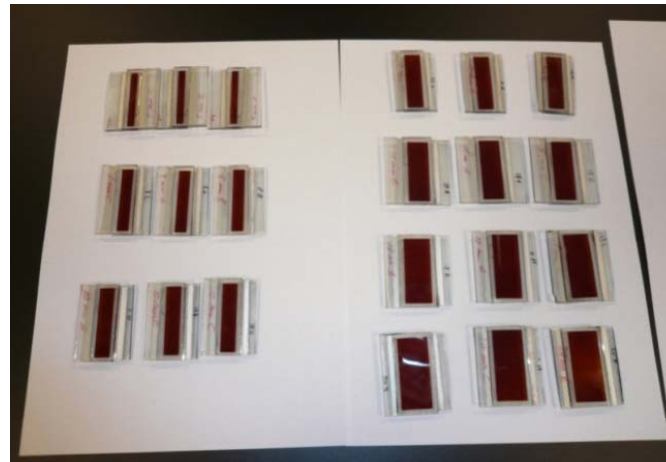
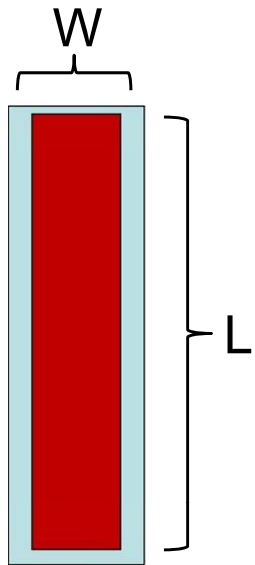


At 0.3 Sun the current is smaller with respect to 1 Sun and consequently ΔV is smaller.



Single Cell - experimental data

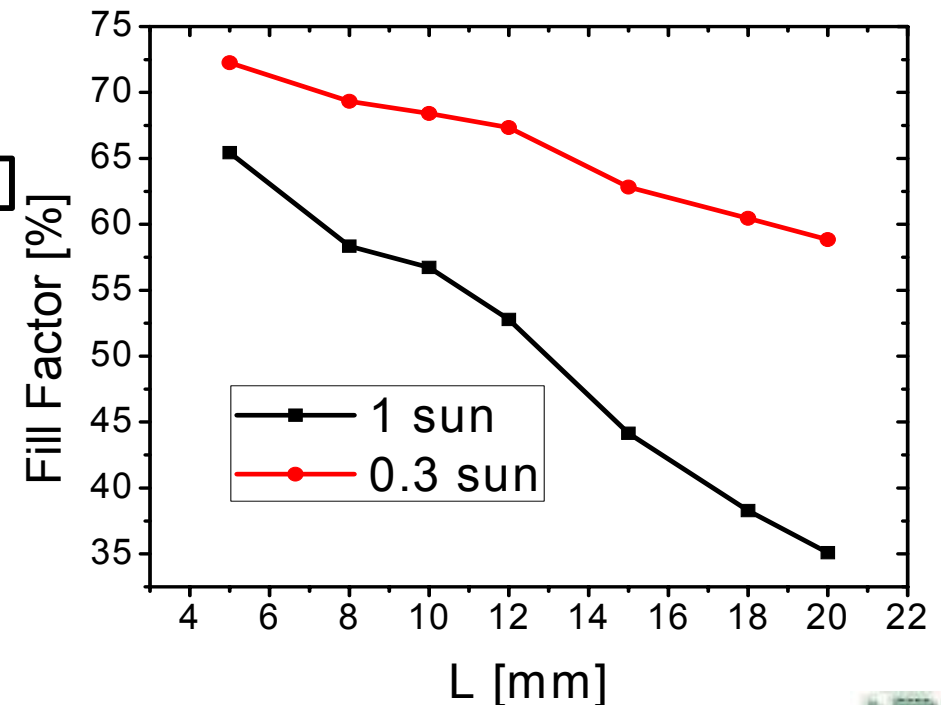
F. Giordano et al, HOPV conference 2009



1 set of cells $L = 44\text{mm}$,
 $W = 5, 8, 10, 12, 15, 18, 20\text{ mm}$
Single titania layer of 6 microns
 $J_{sc} = 10\text{ mA/cm}^2$ $V_{oc} = 730\text{ mV}$
starting efficiency = 4.7%
($W = 5\text{ mm}$, total area 2.2cm^2)

$\frac{\rho}{d} = TCO\text{ sheet resistance} = 8\Omega / \square$

$$R_s = \frac{\rho W}{d L}$$



From large area cells to (sub)module

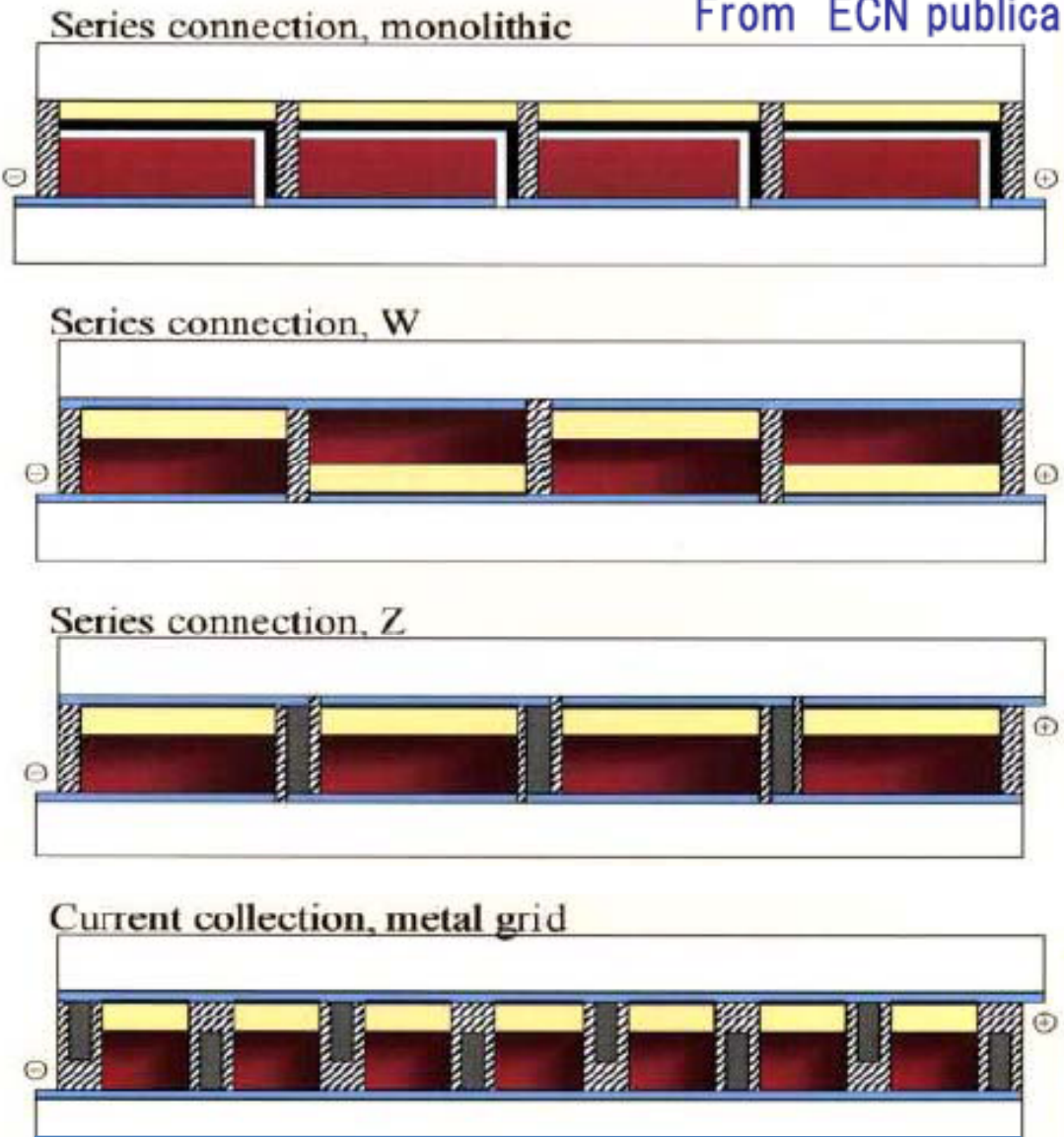
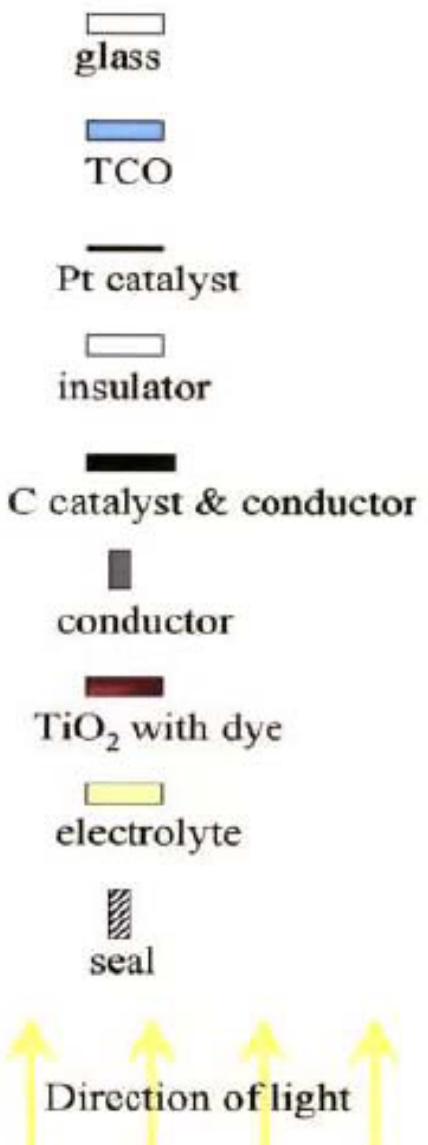
Well ...and now ...

How can we realize a large area module with a certain open circuit voltage and a certain short circuit current ?

There are several ways to do it.

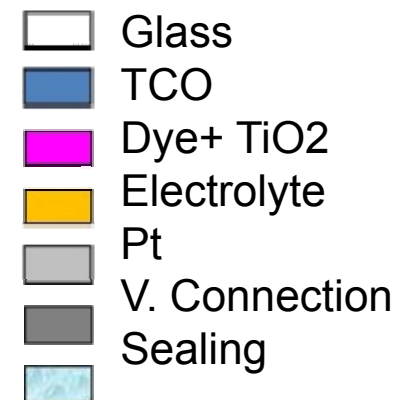
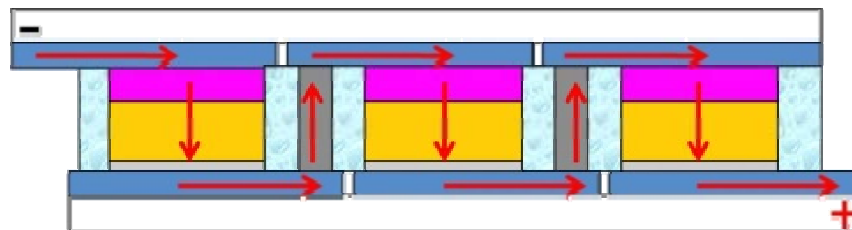


From ECN publications



W and Z schemes

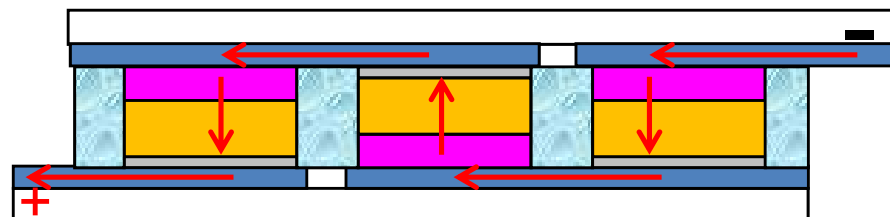
✓ Optimized and separated processes for WE and CE substrates



- Vertical interconnections resistance decreases FF
- Sealing more complex
- Lower aperture ratio

Z

✓ No vertical connections
✓ High AR

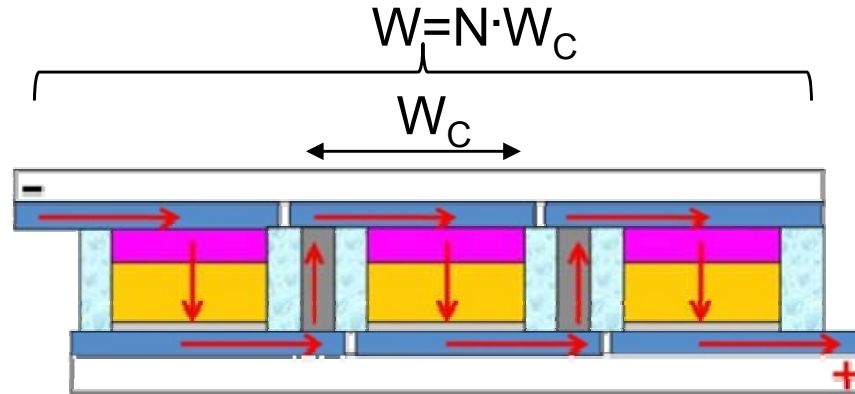


- One half of the cells is illuminated on the CE side (Current matching problem)
- CE and WE processes are on the same substrate

W



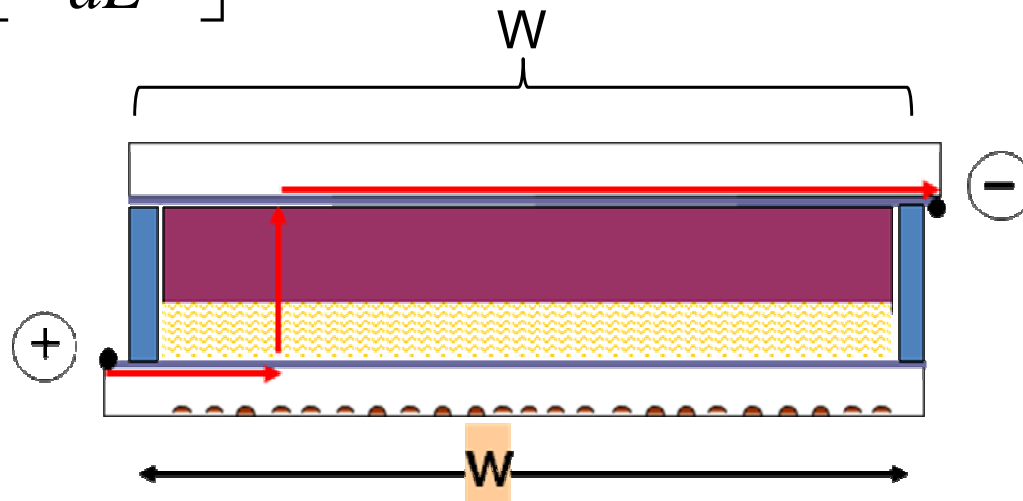
Module with N cells connected in series



$$R_{\text{interconnects}} = 0$$

$$\Delta V_M = RI = \left[\frac{\rho N W_C}{dL} \right] [J \cdot L \cdot W_C] = J \cdot N \cdot W_C^2 \cdot R_{\text{square}} = J \cdot \frac{W^2}{N} \cdot R_{\text{square}}$$

Large area cell

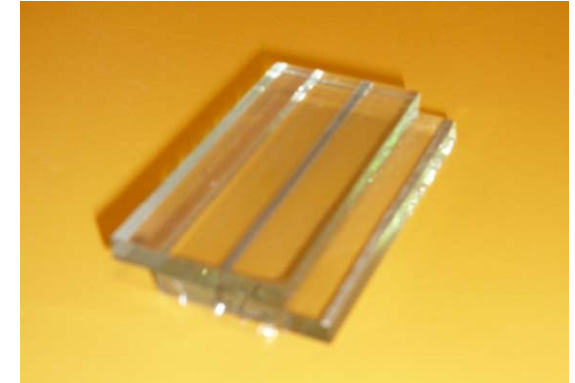
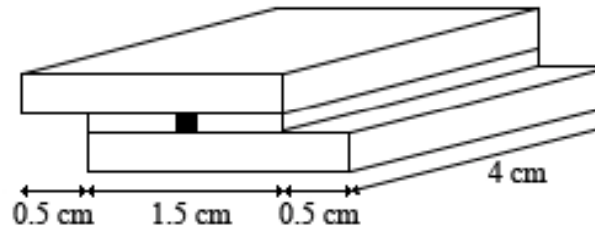
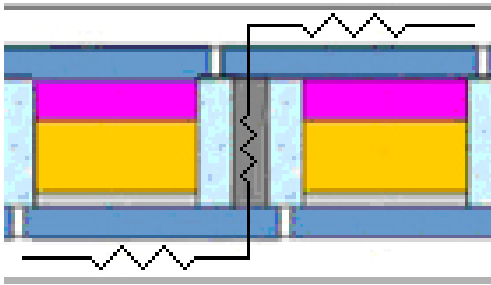


$$\Delta V_M = \frac{\Delta V_{\text{LargeCell}}}{N}$$

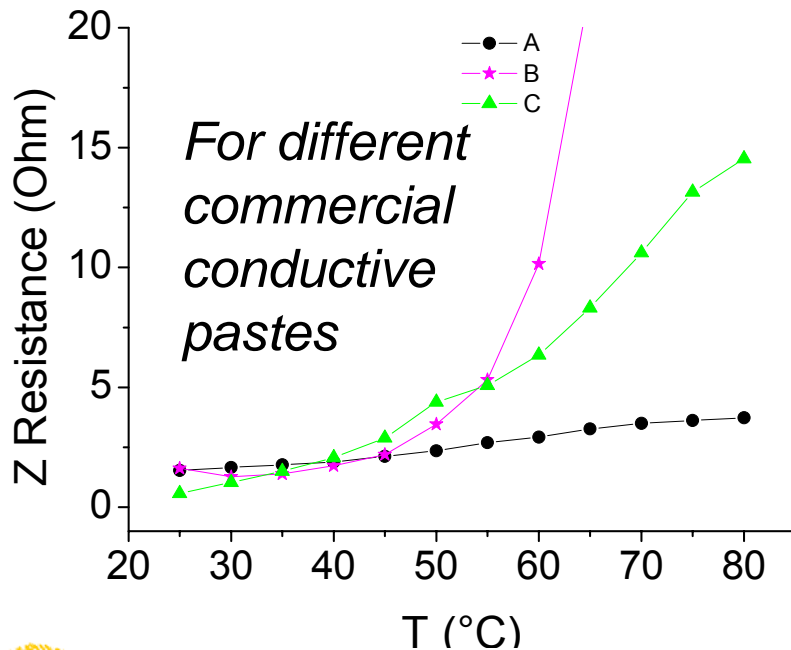
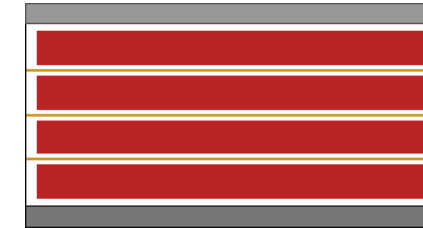
$$\Delta V = RI = \left[\frac{\rho W}{dL} \right] [J \cdot L \cdot W] = J \cdot W^2 \cdot R_{\text{square}}$$



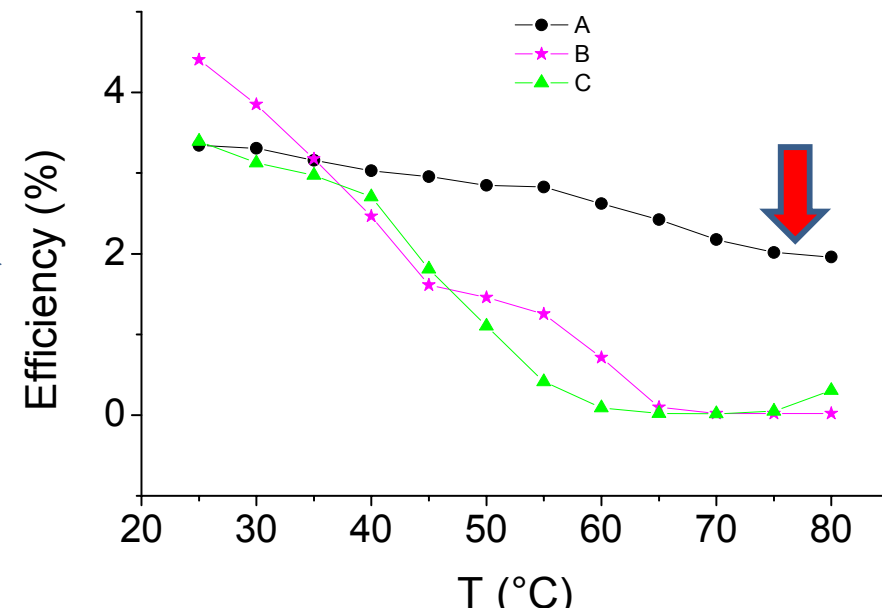
Z scheme - Vertical interconnections



Mismatch in thermal expansion coefficient between sealing and interconnection affects the value of electrical resistance

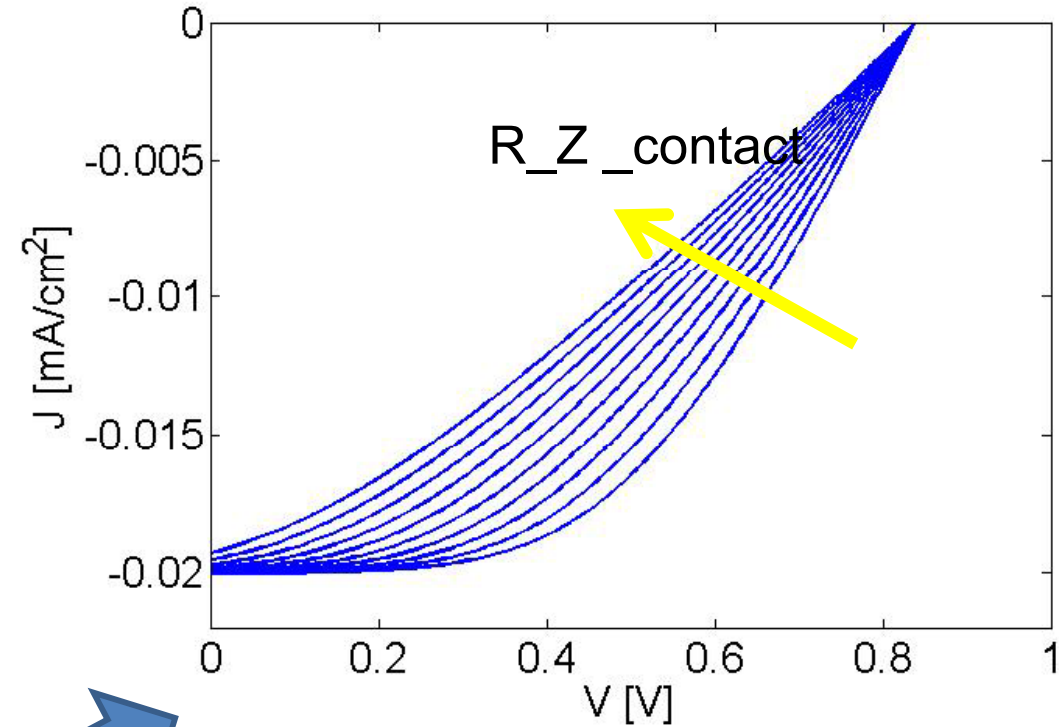
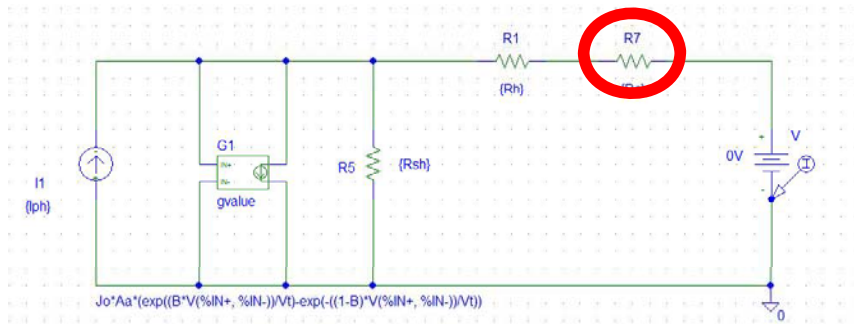


module

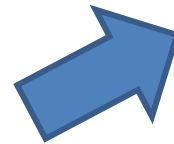


Vertical interconnections- simulated data

R_interdistance+R Z contact

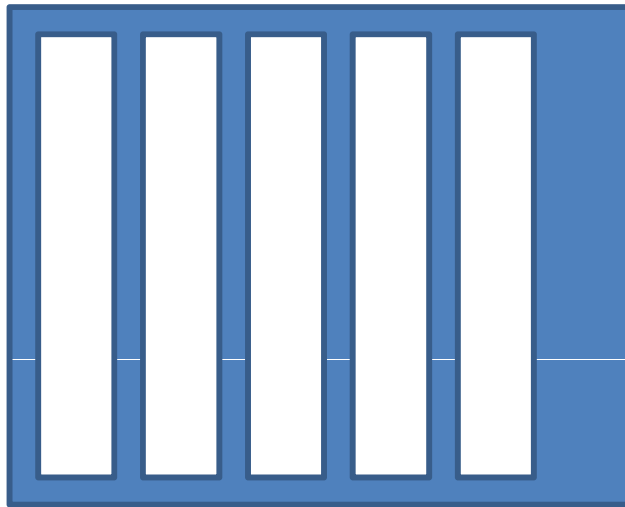


Z(Ω)	Rs(Ω)	FF	eff
0.4	2.5	49	8.2
0.8	2.9	46.1	7.7
1.2	3.3	43.3	7.3
1.6	3.7	40.7	6.8
2.0	4.1	38.3	6.4
2.4	4.5	36.1	6.1
2.8	4.9	34.1	5.7

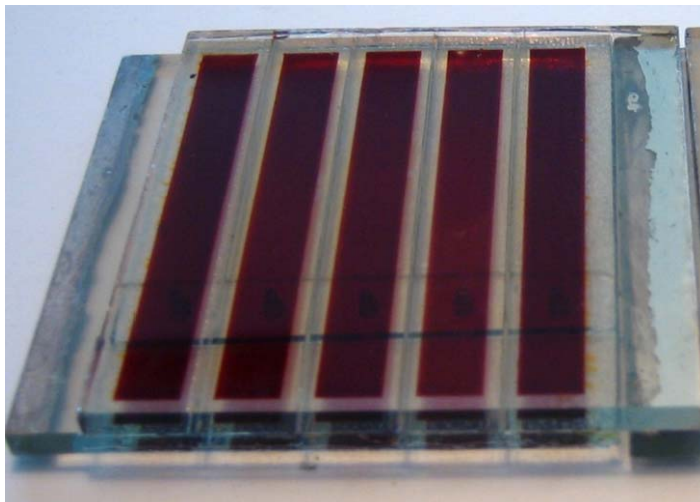


Z and W projected layout

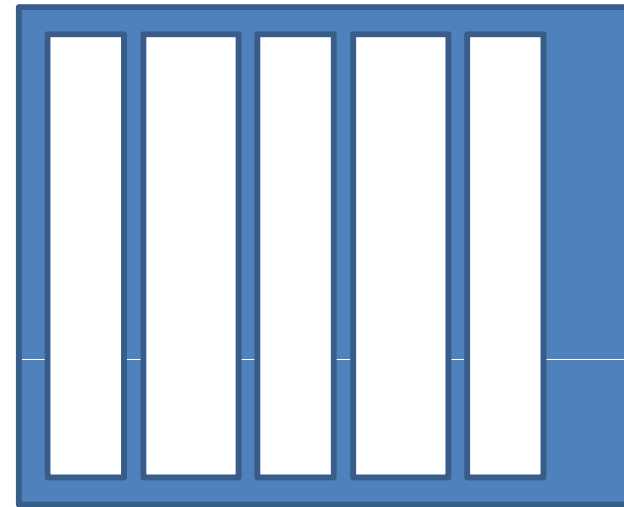
Z



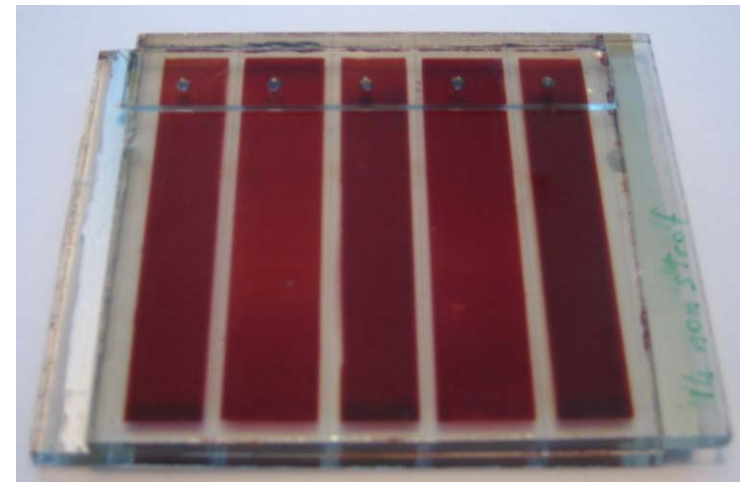
$L = 8 \text{ mm}$ $d = 3$
Vertical connection Paste A



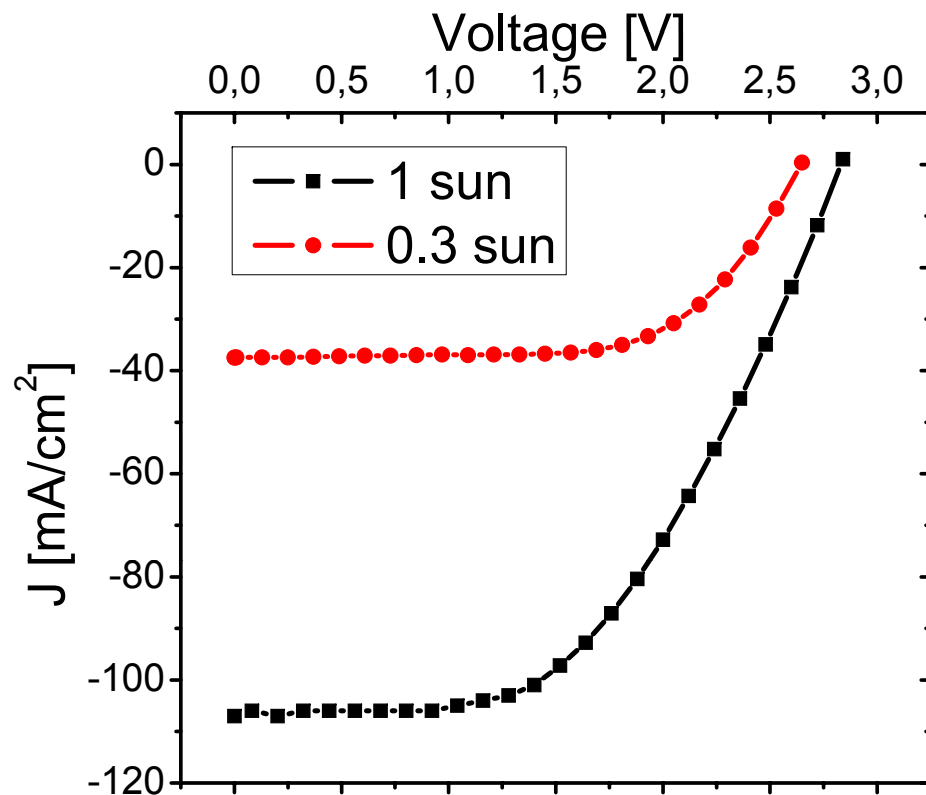
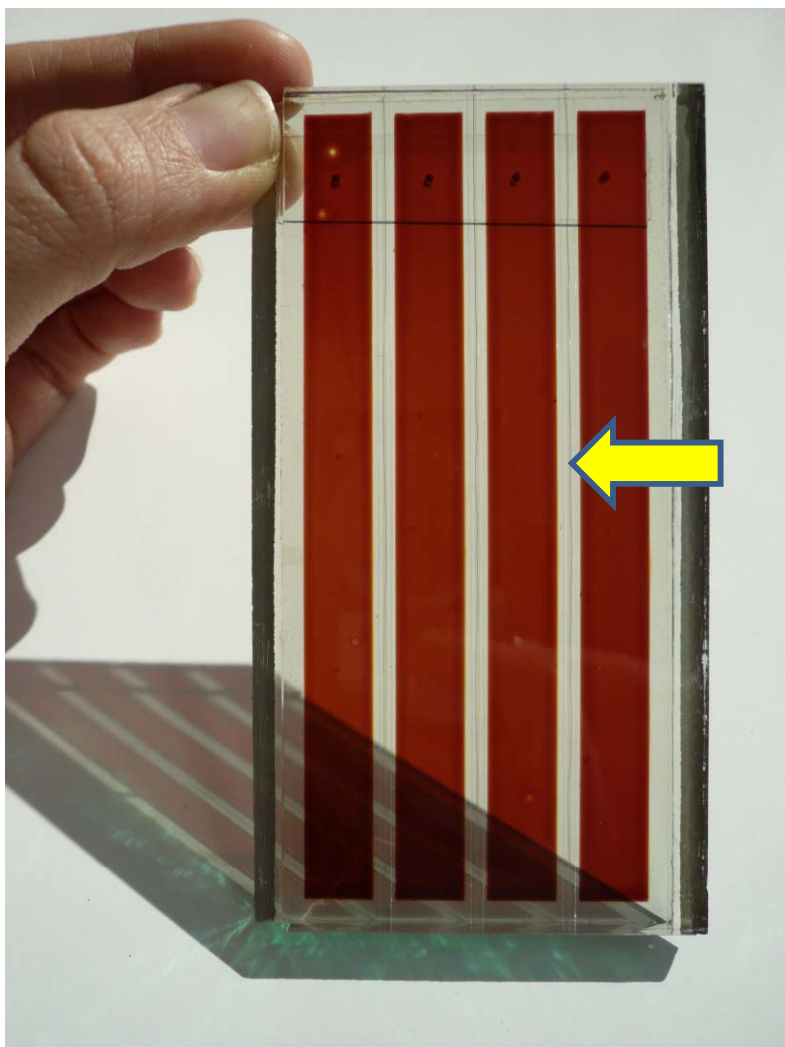
W



$L_1 = 8 \text{ mm}$ $L_2 = 10 \text{ mm}$ $d = 2$
Electrolyte B



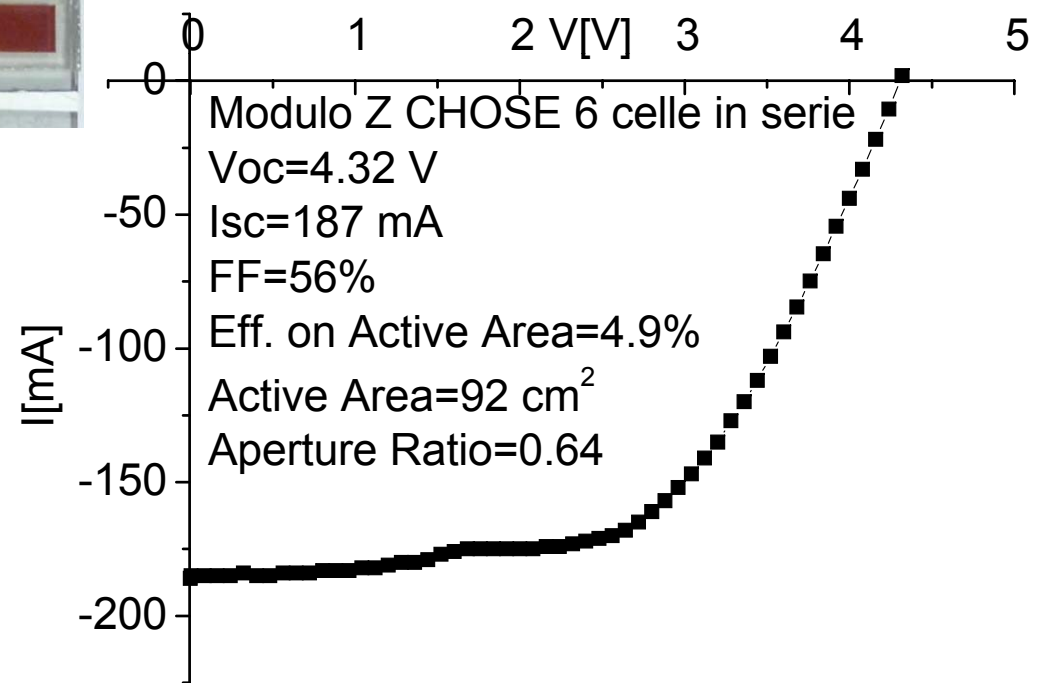
Z-module – micrometer interconnections



	1 sun	0.3 sun
Isc [mA/cm ²]	1.06E-1	3.77E-2
Voc [V]	2.84	2.65
FF [%]	51.01	64.34
η [%]	4.15	5.8



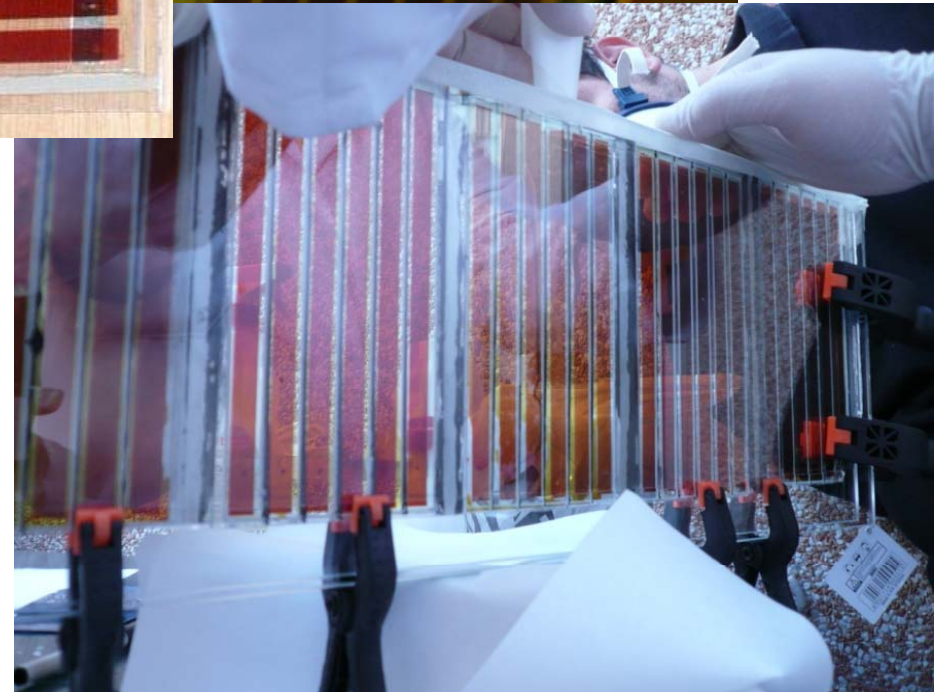
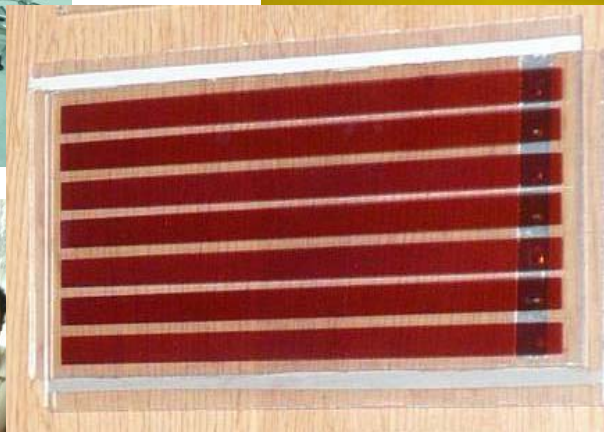
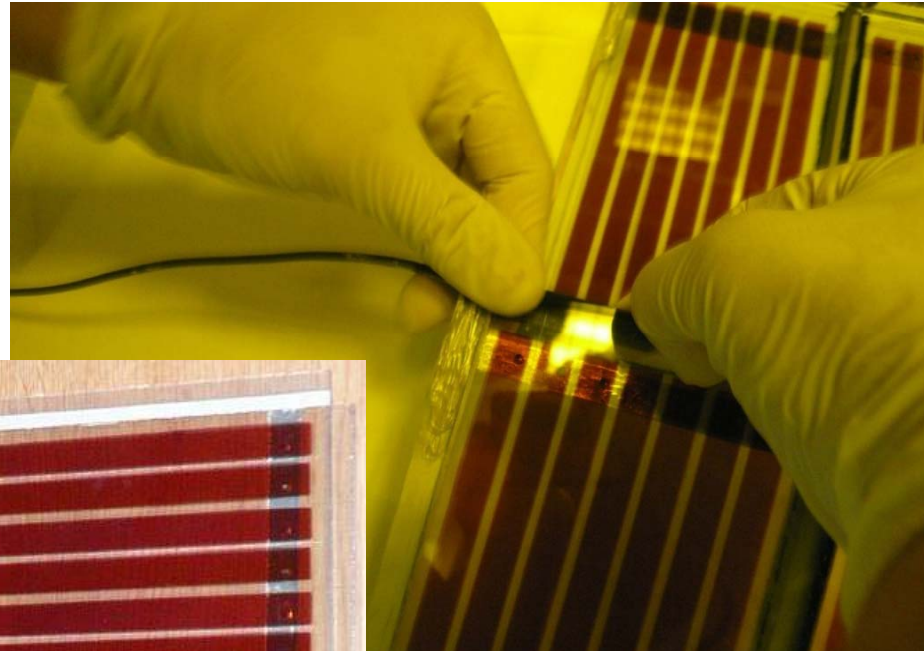
Z module 6 cells



From Modules to Panels

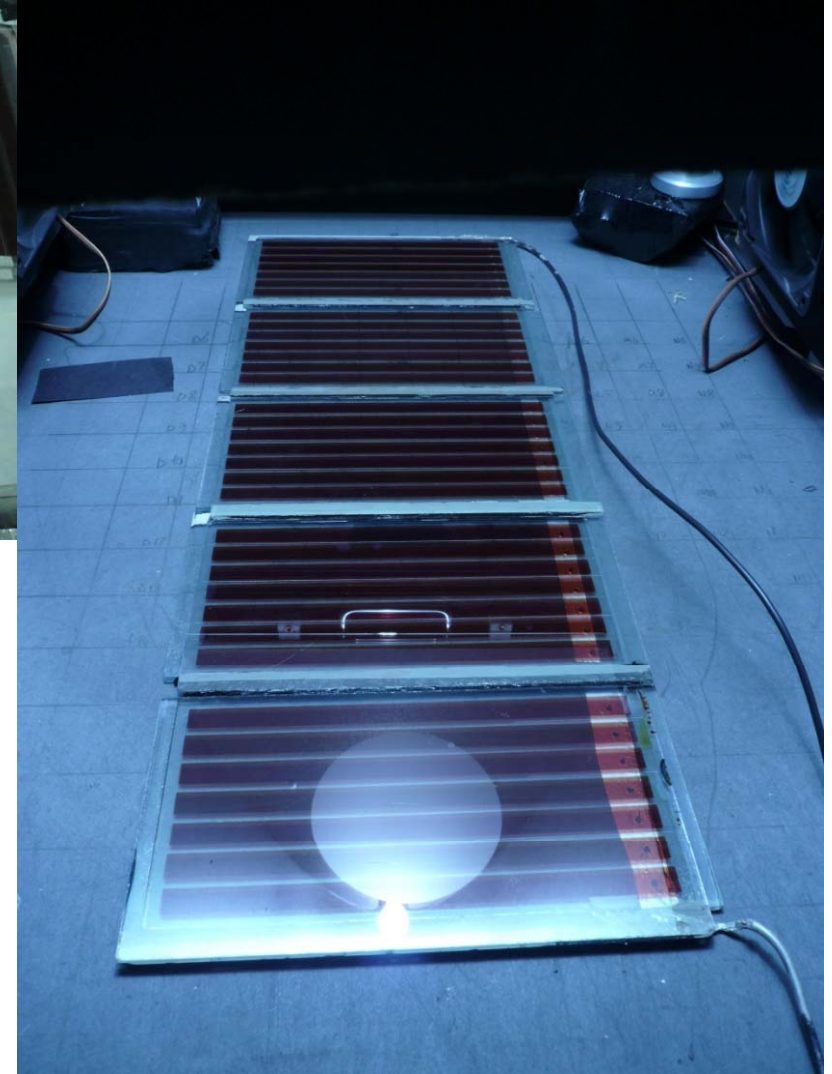


Modules Assembly, bus bar connections

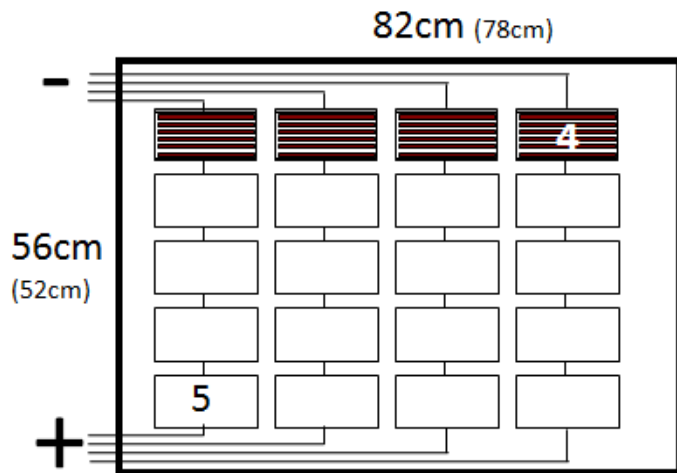
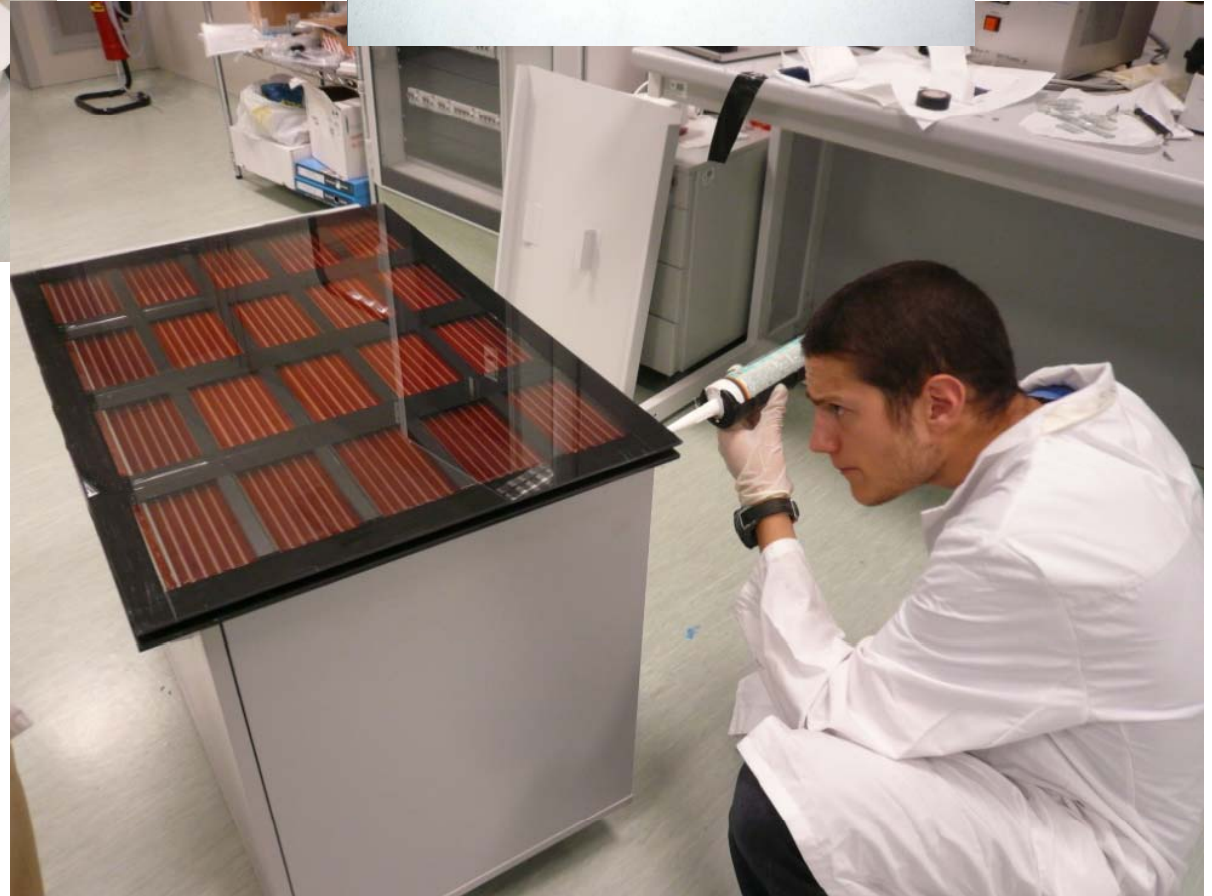
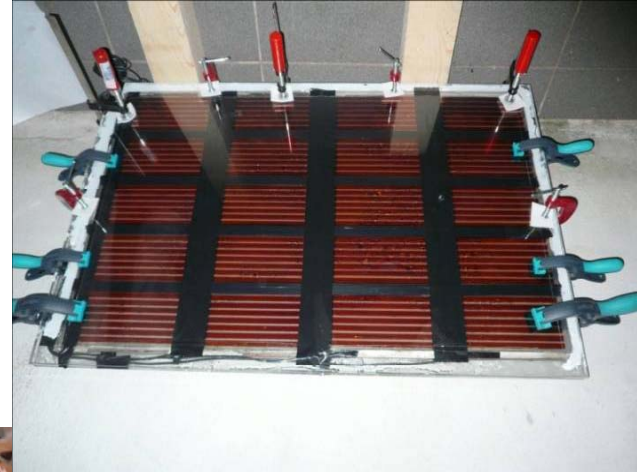
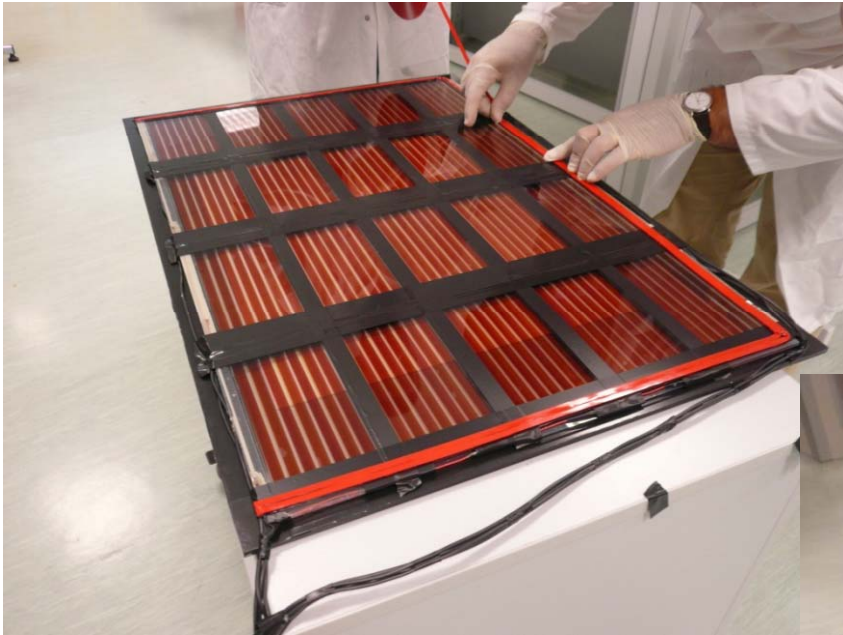


CHOSE

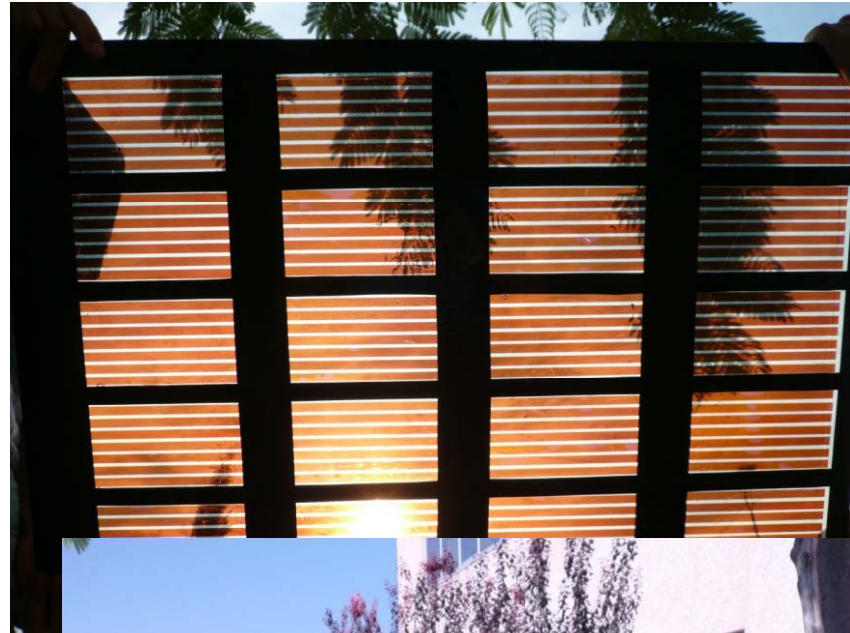
Strings



Panel assembly



Final panel



Fabrication



Automatic Screen-Printing (Baccini)



A. Di Carlo

CHOSE



Batch fabrication facilities



- a) Belt oven
- b) Hole drilling machine
- c) Dye Applicator



Batch fabrication facilities



- a) Dye profiling
- b) Electrolyte applicator
- c) Sealing applicator



Pilot line



Toward Industrialization



Applications Dyesol



DSSC Façade System
at the CSIRO Energy Centre
Newcastle, Australia



Applications (AISIN-Toyota)

AISIN - Japan



A. Di Carlo

CHOSE



Applications (Sony)



A. Di Carlo

CHOSE



Outdoor measurements



ENERGIA SOLARE TEST E RICERCA
LABORATORI DI FISICA TECNICA AMBIENTALE
UNIVERSITÀ DEGLI STUDI DI ROMA 'TOR VERGATA'

Prof. Spina – Dr. Cornaro



Outdoor PV Test and meteorological station

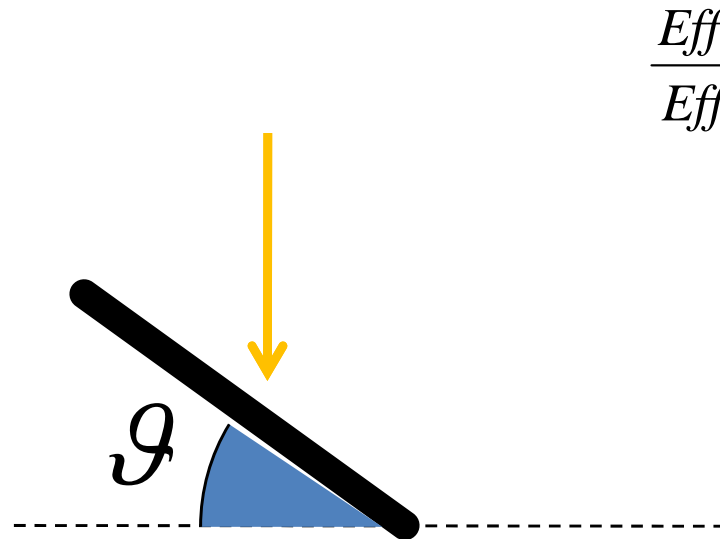


Main Characteristics:

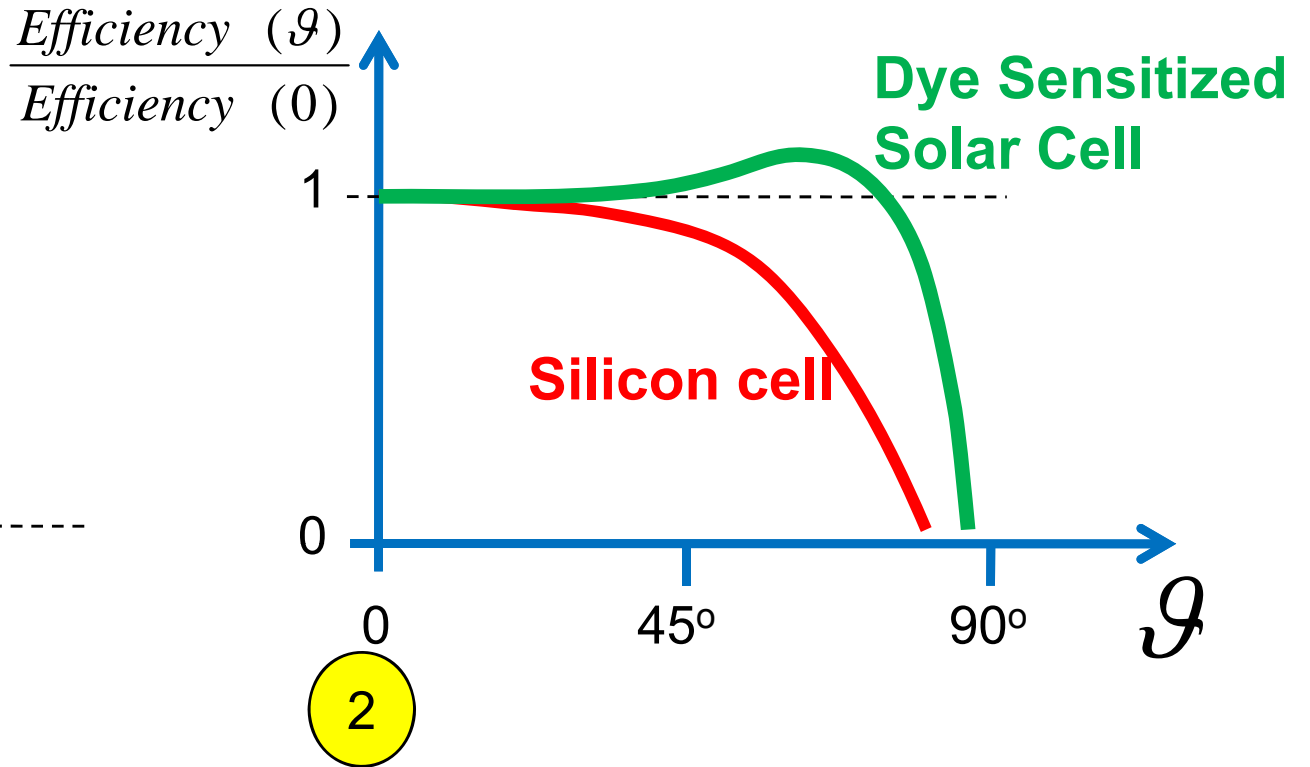
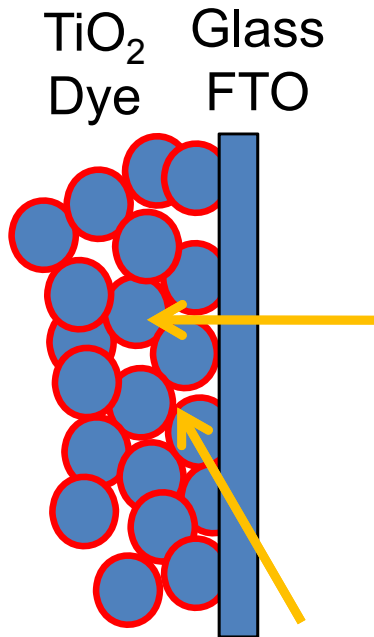
- Meteorological station with also direct/indirect light intensity meas.
- up to 6 panel contemporary measurement with also DSC cell meas.
- 2 rotation axis
- Solar spectra measurement



Angular dependence



1

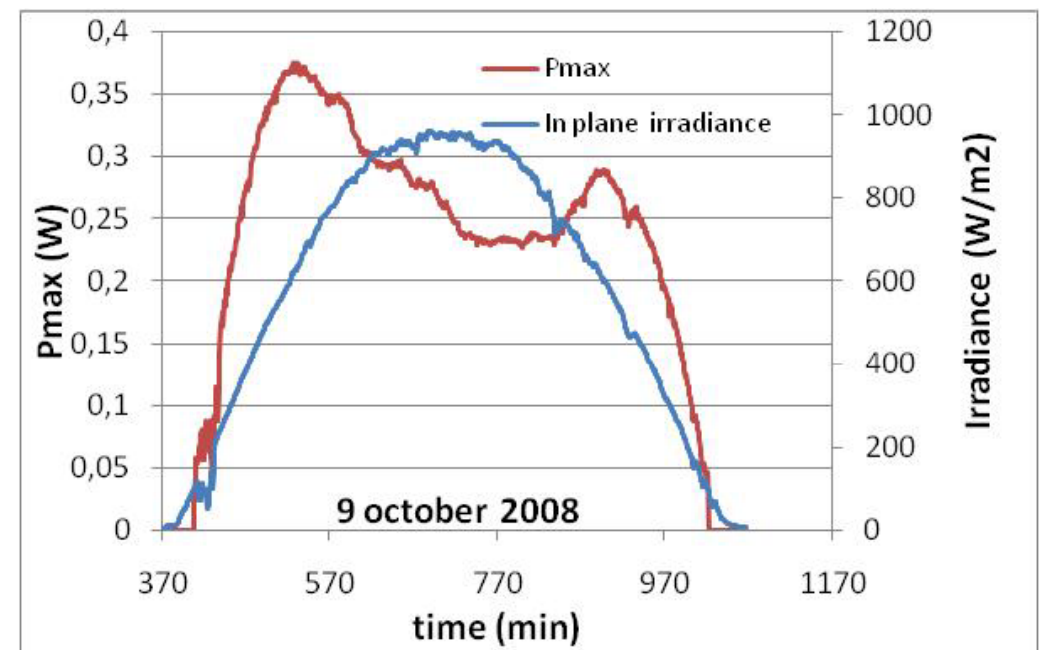
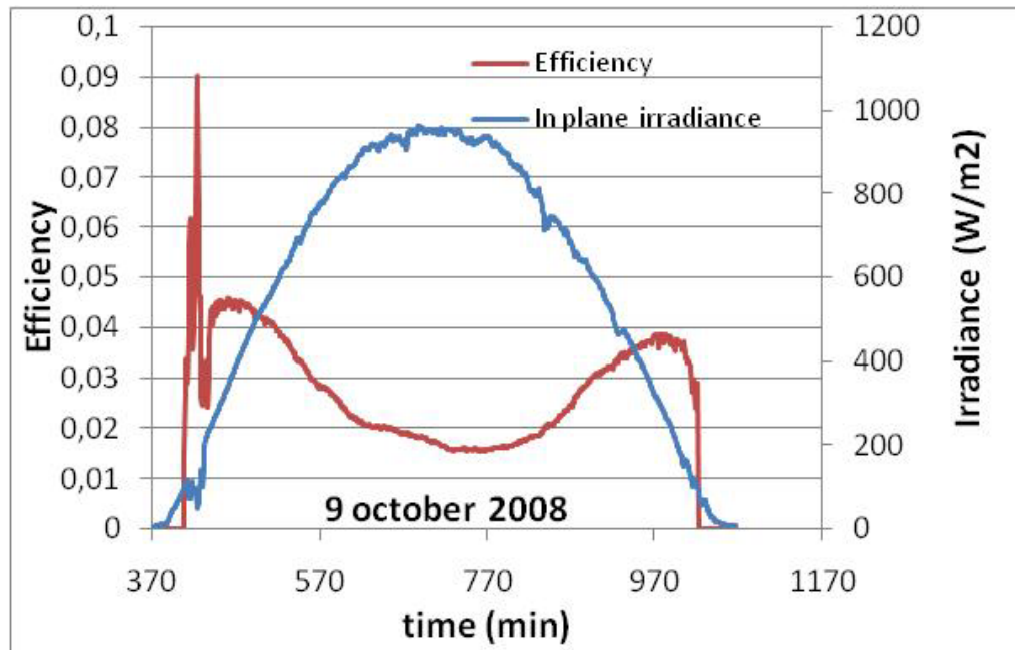


Lower is the light intensity
higher is the efficiency of the
electrolyte to sustain the
generated carriers

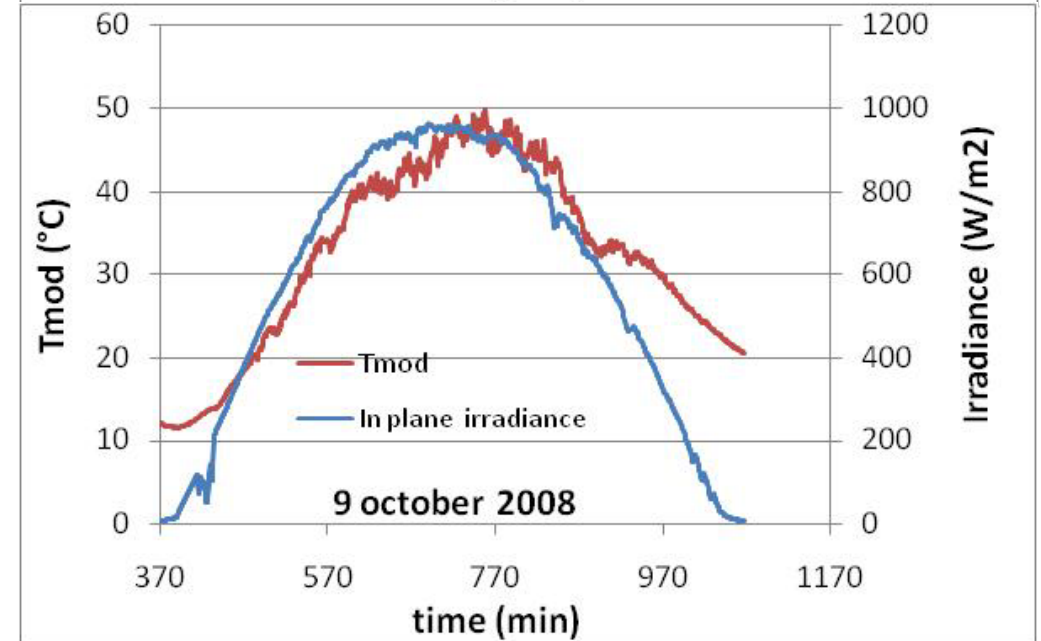
Path length increases with increasing angle



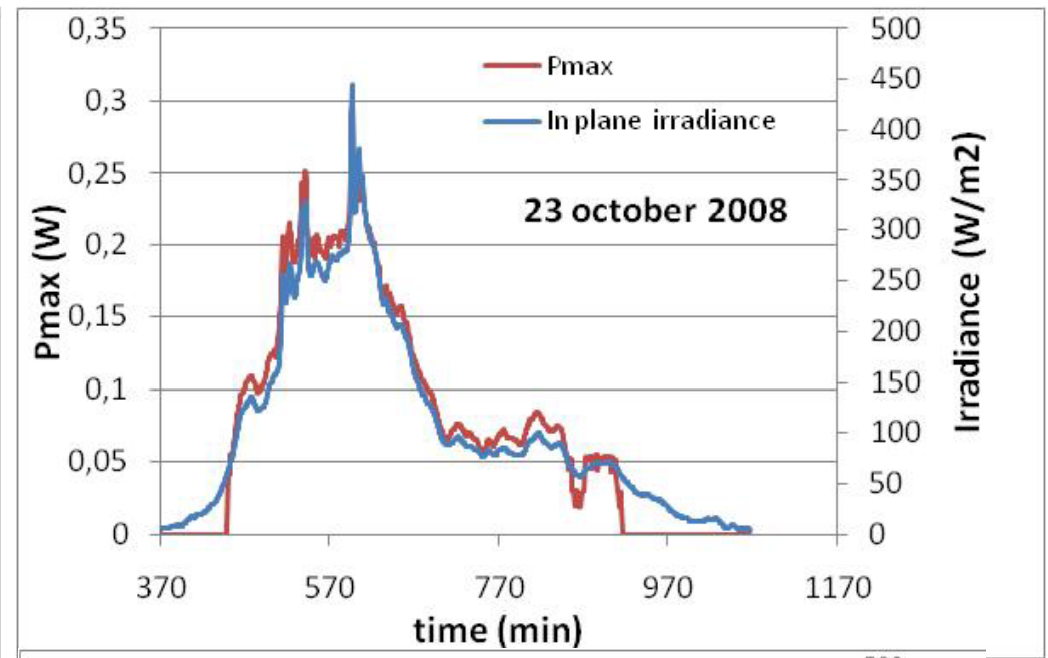
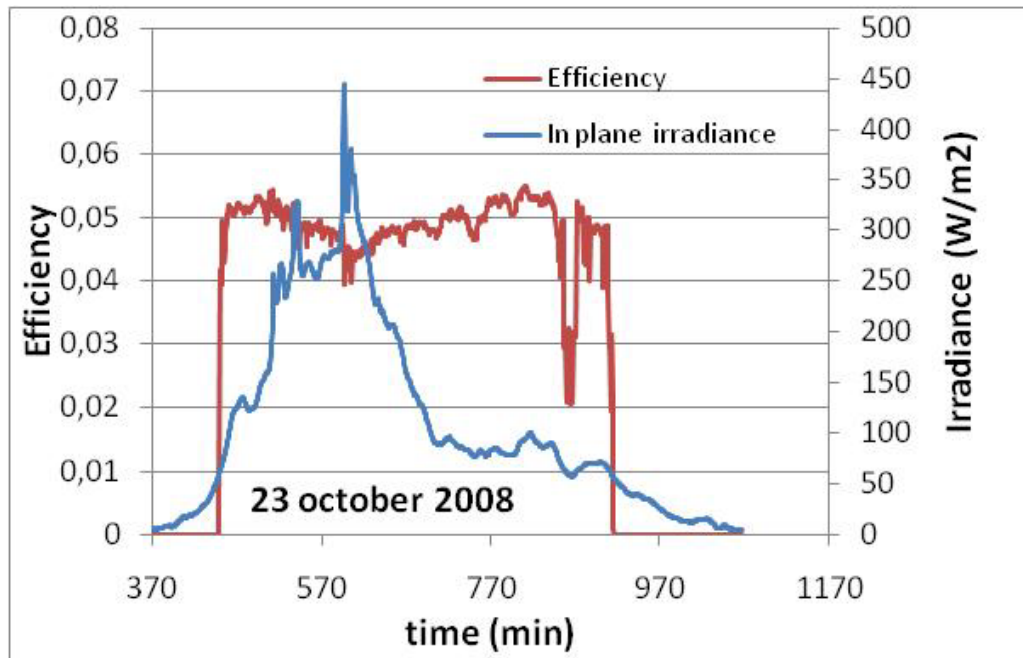
Outdoor Module test – Clear day



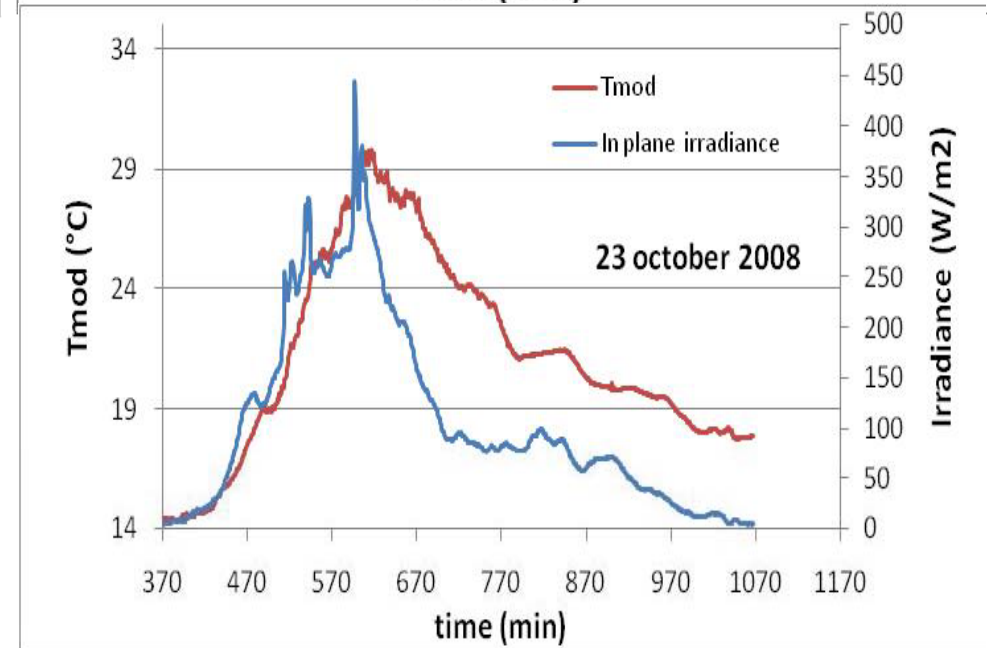
Light is mainly direct



Outdoor Module test – Cloudy day



Light is mainly diffused



Energy production

[T. Toyoda et al. / Journal of Photochemistry and Photobiology A: Chemistry 164 (2004) 203–207]

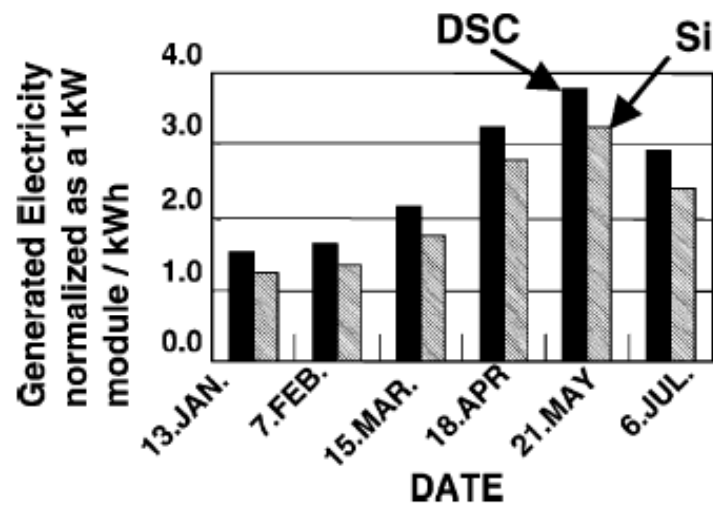


Fig. 5. Example of generated electricity for cloudy days between December and July for the DSC modules and the Si module. Output power is converted as a 1 kW module.

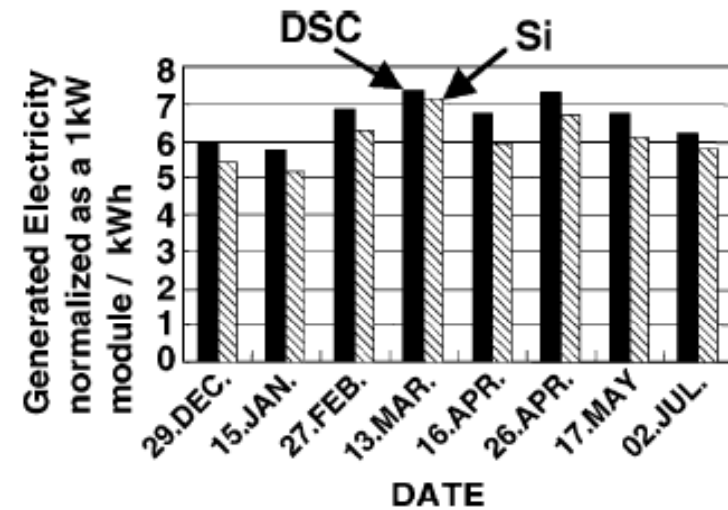


Fig. 4. Example of generated electricity for clear and sunny days between December and July for the DSC modules and the Si module. Output power is converted as a 1 kW module.

1 kWp of silicon based PV modules produce 1400 kWh / year.

1 kWp of DSC based PV modules produce 1600 kWh / year



Build integrated PV

Compared to traditional photovoltaics, DSC has the following differentiation advantages:

- Low dependence on angle of light
- Stable operating voltage in all light conditions
- Natural colours
- Optional transparency
- Aesthetically pleasing
- Manufactured as a building product
- Provides additional functionality for energy efficiency



Building Integration of Photovoltaics is quite convenient for DSC technology

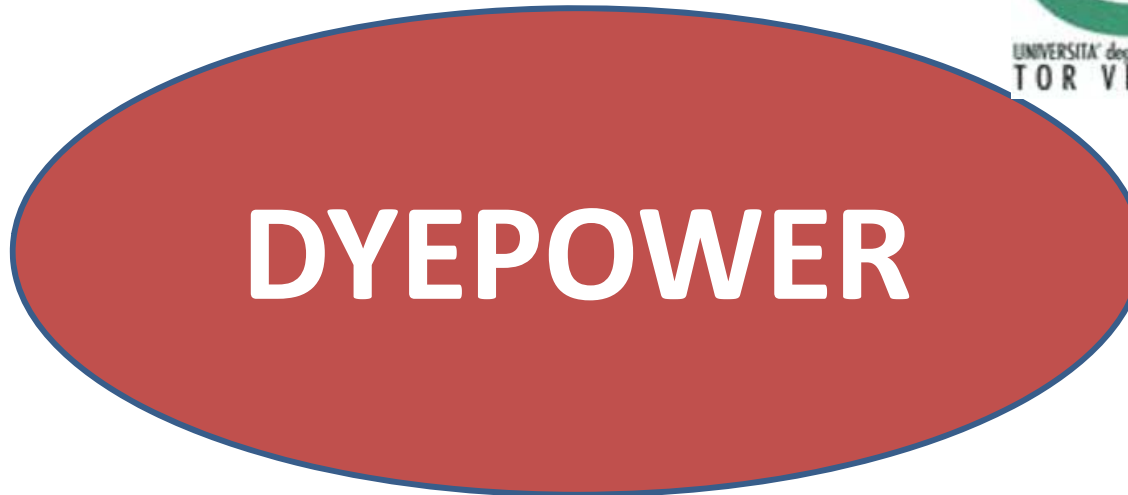
Facade DSC photovoltaic façade glass can be manufactured on volume production with low impact on a typical glass façade.

Silicon based PV glass Façade has 50-70 Wp/sqm quite comparable with DSC !!!!!

A continuous Glass Façade WITHOUT PV costs 1000 euro/sqm



DYEPOWER Consortium



1 July 2009: Dyepower Consortium has been established

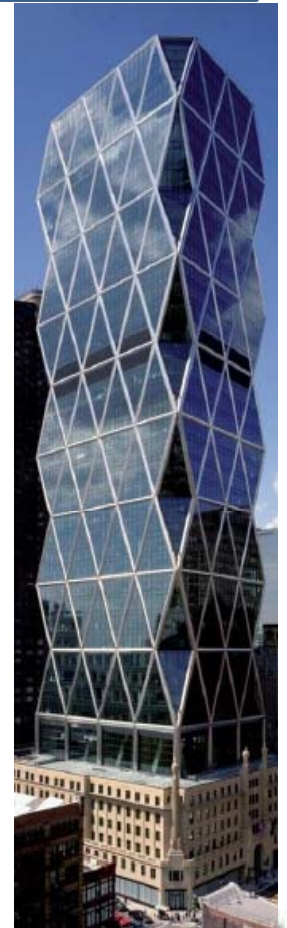


DYEPPOWER: Objectives

The objective of the consortium is the development of an industrial manufacture capability for the fabrication of DSC panels particularly for photovoltaic glass building envelope. This involves identifying materials, processes and technological solutions that will enable these panels to reach the appropriate levels of cost effectiveness, stability and energy efficiency.

Main Milestones

- Prototype of Photovoltaic Glass Envelope based on DSC technology
- Pilot Plan for the production of such DSC Photovoltaic Glass Envelope



Material Costs

Material	Actual Cost / m ²	
Glass + TCO (2x)	25,00 €	
TiO ₂ paste	20,00 €	→ 7 euro
Pt paste	3,00 €	
Dye	30,00 €	→ 5 euro
Sealing paste	2,00 €	
Conductive paste	4,00 €	
electrolyte	10,00 €	→ 3 euro
external sealing	5,00 €	
other	1,00 €	
TOT.	100,00 €	TOT 55 euro

In few years
after material scaling up

For 50 W / m² panel we have a cost of 2 euro/watt of materials considering an annual production of 10.000 m².

This reduces to 1.6 euro/Wp for a production of 100.000 m²

Dye, TiO₂ paste and Electrolytes are under industrial scaling up and we expect a strong reduction of their retail prices (< 1 euro/watt).

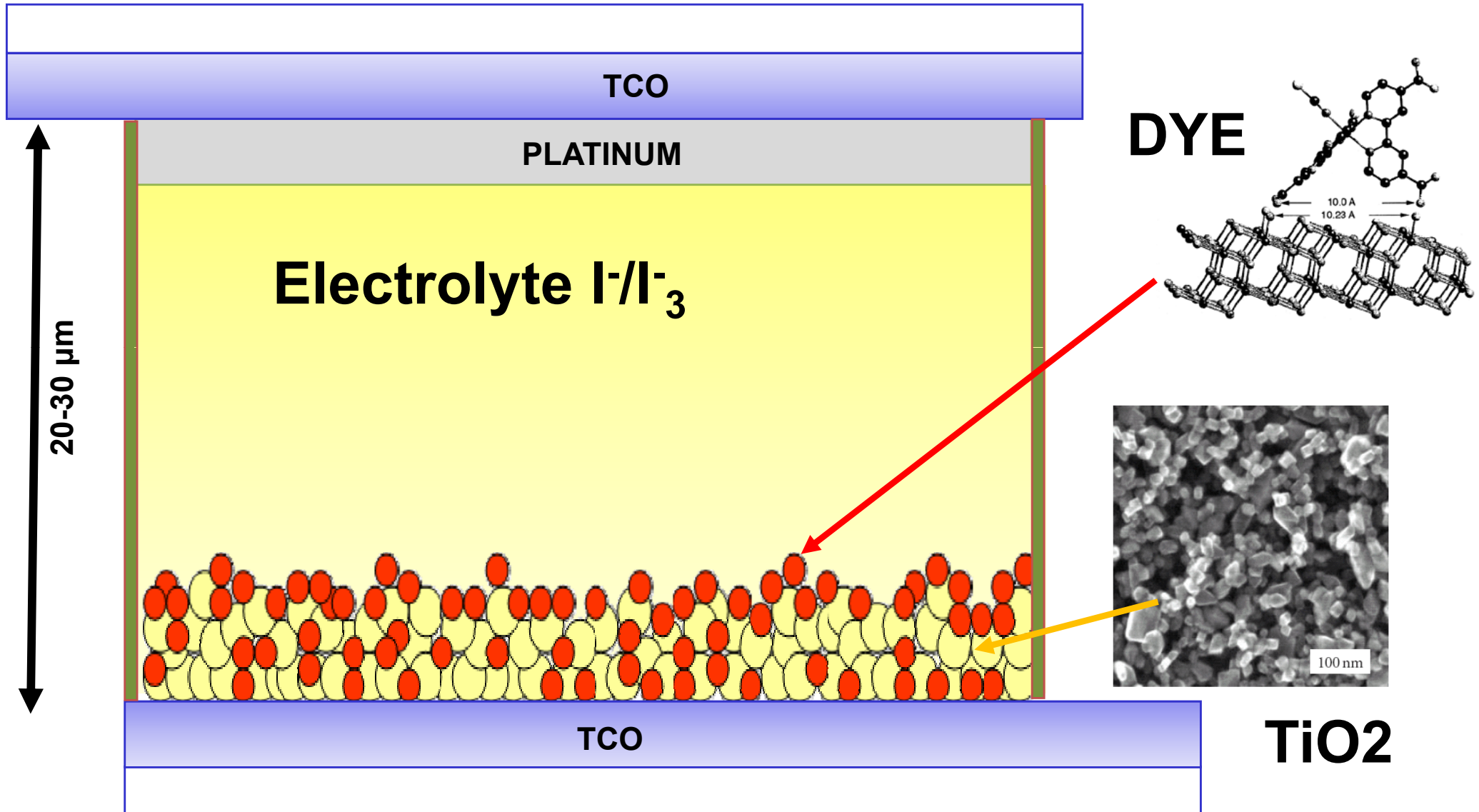
More critical is the situation for the glass-TCO where no strong reduction of the price is forecast (Pilkington)



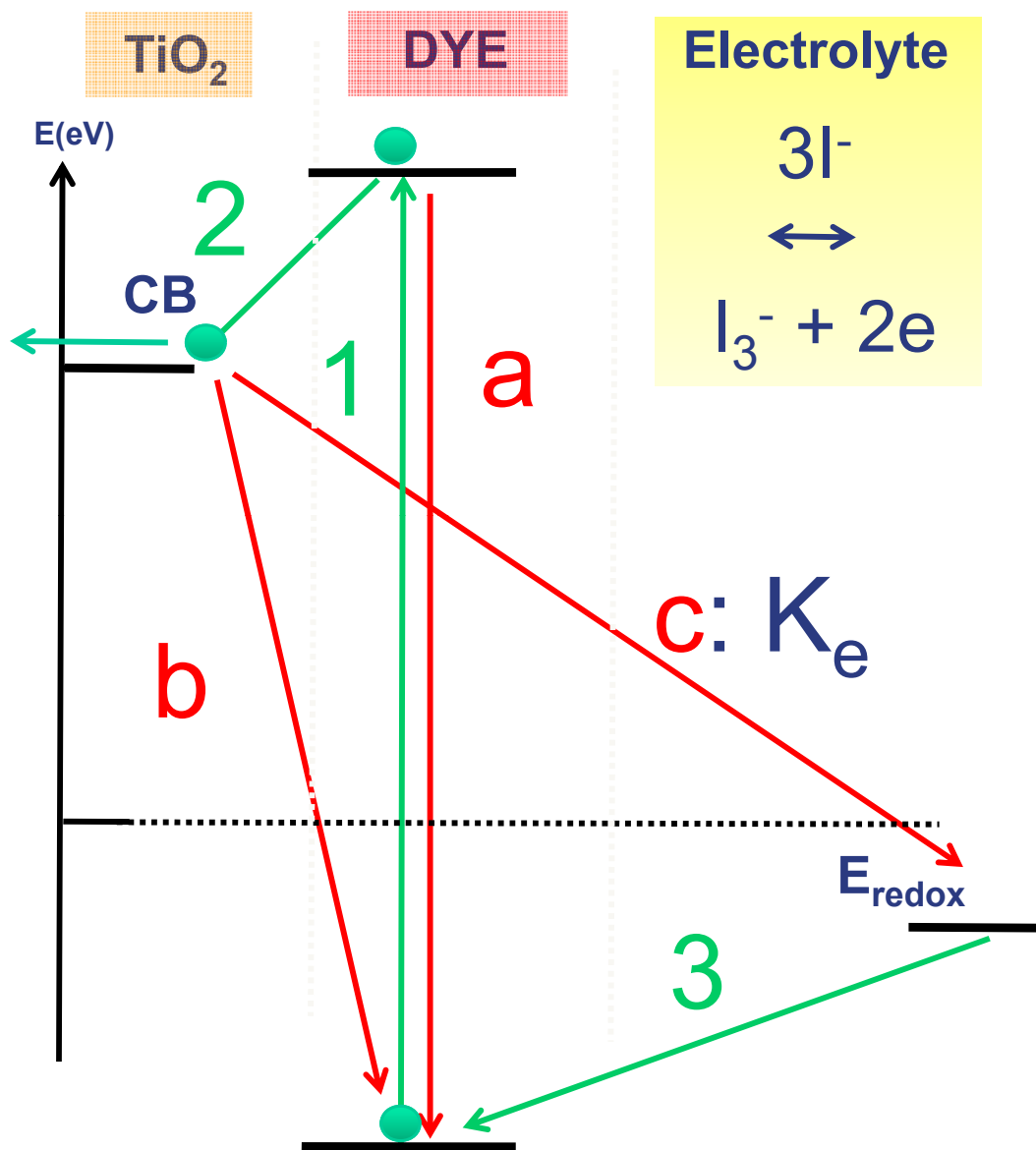
Computer Aided Design (CAD): Simulation of DSCs



Scheme of a DSC



Kinetic: Important rate constants



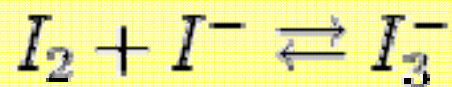
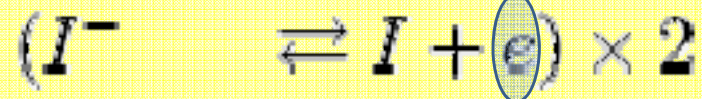
1. Dye Excitation ✓
2. Electron Injection into TiO₂ Conduction Band
3. Oxidation of the electrolyte

- a. Dye relaxes into its ground state ✗
- b. Dye regenerated by TiO₂
- c. Electrolyte Reduces at TiO₂ surface



Oxidation-Reduction reactions

DYE



ELECTROLYTE



COUNTER ELECTRODE



Transport: a challenging issue

- ❖ Two different phases involved (TiO_2 and electrolyte)
- ❖ Three charge carriers contribute to the current (e , I^- , I_3^-)
- ❖ Handling of the electrolyte regeneration at the cathode

The electron in the conduction band exhibits anomalous properties:

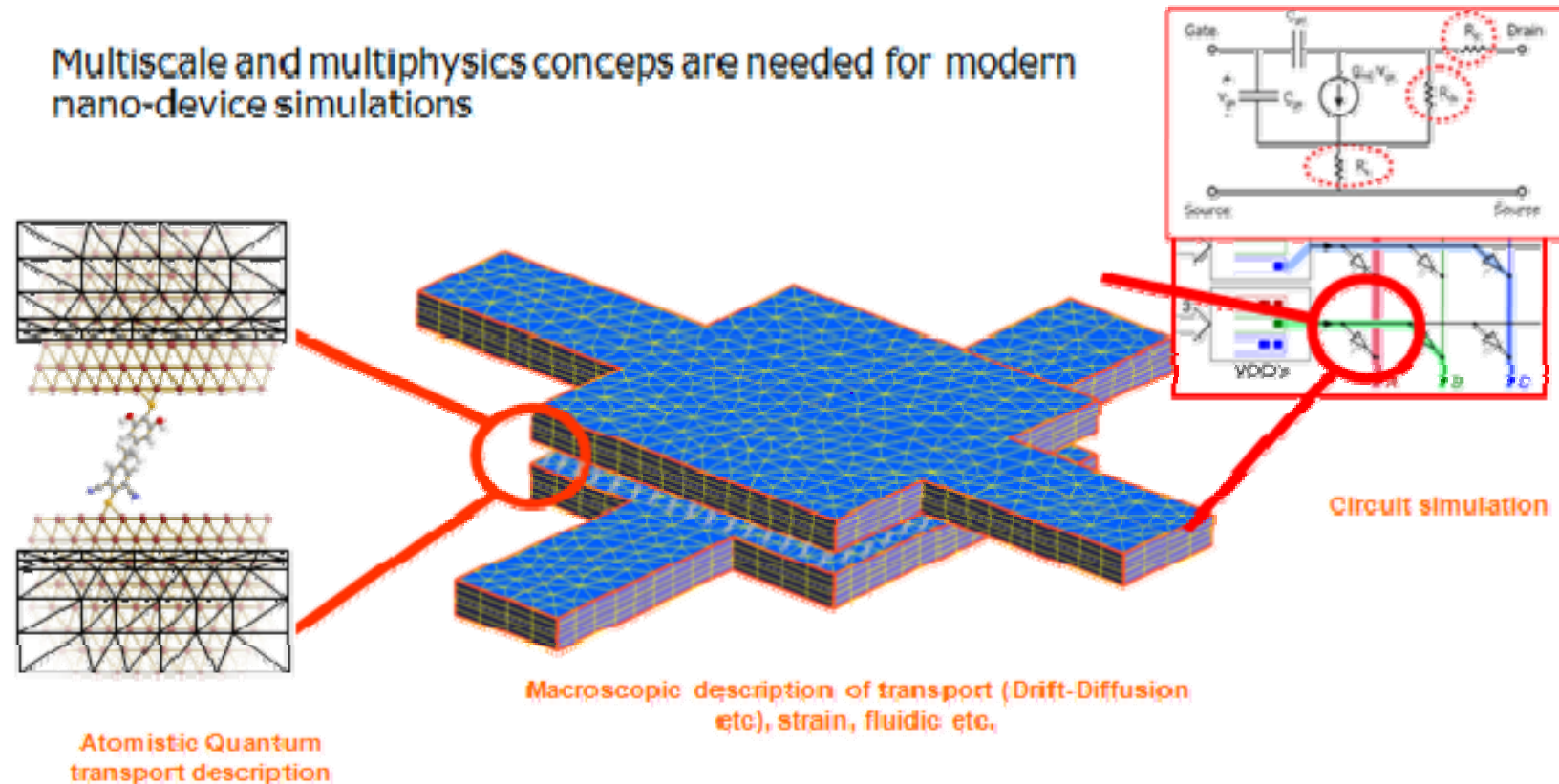
- ❖ Extremely long propagation time (ms)
- ❖ Non-exponential current and recombination transient
- ❖ Intensities-dependent response times



Physical Device Modeling - TiberCAD

DSC devices are getting complicate (3D, Tandem, Back contact etc. etc.)

TiberCAD is a multiscale device simulator : www.tibercad.org



TiberCAD have been extended to account also for simulation of DSC



Theoretical model

Cathode:

$$-e\mu_r n_r \nabla \phi_r = \frac{3}{2} \frac{V}{R_L}$$

$$-e\mu_{I_3^-} n_{I_3^-} \nabla \phi_{I_3^-} = -\frac{1}{2} \frac{V}{R_L}$$

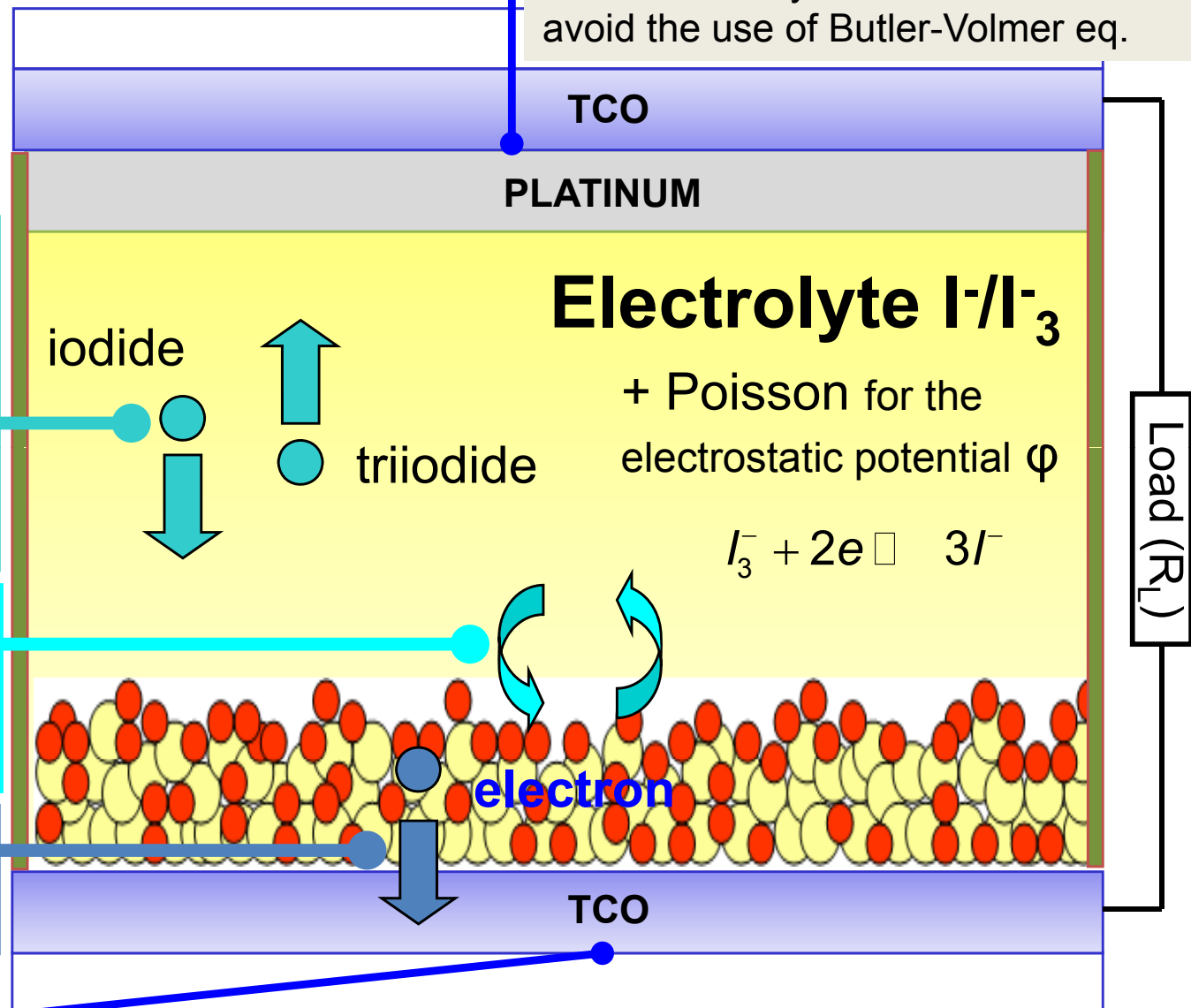
$$\nabla \cdot (\mu_{I_3^-} n_{I_3^-} \nabla \phi_{I_3^-}) = \frac{1}{2} (R - G)$$

$$\nabla \cdot (\mu_r n_r \nabla \phi_r) = -\frac{3}{2} (R - G)$$

$$R = k_e \left[n_e \sqrt{\frac{n_{I_3^-}}{n_r}} - \bar{n}_e \sqrt{\frac{\bar{n}_{I_3^-}}{\bar{n}_r^3} n_r} \right]$$

$$\nabla \cdot (\mu_e n_e \nabla \phi_e) = (R - G)$$

Local boundary conditions allows to avoid the use of Butler-Volmer eq.



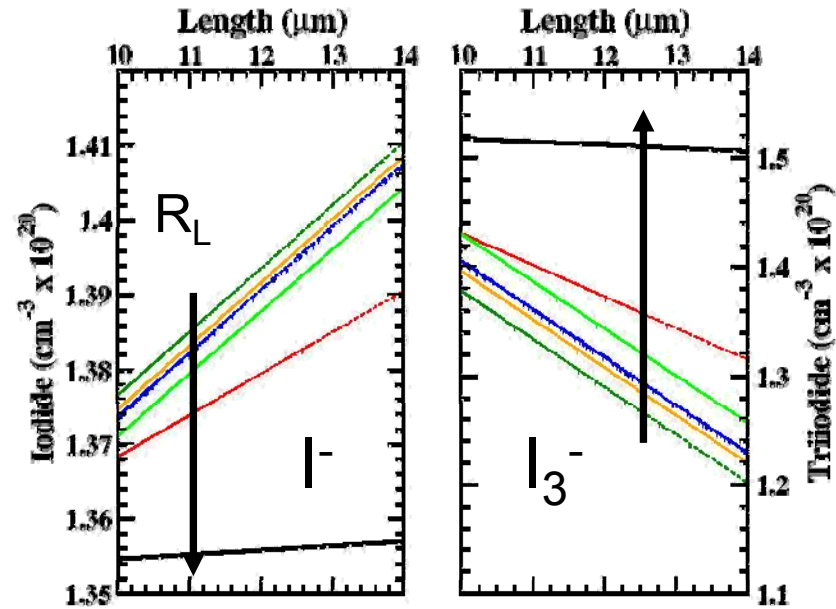
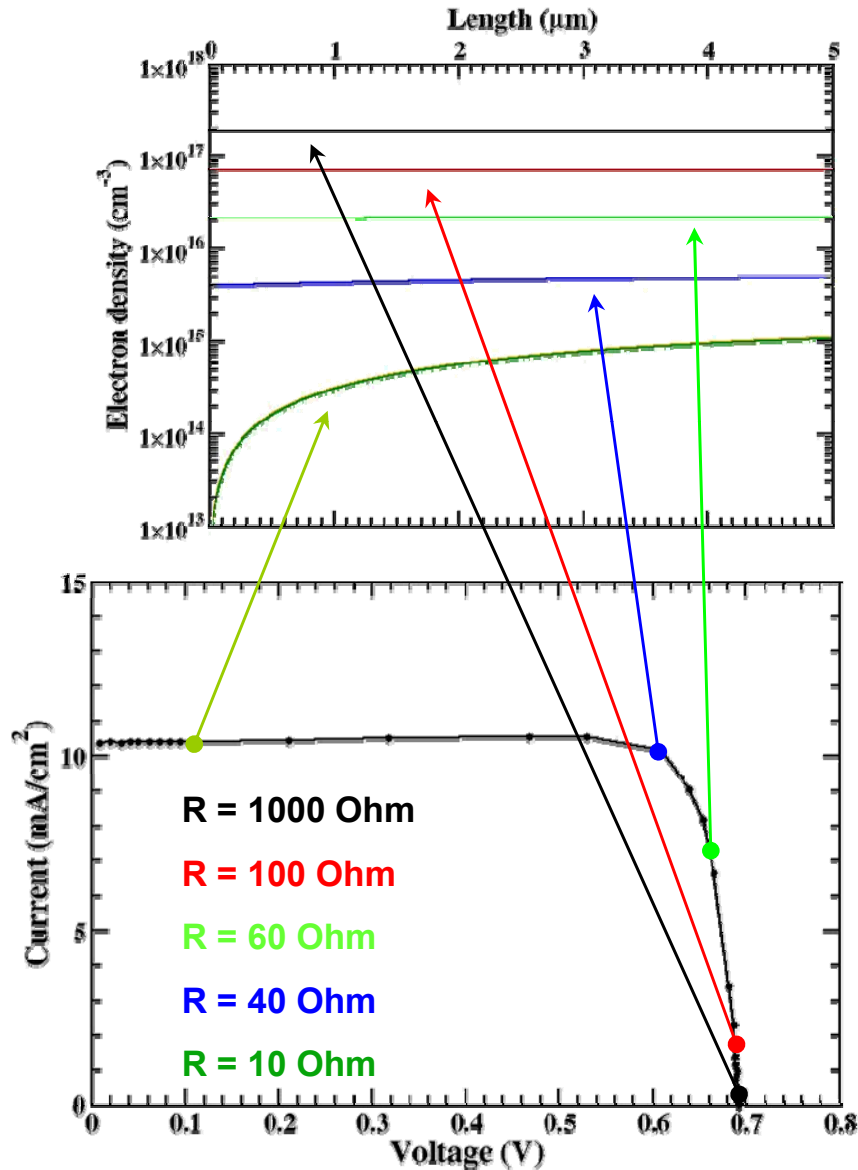
Anode:

No ionic current: $\nabla \phi_{I_3^-} = \nabla \phi_r = 0$ Ohmic contact: $\nabla \phi = 0$



Diffusion driven device

- ❖ The DSC is driven by a concentration unbalance between electrons and redox pair induced by the illumination. The drift component is negligible.



Concentration profile in the electrolyte region close to the cathode

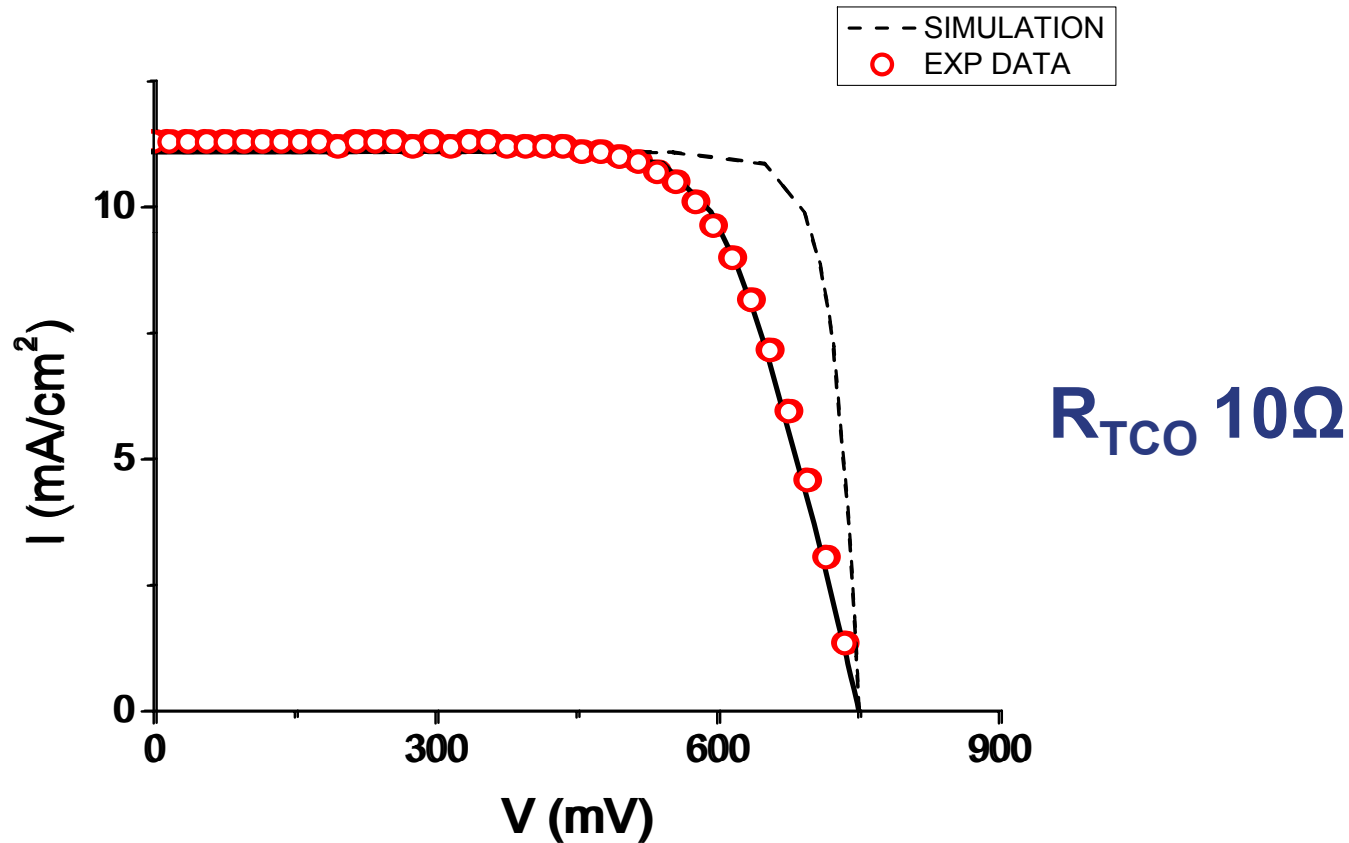
- ❖ The effect on the redox pair is much smaller due to the larger concentration. On the other hand the bottleneck results to be the electrons in the oxide.



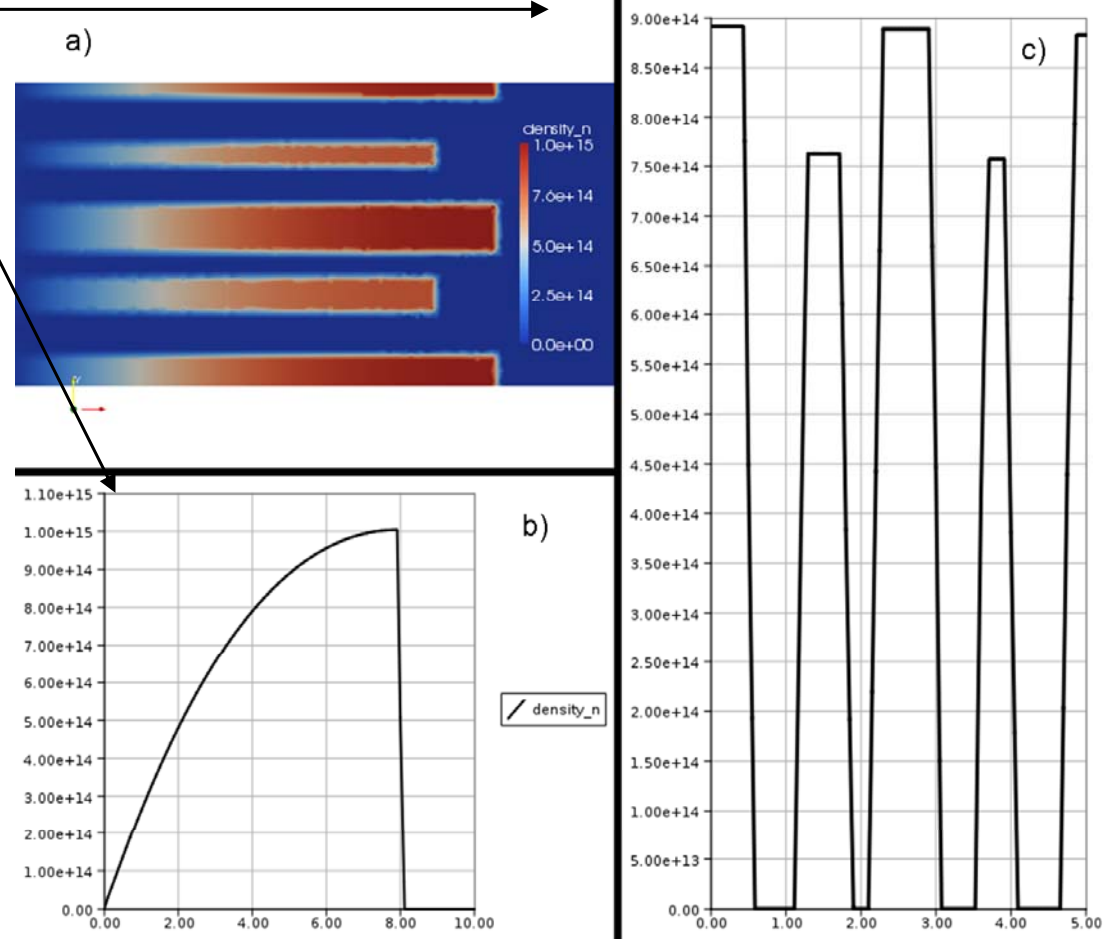
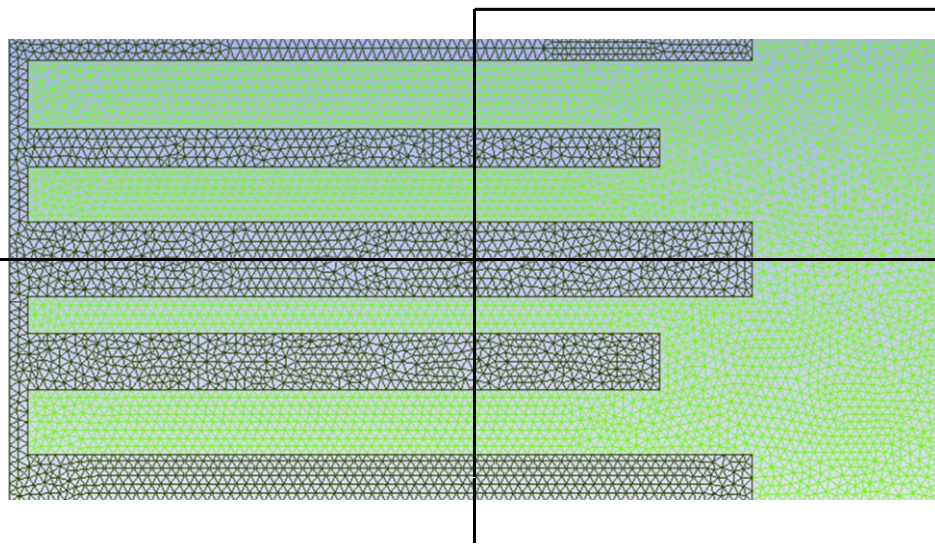
Fit to experimental data

Fitting of sperimental I-V curve of a standard cell (10 μm)

PARAMETERS: $\mu_e = 0.8 \text{ cm}^2/\text{Vs}$
 $K_e = 10^3 \text{ 1/s}$



From 1D model to 2D...

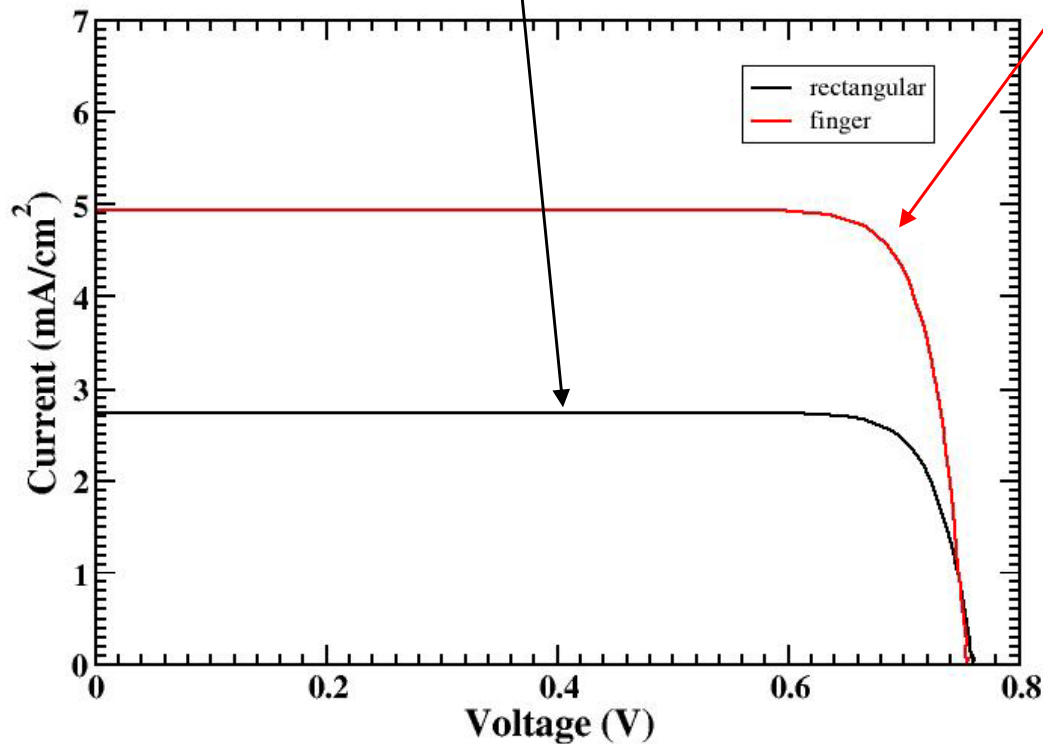
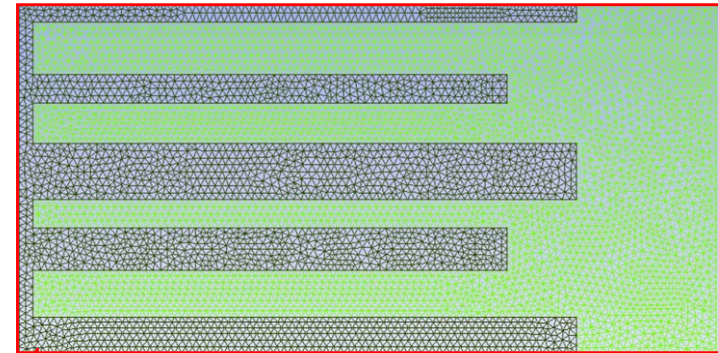
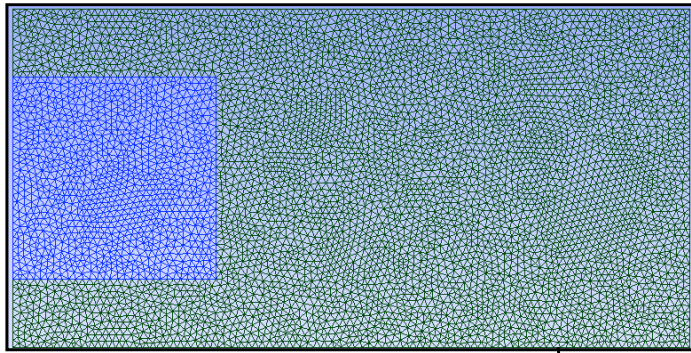


- ❖ Electron density concentration in a fingered mesoporous structure
- ❖ Mesh: 11,400 elements

Several different topology can be investigated, with particular interest to the shape of the titanium oxide and the position of the photoanode and platinum layer.



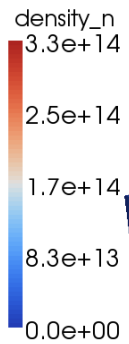
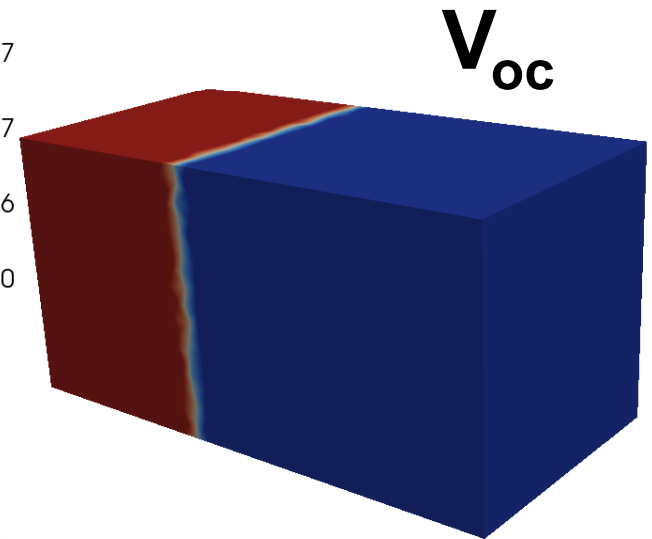
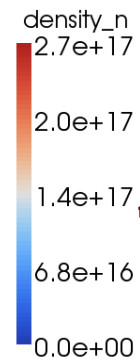
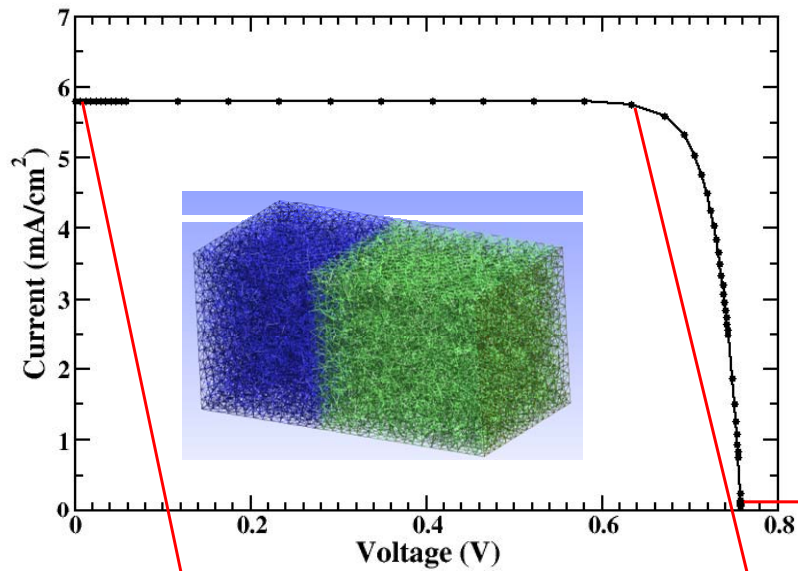
From 1D model to 2D...



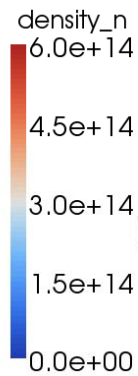
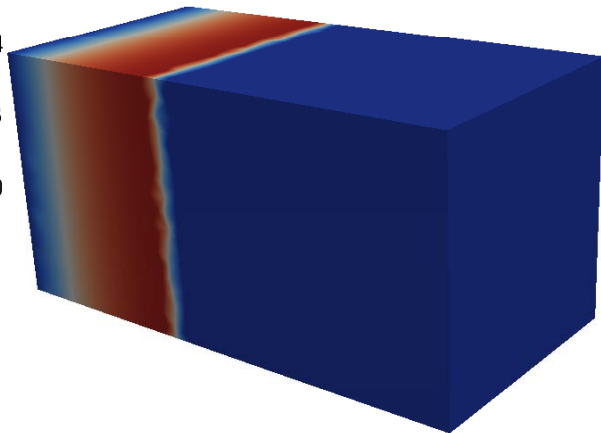
- ❖ Interesting effects can be seen changing the topology of the cell, especially the titanium oxide
- ❖ two different geometries are shown with the same parameters but different topology
- ❖ The lack of TiO₂ for the rectangular geometry reduces the total current



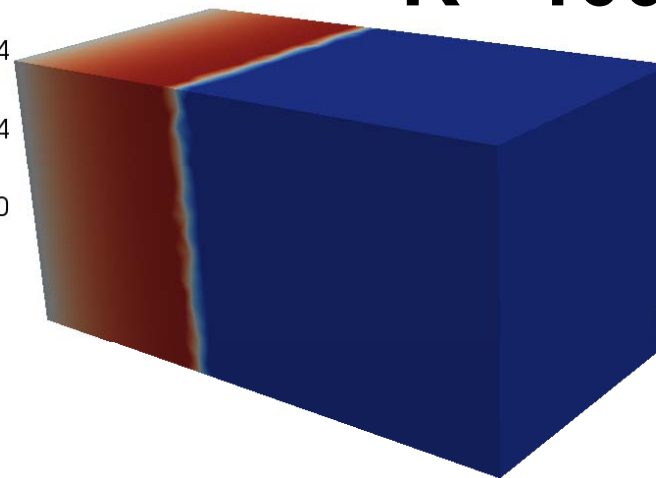
.... up to 3D



J_{sc}



R = 100 Ω



Conclusions

- DSC represents a new way for silicon free photovoltaics. Large tunability, easy manufacture, low plant and material costs.
- Large area devices is not trivial and many issues are still open
- Industrialization is very close
- Scale up of the materials with price reduction is request.
- Many applications. DSC is well suited for building glass envelopes



Acknowledgments

- UniFerrara (Bignozzi team)
- UniRoma 1 (Decker team)
- UniTorino (Viscardi-Barolo team)
- DYESOL



REGIONE LAZIO



Tor Vergata team

www.chose.it

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T. Denaro (Dyesol)

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