



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



2234-25

**Meeting of Modern Science and School Physics: College for School
Teachers of Physics in ICTP**

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Photovoltaics and sun energy

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Photovoltaics and sun energy

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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



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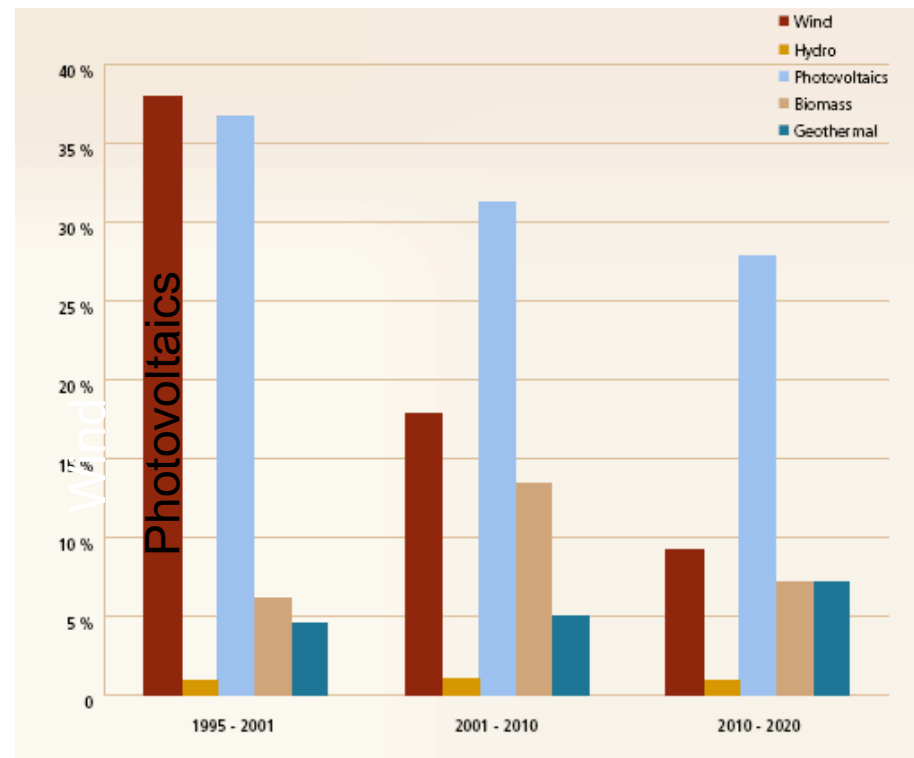


Renewable energy objectives (2020)

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



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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



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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.

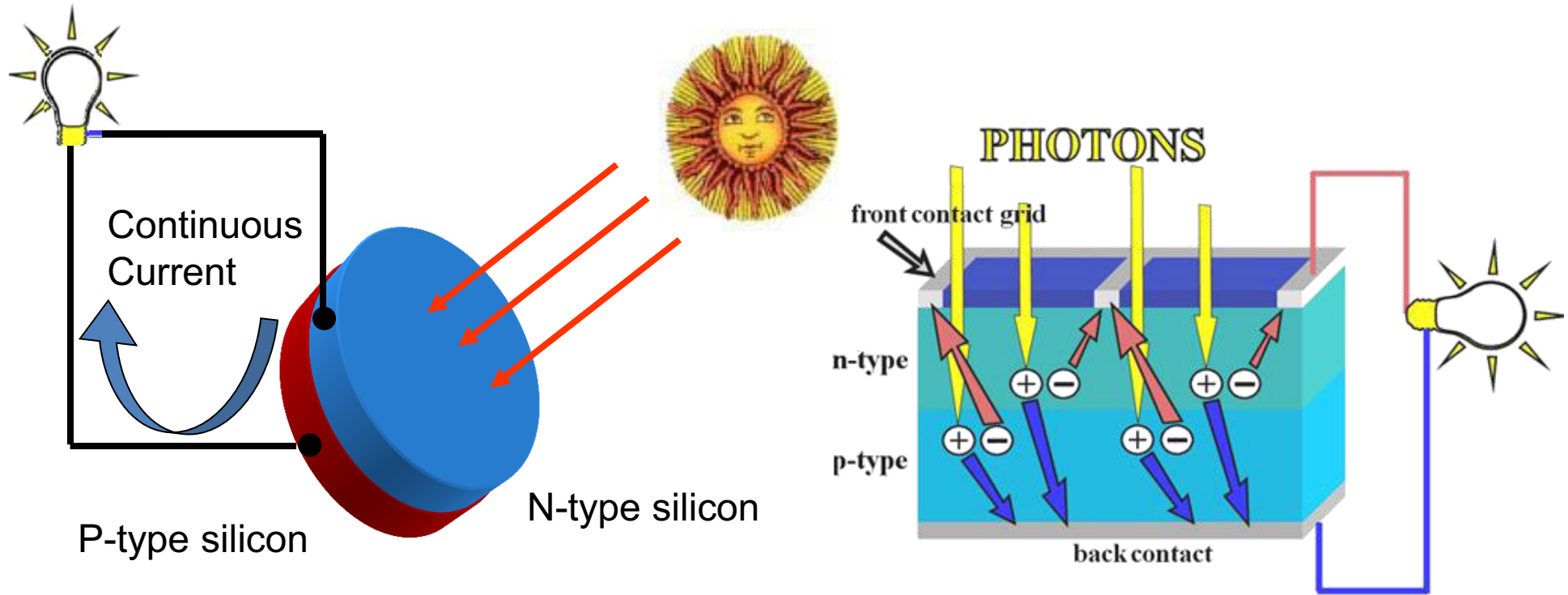
Besides increasing the efficiency of silicon modules, EPIA identifies the development of new materials and concepts as a crucial step for achieving these objectives.

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.



Photovoltaic cell: working principle



“Conventional” photovoltaic cells are based p-n junction between semiconductors.



Photovoltaic cell: short history



1941

Russell Ohl (Bell Labs) discover the silicon p-n junction and the effect of light on the junction

1954

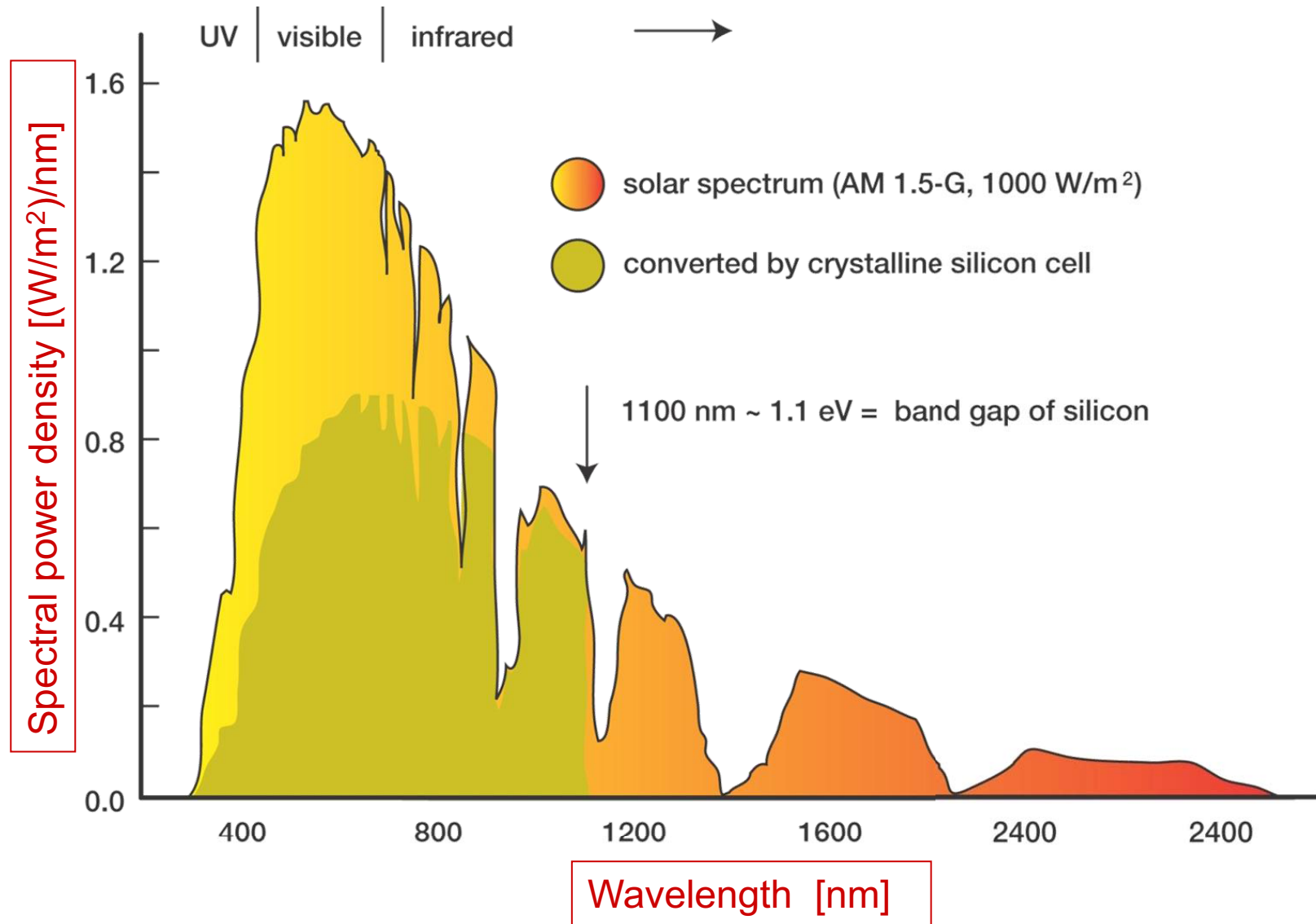
Bell Labs researchers Pearson, Chapin, and Fuller demonstrated the photovoltaic cell with 4.5% efficiency



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Solar Spectrum



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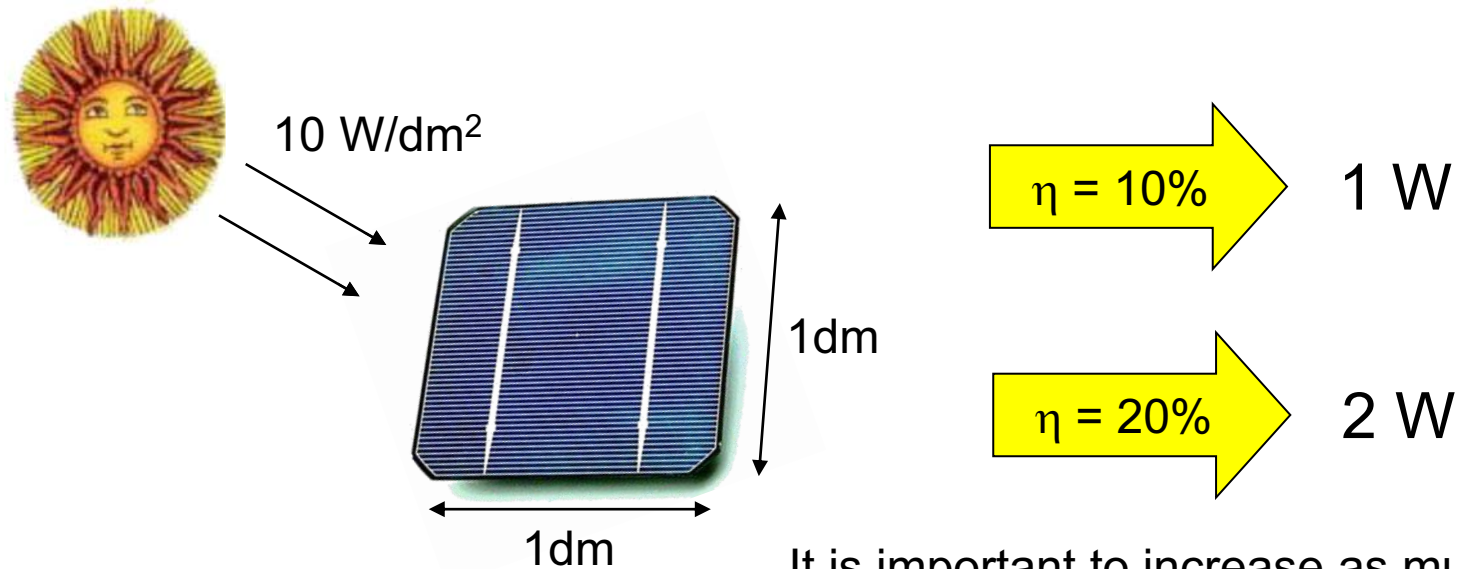


Efficiency

One of the most important parameters of the photovoltaic cell is the efficiency defined as:

$$\text{EFFICIENCY} = \eta = \frac{\text{Max electrical power produced by the cell}}{\text{Total solar power impinging on the cell}}$$

Example:

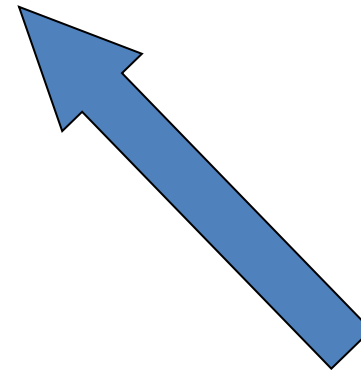
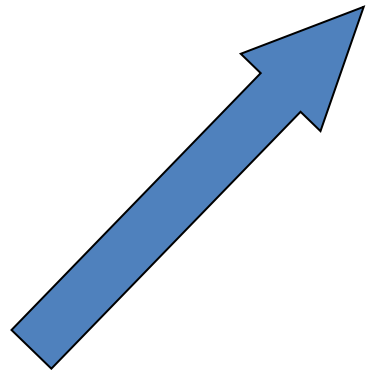


It is important to increase as much as possible the efficiency.



Which are the factors influencing the cell efficiency ?

EFFICIENCY



MATERIALS

Silicon
GaAs
CdTe
.....
.....

TECHNOLOGY

Single junctions
Multiple junctions
.....
.....



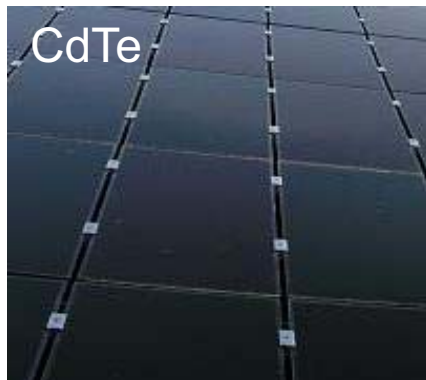
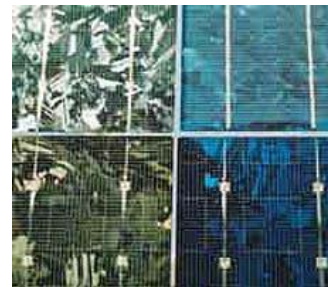
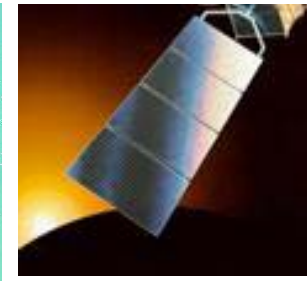
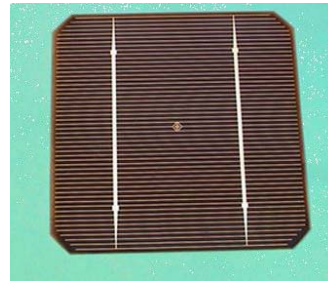
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Materials for photovoltaic cells

Bulk semiconductors

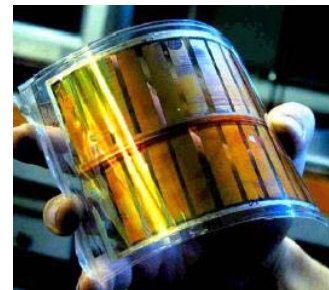
- **Silicon**
 - Single crystal
 - Multi crystalline
- **Gallium arsemide (GaAs)**
- **Other III-V semiconductors**



CdTe

Thin Films semiconductors

- Amorphous silicon (a-Si)
- Cadmium telluride (CdTe)
- Copper-Indium diselenide (CuInSe₂, o CIS)
- Coper-Gallium-Indium diselenide (CIGS)



Organic and hybrid materials

- Small molecules
- Polymers
- Dye Sensitized Solal Cell



Beyond the Shockley-Queisser limit

The maximum thermodynamic efficiency for the conversion of unconcentrated solar irradiance into electrical free energy in the radiative limit, assuming detailed balance, a single threshold absorber, and thermal equilibrium between electrons and phonons, was calculated by Shockley and Queisser in 1961 to be about 31%.

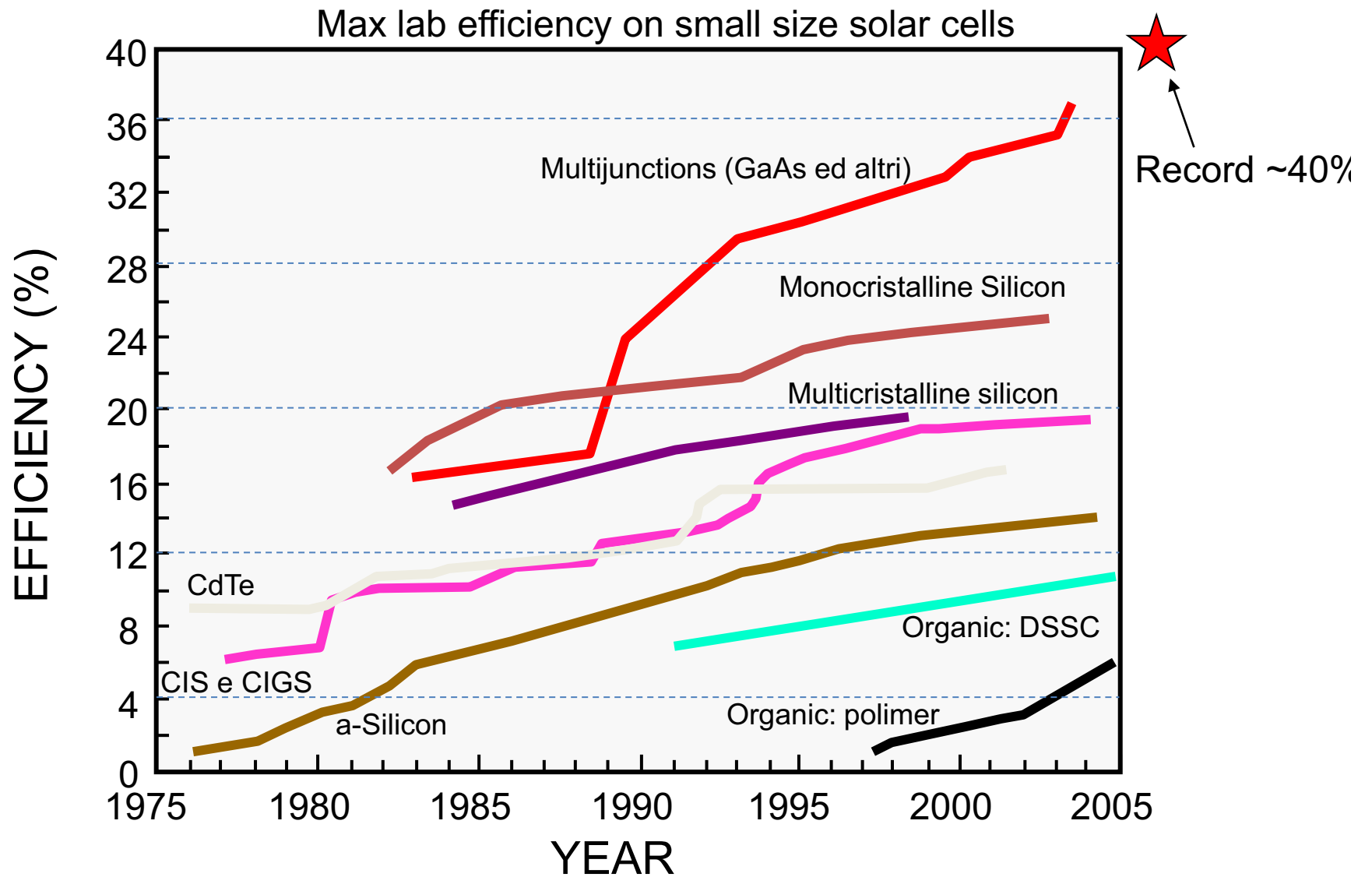
W. Shockley and H. J. Queisser. *J. Appl. Phys.* 32 (1961) 510.

What do we do to achieve efficiencies $> 31\%$?

- Concentration
- Multijunction
- No thermal equilibrium



Lab Cell efficiency



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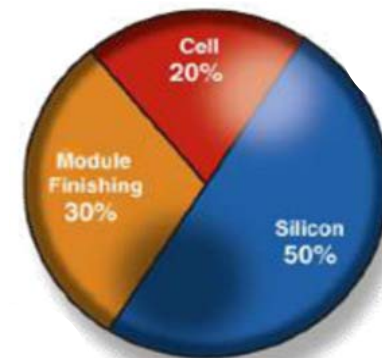
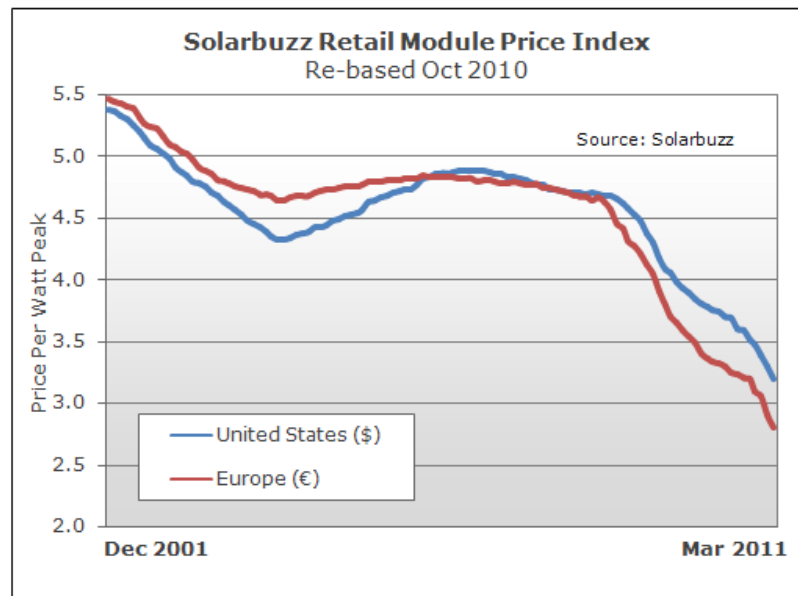
Energy from the sun



To satisfy the electricity needs of a typical family one needs 3kWp PV system, i.e. ~20m² of photovoltaic surface (assuming system efficiencies of 15%).

COST → 12.000 euro

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



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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

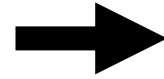


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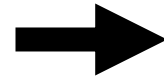
“New” manufacture processes

Conventional Electronics

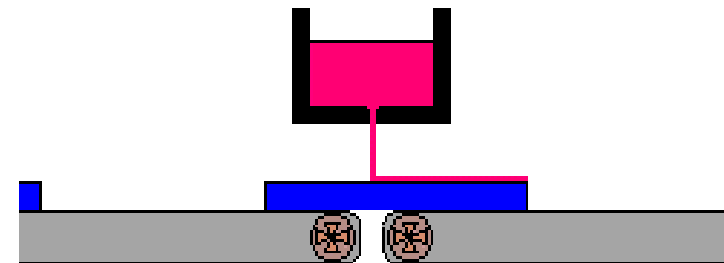
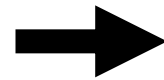
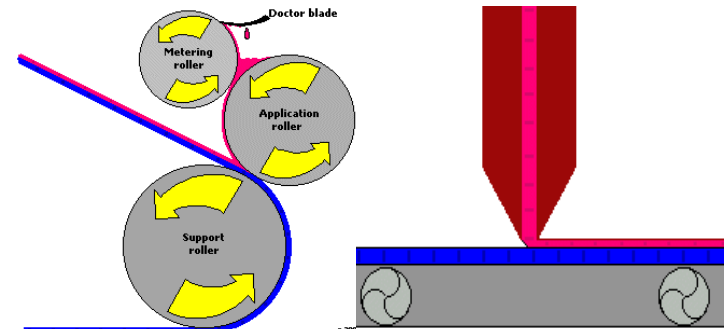


Organic Electronics

**Conventional
semiconductor industry**



Printing methods



**High temperature, doping,
vacuum**

Very Large enterprises



Liquid deposition

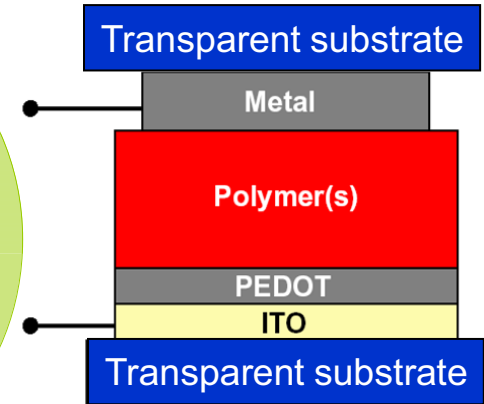
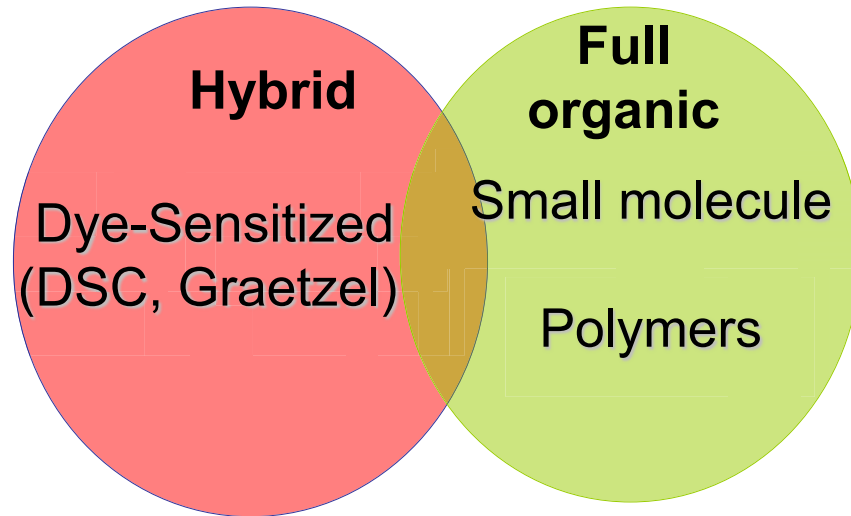
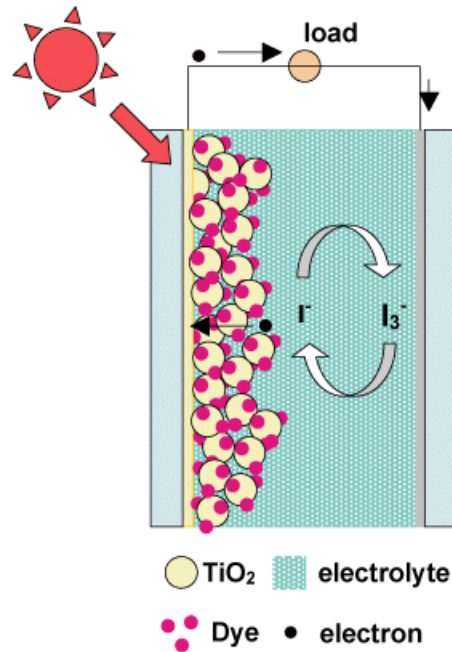
**Small Medium
enterprises /
local productions**



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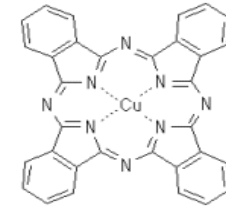
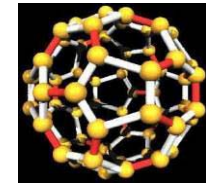
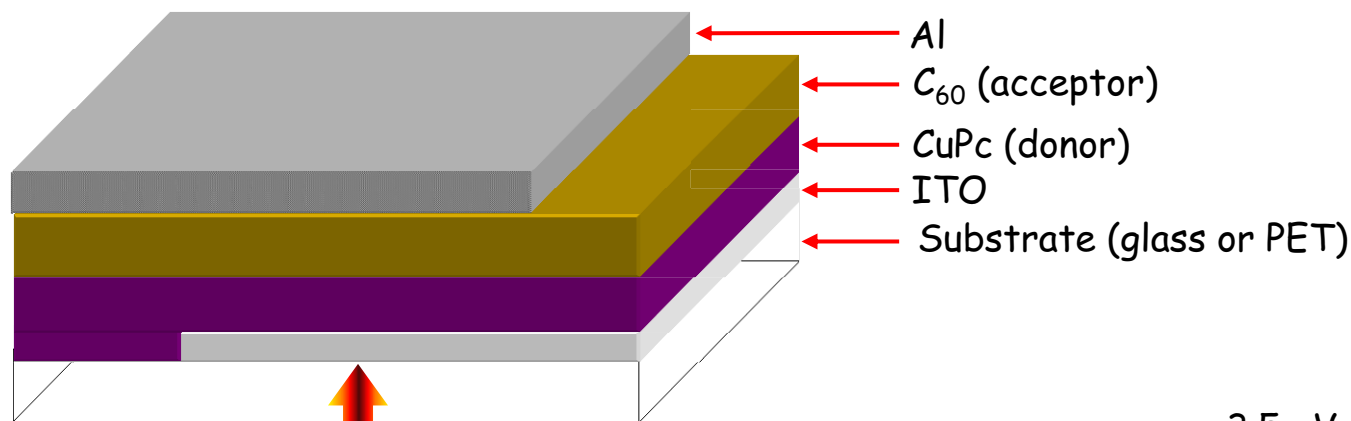
Organic photovoltaics



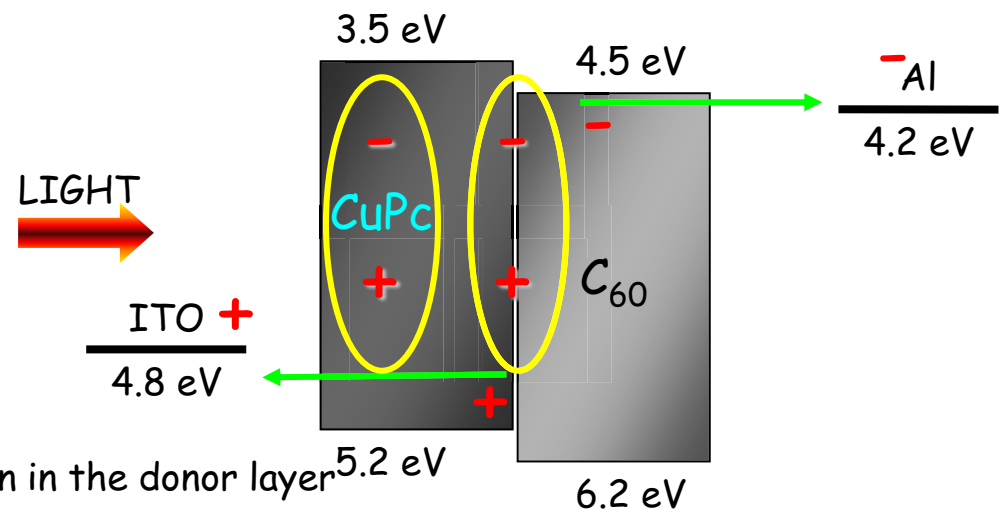
Type	Max lab efficiency	Stability	R&D
Hybrid Dye Sensitized (Graetzel)	~ 11-12%	20 years	University and industry
Full organic solar cells	~ 8%	3 years	University and industry



Small Molecules Organic Solar Cell



How it works



- 1) Creation of an exciton via absorption of a photon in the donor layer
- 2) Diffusion of the exciton to the interface with the acceptor.
- 3) Dissociation of the exciton in a e^- and a h^+ at the interface (charge transfer).
- 4) Transport of the free charges to the opposite electrodes (electrons towards Al and holes towards ITO).

Charge separation at the 2D interface between donor and acceptor



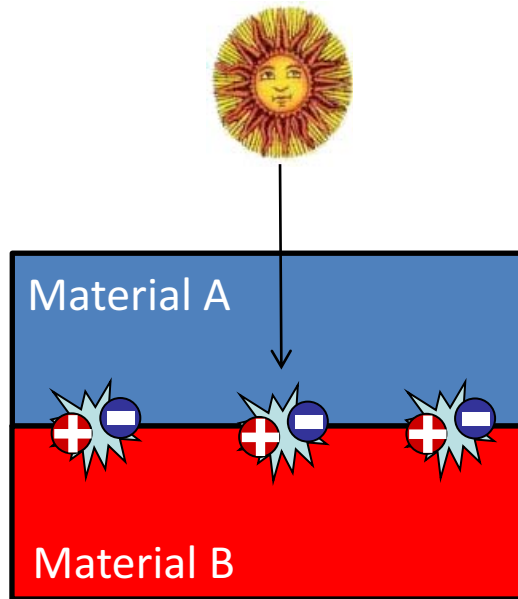
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Breakthrough concept: bulk heterojunction

Heeger - Friend

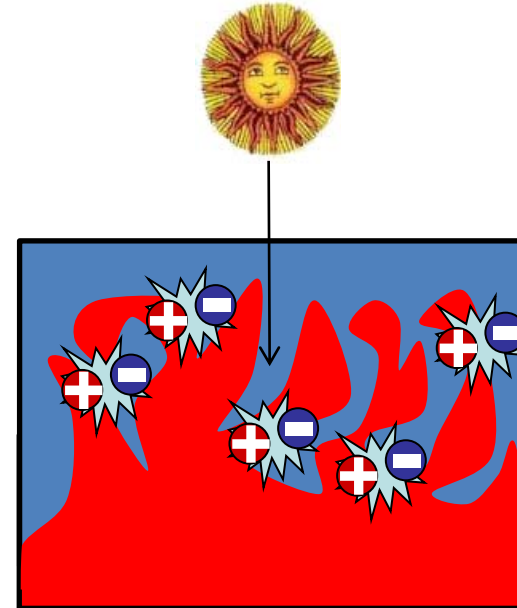
Classical Heterojunction



Interface between A and B materials is two dimensional (2D)

After absorption of light, e-h dissociate at the interface

Bulk Heterojunction



Interface between A and B material tends to be three dimensional (3D) !!!

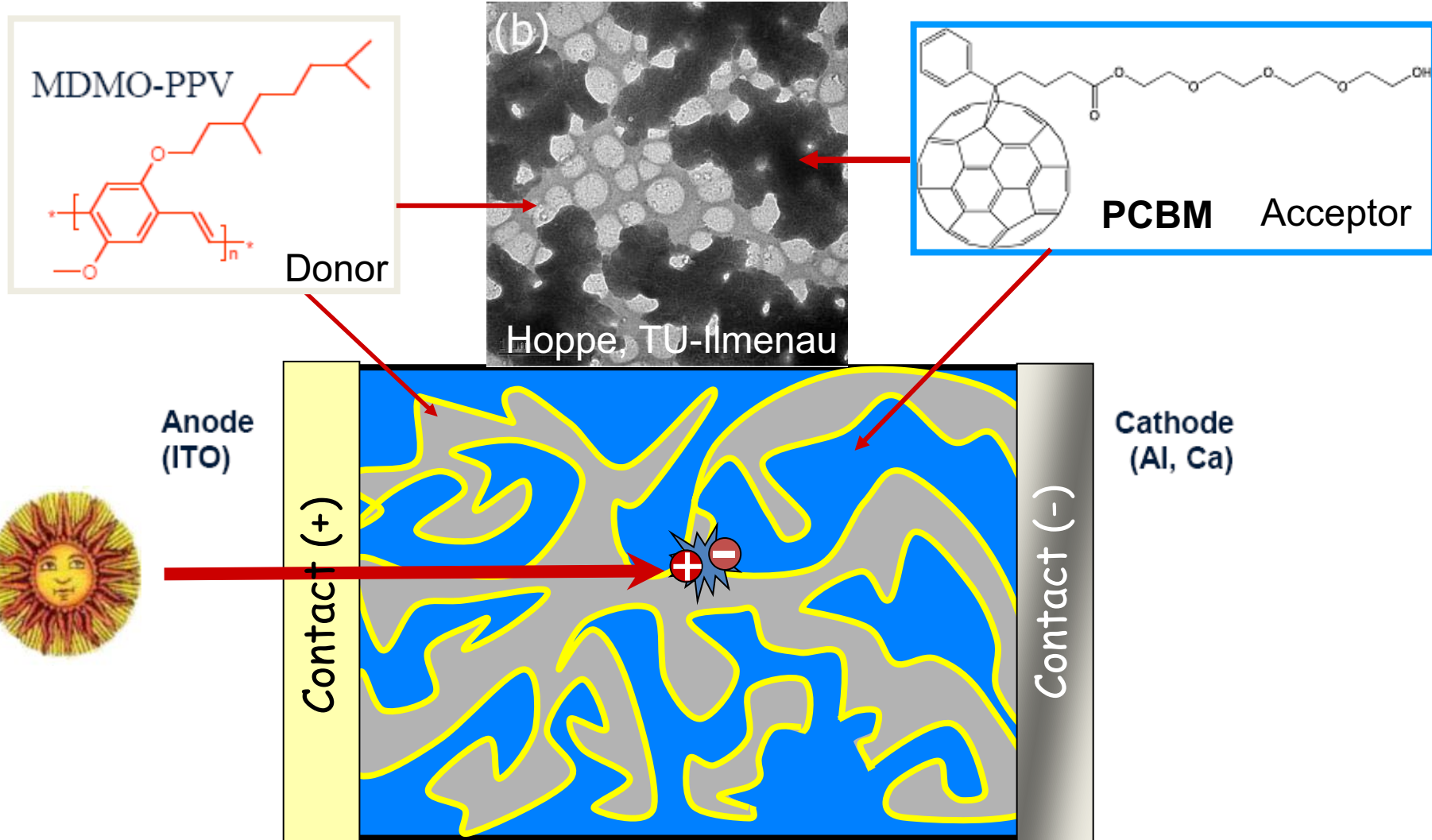
Absorption surface and dissociation interface increase. More efficient



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Polymer Solar Cells (Bulk heterojunction)



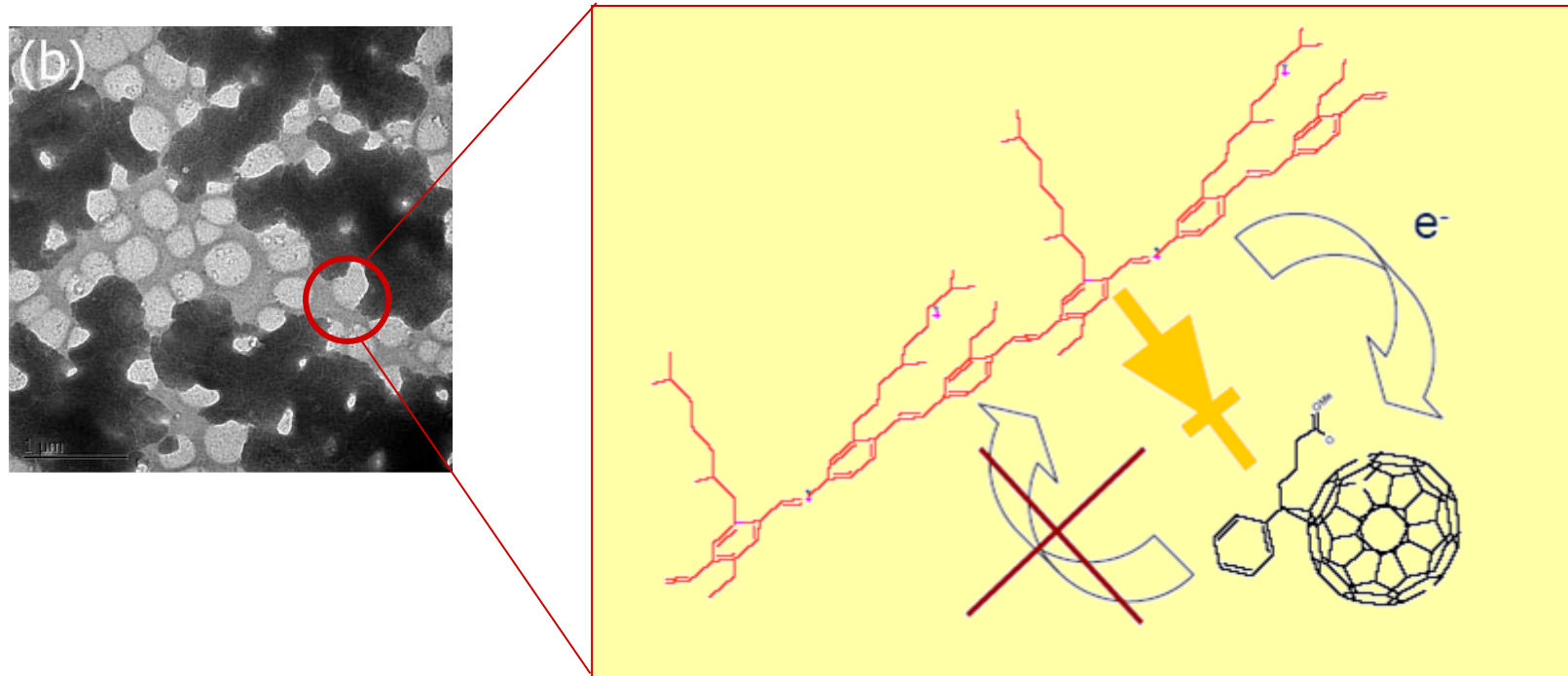
Intimate mixture of electron donor and acceptor materials

Charge separation at the distributed interface + percolation to the contacts

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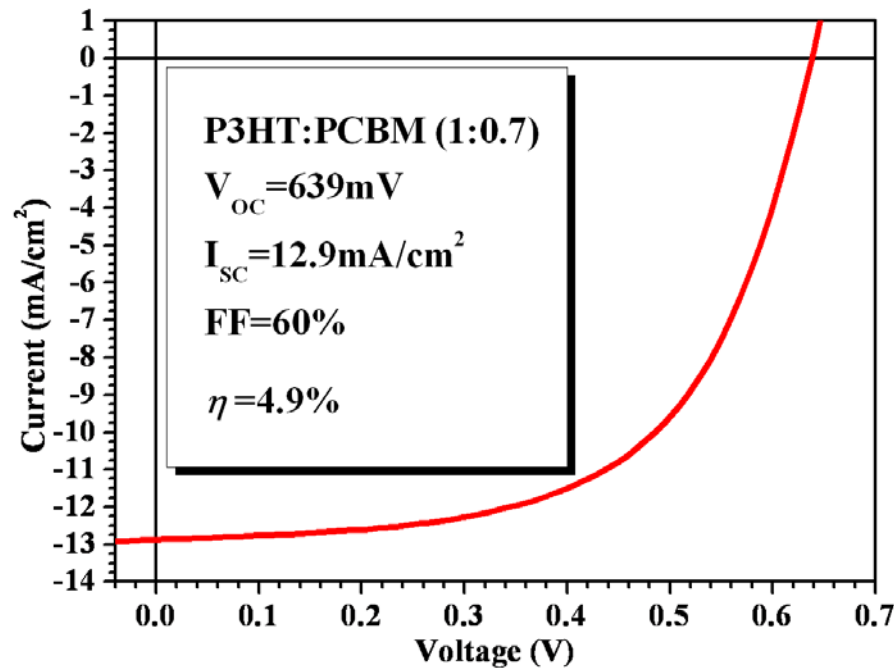
Bulk heterojunction=distributed molecular diode



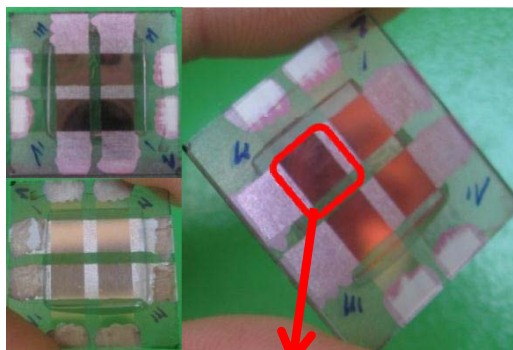
- Any PV device must have a rectifying interface which separates charges (== current/voltage asymmetry == diode).
- A “bulk heterojunction” is the homogenous distribution of molecular diodes (hetero interfaces) within a semiconductor bulk.



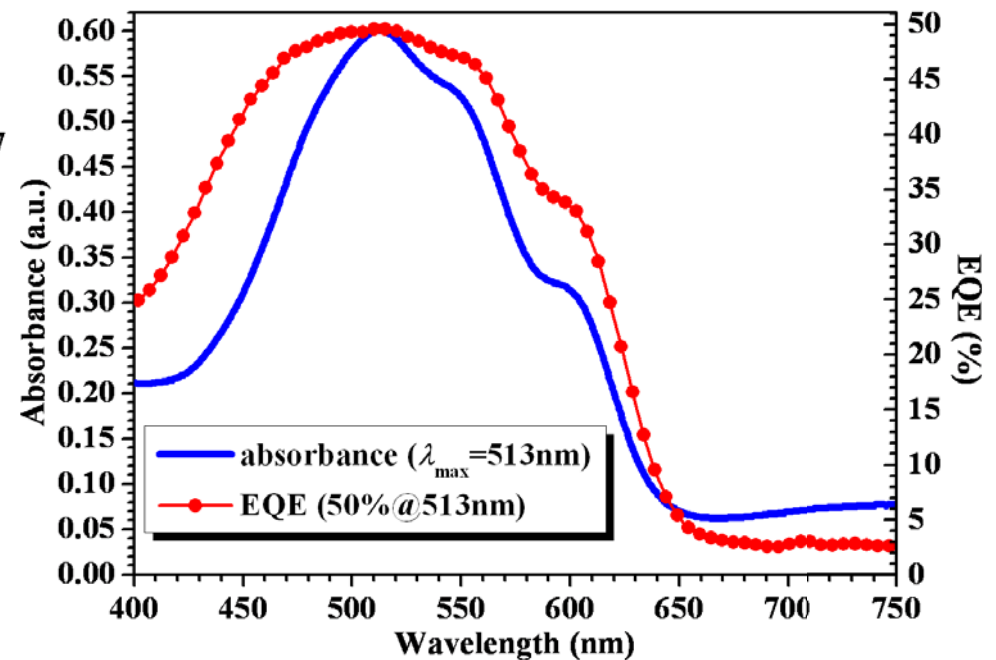
Organic Solar Cell (OSC)



Best realized device ($\eta \sim 5\%$)
Pedot:PSS (2000rpm \rightarrow drying at $150^\circ\text{C} \times 10\text{min}$)
P3HT:PCBM (400rpm \rightarrow drying at $\text{RT} \times 2\text{h}$)
Thermal annealing ($150^\circ\text{C} \times 10\text{min}$ after Al)

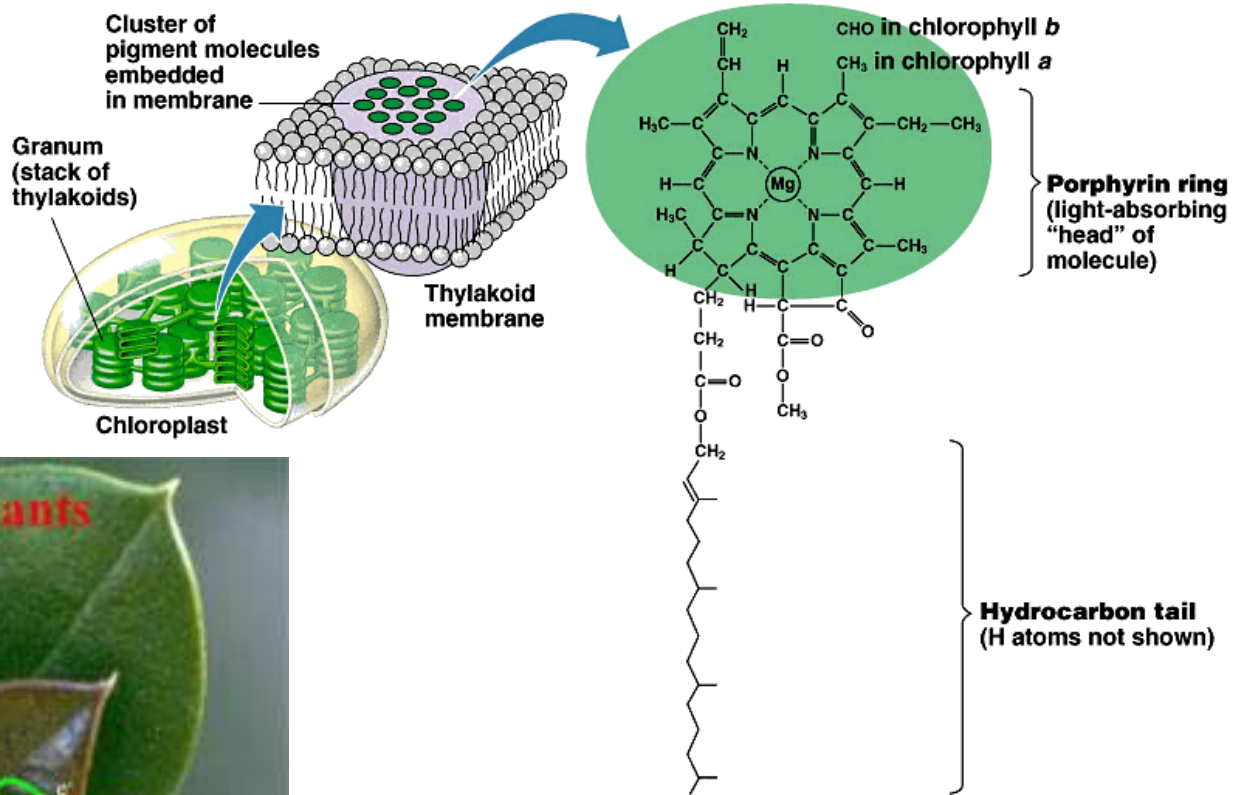


Area $\approx 5 \times 5 \text{mm}^2$



Bio-Inspired Solar Cell

From Photosynthesis to ...



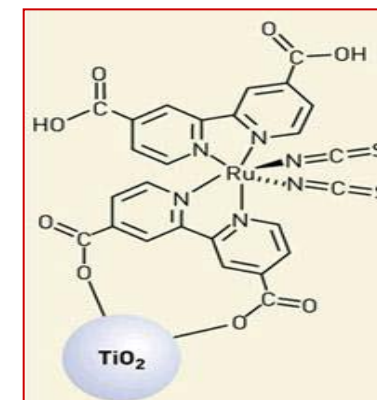
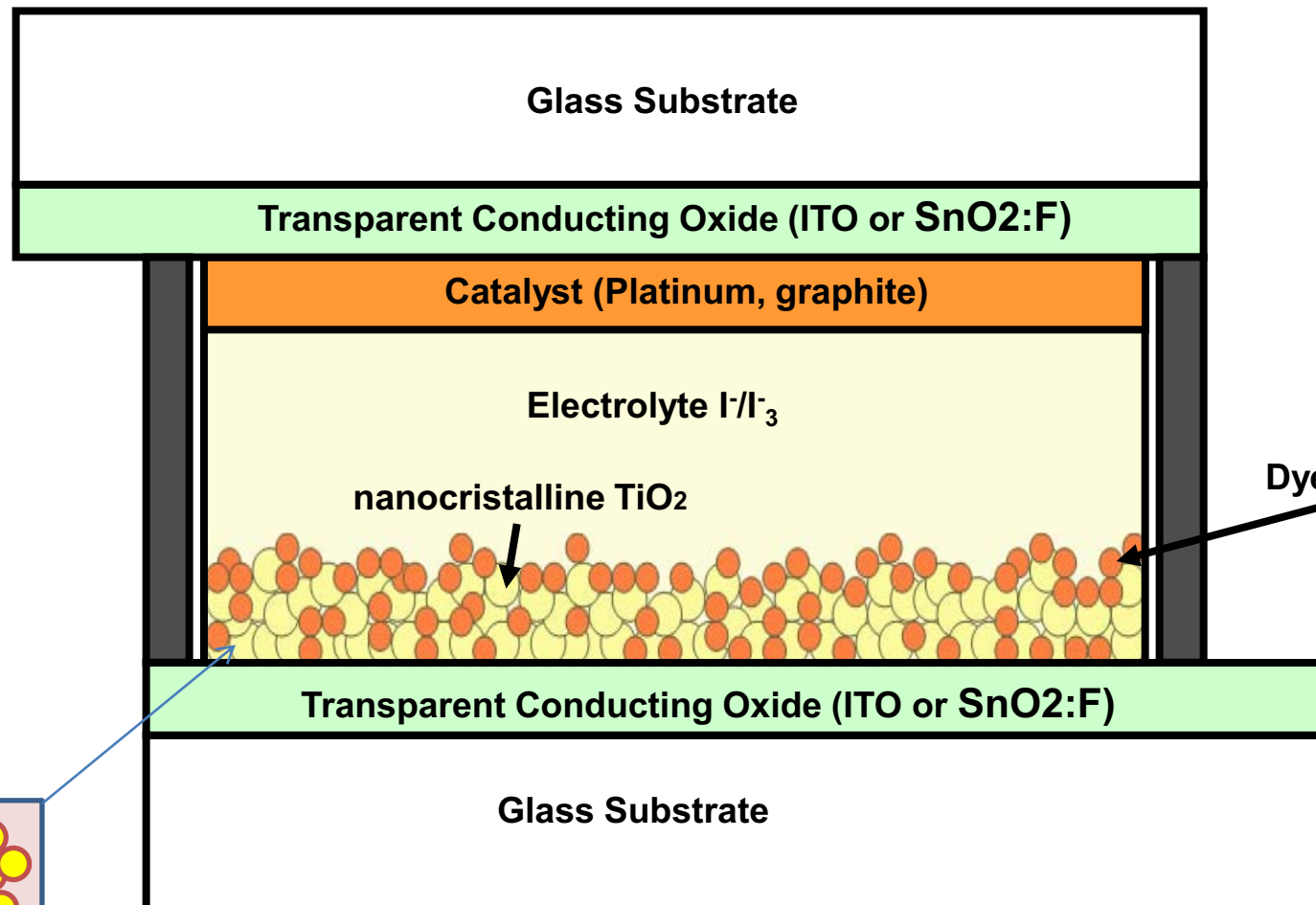
... Dye Sensitized Solar Cells



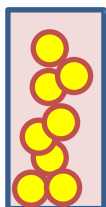
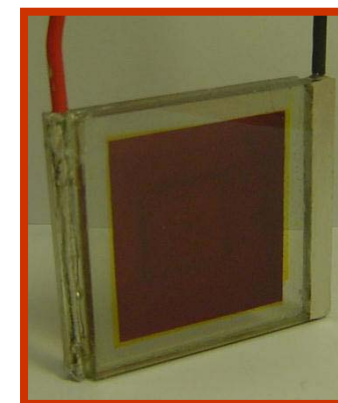
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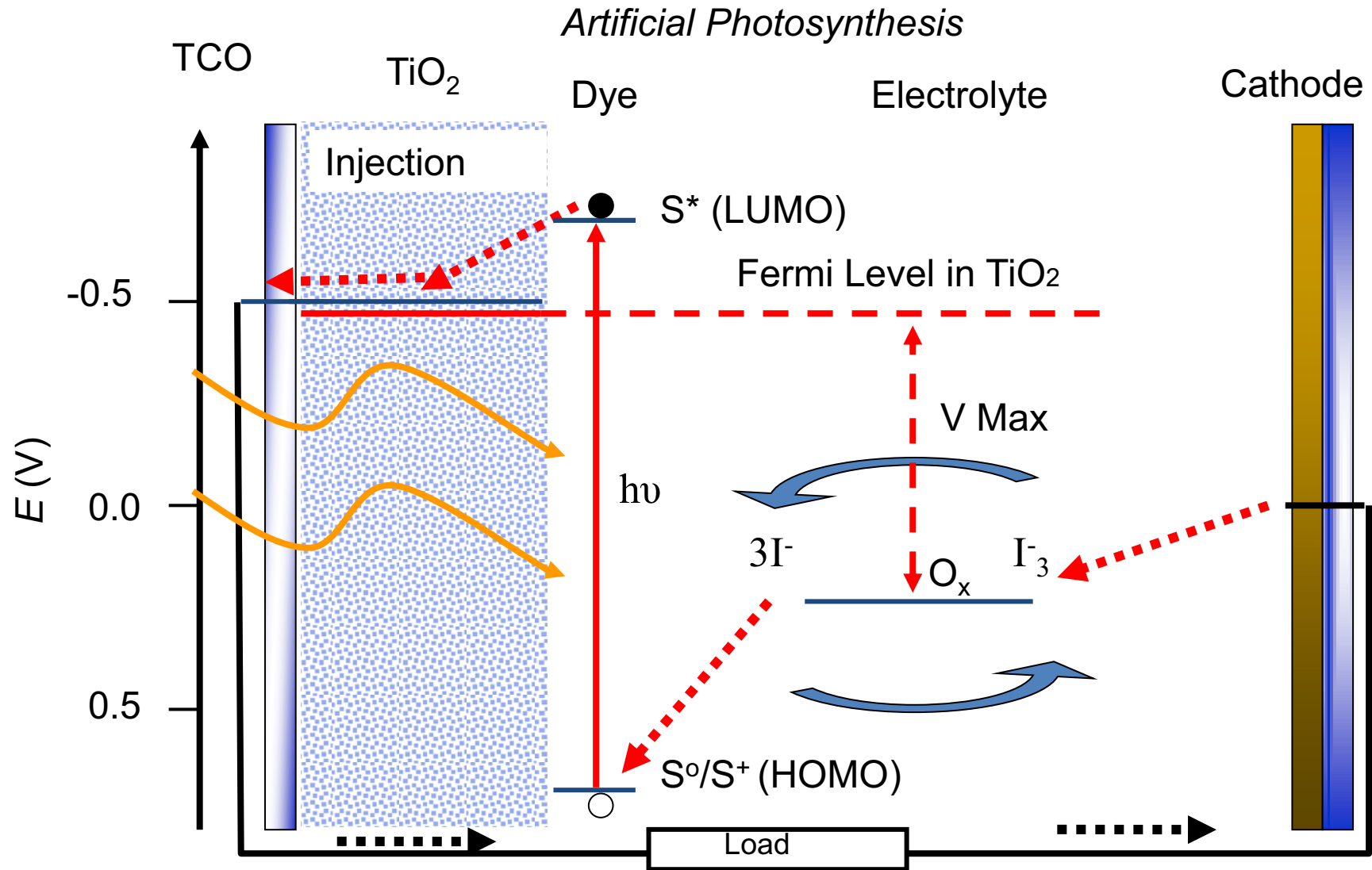
Dye Sensitized Solar Cells



Dye Molecules on TiO₂



Working principle of DSC



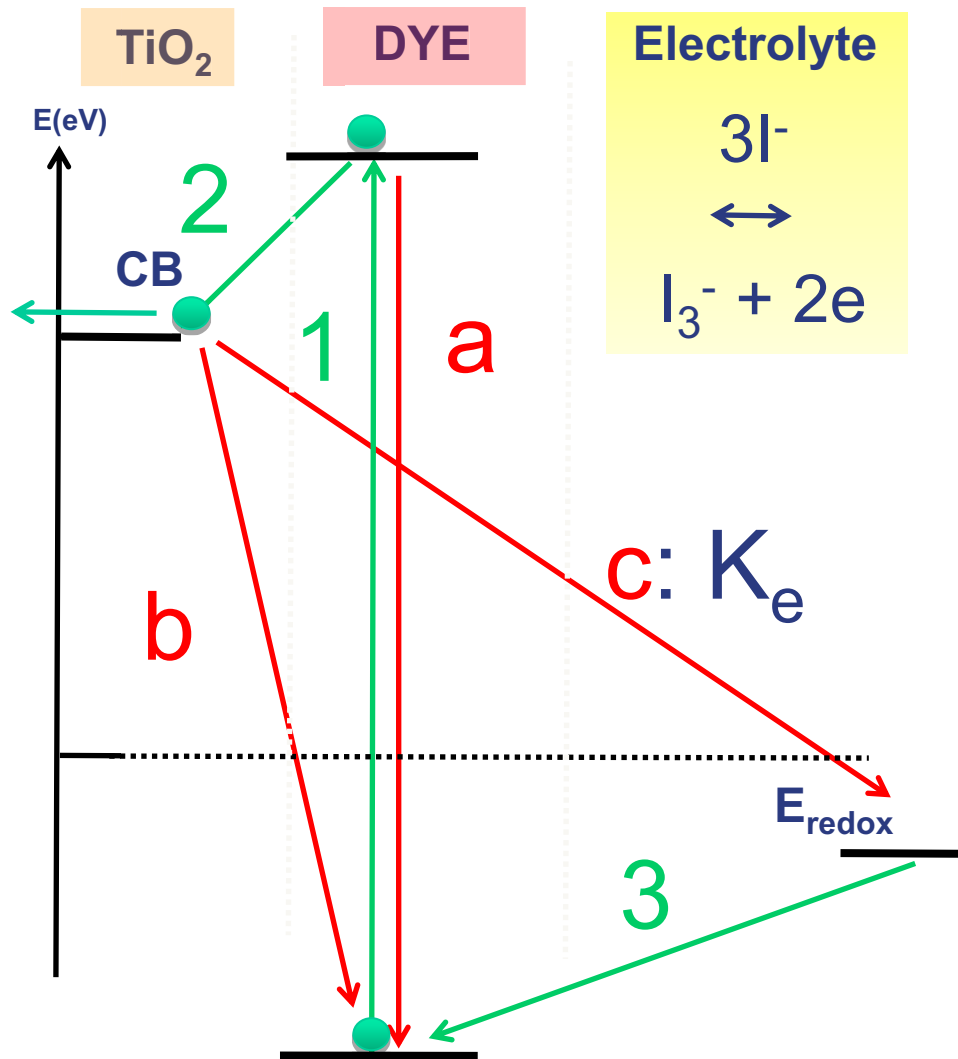
No permanent chemical transformation in the materials composing the cell



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DSC Kinetics

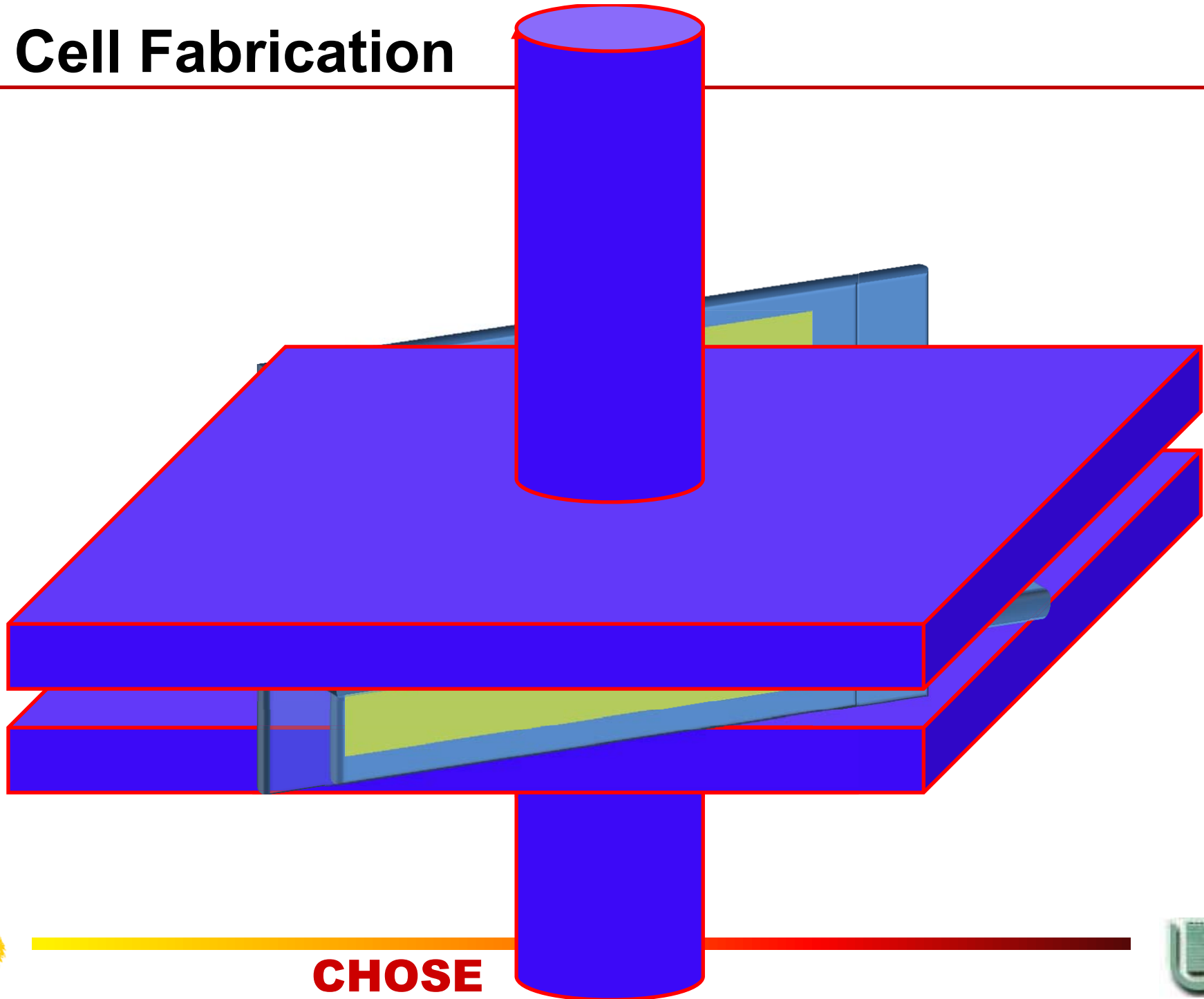


1. Dye Excitation ✓
2. Electron Injection into TiO₂ Conduction Band
3. Oxidation of the electrolyte

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



Cell Fabrication



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Automatic Screen-Printing (Baccini)



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Cell optimization

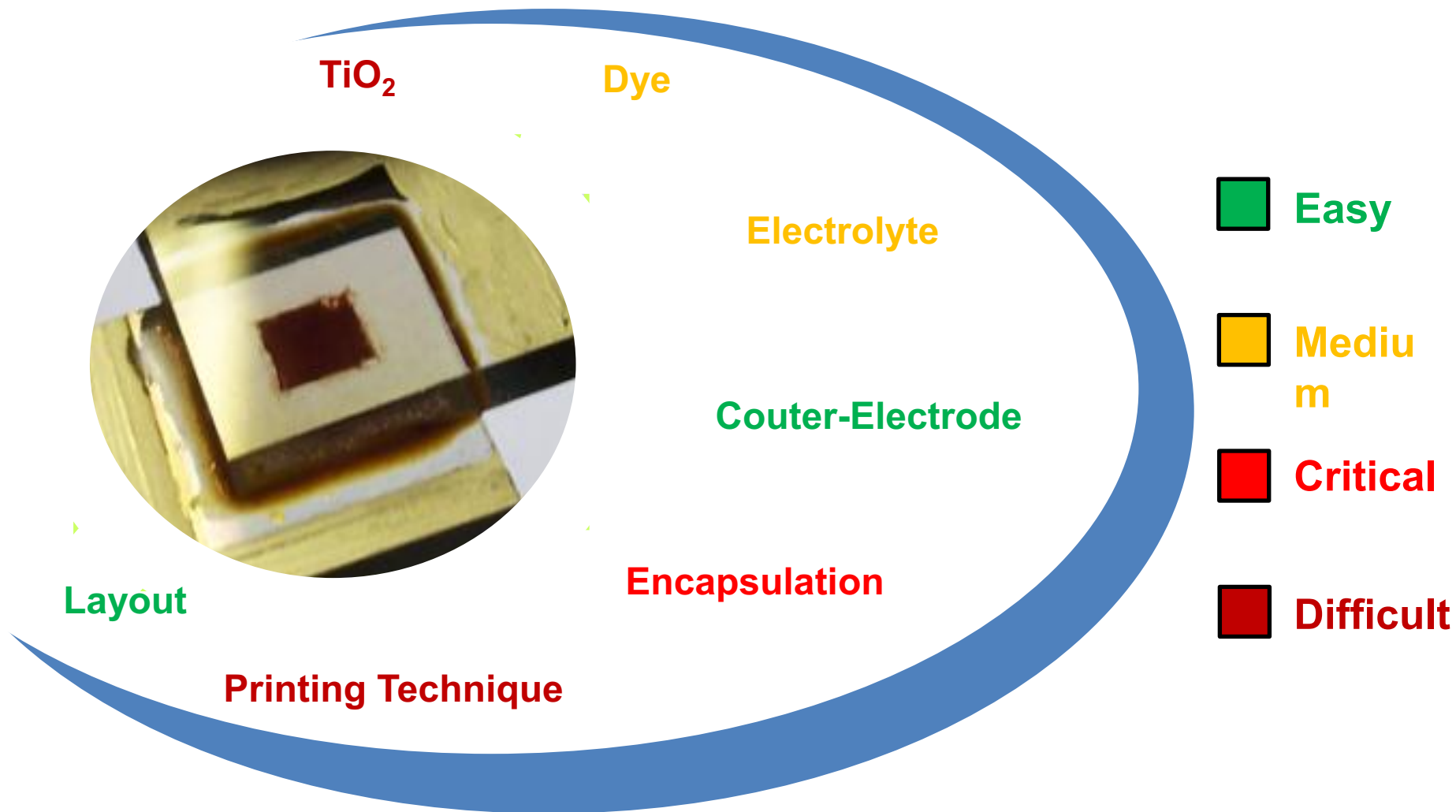


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Optimization parameters

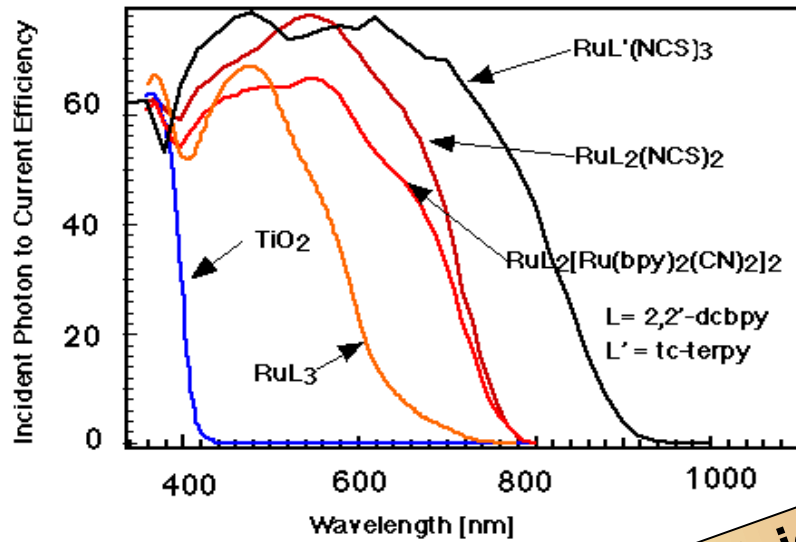
(an engineer view)



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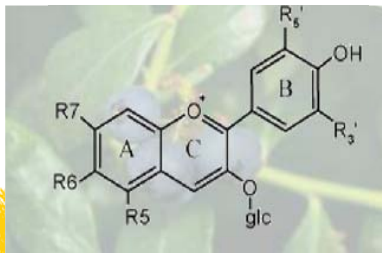


Dyes

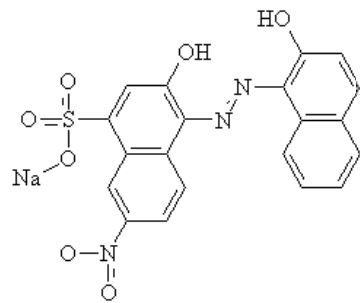


1%

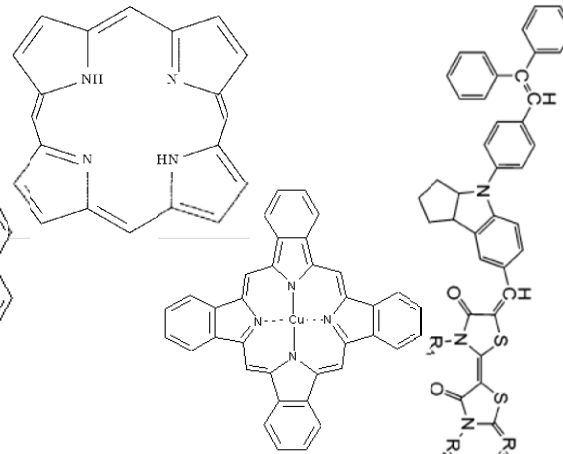
Natural Dyes



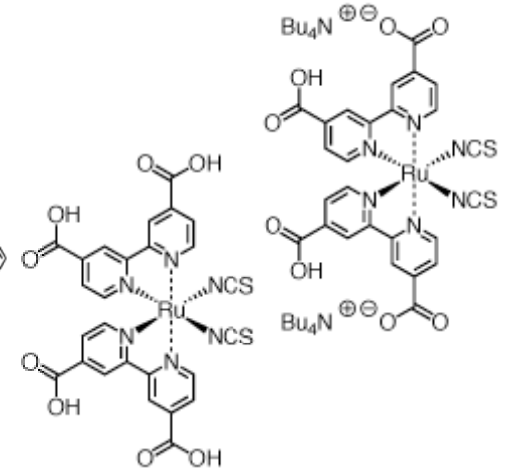
Industrial Dyes



Organic Dyes



Ruthenium-Based Dyes



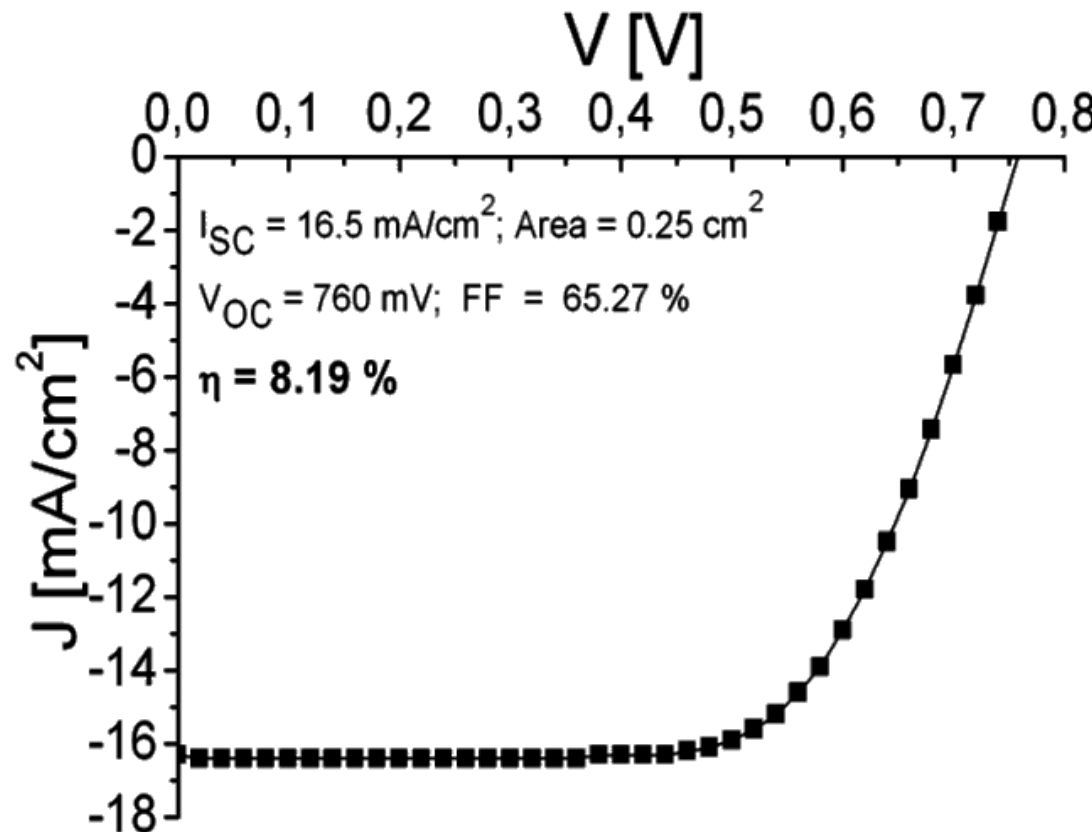
11%

Efficiency

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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

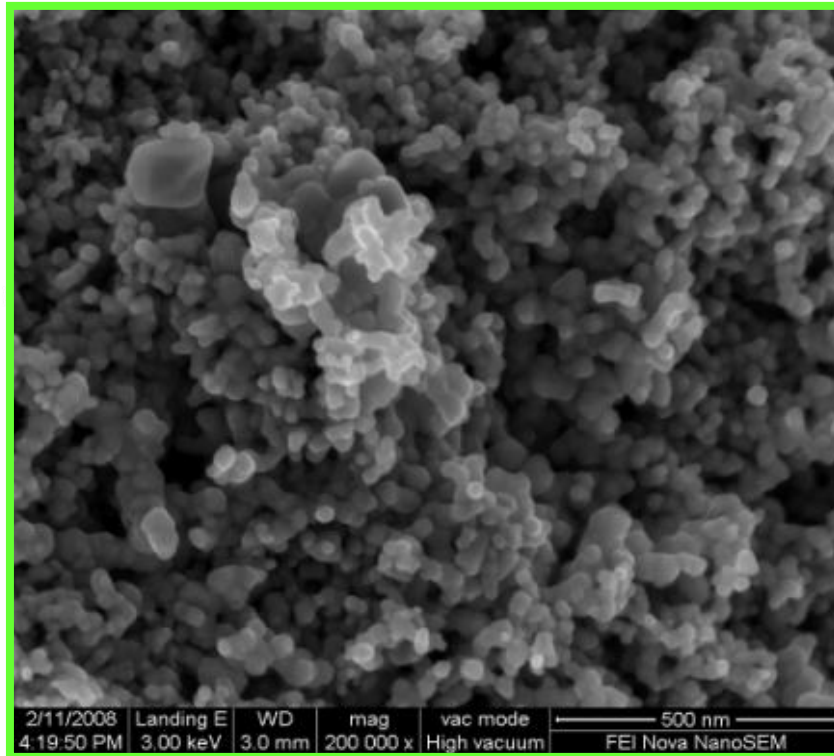


Process Improvements 1/2

Introduction of TiCl_4 treatments

Pre TiO_2 deposition + post sintering treatments

TiCl_4 solution 40mM 30' @ 70°C

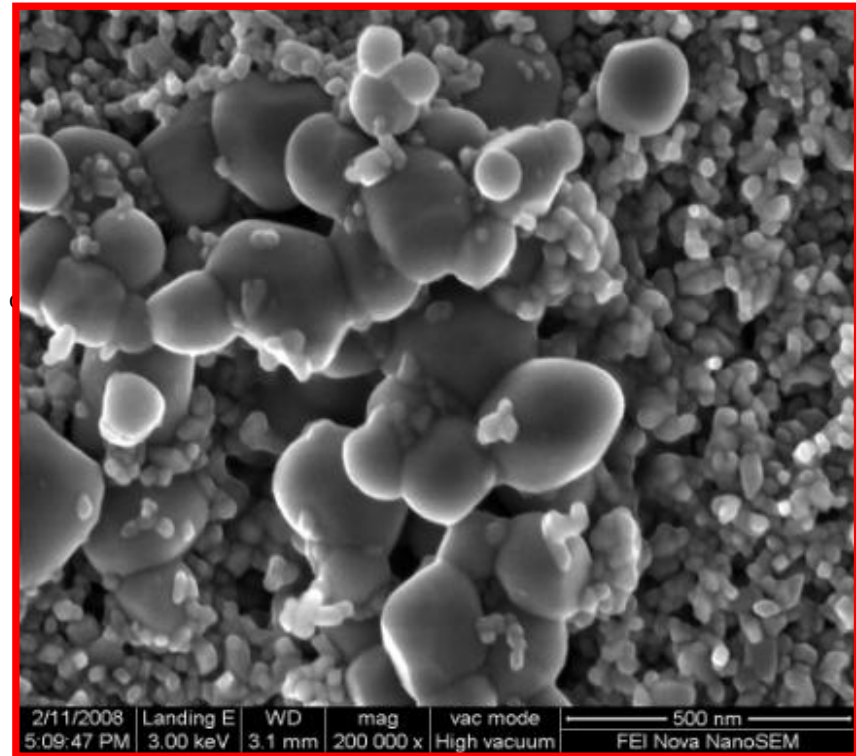


Transparent

Introduction of scattering layer

TiO_2 Dyesol scattering paste WER4-0

Thickness 8 μm^*



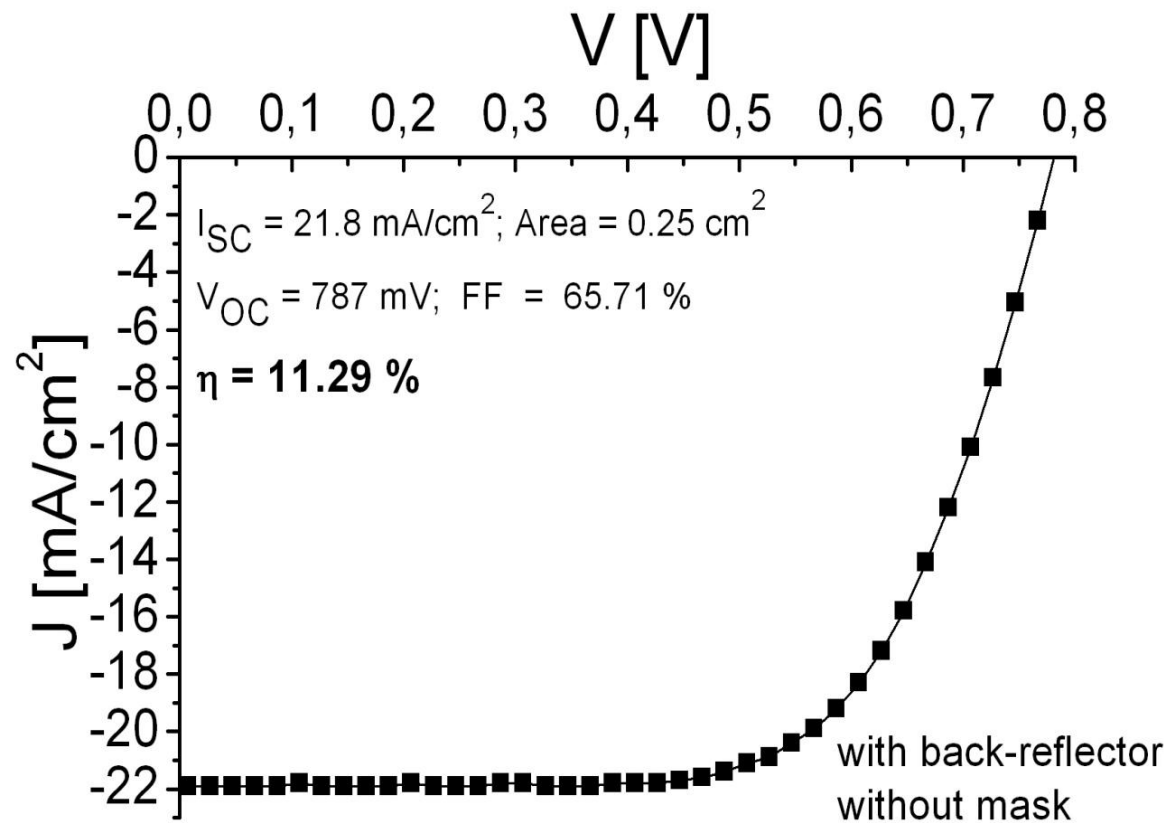
Not Transparent



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Process Improvements 2/2



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

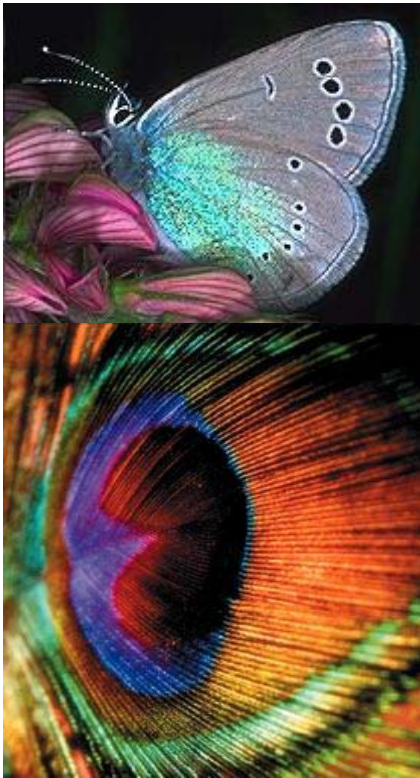
Good reproducibility within 2% deviation



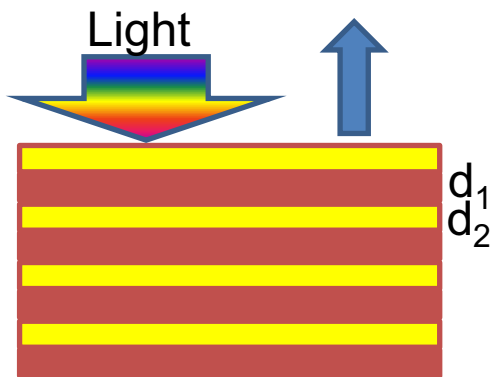
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Artificial colors with Photonic Crystals

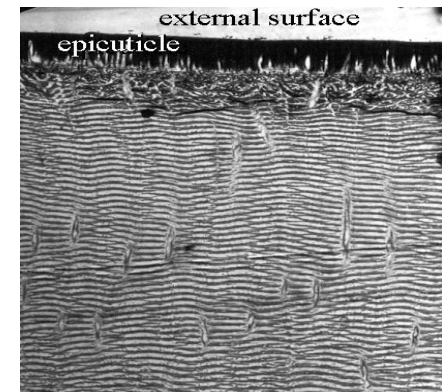


Photonic Crystals are periodic structures, there are natural examples already existing in nature, for instance, the microstructure in the wings of some butterflies causes their remarkable iridescent colours. These structures reflect electromagnetic radiation as propagation through them is prohibited. The action of electromagnetic repulsion / reflection, whatever the frequency at which it occurs, is due to the fabric of the crystal. The periodicity of the crystal plays a very important role in the formation of a useful band gap. The actual width of this band gap depends on the geometry, feature size, spacing and the materials which make up the crystal. The manipulation of light with artificially manufactured photonic crystals is an important new research area.

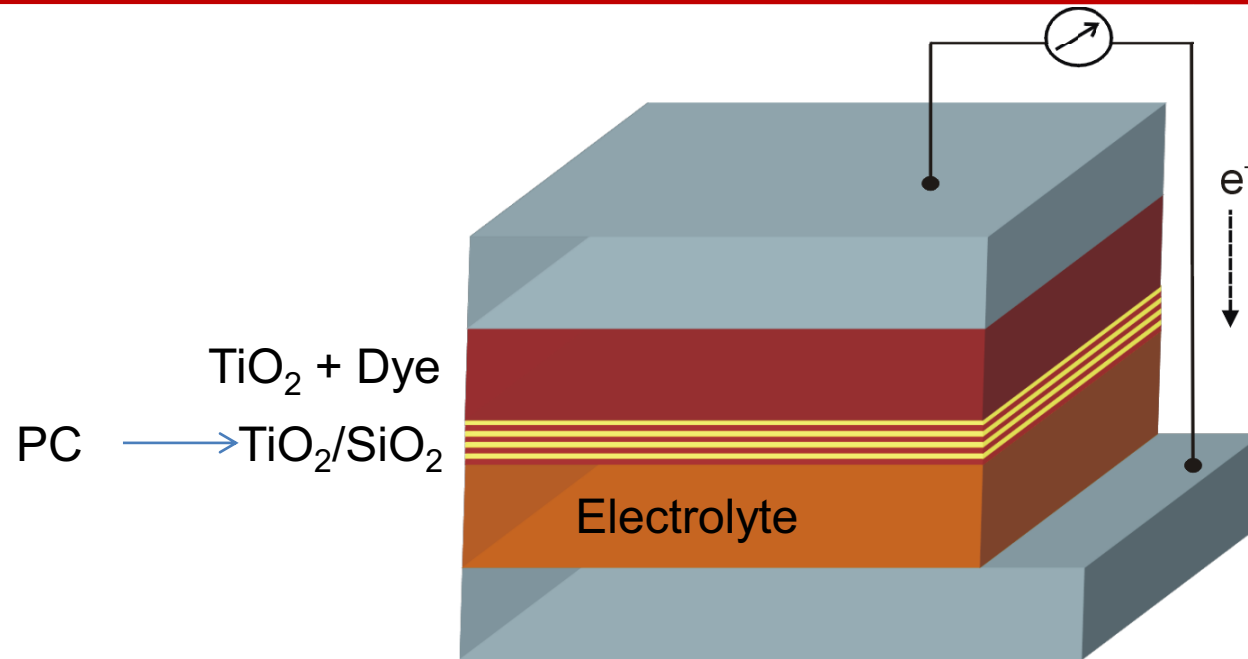


1D Photonic Crystal

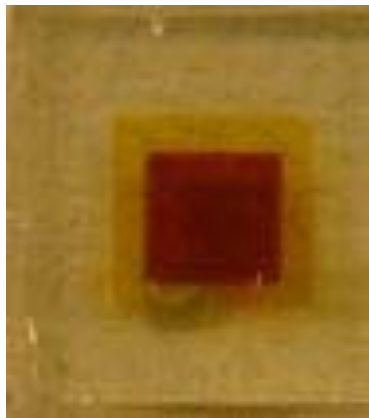
$$\lambda_{BRAGG} = 2(n_1d_1 + n_2d_2)$$



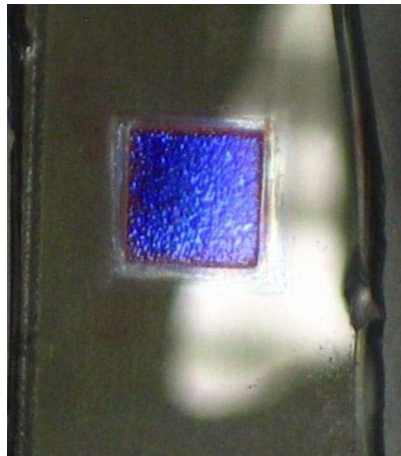
Dye Solar Cells with Photonic Crystals (PCs)



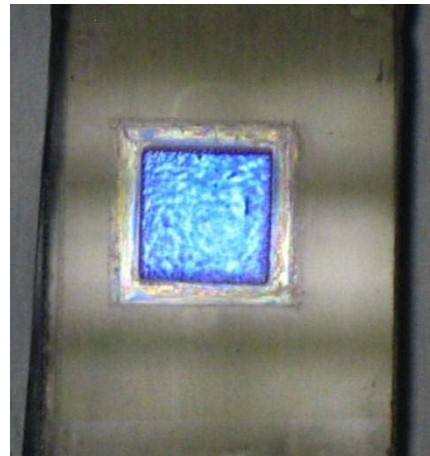
Without PC



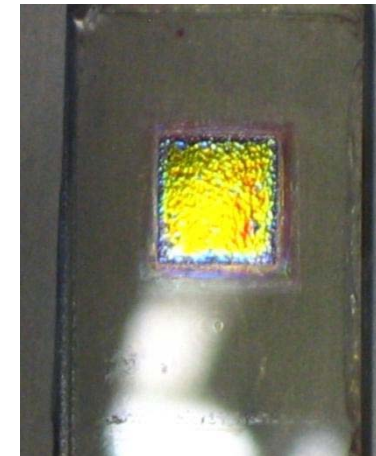
DSC + PC1



DSC + PC2



DSC + PC3



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From cells to modules

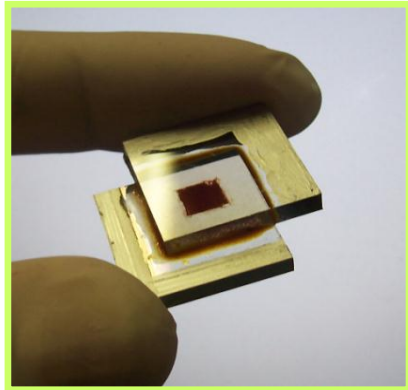
Large Area



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From small cell to (sub)module



The easiest
(and wrong) way:
simple scale up



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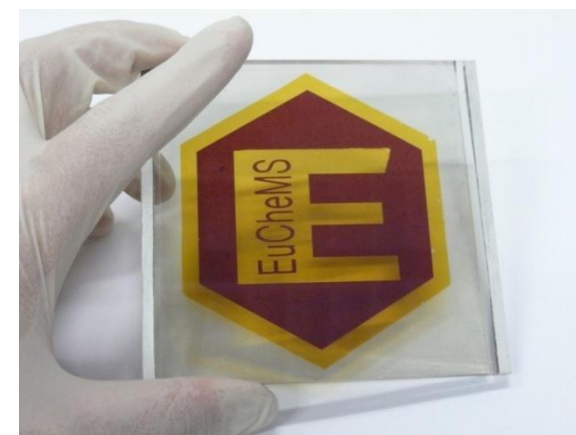
Cell scaling up and colours



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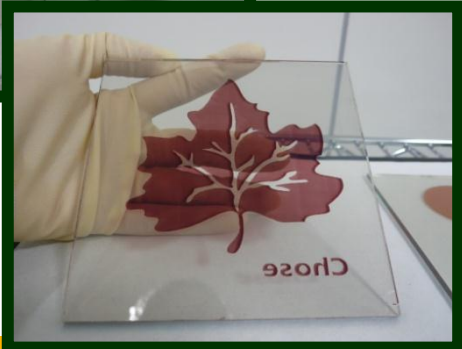
Cells with pattern



CHOSE



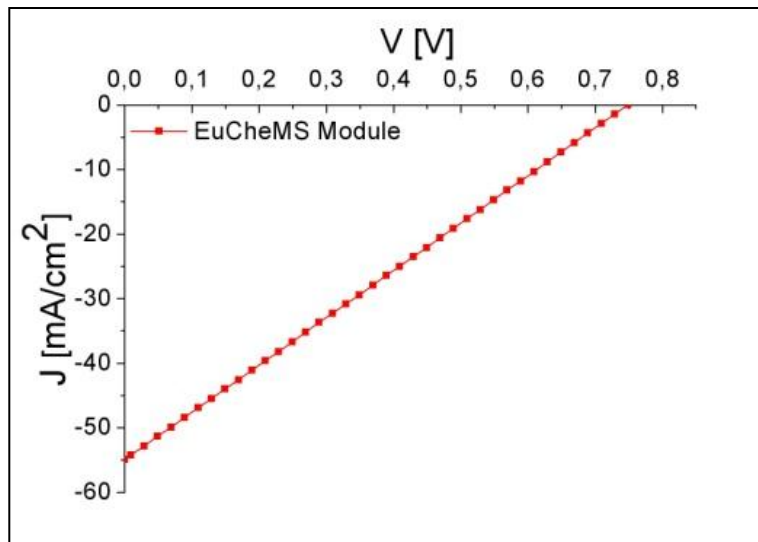
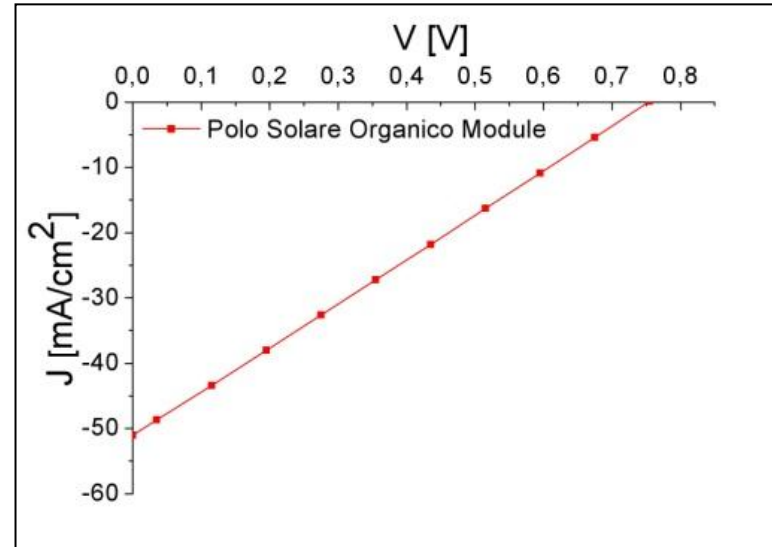
Cells with pattern



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Example of patterned DSC (single cells)



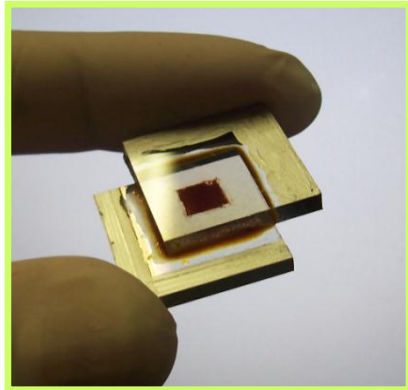
Very Very low efficiency



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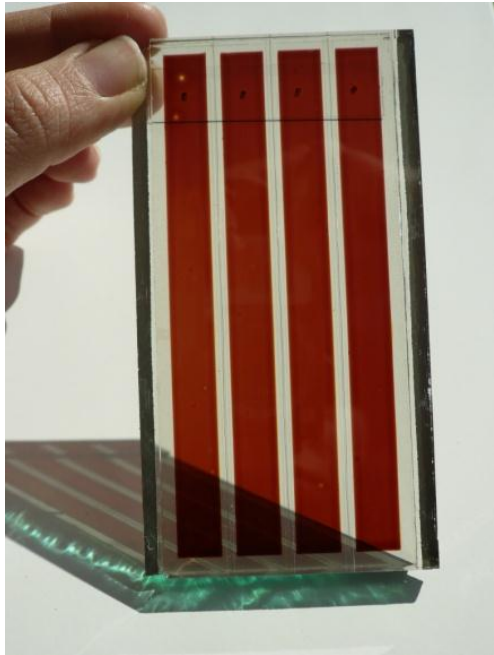
From small cell to (sub)module



The easiest and wrong way: simple scale up



The right way: proper aspect ratio

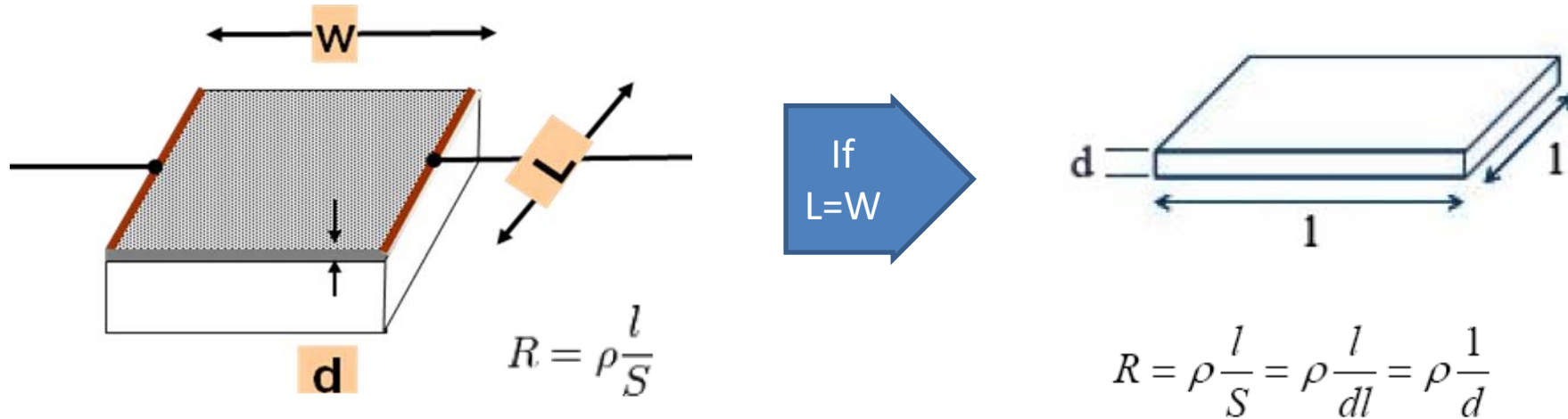


CHOSE



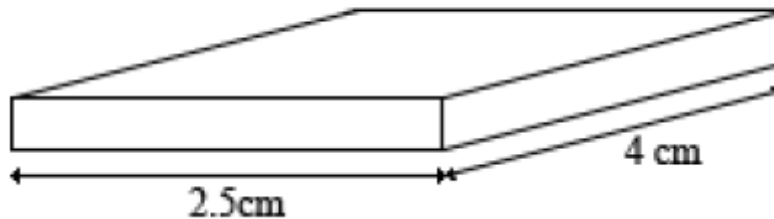
Large area cells: The sheet resistance

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



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

Example

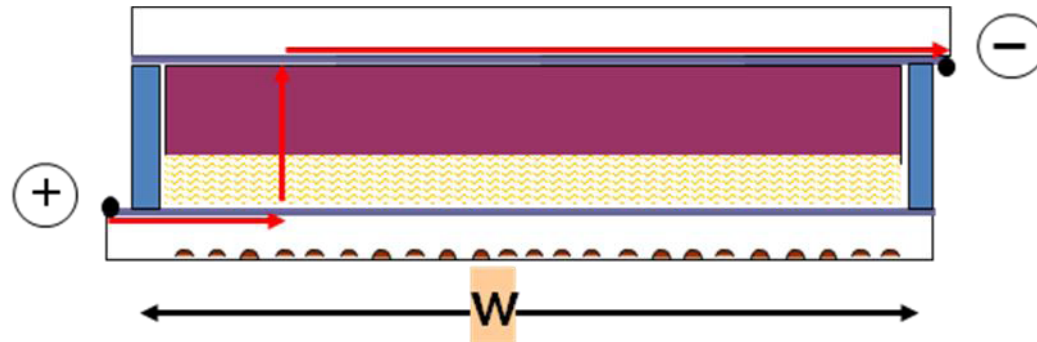


$$R = 8(\Omega / \text{square}) * \frac{2.5(\text{cm})}{4(\text{cm})} = 5(\Omega)$$

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



Sheet resistance influence



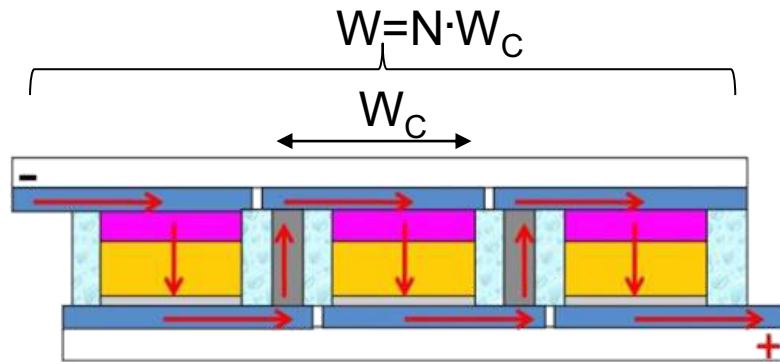
$$\Delta V = RI = \left[\frac{\rho W}{dL} \right] [J \cdot L \cdot W] = J \cdot W^2 \cdot R_{square}$$

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



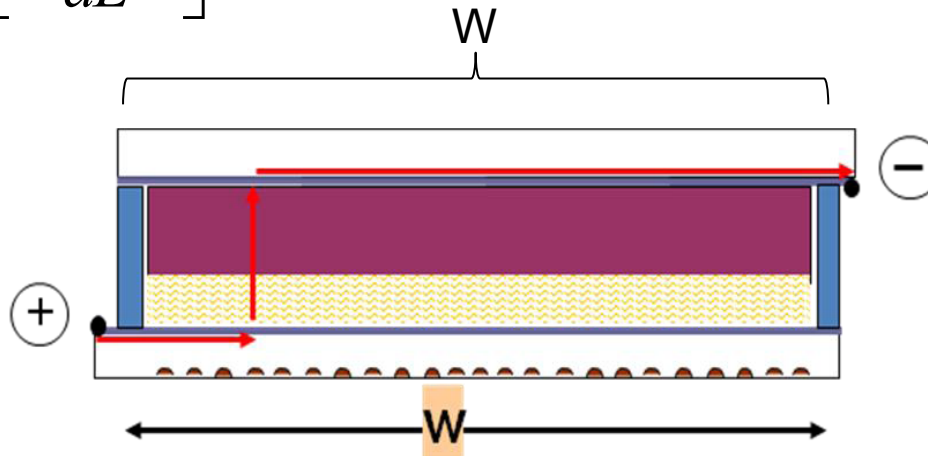
Module with N cells connected in series



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

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

Large area cell



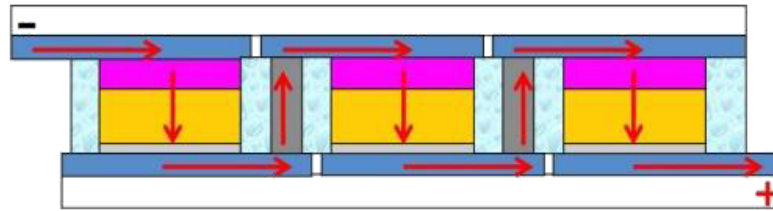
$$\Delta V_M = \frac{\Delta V_{\text{Large Cell}}}{N}$$








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



W and Z schemes

✓ Optimized and separated processes for WE and CE substrates

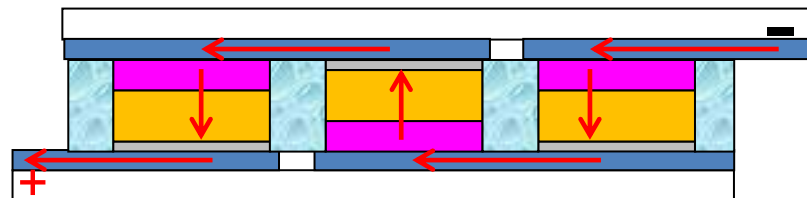


-  Glass
-  TCO
-  Dye+ TiO₂
-  Electrolyte
-  Pt
-  V. Connection
-  Sealing

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

Z

✓ No vertical connections
✓ High AR



-  Glass
-  TCO
-  Dye+ TiO₂
-  Electrolyte
-  Pt
-  Sealing

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

W



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Strutture dei moduli

TiO₂ + Dye

Elettrolita

TCO

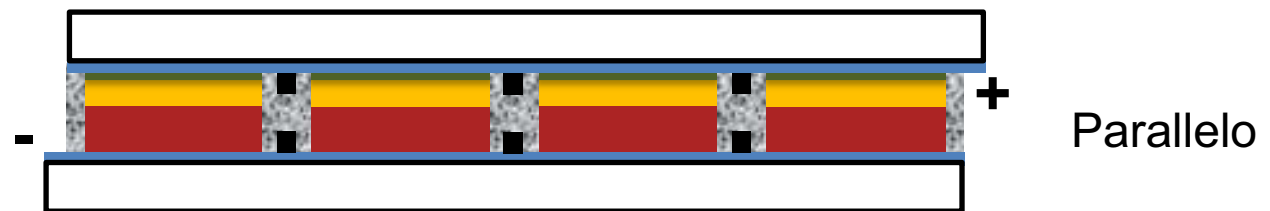
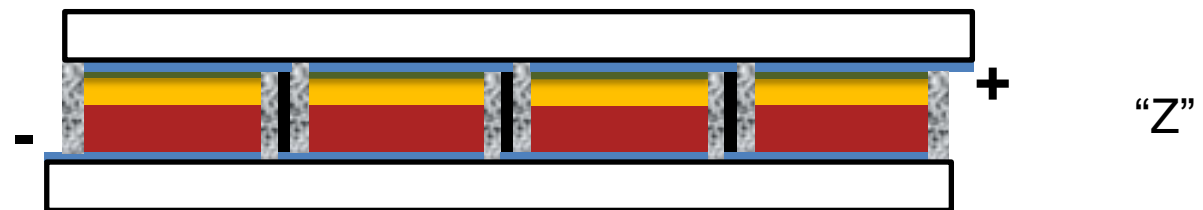
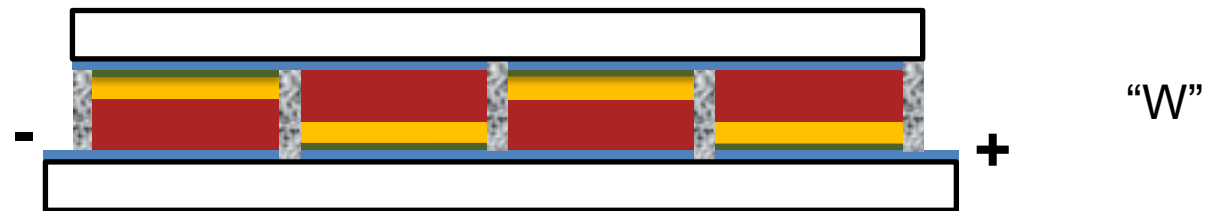
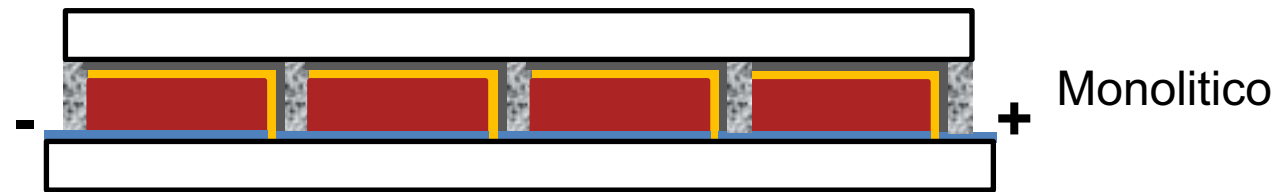
Incapsulante

Conduttore

Grafite

Substrato
(vetro, plastica etc.)

Catalizzatore

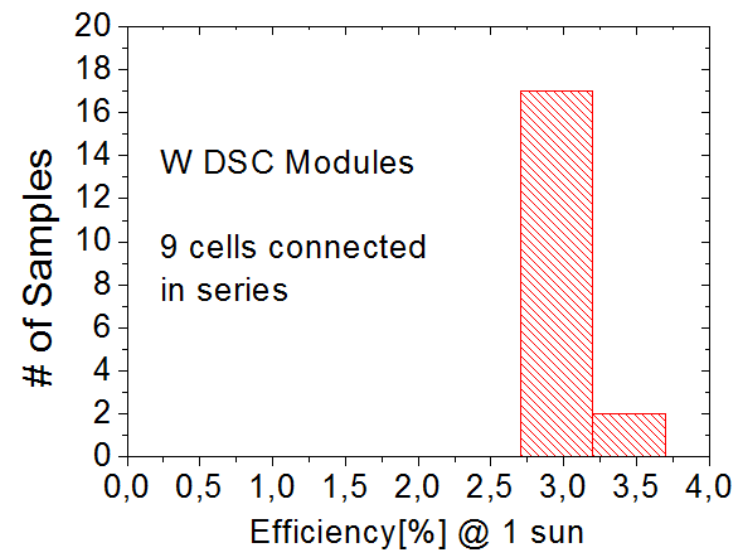
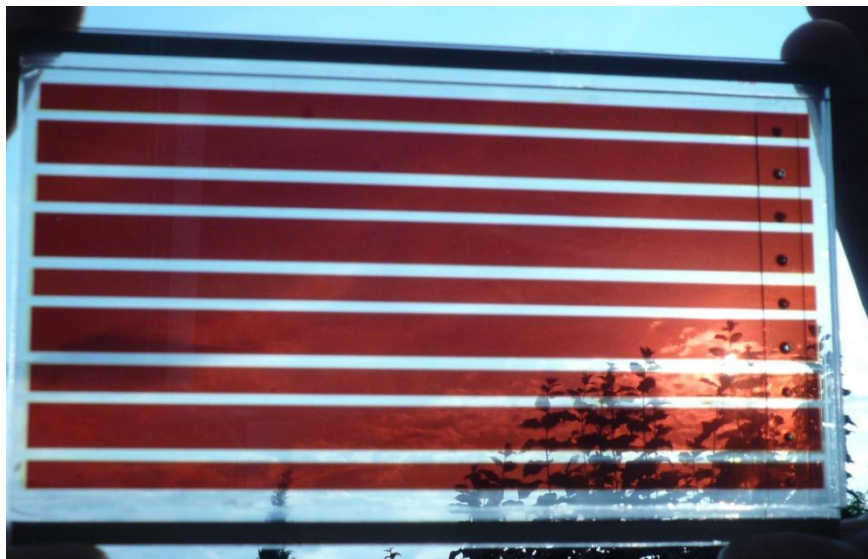


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Optimized W module

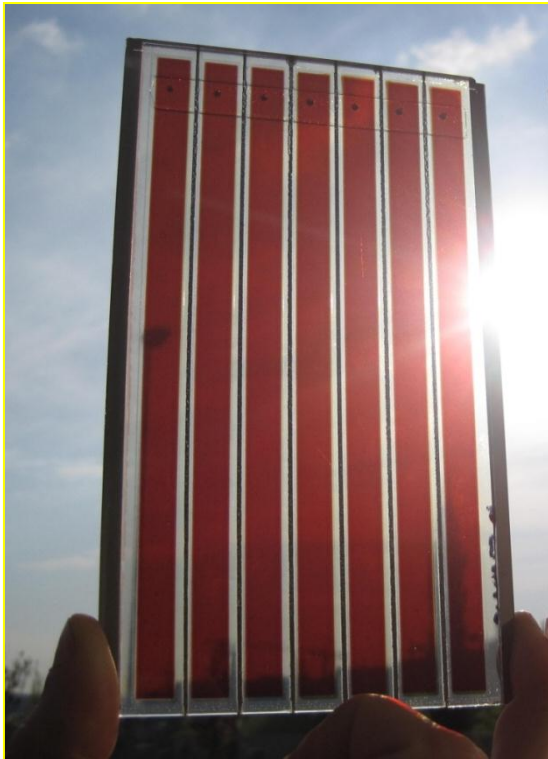
	N total	Mean	Upper 95%	Minimum	Maximum
Isc [mA]	19	112	115	100	124
Voc [V]	19	5.79	5.83	5.6	5.97
FF [%]	19	53	54.3	48	59
Eff [%]	19	2.9	3	2.9	3.3
Pmax [mW]	19	347	358	317	383



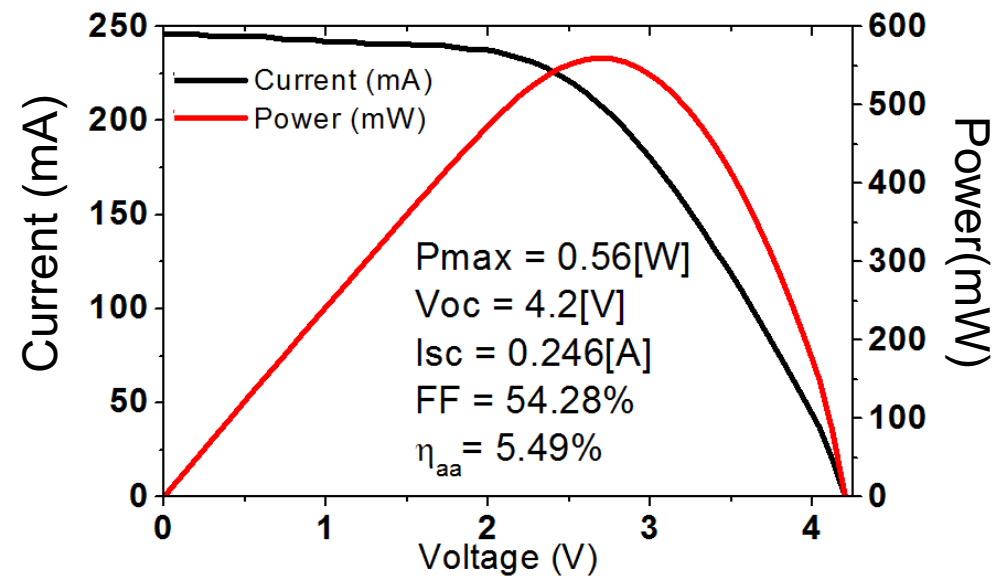
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Z module



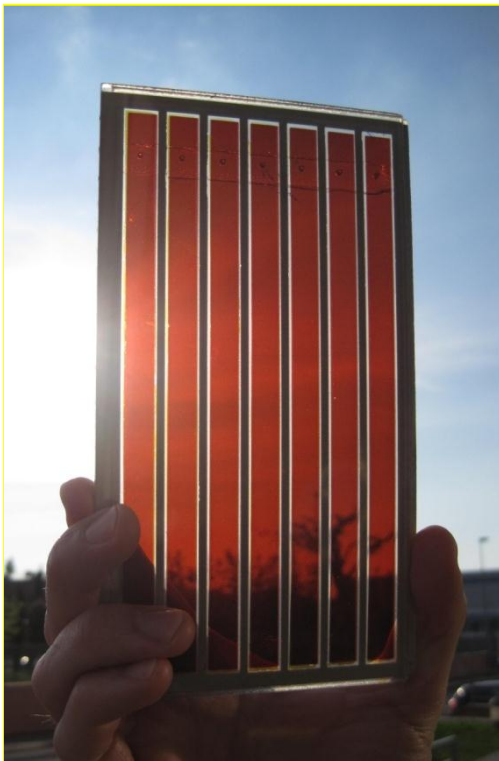
	N total	Mean	Upper 95%	Minimum	Maximum
Isc [mA]	16	236.275	243.537	210	252
Voc [V]	16	4.12625	4.16331	3.98	4.2
FF [%]	16	52.3625	54.13557	43.18	56.96
Eff [%]	16	5.0125	5.2509	3.59	5.49
Pmax [mW]	16	511.1875	535.50473	366	560



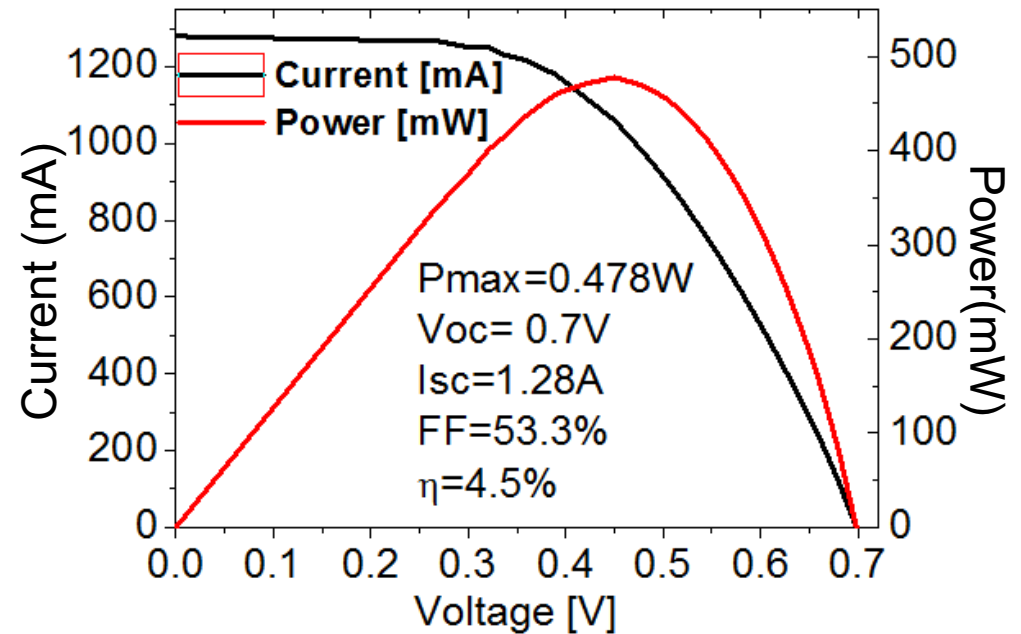
- ✓ Optimized and separated processes for WE and CE substrates
- ✓ High Voltage, Low Current
- ✗ Vertical interconnections resistance decreases FF
- ✗ Sealing more complex
- ✗ Lower aperture ratio
- ✗ Metal-Electrolyte corrosion



Parallel module



	N total	Mean	Upper 95%	Minimum	Maximum
Pmax [mW]	18	461.25	471.9	426.825	507.93
Eff	18	4.31	4.419	4	4.75



- ✓ No vertical interconnection
- ✓ Simpler processes

- X Low voltage Output
- X Metal-Electrolyte corrosion



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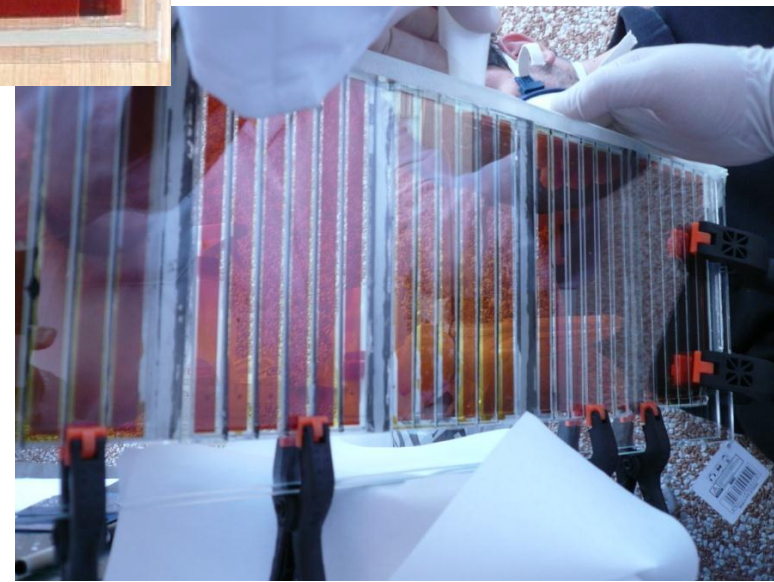
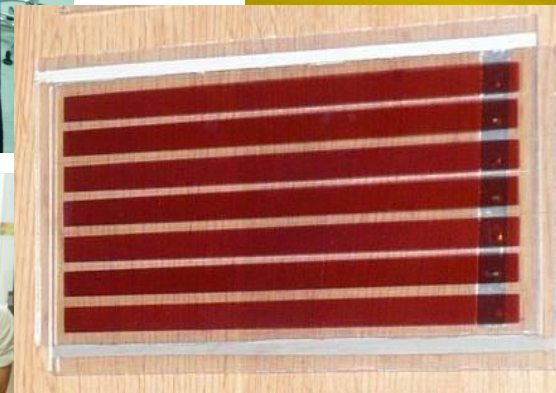
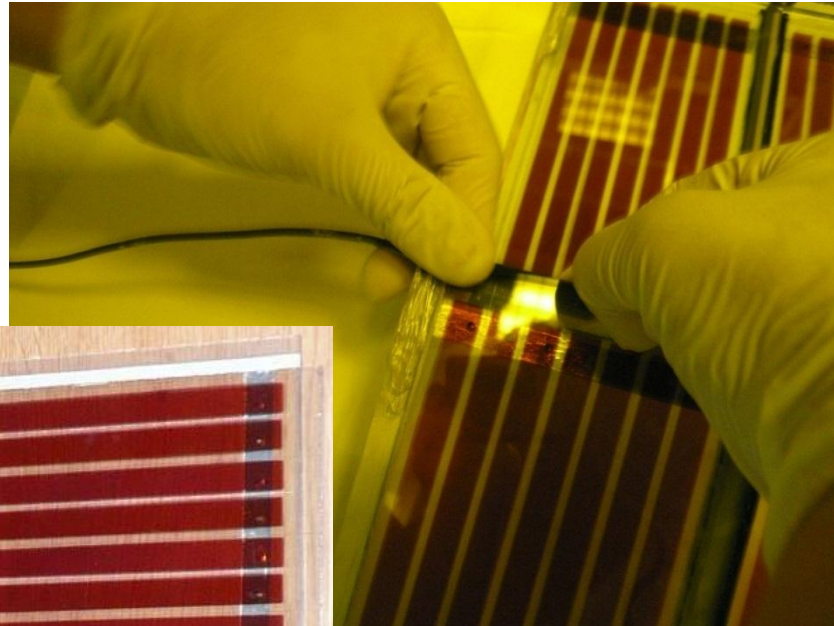
From Modules to Panels



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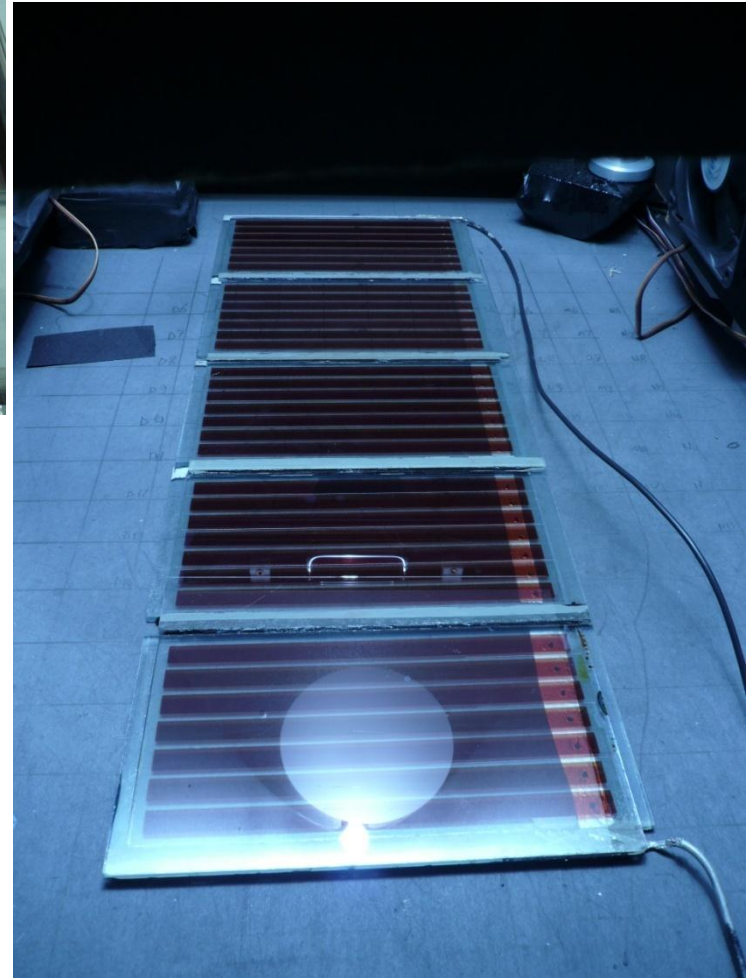
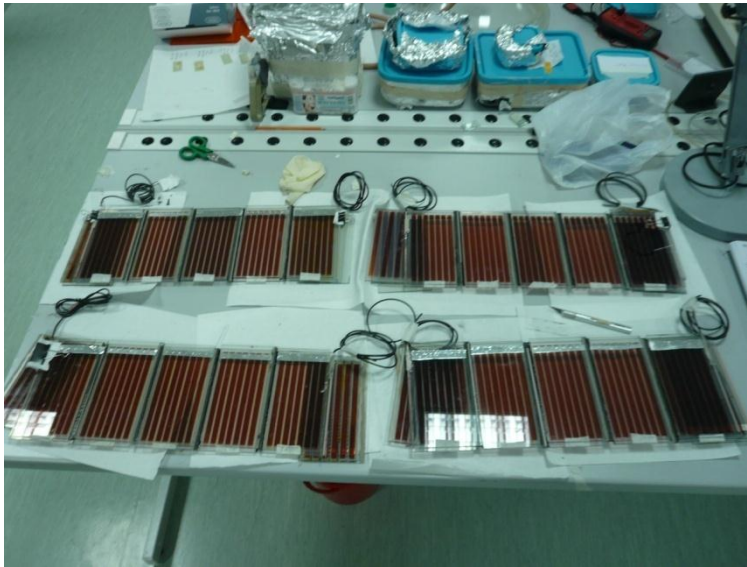
Modules Assembly, bus bar connections



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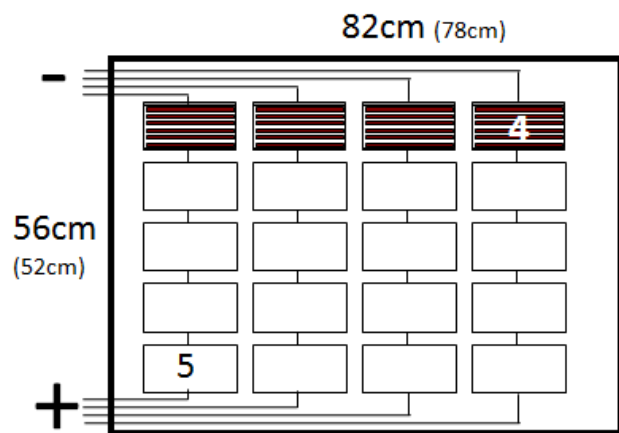
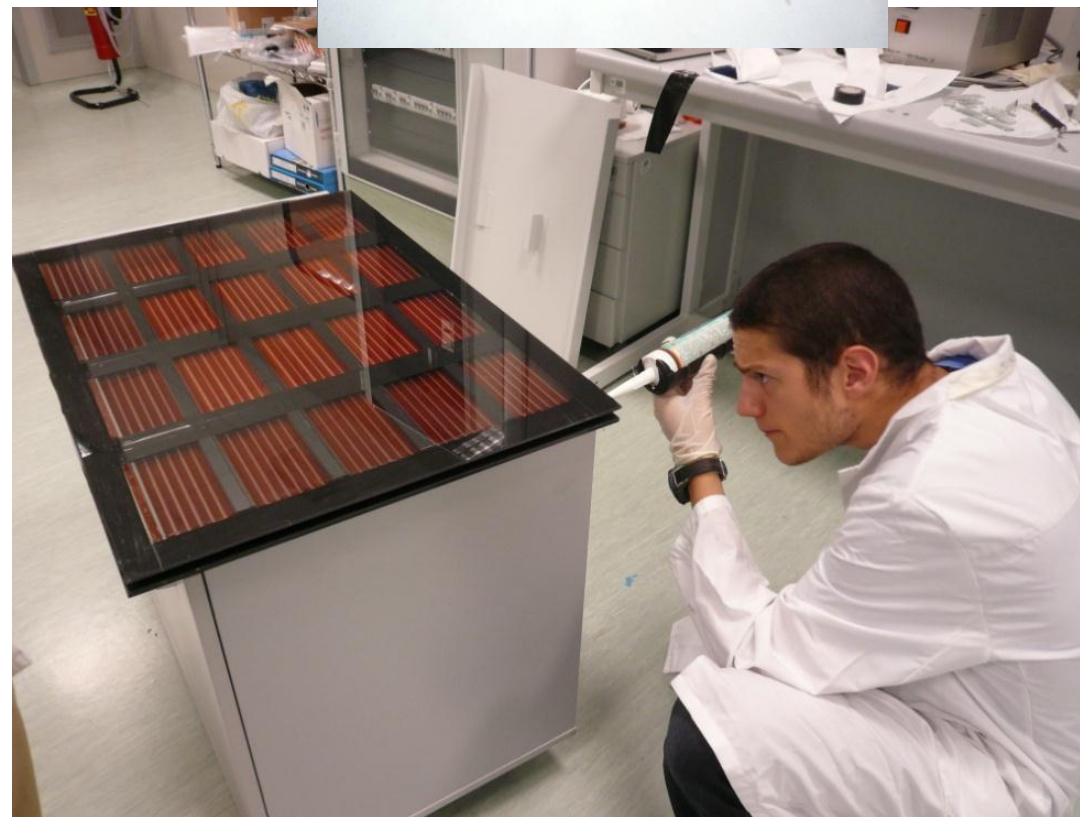
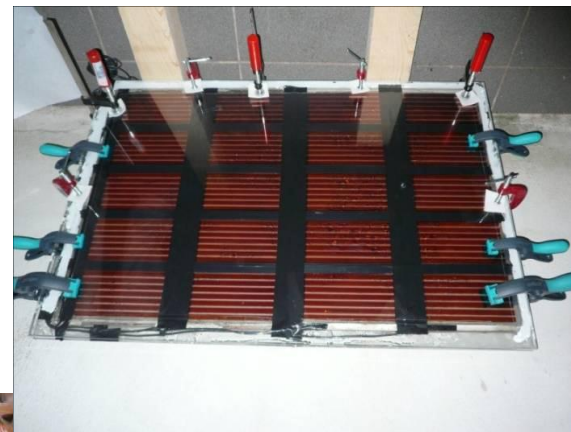
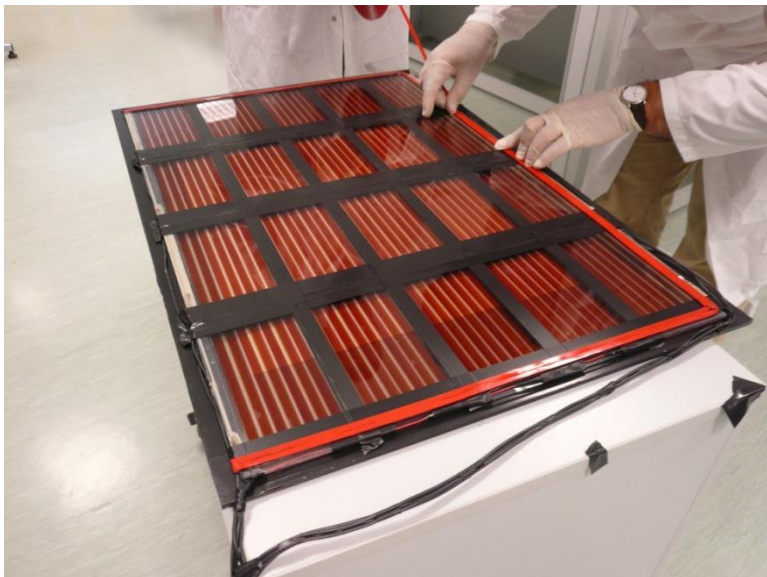
Strings



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Panel assembly



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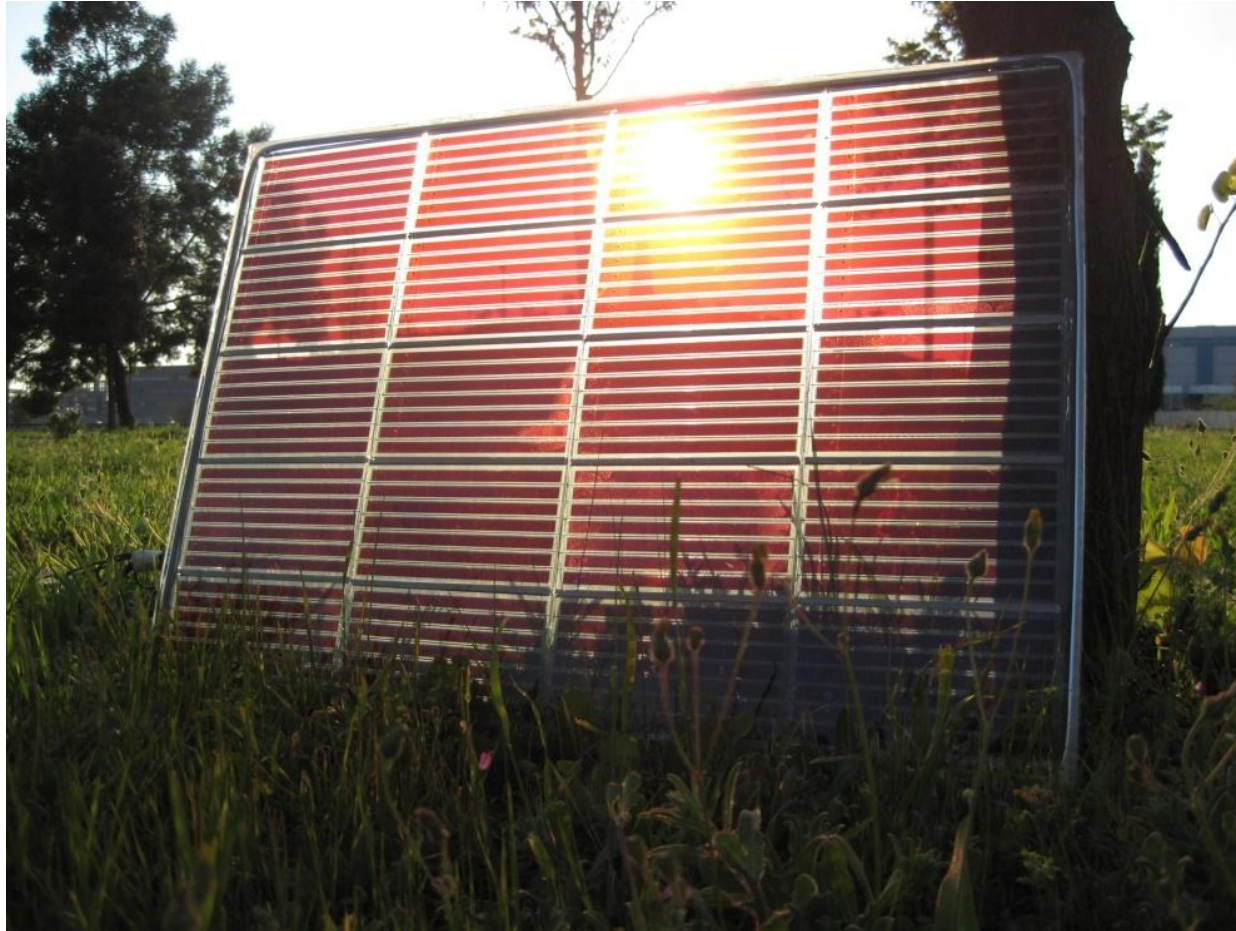
Final panel (August 2009)



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Panel v2: April 2010



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Outdoor measurements



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



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



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Outdoor measurements

Z panels

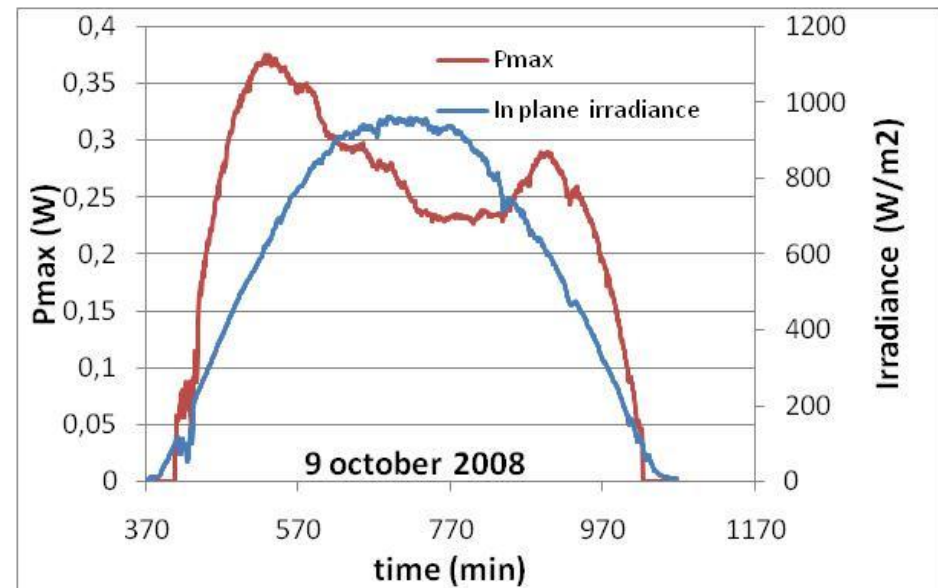
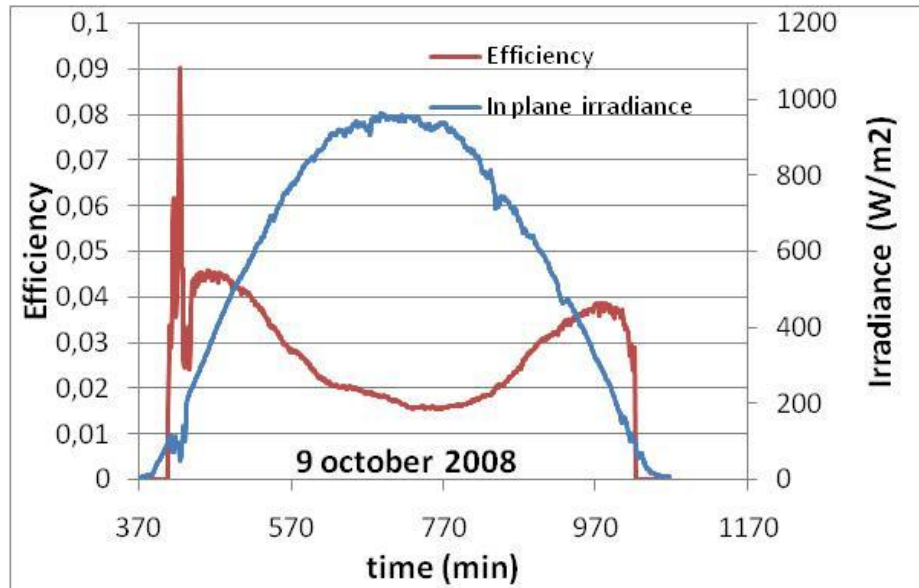
W panel



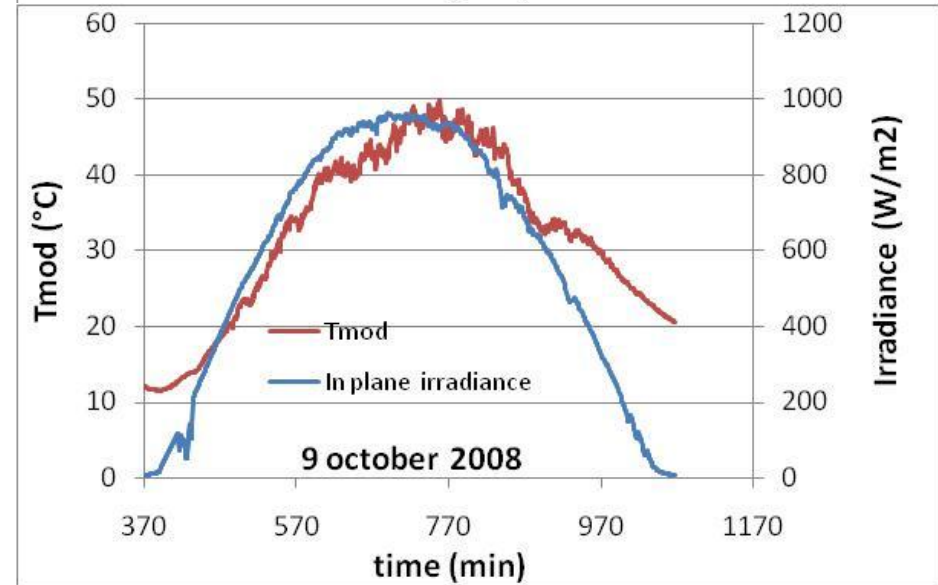
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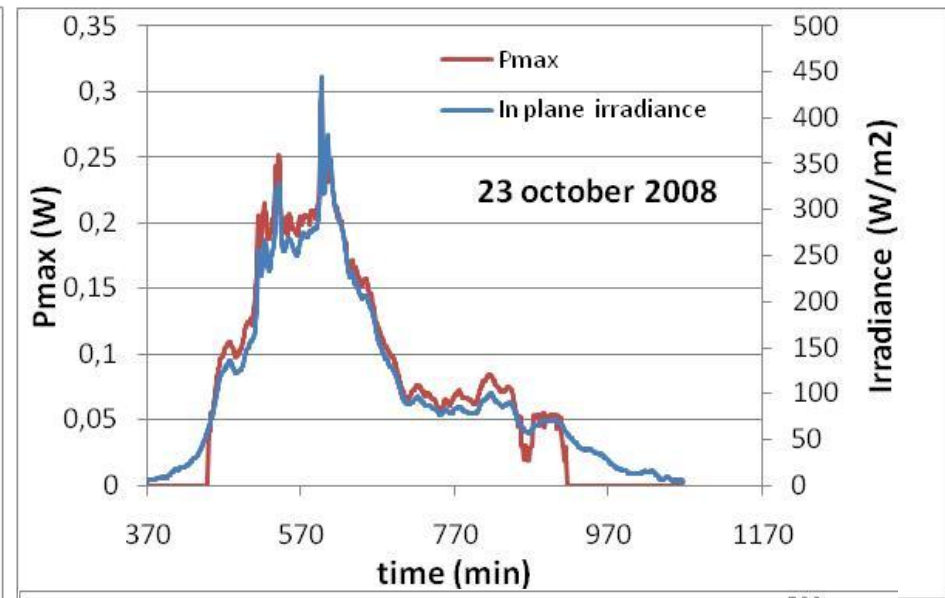
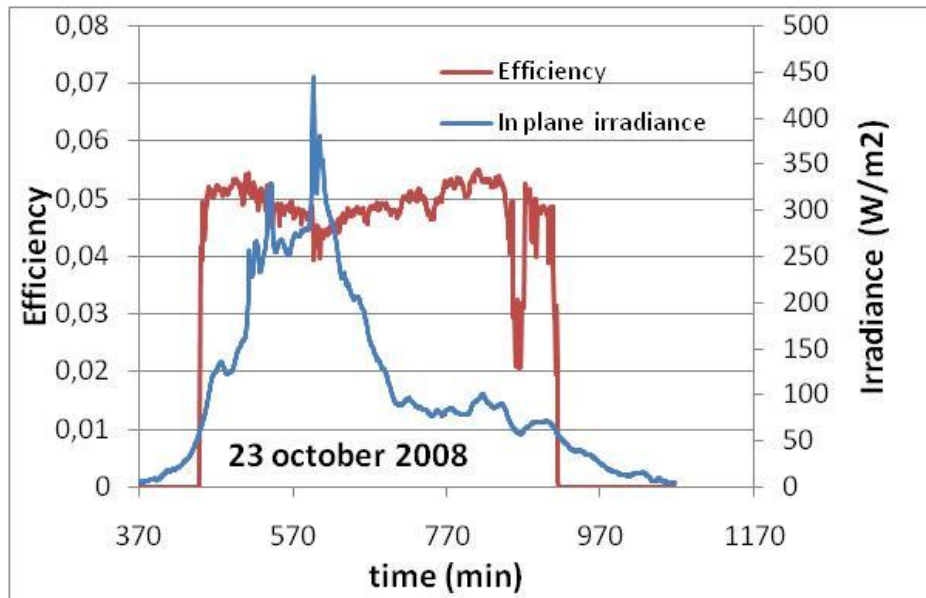
Outdoor Module test – Clear day



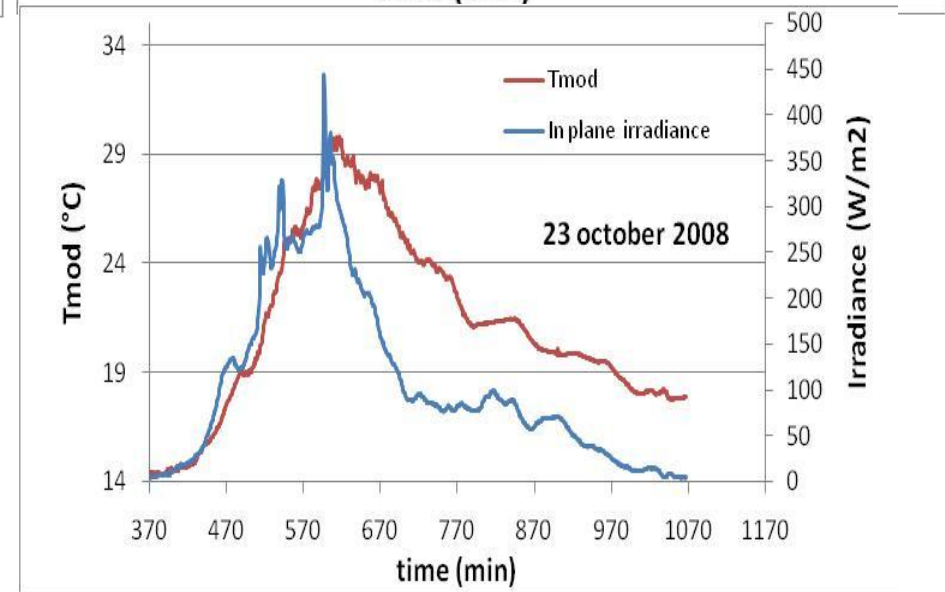
Light is mainly direct



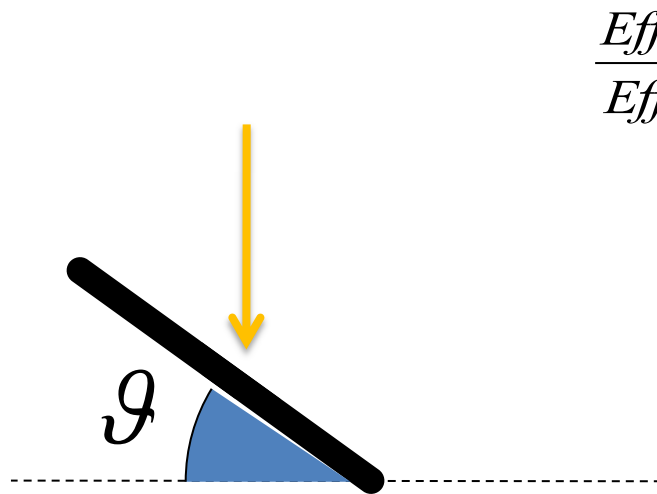
Outdoor Module test – Cloudy day



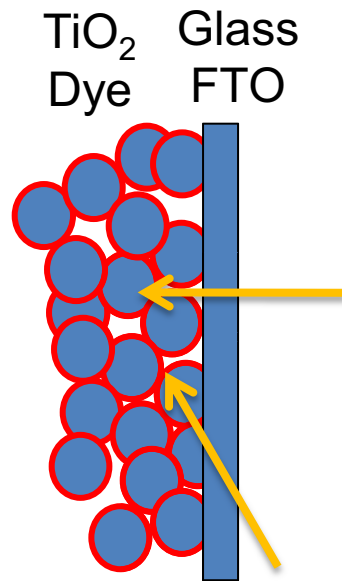
Light is mainly diffused



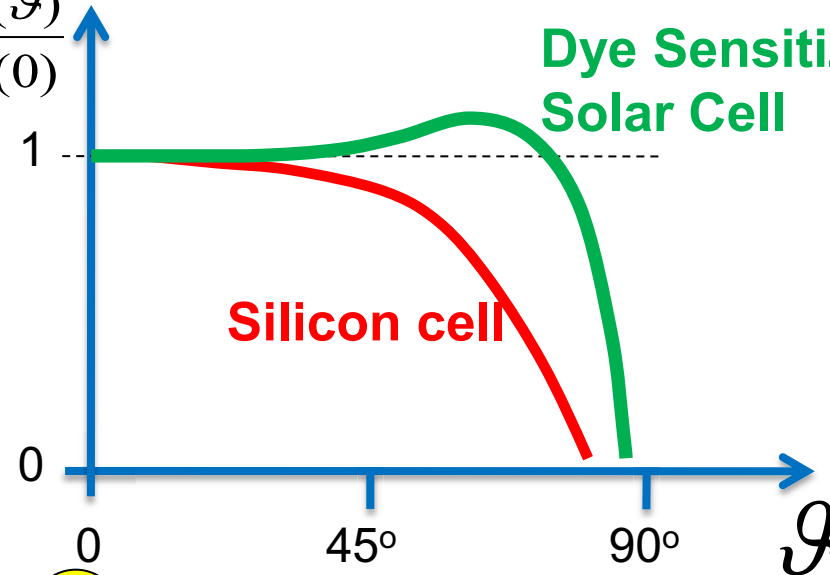
Angular dependence



1



$\frac{\text{Efficiency}(\theta)}{\text{Efficiency}(0)}$



2

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

Path length increases with increasing angle



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

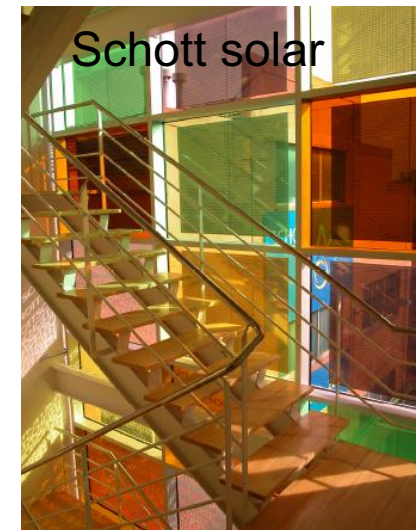


Building Integration of Photovoltaics is quite convenient for DSC technology

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



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Applications (Sony)



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- UniFerrara (Bignozzi team)
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REGIONE LAZIO

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T. Denaro (Dyesol)

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Vesce, Mastroianni, Gentilini
etc.)



Tor Vergata team

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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

