# Dye sensitized solar cells: from research to industrialization

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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 20**20** EU have to reduce by **20**% the $CO_2$ 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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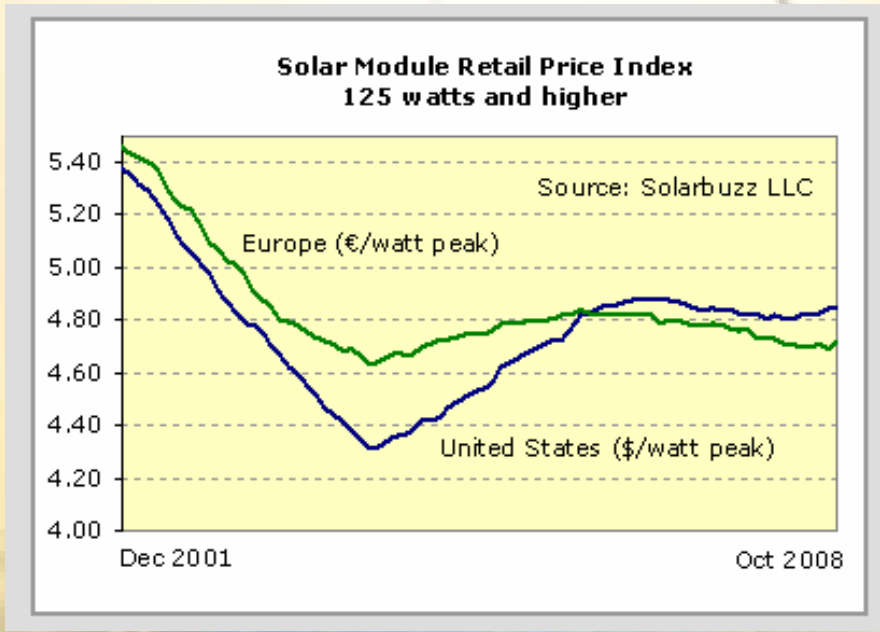
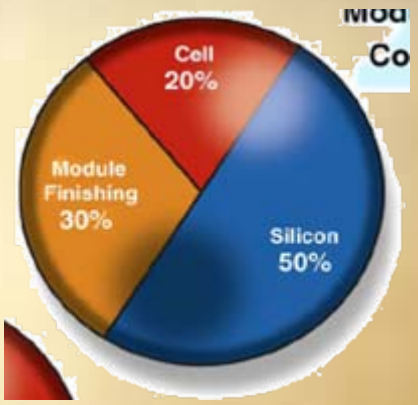
# Energy from the sun

To satisfy the electricity needs of a typical family one needs 3kWp PV system, i.e. ~20m$^2$ of photovoltaic surface (assuming system efficiencies of 13%).

**COST** → 20.000 euro

**Cost reduction of PV systems per Wp/m$^2$ becomes paramount in order to make PV technology an important instrument for energy production.**



# Could we reduce cell cost ?

**Silicon is quite expansive (2 euro/ Wp, one doping level)**

**Production plant are expansive (100 Meuro for 40 MWp/year amorphous silicon, 15Meuro for 30 MWp/year bulk silicon)**

**Energy payback is around 4 years for silicon cells**

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

**This is possible but we have to re-invent the cells**

**Organic photovoltaics**

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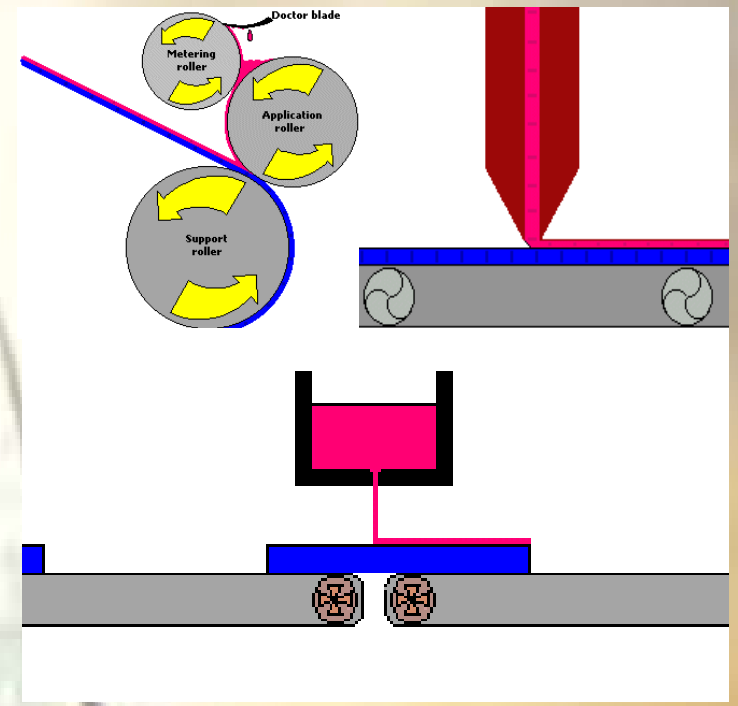
# “Nuovi” processi di realizzazione

**Conventional Electronics** → **Organic Electronics**

**Conventional semiconductor industry** → **Printing methods**

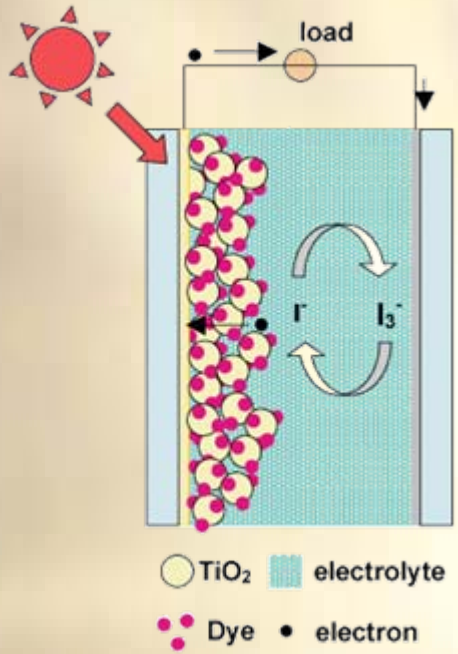


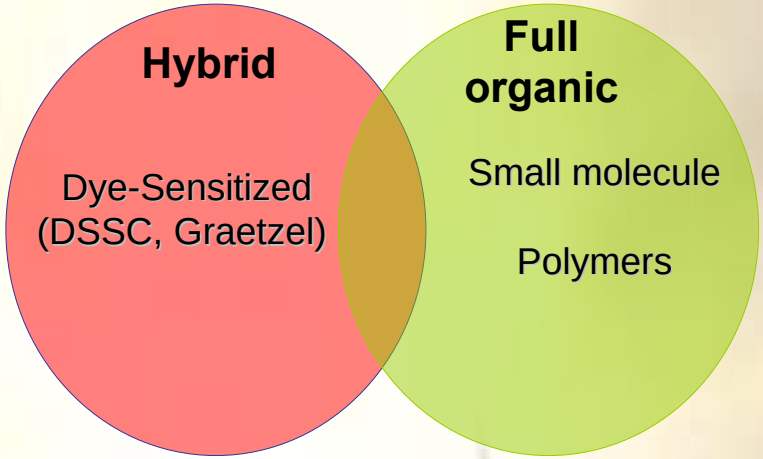

**High temperature, doping, vacuum**

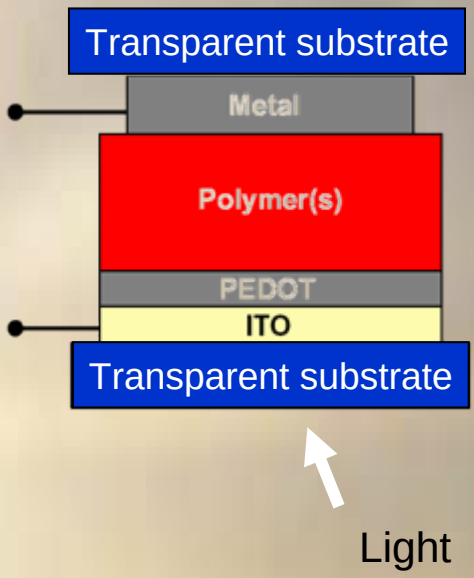
**Liquid deposition**

**Large enterprises** → **Small Medium enterprises**

# Organic photovoltaics

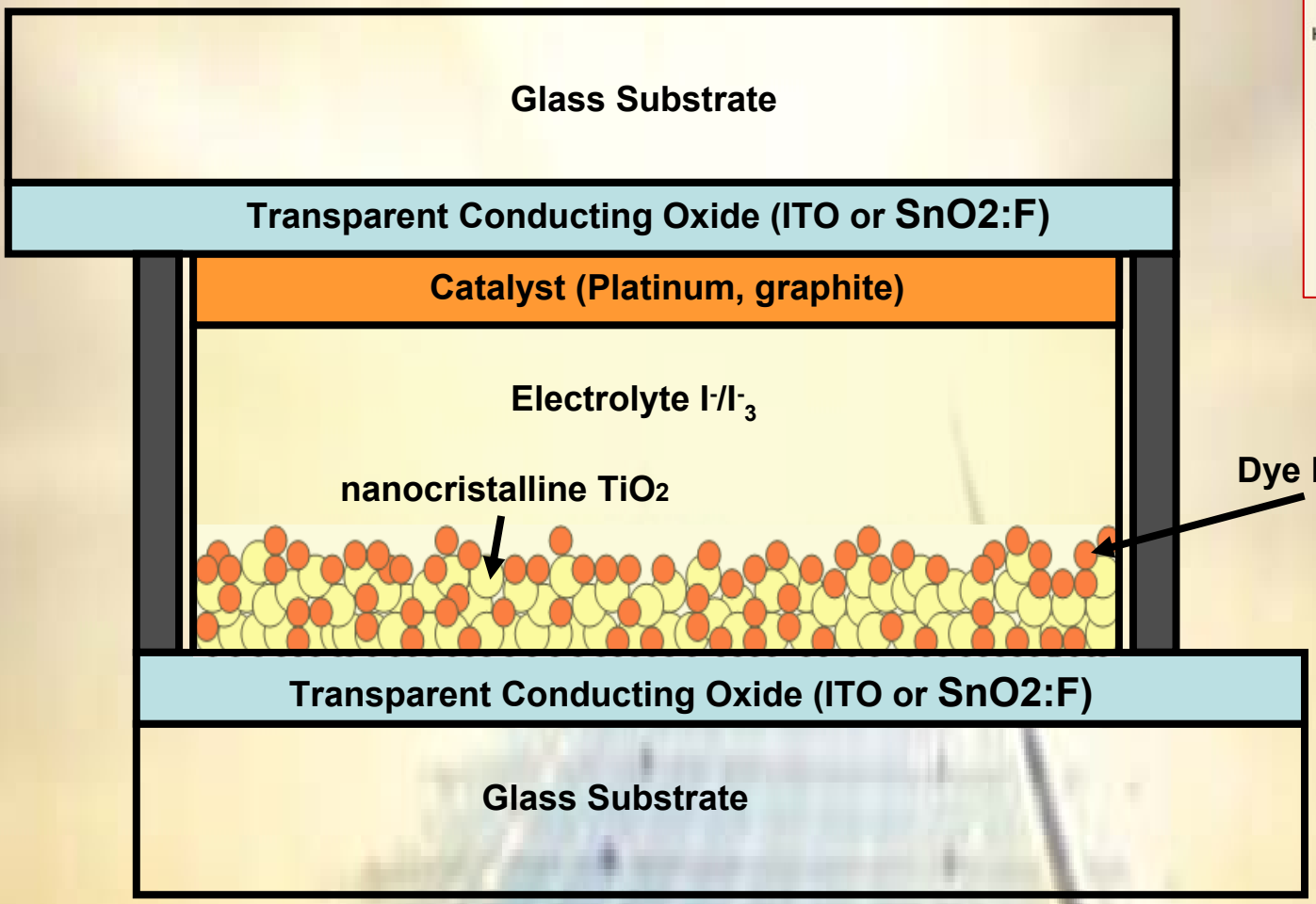


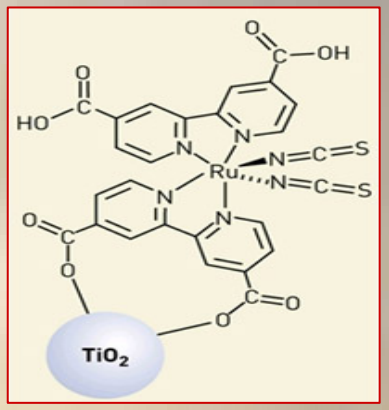



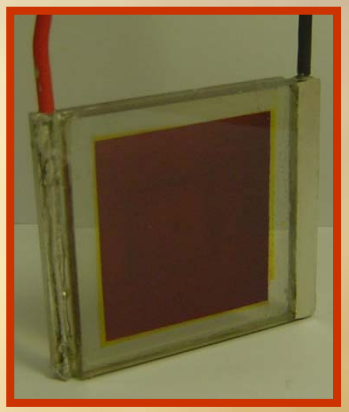

| Type | Max lab efficiency | Stability | R&D |
|---|---|---|---|
| **Hybrid Dye Sensitized (Graetzel)** | ~ 11-12% | 15 years | University and industry |
| **Full organic solar cells** | ~ 5% | 3 years | University and industry |

# Structure of Dye Sensitized Solar Cells



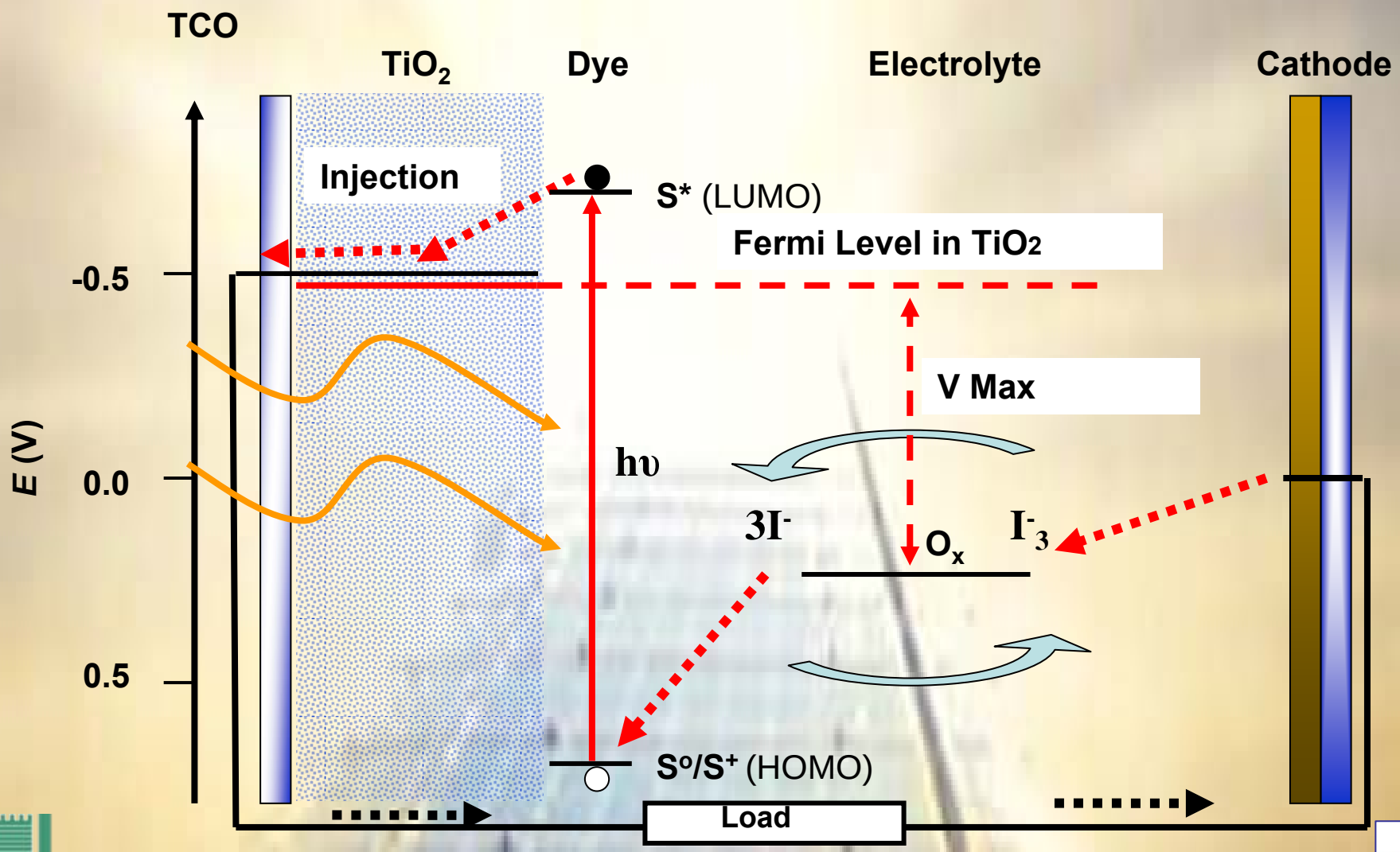




Dye Molecules on $TiO_2$

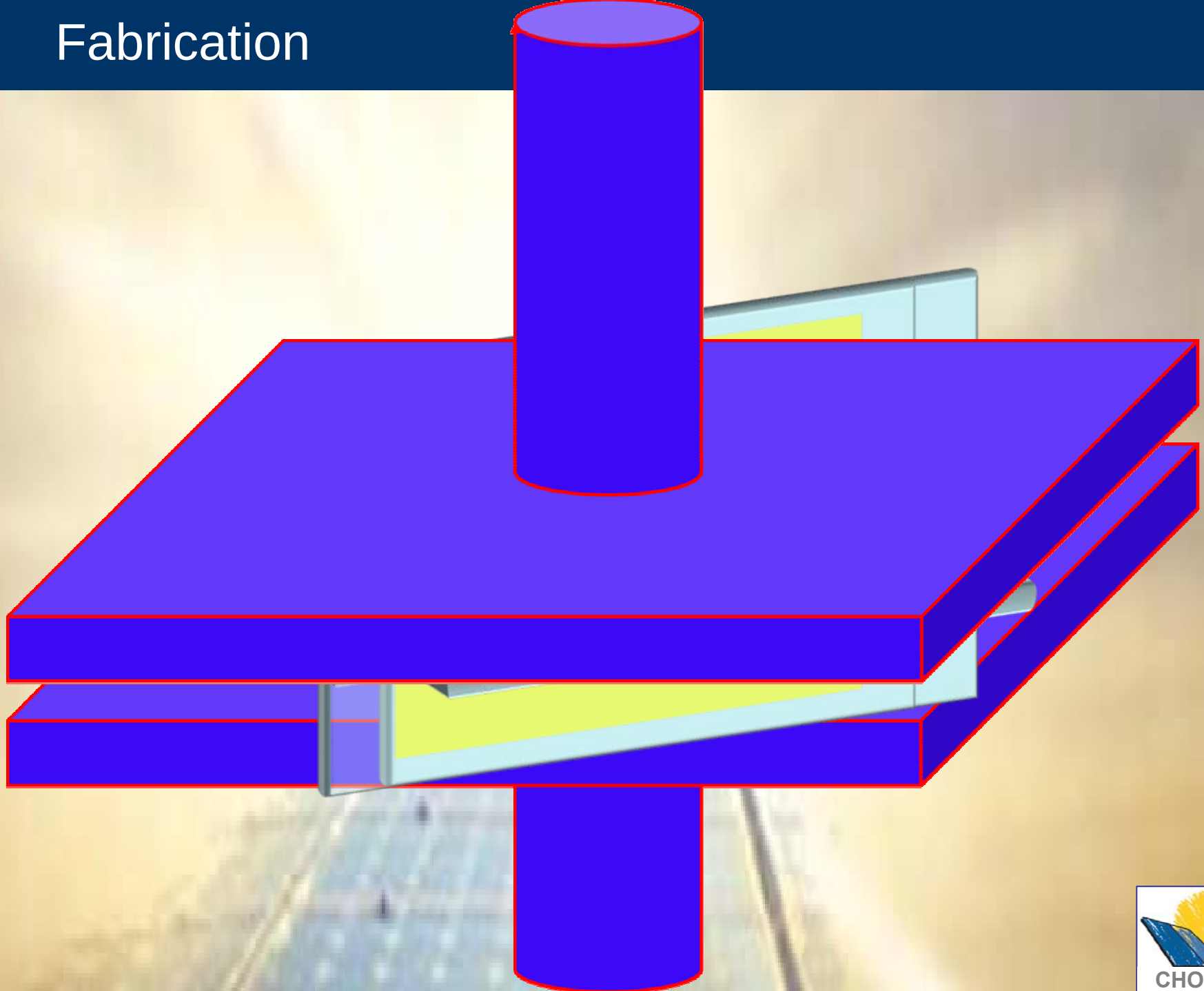


# Principle of Dye Sensitized Solar Cells

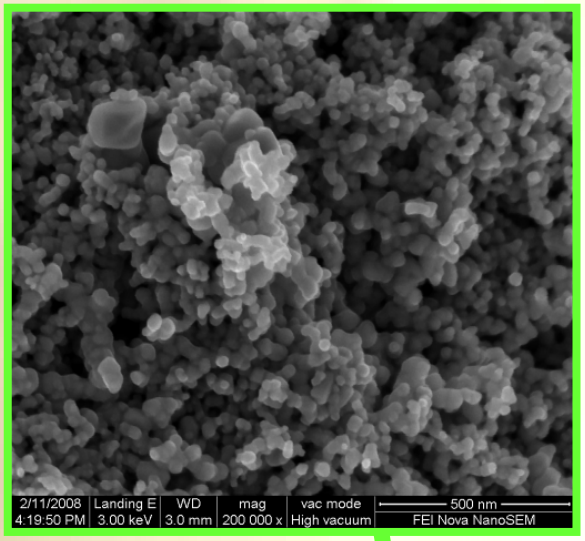
**No permanent chemical transformation in the materials composing the cell**



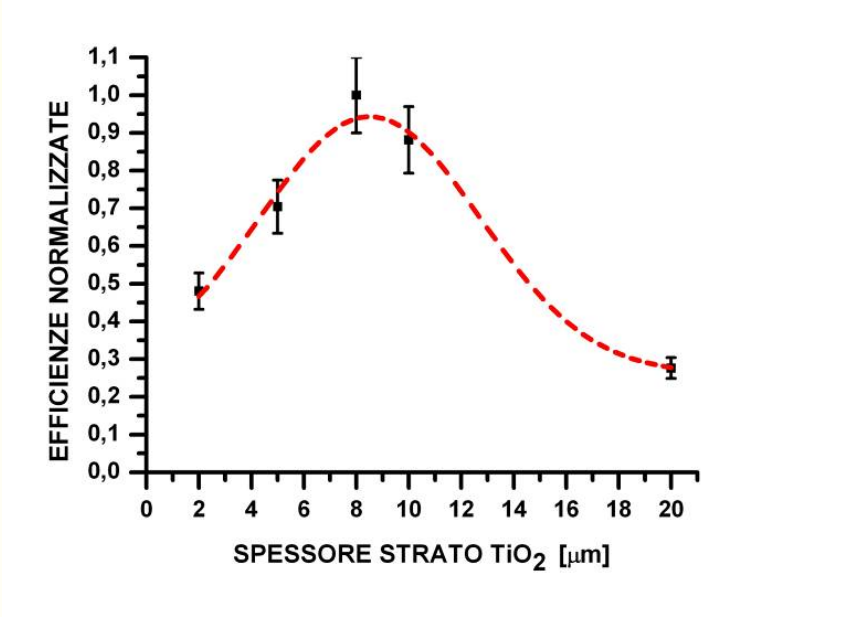
# Fabrication

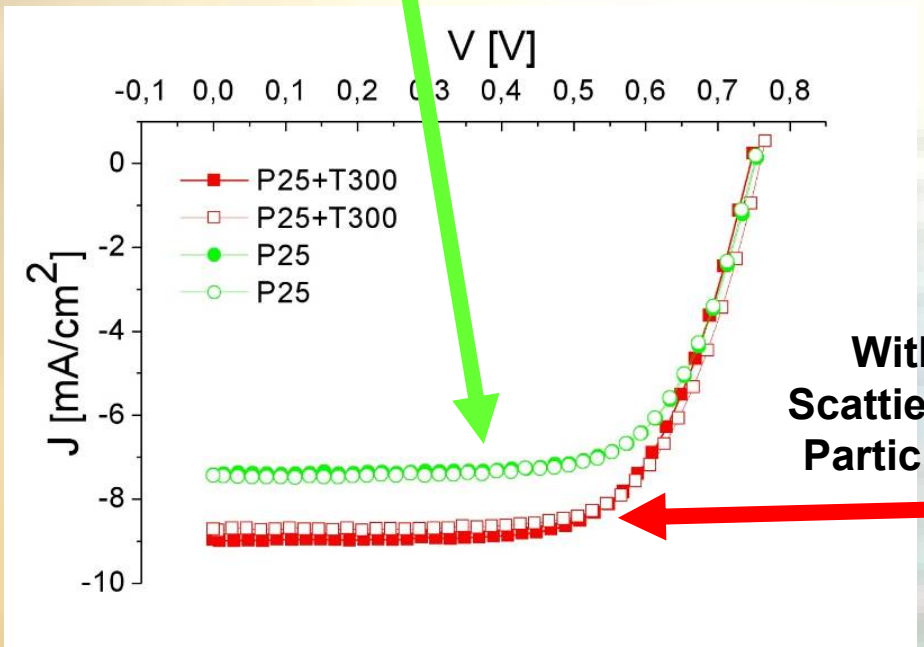


# Optimizarion of TiO2 layer

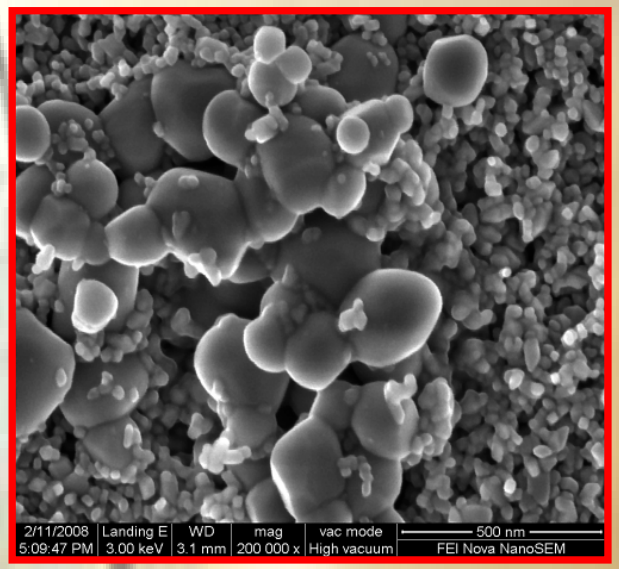



**Ottimizzazione Spessori**




**With Scattering Particles**

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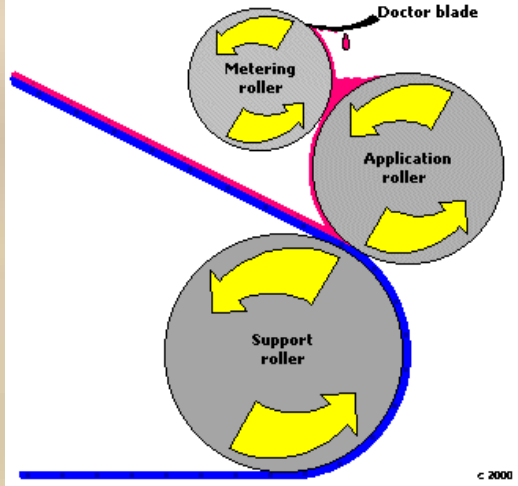
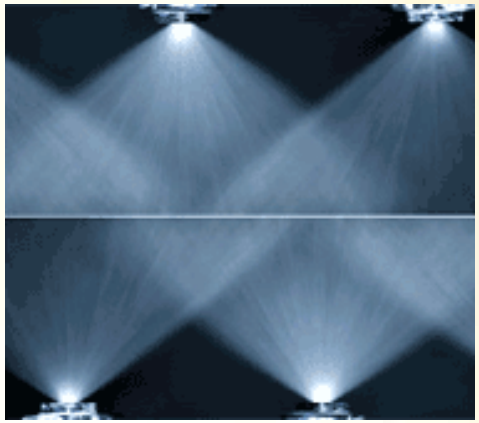
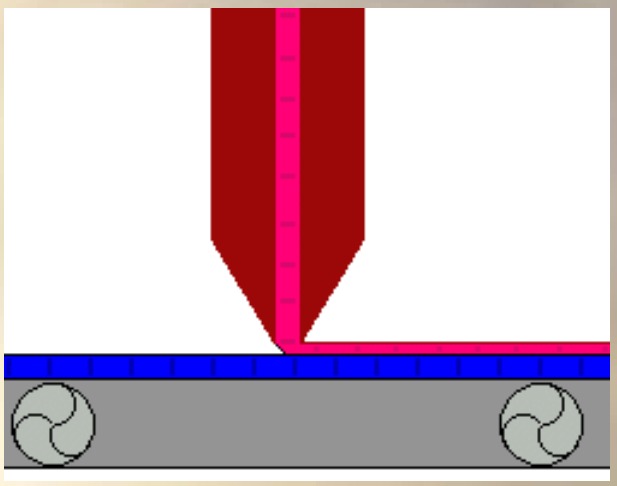
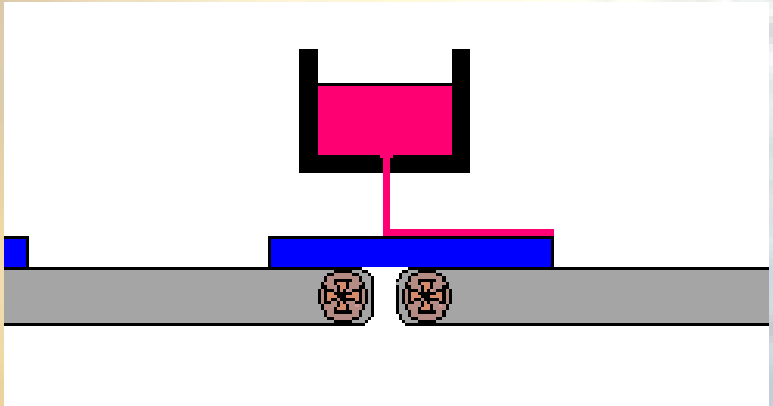
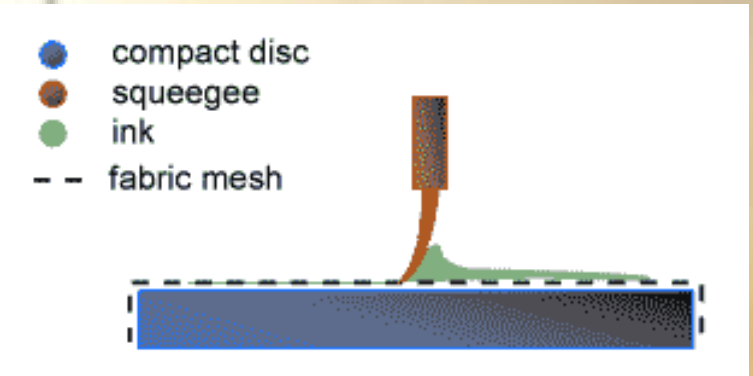
# Available printing technologies for DSC



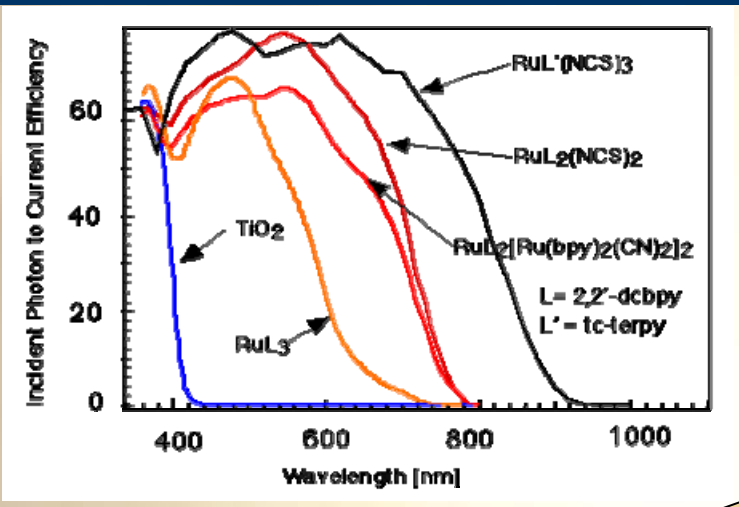









# Dyes

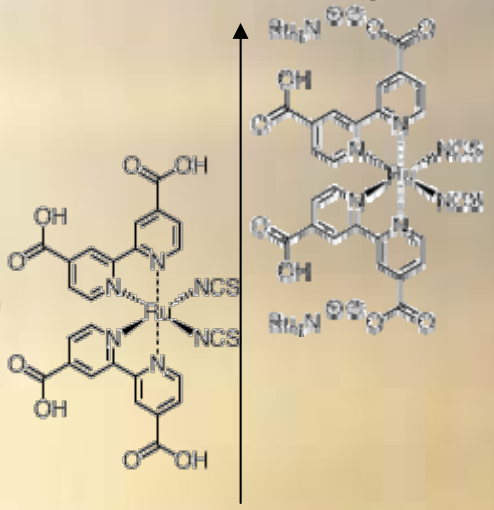



**Efficiency**

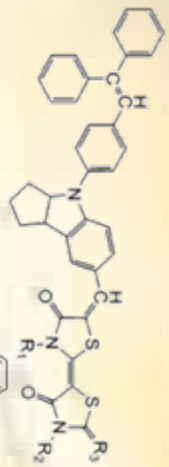
**1%**

**11%**

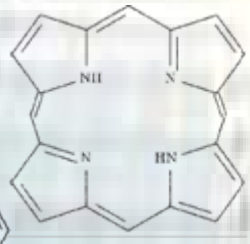
**Rutenium-Based Dyes**

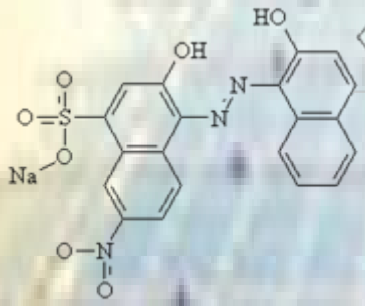


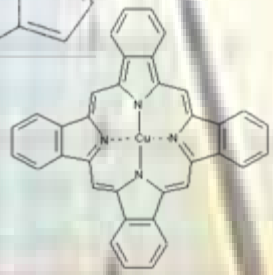
**Organic Dyes**



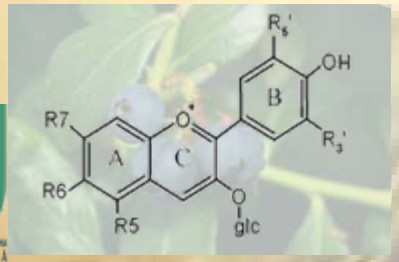
**Industrial Dyes**





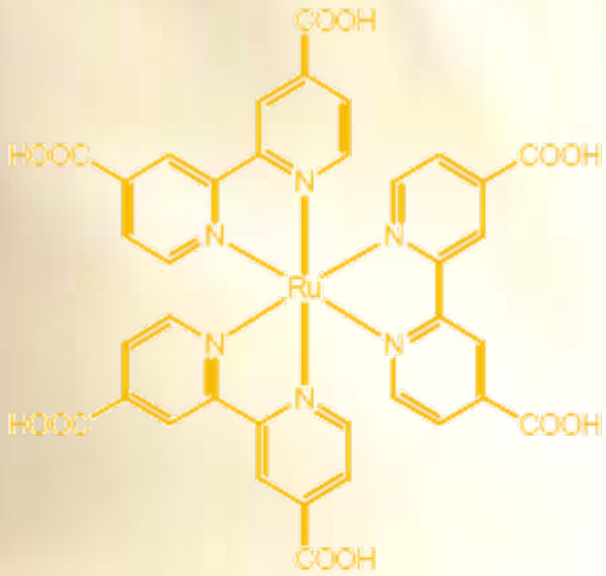


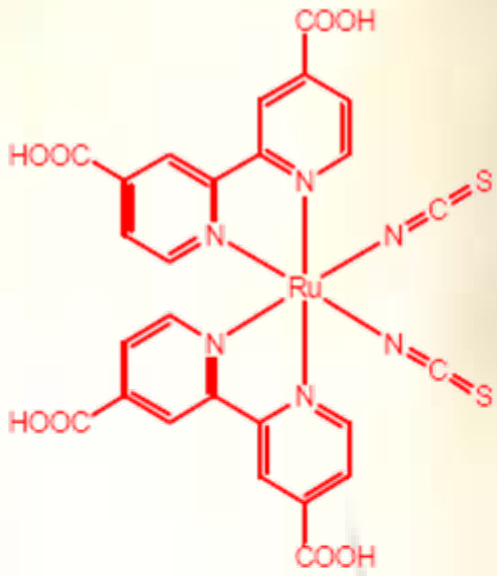
**Natural Dyes**

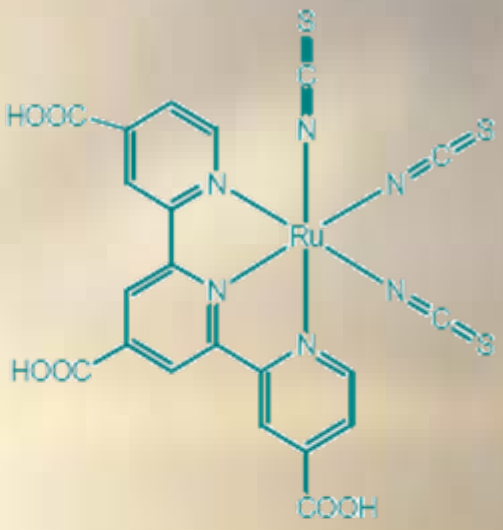


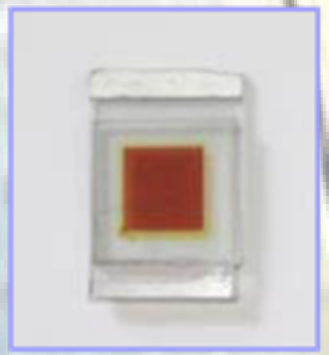
**CHOSE –UniFerrara patent**

# Dyes – color


COOH
HOOC
COOH
N
N
N
Ru
N
N
N
HOOC
COOH
COOH


COOH
HOOC
N
N
N=C=S
Ru
N
N
N=C=S
HOOC
N
COOH


S
C
N
HOOC
N
N
N=C=S
Ru
N
N
N=C=S
HOOC
N
COOH



# Electrolyte – requirements

- Chemically stable;
- Buffer to stabilise pH and thus voltage;
- Additives to reduce recombination and maintain dye integrity;
- Secondary cations to screen electronic charge of electrons injected into $TiO_2$ nanoparticles to enable higher photocurrents;
- Good transparency, particularly for inverse designs
- Processability;
- Low volatility, even at 70oC or 80oC;
- Low toxicity and cost.

# Electrolyte – Development @ CHOSE

- **Electrolyte form**: Liquid, quasi-solid (gel), and solid electrolyte;
- **Liquid Electroyte**: organic solvent electrolyte and ionic liquid electrolyte;
- **Liquid Electrolyte Composition**:
  - *organic solvent*: ACN, MPN, EC, PE, ecc....
  - *redox couple*: $I^-/I_3^-$, $Br^-/Br_2$, $Co^{II}/Co^{III}$, $SCN^-/(SCN)_2$, $SeCN^-/(SeCN)_2$;
  - *additive:* 4-tert-butylpiridine, N-Methylbenzimidazole, guanidine thiocyanate

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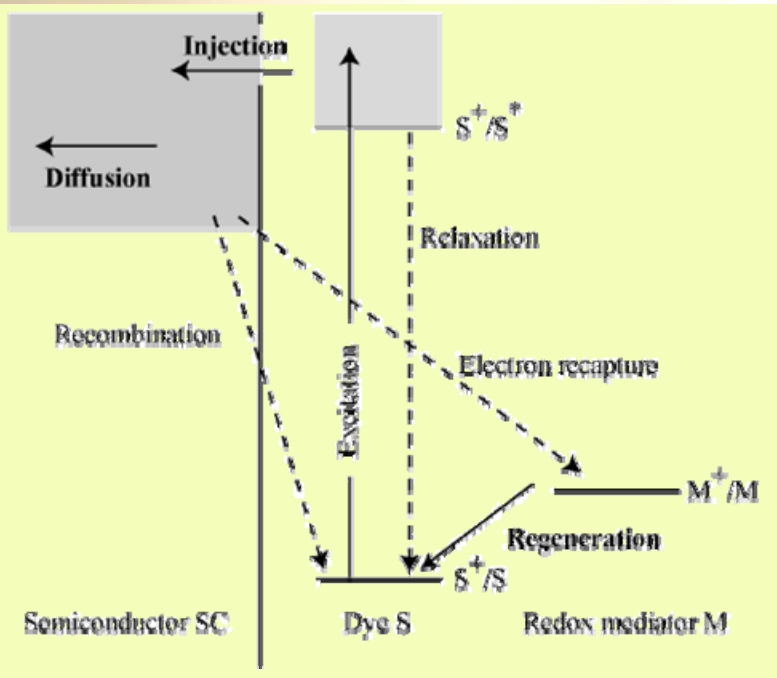
# Electrolyte - Kinetics

**The $I^-/I_3^-$ couple works well in the DSSCs because of a fortunate confluence of the right kinetics for at least four different heterogeneouselectron-transfer reactions:**




**(1) The photoexcited dye must inject an $e^-$ faster than it reacts with the mediator;**

**(2) The oxidized dye must be reduced by the mediator more rapidly than it recombines with the photoinjected electron;**

**(3) The oxidized mediator must, itself, react slowly with electrons in both the $TiO_2$ and the fluorine-doped tin oxide (SnO2:F) contact;**

**(4) Finally, the reduction of the oxidized mediator at the cathode (CE) must be rapid.**

# Electrolyte – Forms

**Gel Electrolyte:**

- High ionic conducibility;
- High chemical and electrochemical stability;
- Easy to prepare; Low cost;

**PEO(polyethyleneoxide)**
**PEG(polyehtyleneglycole)** **+ LiI / $I_2$**

**Liquid Electrolyte:**

- High volatility of the solvent;
- Maybe Ionic Liquid to replace the solvent;
- Low viscosity;
- Additives;
- Easy to put into the cells;

# Ionic Liquid based Electrolytes

**In collaboration with the Chemistry Group of Tor Vergata we can synthesize different Ionic liquid. Suitable ionic liquid are for examples:**

Ref. Iolitec

- **PMII : 1-methyl – 3 propylimidazolium iodide;**
- **HMII : 1-hexyl – 3 methylimidazolium iodide;**
- **BMIM : 1- butyl – 3 methylimidazolium iodide;**

**= High viscosity -> low conducibility**

- **EMIm-I : 1 ethyl - 3 methylimidazolium iodide;**
- **EMIm-SCN: 1 ethyl - 3 methylimidazolium thiocyanate;**
- **EMIm-DCA: 1 ethyl - 3 methylimidazolium dicyanamide;**
- **EMIm-BF4 : 1 ethyl - 3 methylimidazolium tetrafluoroborate;**

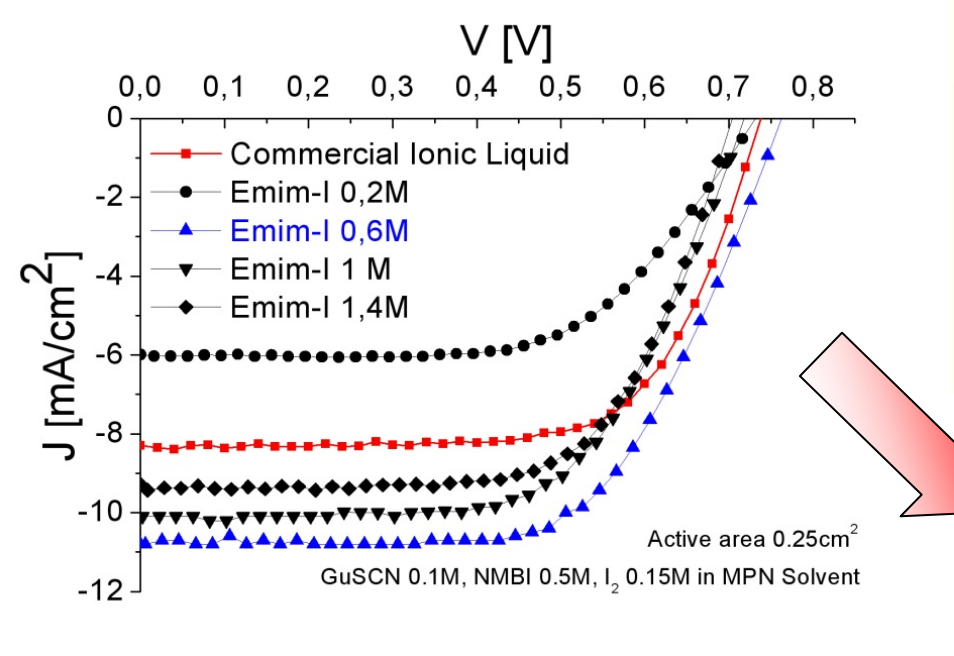
**= Low viscosity -> high conducibility**

## *Ionic Liquid Electrolyte typical composition:*

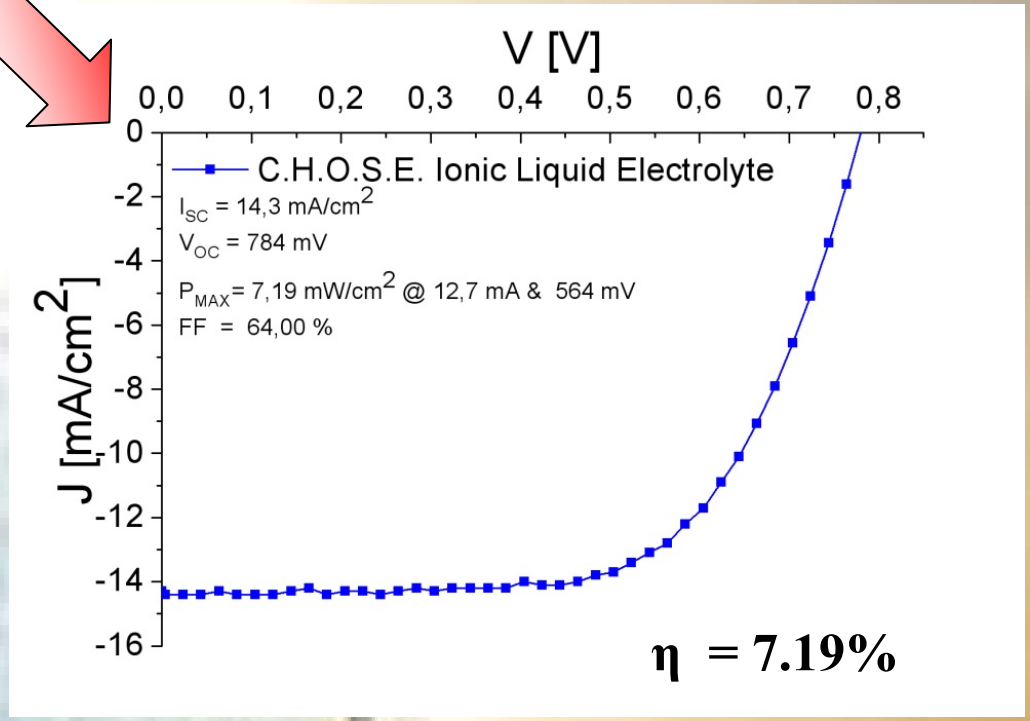
**EMIm + $I^-$, Dicyanamide, Trifluorometanesulfonilmide + $I_2$**

*cation* — *anion* — *mediator*

# Ionic liquid based DSC

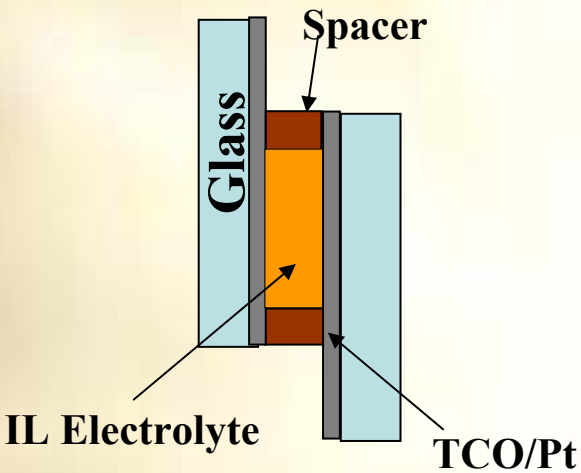


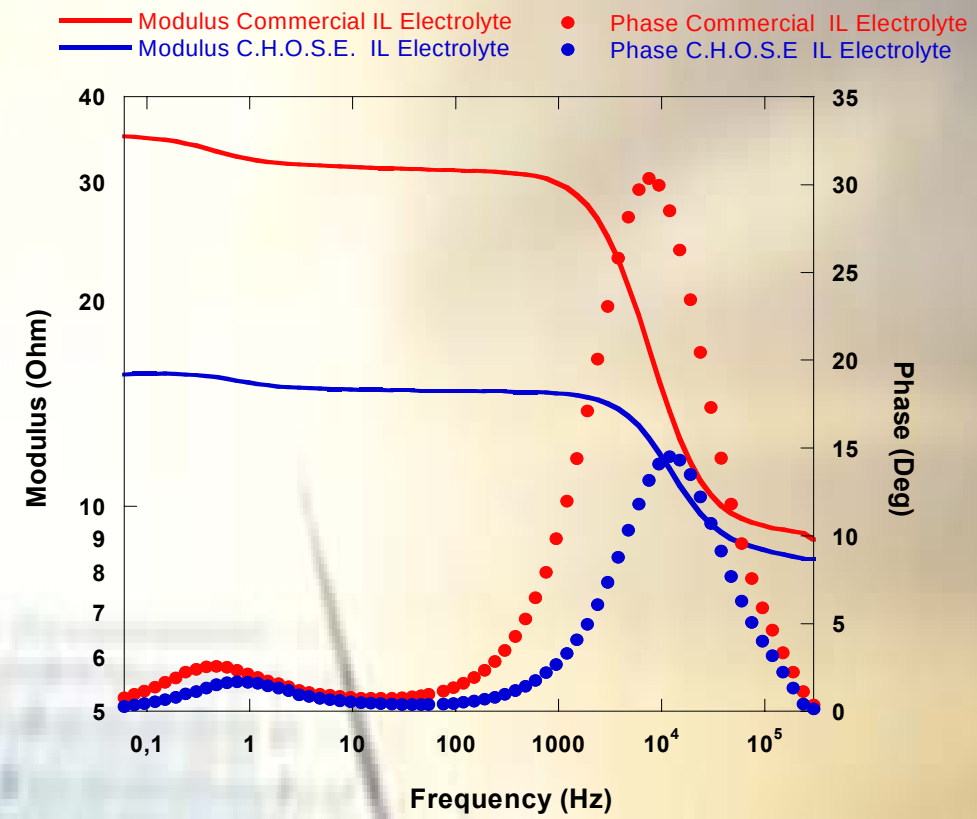

**In collaboration with the Chemistry Group of Tor Vergata (Conte, Mirruzzo) we have synthesize different Ionic liquid.**



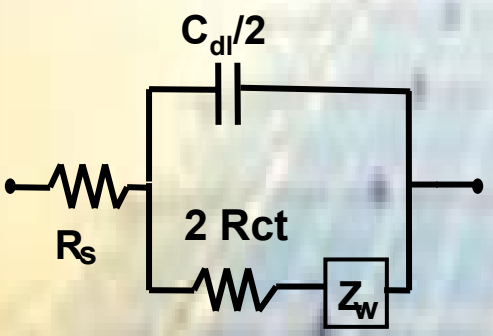
# Electro-Impedance Spectroscopy

## *Symmetric cell*



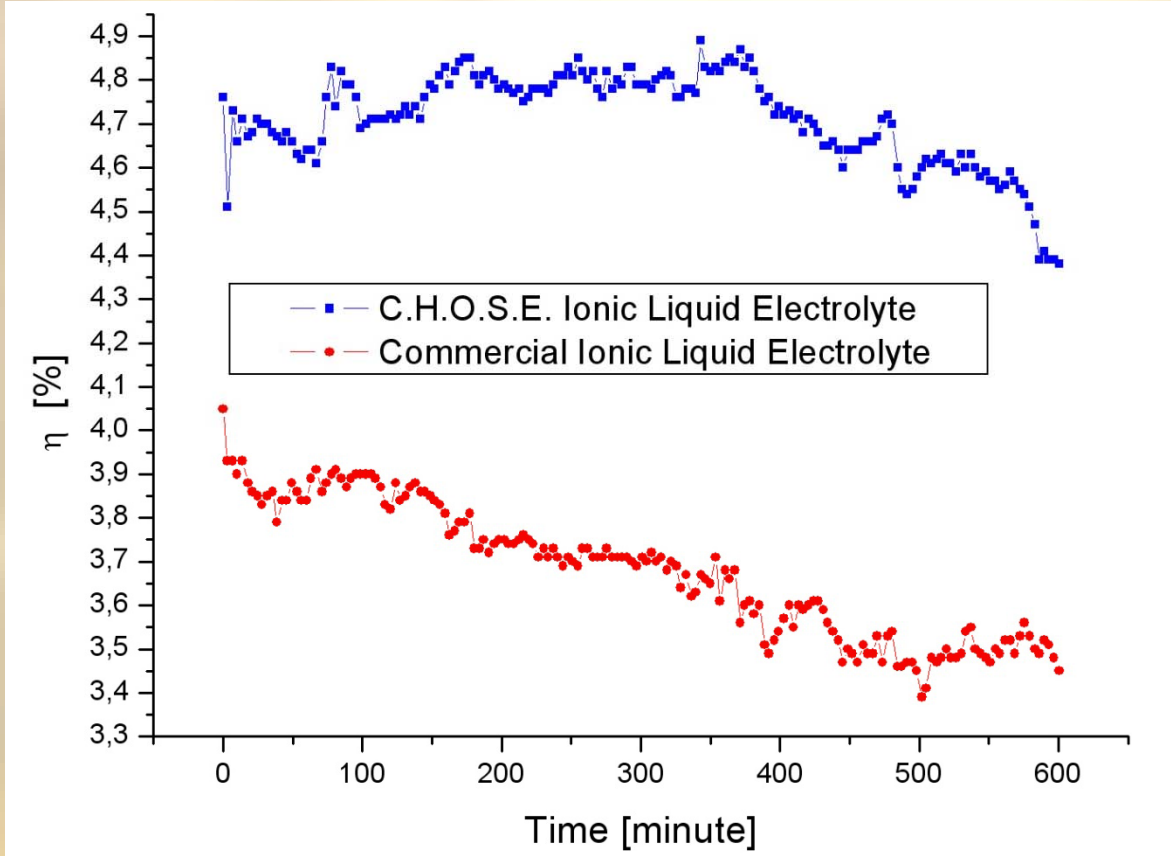




## *Equivalent circuit*




| Sample | $R_{ct}$ (Ohm*cm$^2$) |
|---|---|
| Commercial IL | 5.0 |
| C.H.O.S.E. IL | 1.5 |

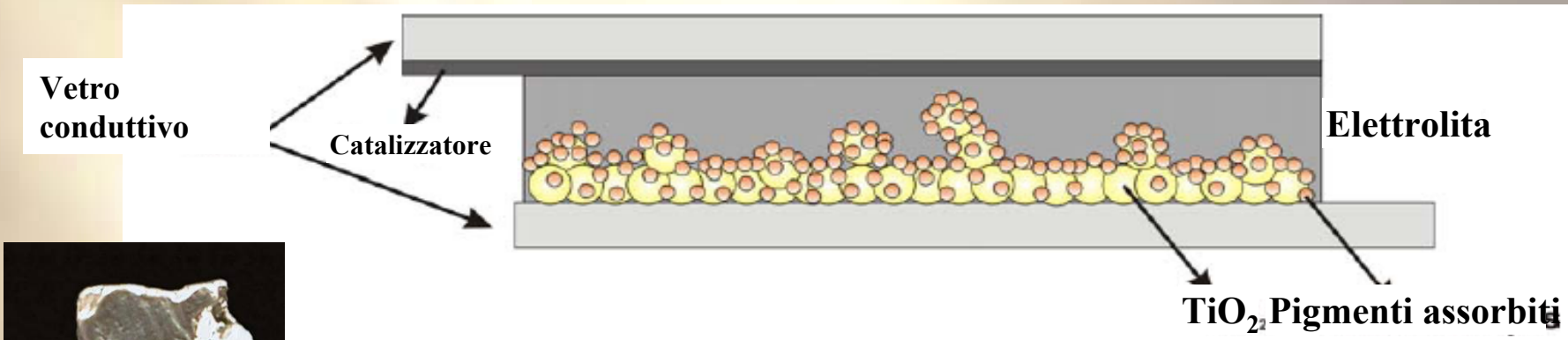
# Confronto Efficienza / Durata Liquidi Ionici

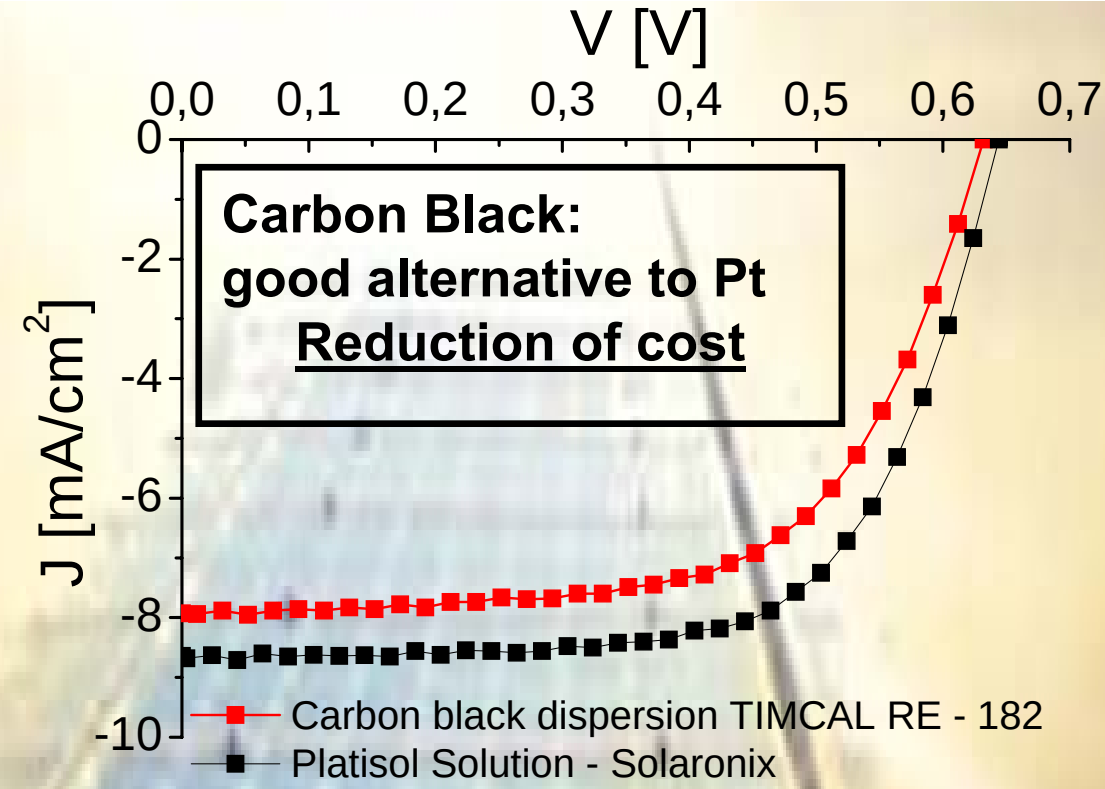


**Confronto tra:**

- **Liquido Ionico prodotto in C.H.O.S.E**
- **Liquido Ionico Commerciale**

# Counterelectrode development

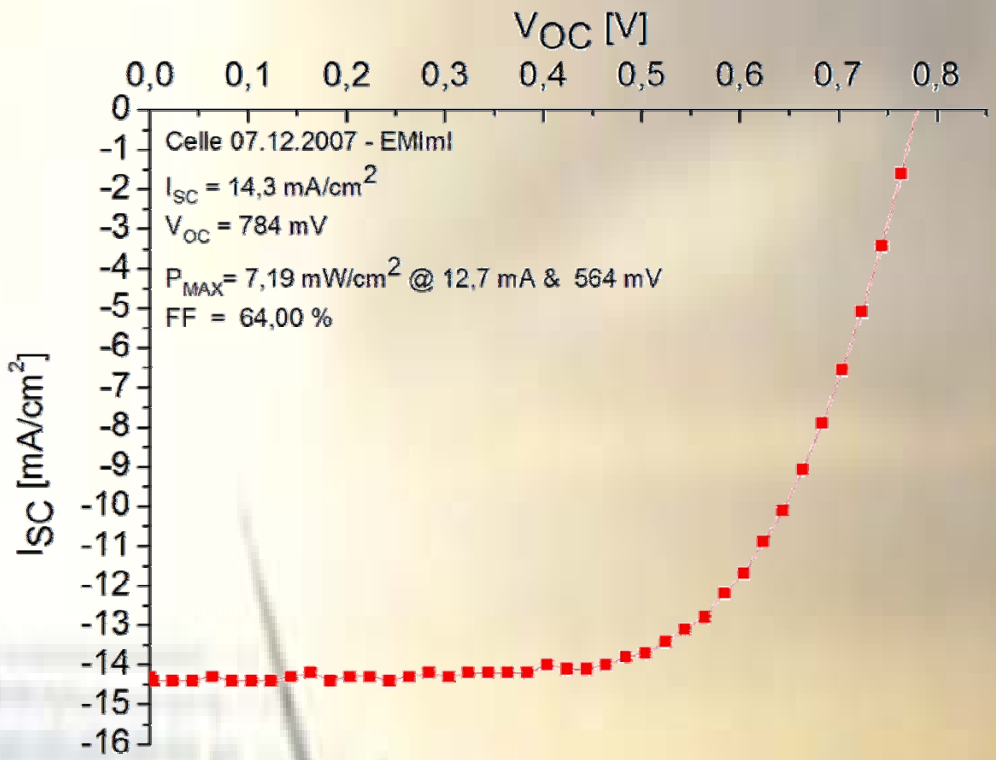




# Typical Photovoltaic performance

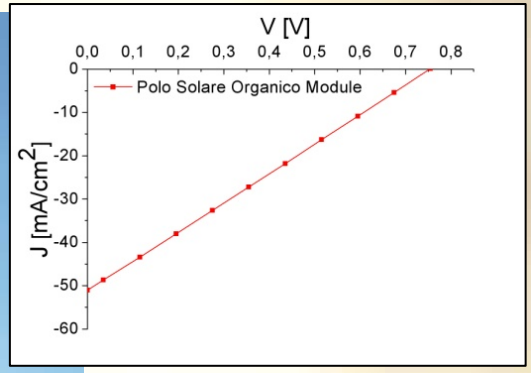
- QE = 70-80%
- $J_{sc}$ = 15-20 mA $cm^{-2}$
- $V_{oc}$ = 0.8 V

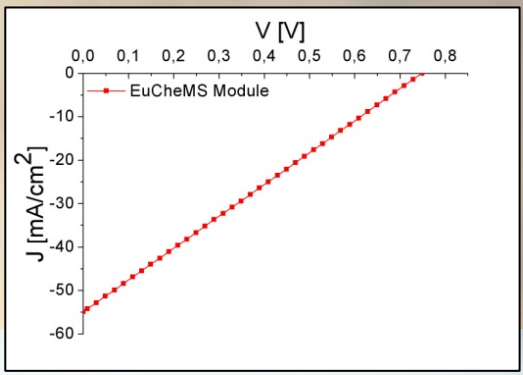
- $\eta$ = 7 %

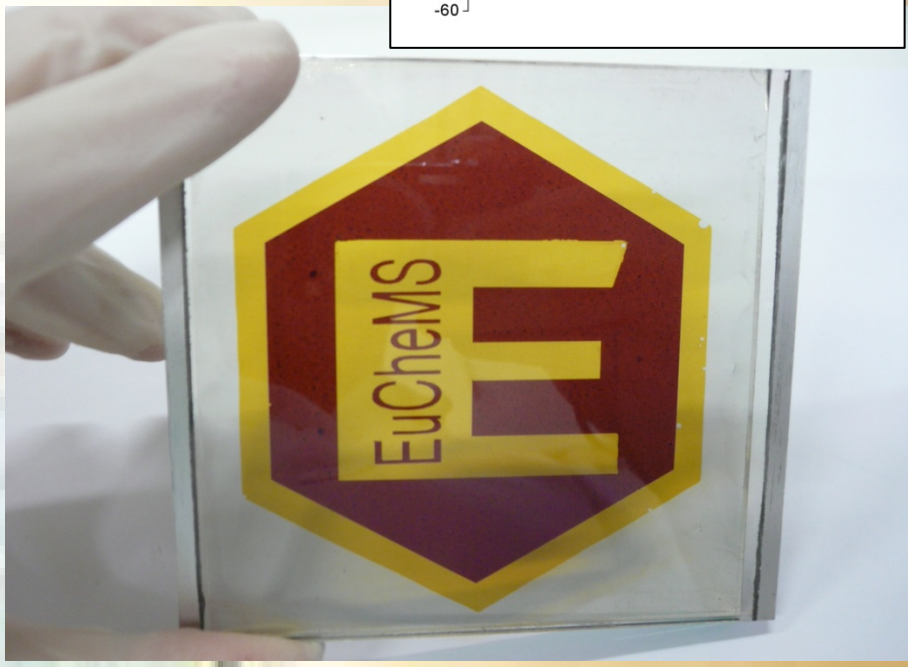



- Challenges:
  - Improving photocurrent: dyes, light management
  - Improving photovoltage : minimise recombination
    alternative materials

# Example of DSC (sigle cells)

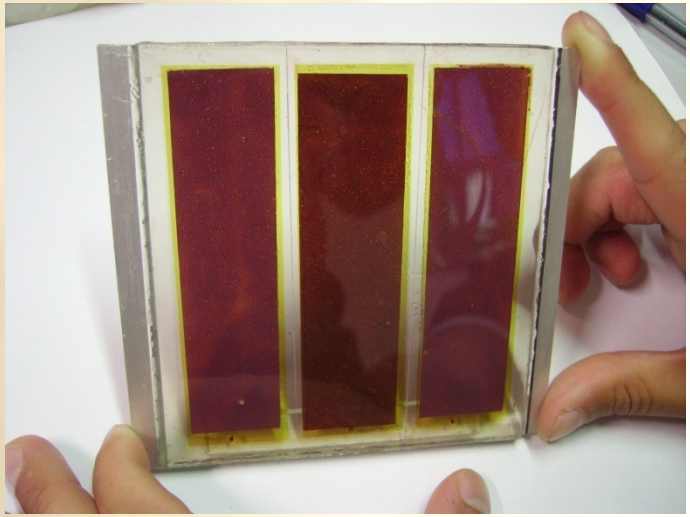


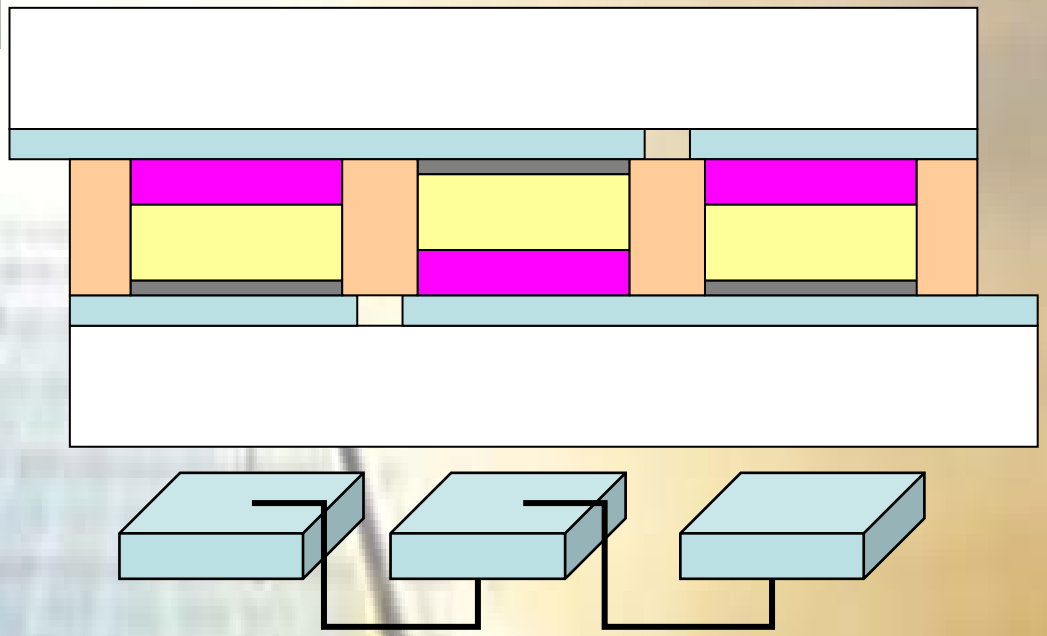



**Series resistance is very critical !!!**

# 100cm² Module Fabrication with 3 cells series interconnected



- Define contacts
- Coat the different layers
- Leave in Dye Solution
- Seal



Glass

TCO

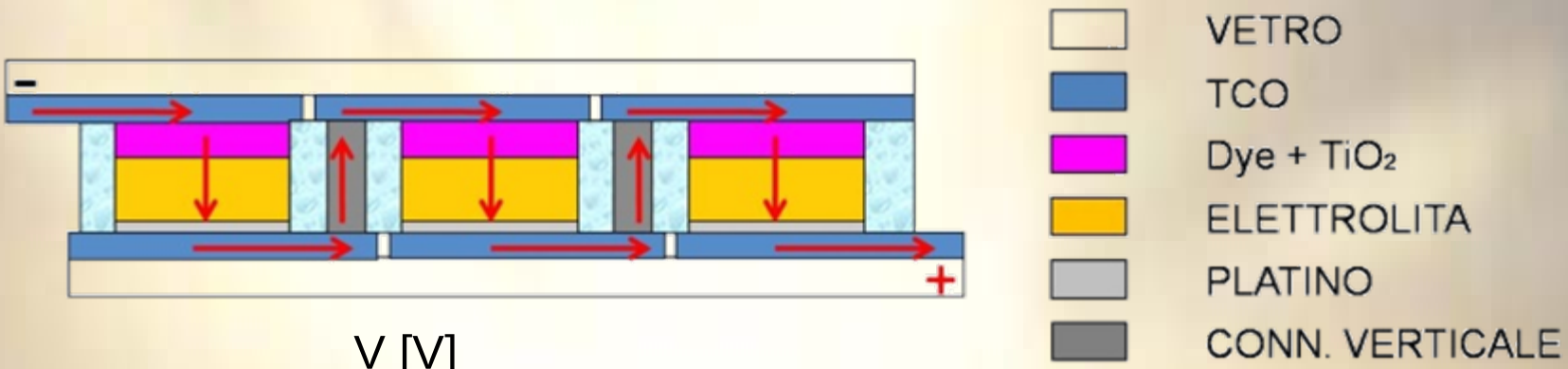
Dye sensitized TiO2

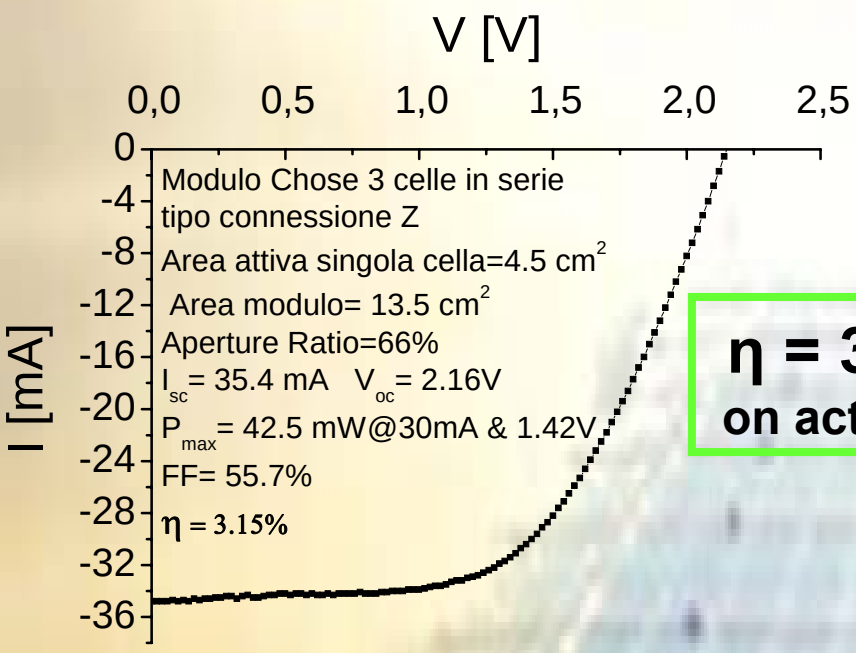
Electrolyte

Pt catalyst

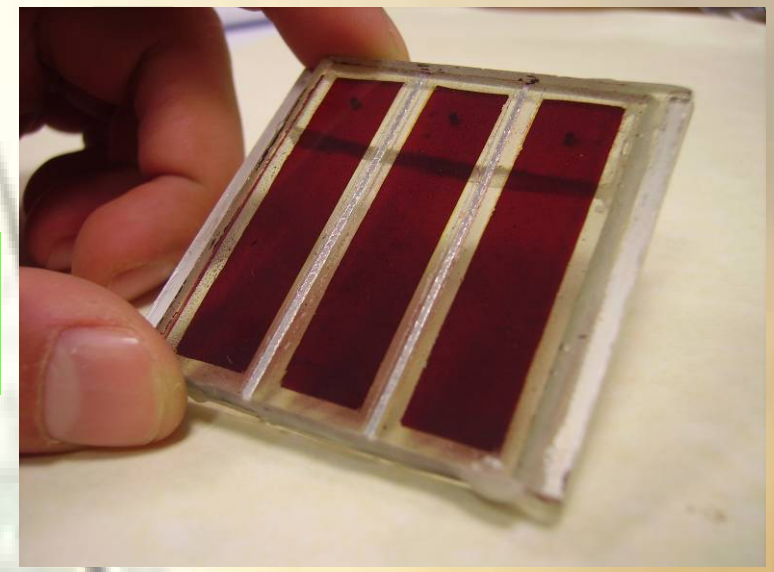
Series interconnect of a number of cells

# DSC Modules with Ionic Liquids



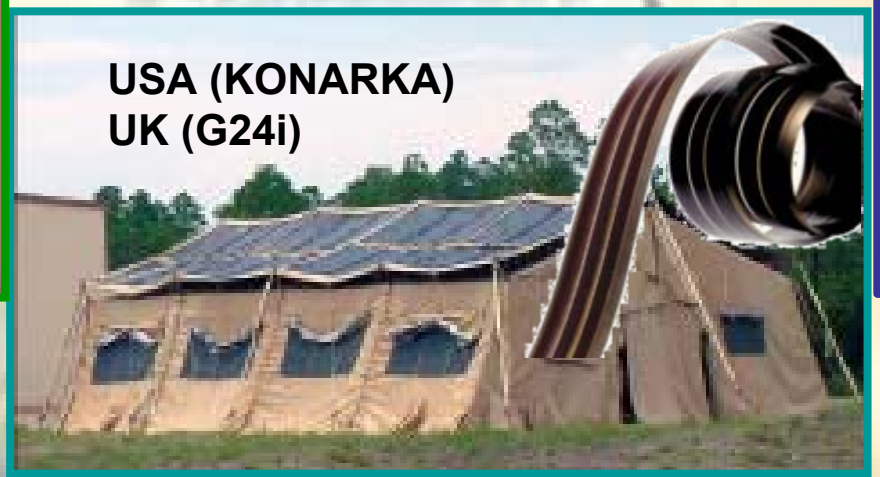




**η = 3.15 %**
**on active area**



**With Ionic Liquid**

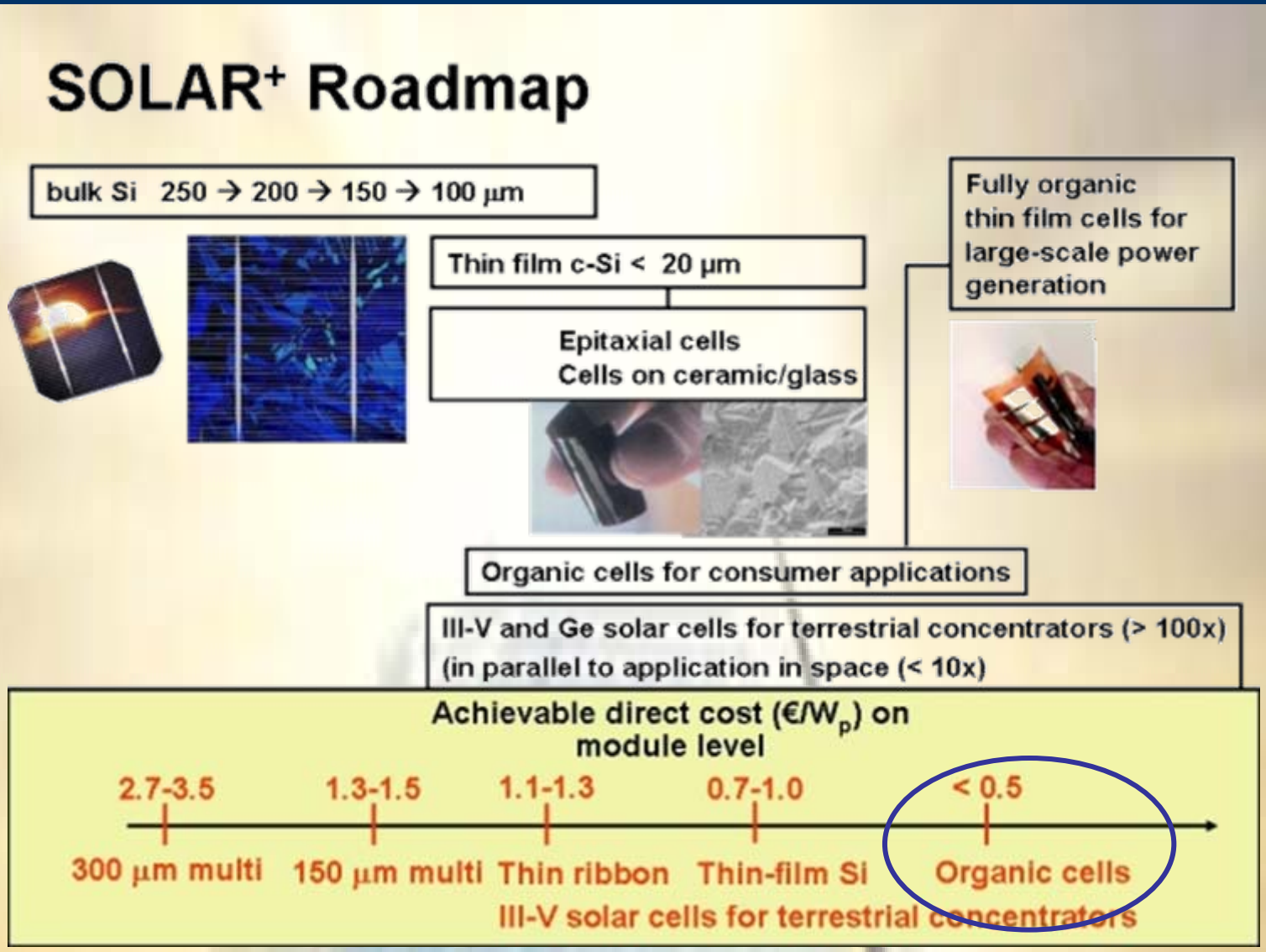
# DSC in the world



3rd INTERNATIONAL CONFERENCE
on the INDUSTRIALISATION of DSC
DSC-IC 2009
Nara, Japan, 22-24 April 2009

CHOSE

# COST: IMEC vision




**For DSC cost of the cell is mainly related to the cost of glass (Pilkington)**

# L’impegno della Regione Lazio alla sfida delle Rinnovabili

LAZIORINNOVABILE
RegioneLazio

POLOIDROGENO
RegioneLazio

REGIONE LAZIO

POLOMOBILITA’
RegioneLazio

POLOSOLAREORGANICO
RegioneLazio
CHOSE

CHOSE

# CHOSE: fatti

- Nasce il 19 dicembre 2006
- Scopi
  - Sviluppare un processo tecnologico per le celle organiche/ibride
  - Definire una processo di industrializzazione del fotovoltaico organico
  - Punto di riferimento sul fotovoltaico nel panorama regionale
  - Trasferimento tecnologico verso le PMI
- Attualmente coinvolge 6 gruppi di Tor Vergata (Ingegneria, Chimica, Fisica), 5 gruppi esterni (UniFerrara, UniSapienza, PoliTorino, UniTorino e CNR) e diverse società di ricerca
- Punto di aggregazione per sviluppo di progetti correlati al fotovoltaico organico (FP7, MAP, FIRB, FIRS, PRIN etc. etc.)

TOR VERGATA

CHOSE

# Laboratorio CHOSE (21 July 2008)

**Tecnopolo Tiburtino**

**Il Polo svilupperà la linea pilota al Tecnopolo Tiburtino dove la vicinanza con la realtà industriale ed imprenditoriale permetterà il trasferimento tecnologico.**

**600 m² di laboratorio di cui 400 m² di camera pulita**

**Il laboratorio è principalmente dedicato allo sviluppo di una linea pilota di produzione DSSC**

# Dettagli di CHOSElab

# Rientro dei “cervelli” e degli investimenti

**La nascita di un centro di eccellenza sul fotovoltaico organico ha permesso il rientro in Italia di giovani “Cervelli” che operavano da anni all’estero**

- Dall’Inghilterra (Dott. Thomas M. Brown) ora Professore a Tor Vergata
- Dalla Francia (Dott. Adalberto Brunetti)
- Dalla Germania (Dott. Massimiliano Liberatore, Dott. Alessio Gagliardi)

**Il team di ricerca si compone di circa 30 ricercatori ( 7 dottorandi, 3 post doc, 6 contrattisti e 4 staff) e circa 10 studenti di laurea**

**La DYESOL australiana, industria leader nei materiali per celle organiche ha deciso di investire in Italia, a Roma, attraverso la DYESOL Italia.**

**Questa iniziativa è stata motivata dalla nascita del Polo Solare Organico con cui intende fortemente collaborare.**

**Sono previste diverse assunzioni nell’ambito di esperti chimici.**

# Master in Ingegneria del Fotovoltaico

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ENEA

CHOSE

# SPIN-OFF: DYERS.srl

- Si è concluso a Giugno 2008 l'iter accademico per la nascita di una spin-off universitario, Dyers, per lo sviluppo e la promozione delle tecnologie fotovolaiche organiche

DYERS

CHOSE

# DYEPOWER consortium

**September 2008:**

**ERG Renew, Permasteelisa, Dyesol Italia, CHOSE (Uni Tor Vergata), Uni. Torino, Uni Ferrara**

**Signed a Framework agreement for the industrialization of DSC for BIPV**

# Conclusion

- Organic materials introduce a new way for silicon free photovoltaics. Large tunability, easy manufacture, low plant cost.
- However, we need chemical company to scale up materials
- Sept. 2007 – BASF and others announced an investment for 400 million euro in this field.
- December 2007 – Dyesol Italia has been established

# Acknowledgments

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

**Regione Lazio**

CHOSE