High efficient Dye sensitized solar cells: A new perspective to the solar energy conversion.

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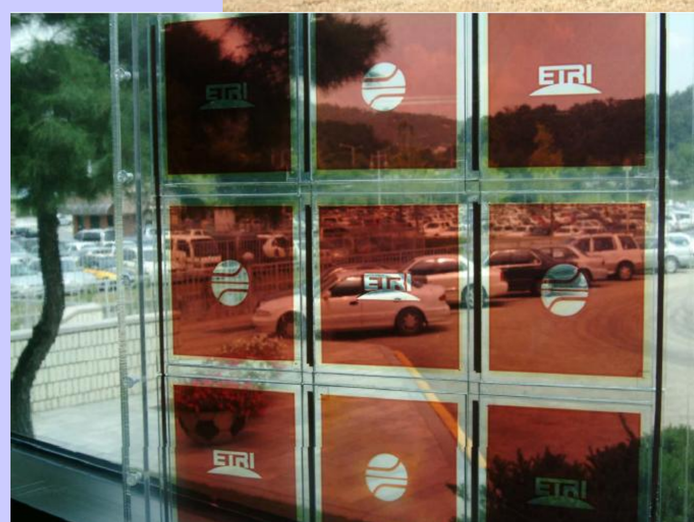
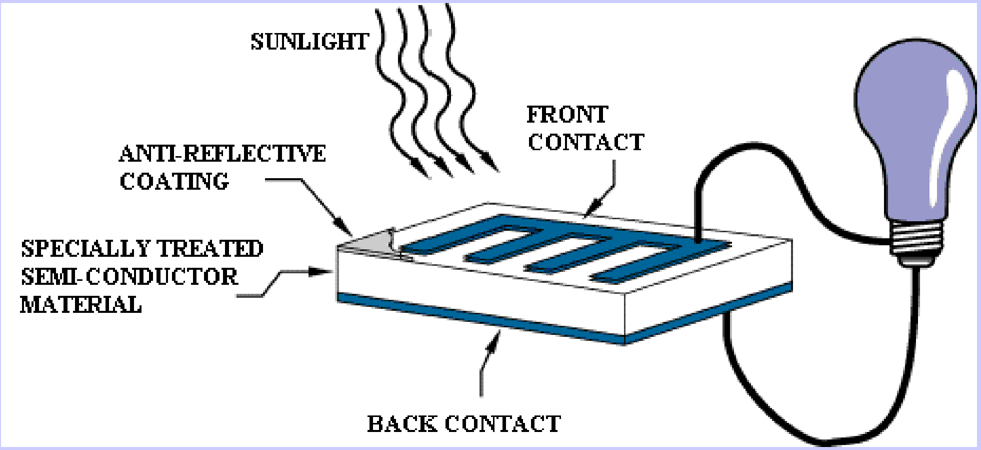


What's a PV

Light energy (photons) ➡ **Electrical energy**

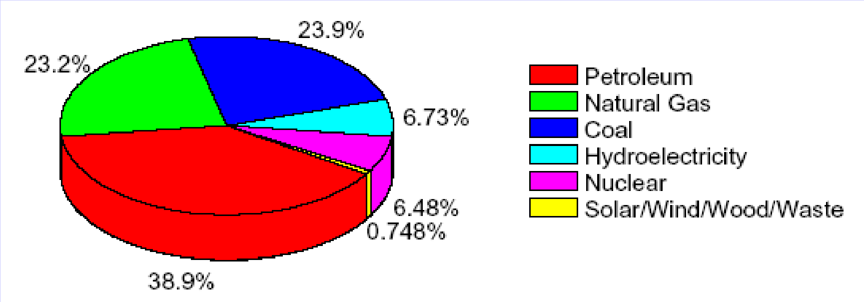


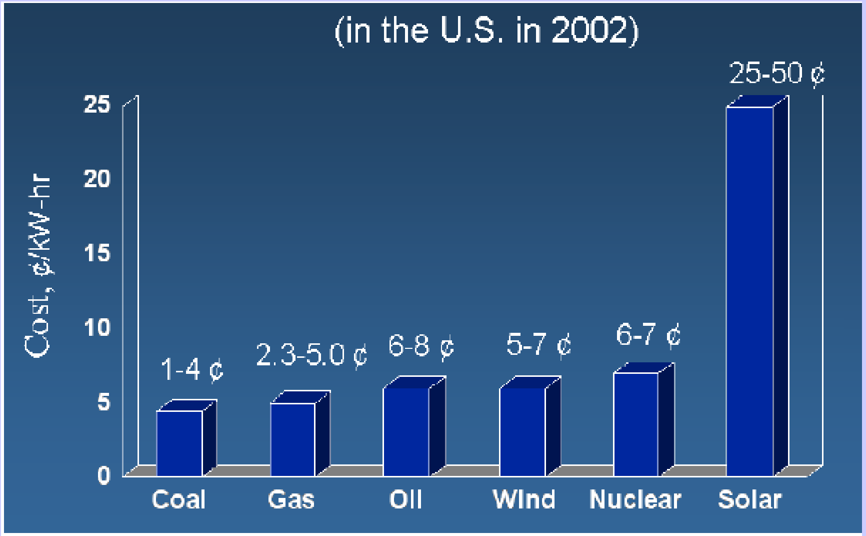
When sunlight is absorbed by some materials, the solar energy knocks electrons loose from their atoms, allowing the electrons to flow through the material to produce electricity.

This process of converting light (photons) to electricity (voltage) is called the ***photovoltaic (PV) effect***.

Solar energy

At earth's surface average solar energy is ~ 4 x 1024 J / year
Global energy consumption is ~ 4.2 x 1020 J / year (increasing ~ 2% annually)





In US, average power requirement is 3.3 TW.
With 10% efficient cells we would need 1.7% of land area devoted to PV (~ area occupied by interstate highways)

History

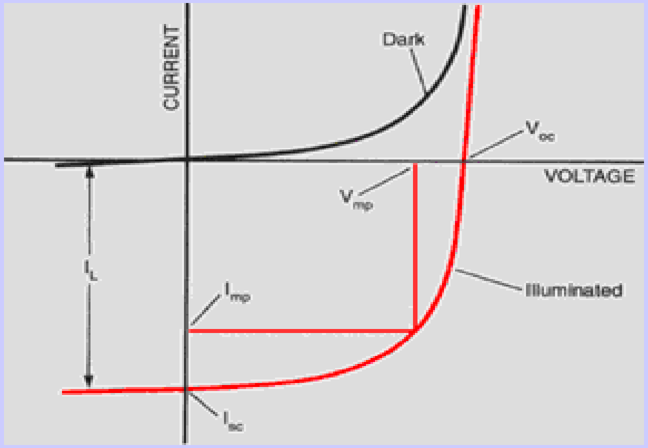
- 1839 : Finding of Photovoltaic effect with liquid (Edmond Becquerel)
- 1876 : Photovoltaic effect in a solid (Heinrich Hertz)
- 1883 : Se solar cell (C. Fritts)
- 1930 : Research of Cu_2O/Cu solar cell
- 1941 : Patent of Si solar cell (R. Ohl)
- 1954 : Crystalline Si solar cell (Bell Lab.) ; 4 % efficiency
- 1958 : Using as assistant power in the spaceship (Vanguard I) ; 5 mW
- 1973 : oil crisis
- 1980 : solar cell using CdTe, $CuInSe_2$,TiO_2 etc.
- 1997 : world product 100MWp
- 2000 : research of advanced materials and structures

  (Dye Sensitized Solar Cell (DSSC) , Organic Solar Cell (OPV))

  ➔ *cheap process , flexible substrate*

Cell efficiency

Power conversion efficiency (η)



$$\eta = \frac{I_{mp}V_{mp}}{P_S} \times 100$$

I_{SC} : Short-circuit current

→ Current value when V = 0

V_{OC} : Open-circuit voltage

→ Voltage value when I = 0

P : Power output of the cell

P = IV

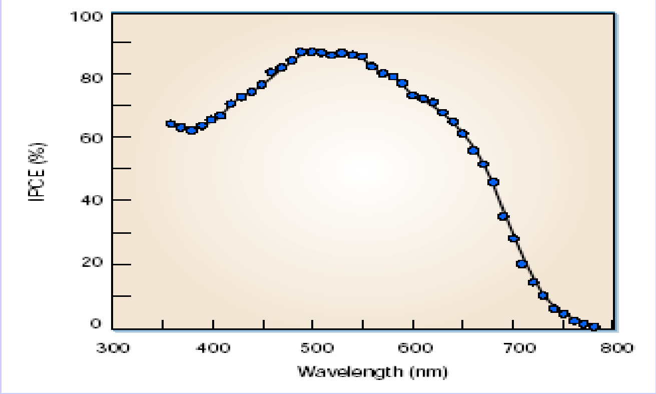
FF : Fill factor

$$FF = \frac{I_{mp}V_{mp}}{I_{sc}V_{oc}}$$

$$\eta = \frac{I_{sc}V_{oc}FF}{P_S} \times 100$$

Under **AM 1.5G** simulated solar illumination

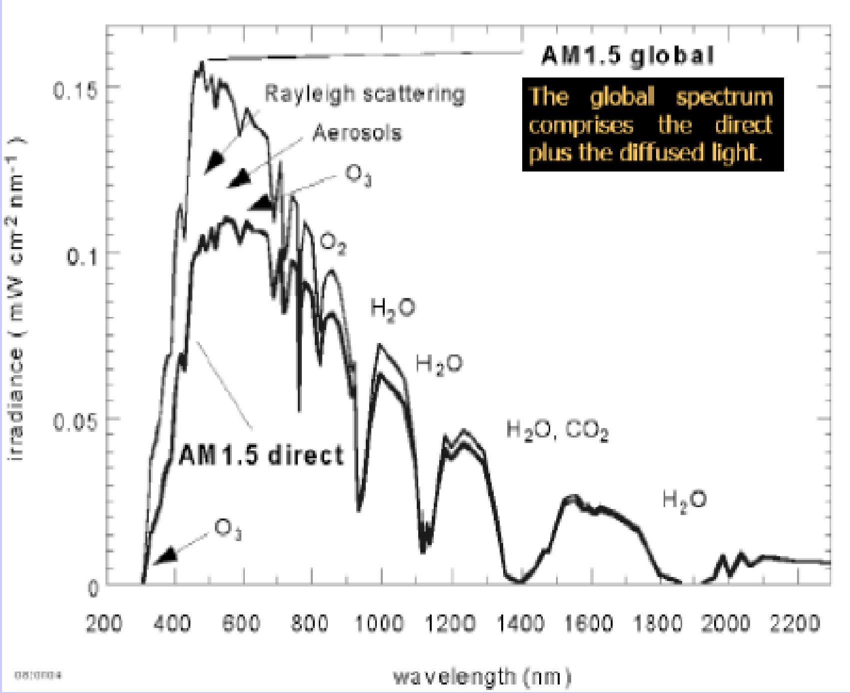
Incident-photon-to-current conversion efficiency (IPCE)

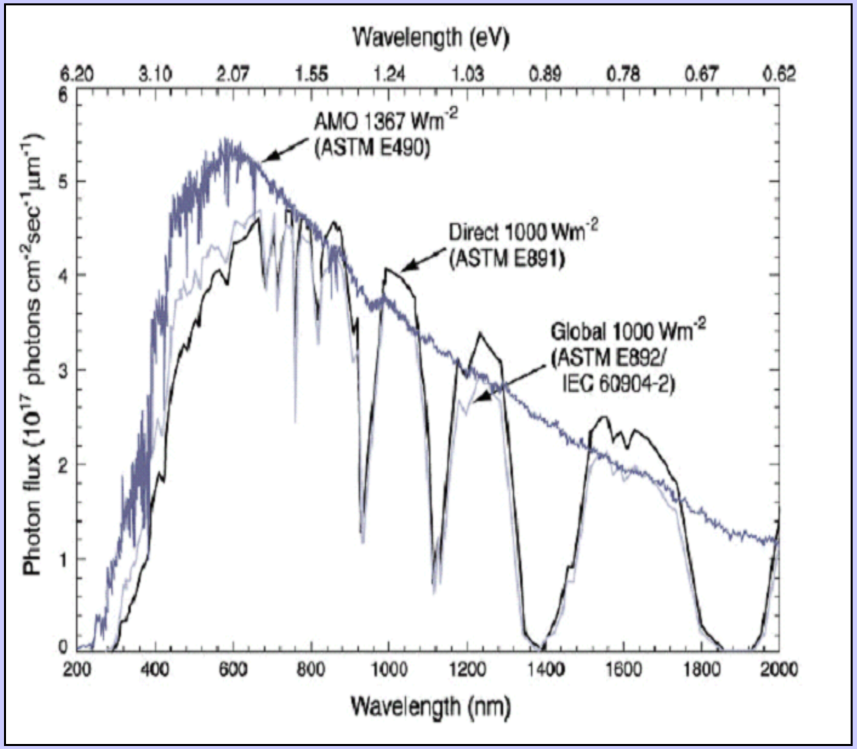


$$IPCE = \frac{\text{no. of electrons through the external circuit}}{\text{no. of photons incident}}$$

$$= \frac{[1240\ eV\ nm][photocurrent\ density\ (\mu A\ cm^{-2})]}{[wavelength\ (nm)][irradiance\ (mW\ cm^{-2})]}$$

Sunlight spectrum

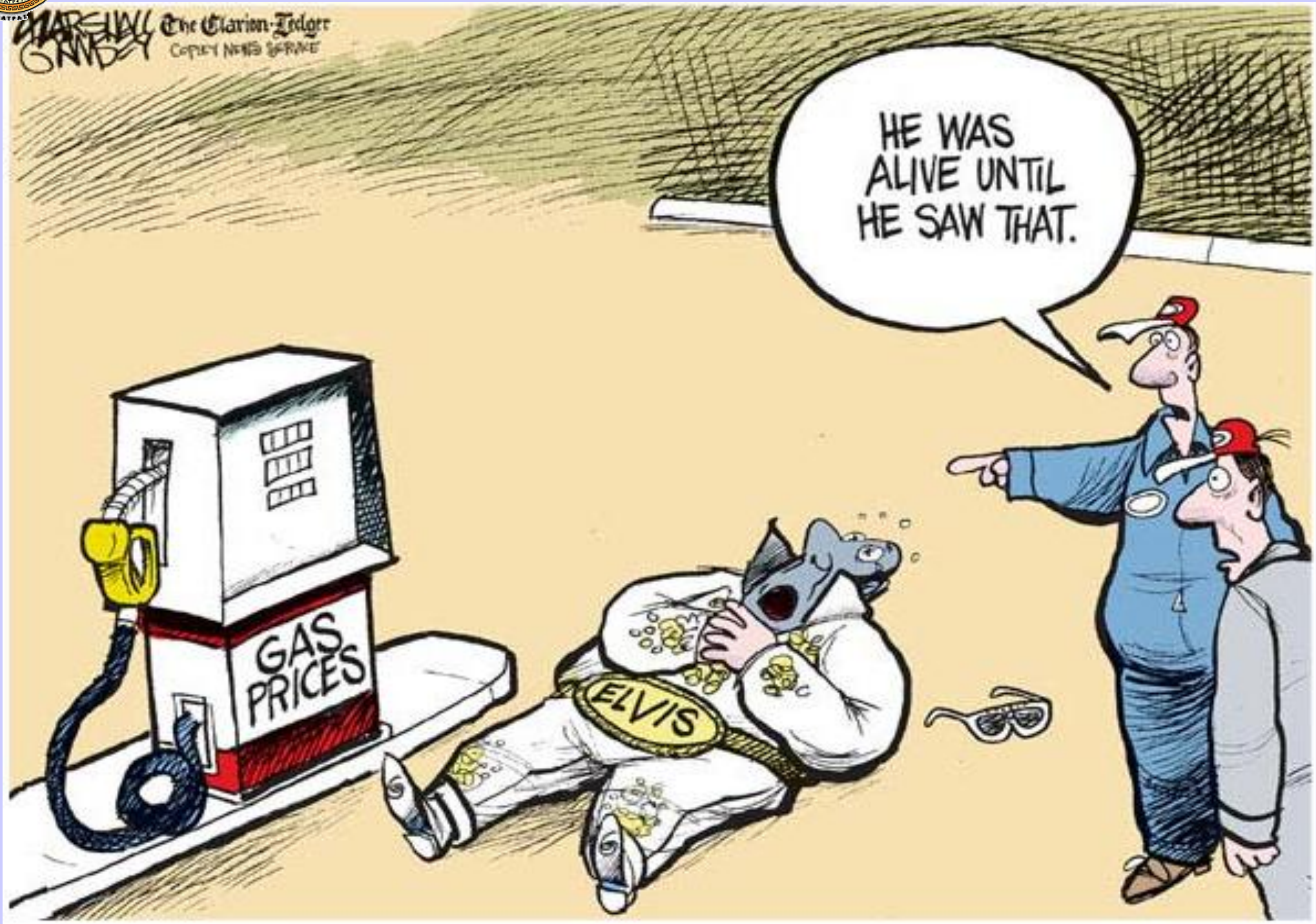




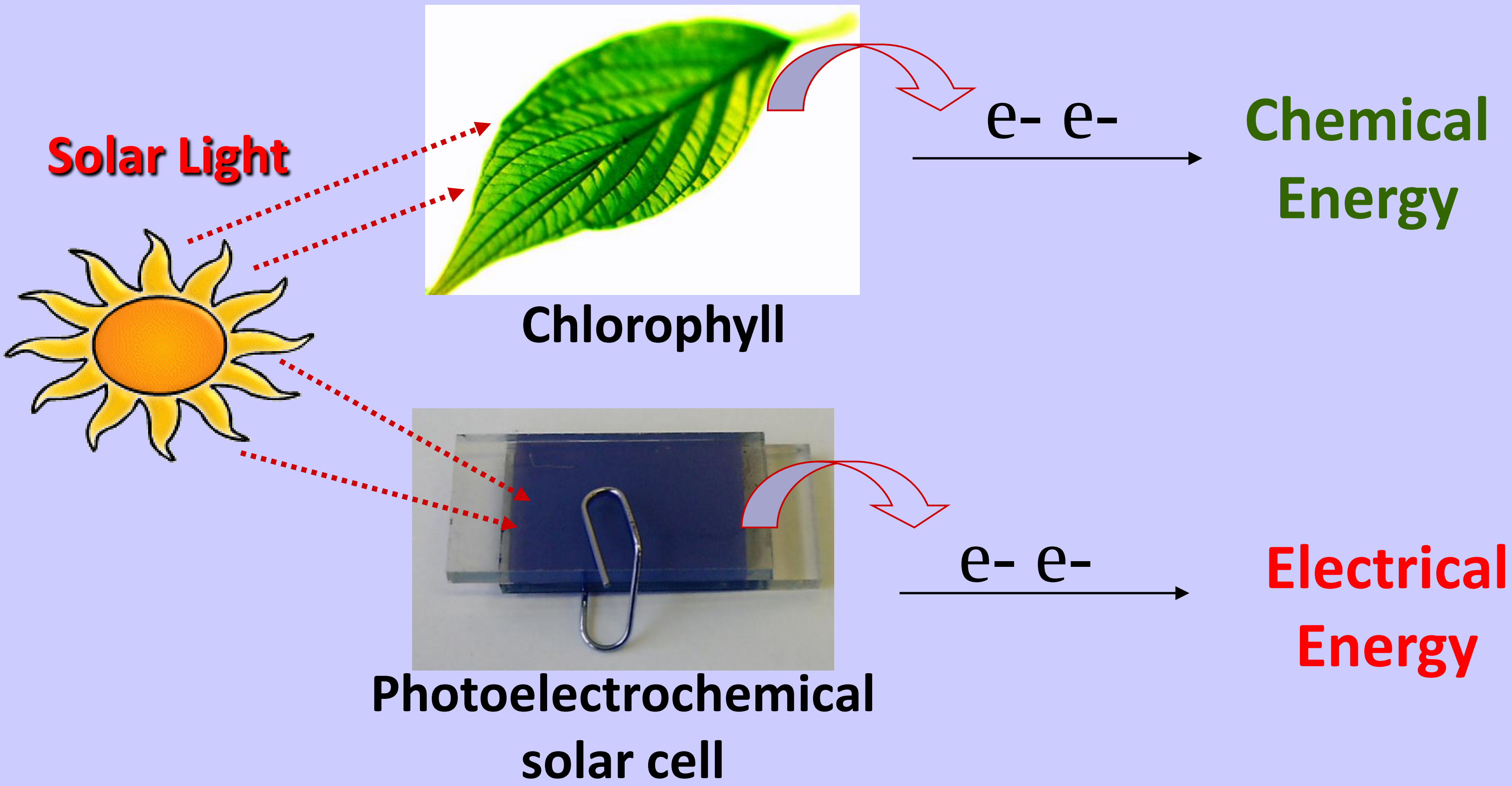
Global condition (G) : **<u>including the diffusion component</u> (indirect component owing to scattering and reflection in the atmosphere and surrounding landscape)**

Direct condition (D) : **without the diffusion component**

We have to find new technologies in renewable energy sources



Photosynthesis and Photoelectrochemical Solar cells

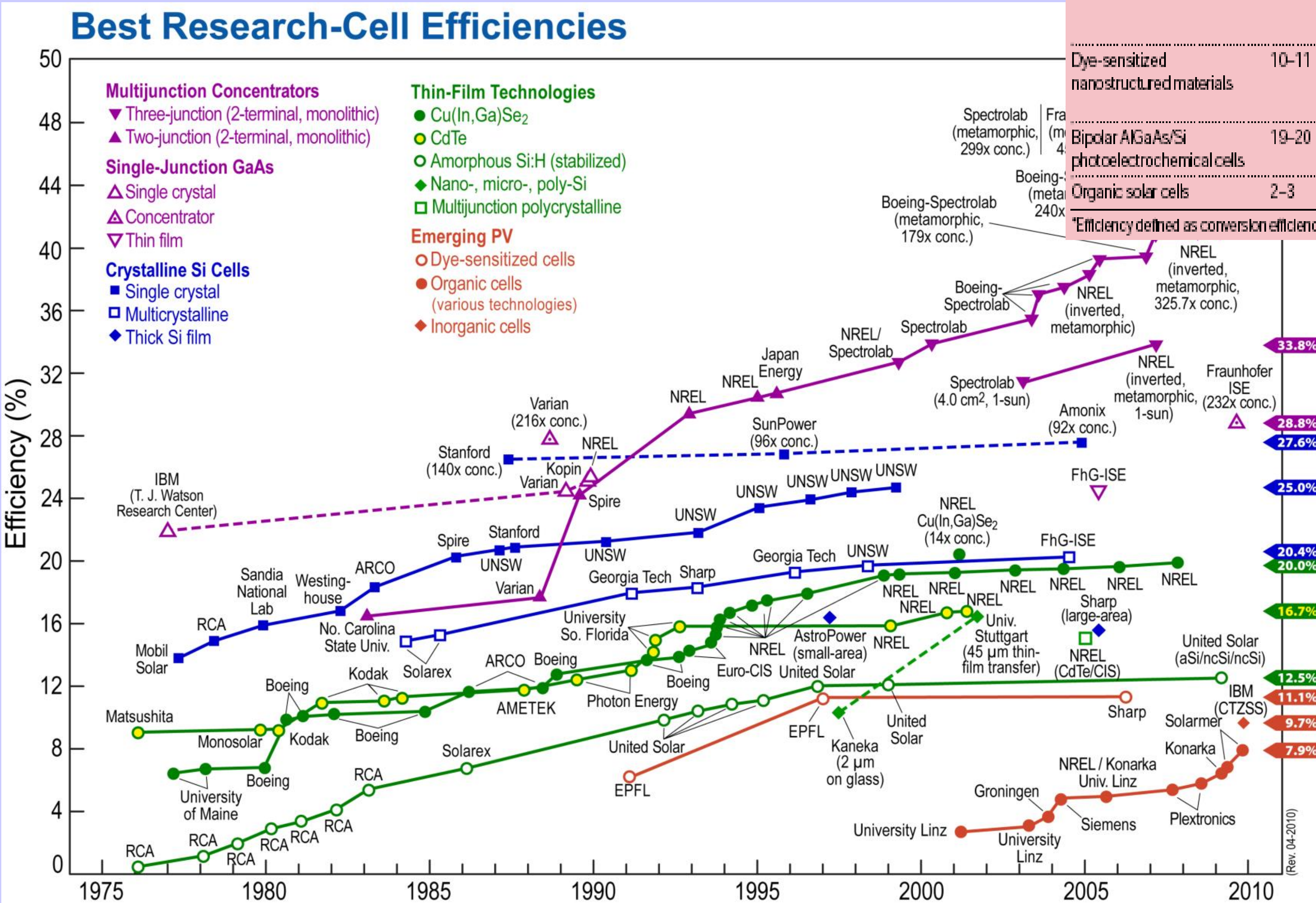


Progress of cell efficiencies

Table 1 Performance of photovoltaic and photoelectrochemical solar cells

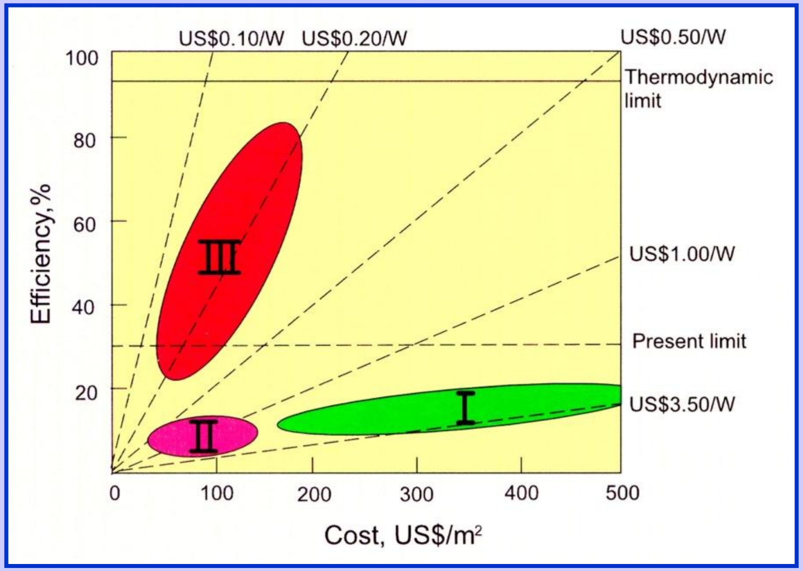
Type of cell	Efficiency (%)* Cell	Efficiency (%)* Module	Research and technology needs
Crystaline silicon	24	10–15	Higher production yields, lowering of cost and energy content
Multicrystalline silicon	18	9–12	Lower manufacturing cost and complexity
Amorphous silicon	13	7	Lower production costs, increase production volume and stability
$CuInSe_2$	19	12	Replace indium (too expensive and limited supply), replace CdS window layer, scale up production
Dye-sensitized nanostructured materials	10–11	7	Improve efficiency and high-temperature stability, scale up production
Bipolar AlGaAs/Si photoelectrochemical cells	19–20	—	Reduce materials cost, scale up
Organic solar cells	2–3	—	Improve stability and efficiency

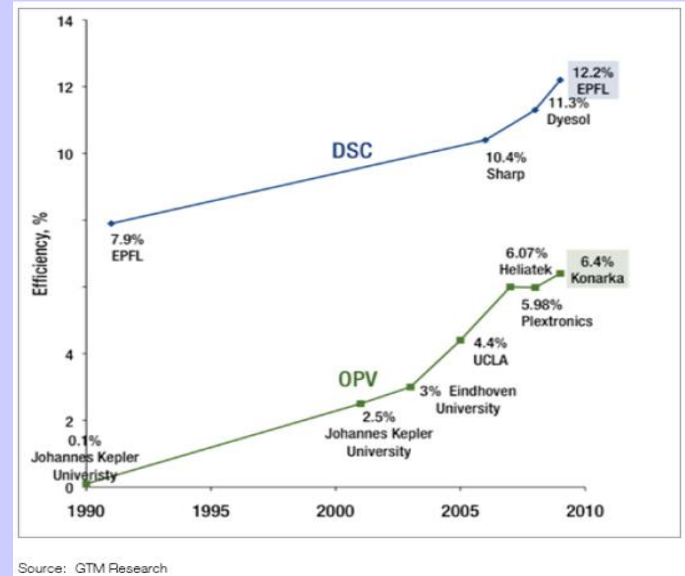
*Efficiency defined as conversion efficiency from solar to electrical power.



Under

AM 1.5G simulated solar illumination

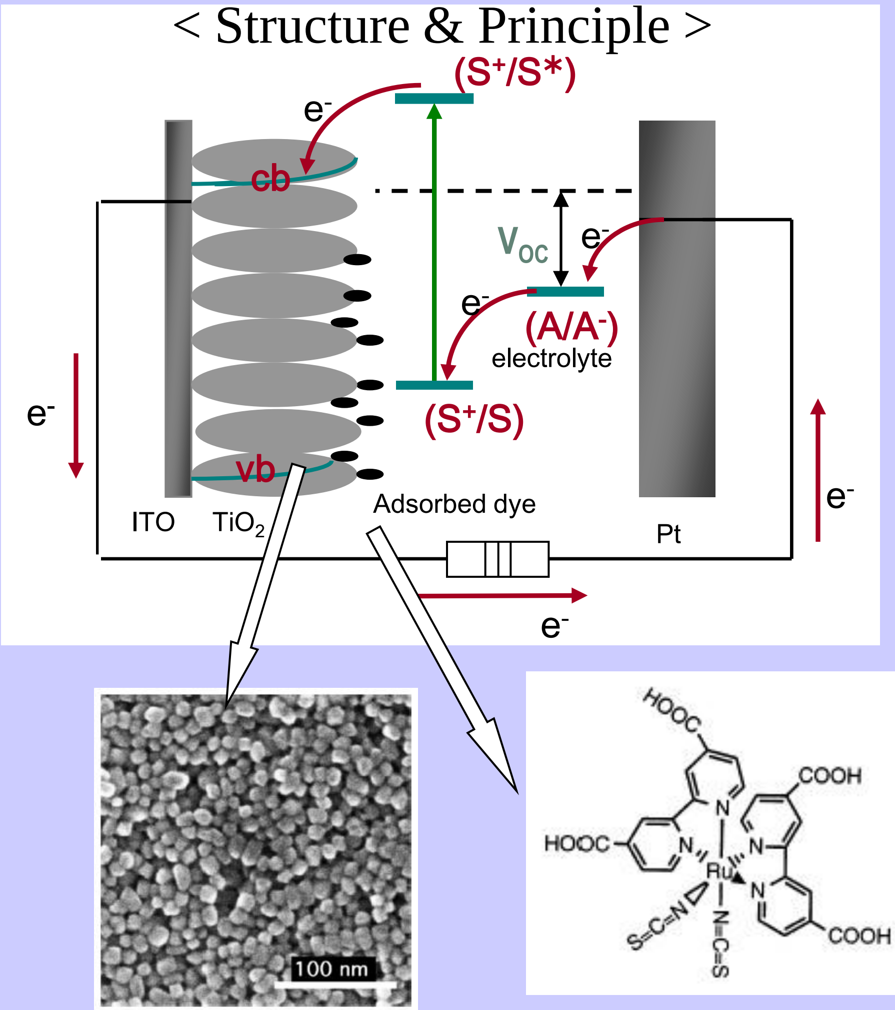




	cost	flexibility	shape factor filling	permeability	color	weight	external-internal use	efficiency
DSSC/OPV (3rd Gen)	High Advantageous	High Advantageous	High Advantageous	High Advantageous	High Advantageous	High Advantageous	High Advantageous	Medium Advantageous
Thin Film (2nd Gen)	Medium Advantageous	Medium Advantageous		Medium Advantageous	Disadvantageous	Medium Advantageous	Medium Advantageous	Medium Advantageous
Crystalline Silicon (1st Gen)	Disadvantageous			Disadvantageous	Medium Advantageous	Disadvantageous	Disadvantageous	High Advantageous

Disadvantageous (red) · Medium Advantageous (olive) · High Advantageous (green)

Dye-Sensitized Solar Cell (DSSC)



< Cell reactions >

- $S_{(adsorbed)} + h\nu \rightarrow S^{*}_{(adsorbed)}$
- $S^{*}_{(adsorbed)} \rightarrow S^{+}_{(adsorbed)} + e^{-}_{(injected)}$
- $S^{+}_{(adsorbed)} + A^{-} \rightarrow S_{(adsorbed)} + A$
- $A_{(cathode)} + e^{-} \rightarrow A^{-}_{(cathode)}$

< Advantages >

Low cost **(<100 euros/m^2 or <0.7€/watt)**

Utilization of visible range of light

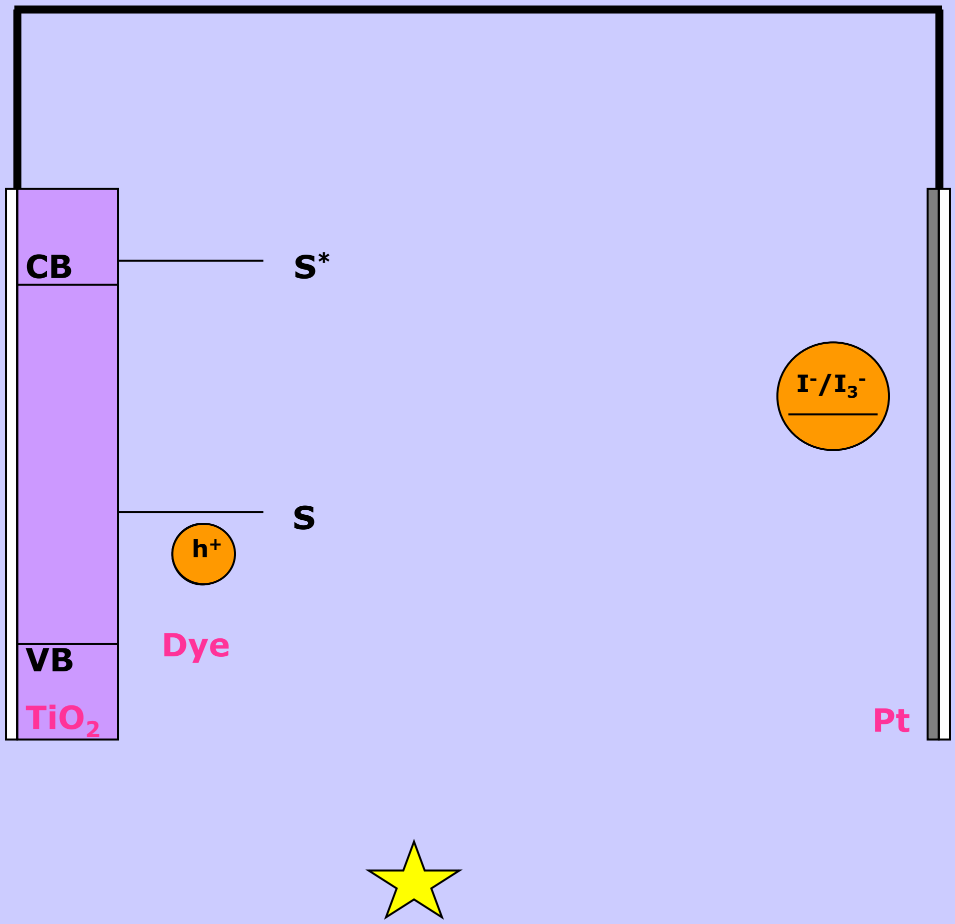
Simple manufacturing process

Environmental compatibility

Transparent solar cell Window

Moderate efficiency ~11%

Principle of Operation



Key Components

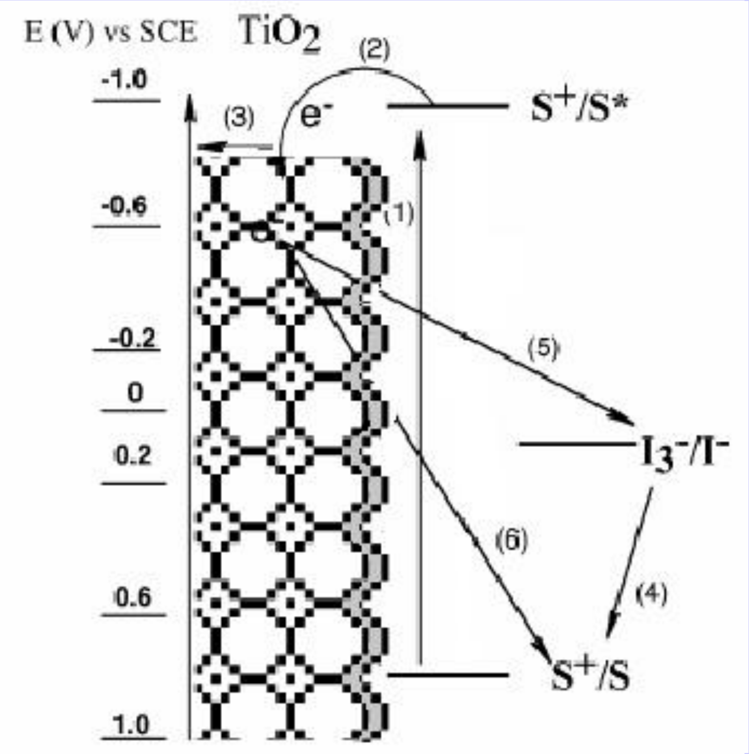
1. Nanocrystalline SC → large surface area, high porosity, pore size distribution, light scattering, electron percolation, **Anatase (TiO_2)**, ZnO, SnO_2, Nb_2O_5

2. Sensitizers (Dye) → distribution of the dyes on the semiconductor surface, spectral properties, redox properties in the ground and excited state, anchoring groups (carboxylate or phosphonate), Polypyridyl, Porphyrins, or Phthalocyanines complexes

3. Electrolyte → ionic conductivity, electron barrier and hole conductor, redox potential, mechanical separator, interfacial contact for dye, TiO_2 and counter electrode (I^-/I_3^-)

4. Extra → transparent conductive oxide (conductivity, transmittance), sealing, metal grid, counter electrode

Dynamics



(1) Excitation of dye under illumination (ns)

(2) Electron injection (ps)

(3) Electron transport (ms)

(4) Regeneration of dye (10 ns)

(5) Recombination with oxidized redox (ms)

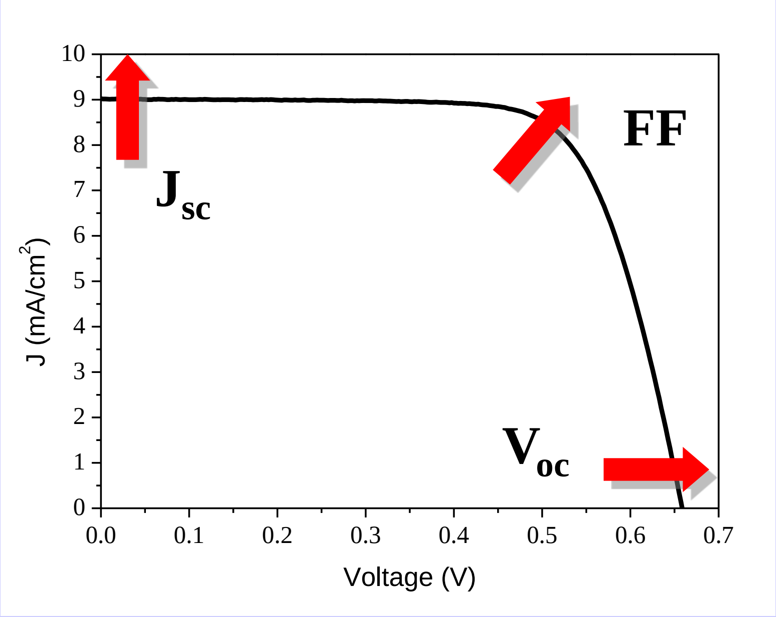
(6) Recombination with oxidized dye (s)

30 mM of I^- is enough to reduce the most of dye cations

Current issues

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

Power curve (I-V curve)



To increase performance of DSSC

J_{sc}: Diffusion coefficient (Length)

H^+ or Li^+ cation on TiO_2

$TiCl_4$ acidic sol. Treatment

Increase in adsorbed dye

V_{oc}: Electron lifetime (Recombination)

TBP, Ammonia in electrolyte

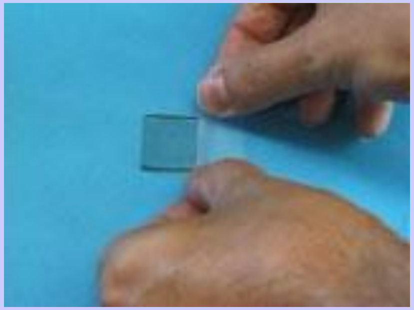
Secondary oxide layer

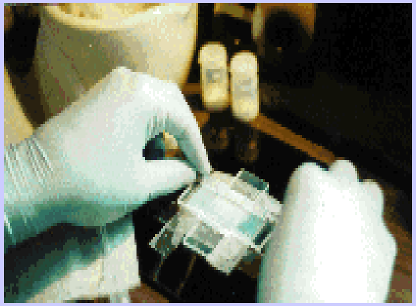
FF: Series and Shunt Resistance (Recombination)

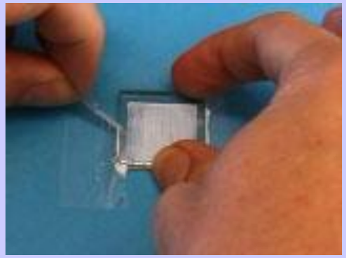
Secondary oxide layer

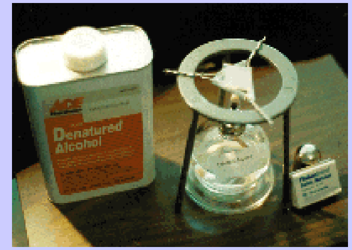
Competition between J_{sc} and V_{oc}: High carrier → High probability of recombination

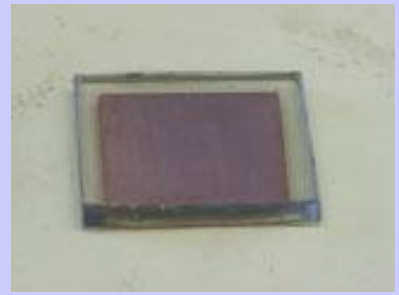
How to easily built a Dye Sensitized Solar cell

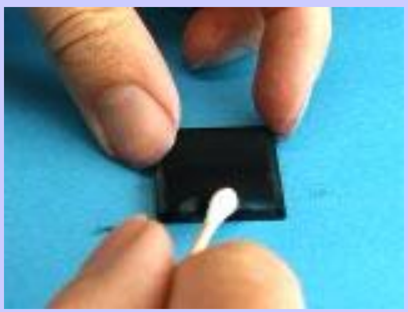


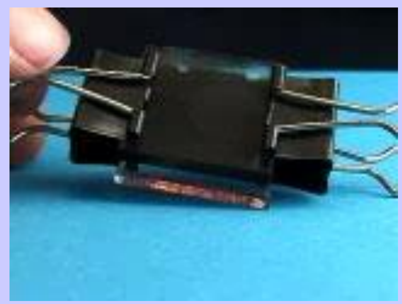


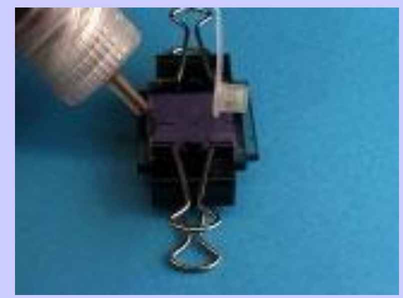



Denatured
Alcohol









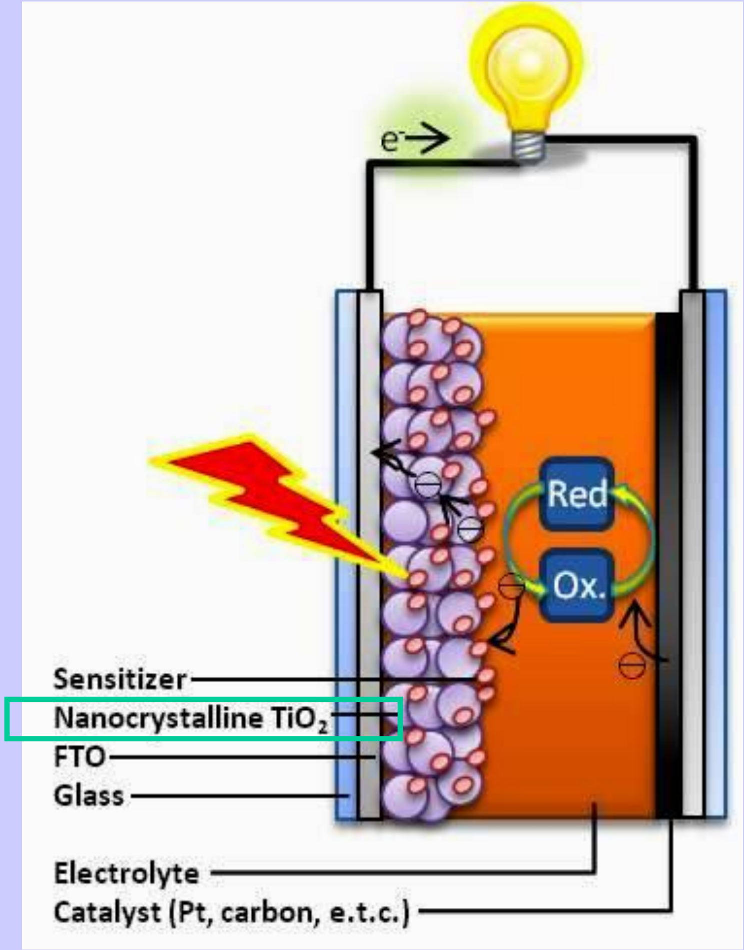

GoldStar
.4085


504

An overview to the Main process steps of Manufacture a standard nc-DSSCell

1. Structuring (electrical insulation) of the TCO-glass plates
2. Screen-printing of conductive silver lines for adequate current collection
3. Screen-printing of colloidal TiO_2 and platinum-containing pastes on the two electrodes
4. Sintering of the TiO_2 and platinum layers between 400 and 500^oC
5. Coloration of the TiO_2 electrode by chemical bath deposition
6. Sealing/lamination of the two electrodes
7. Injection of electrolyte through the two electrodes and device closure
8. Electrical contacting and wiring

Dye-sensitized Photoelectrochemical Solar Cells based on liquid electrolytes or nanocomposite organic/inorganic gels (solid electrolytes).



Preparation method for the TiO_2 wide band gap (3.2 eV) semiconductor and solid electrolytes

GELATION BY INORGANIC SOL-GEL Si-O-Si-O- POLYMERIZATION

- M-OR+$H_2O \rightarrow$ M-OH + ROH — Hydrolysis
- M-OH $\rightarrow$ M-O-M- — Polymerization

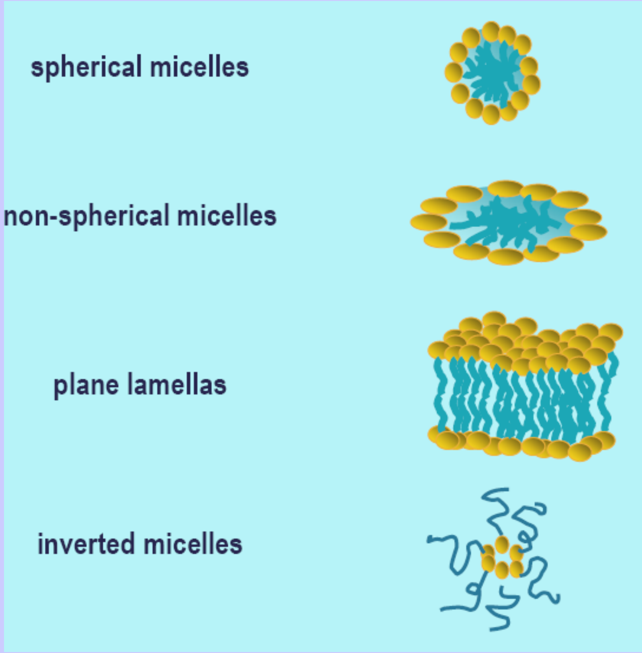
where M = Ti or Si

- ROH+AcOH $\rightarrow H_2O$ + ROAc — Esterification

- Organic acid solvolysis

- M-OR + AcOH $\rightarrow$ M-OAc + ROH
- ROH + AcOH $\rightarrow$ ROAc + H_2O
- M-OAc + ROH $\rightarrow$ ROAc + M-OH
- M-OR + M-OAc $\rightarrow$ ROAc + M-O-M

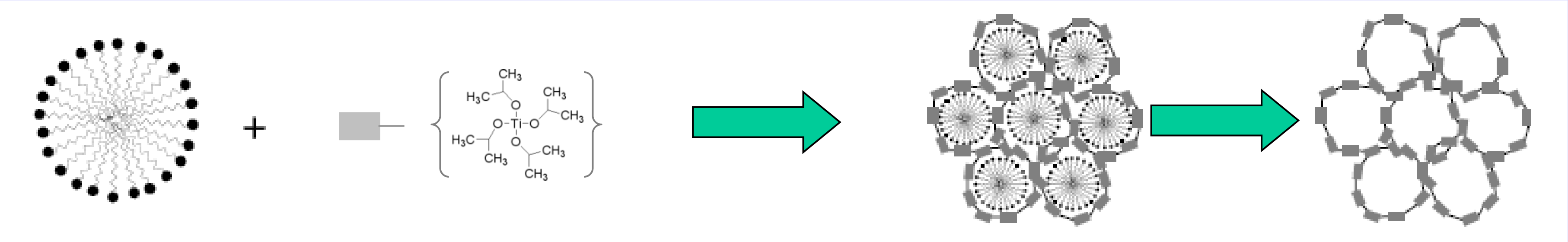
Surfactants as templates in the formation of TiO_2 nanostructure



Micelles

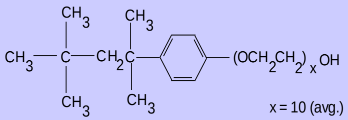
of Triton X-100

TiO_2 precursor

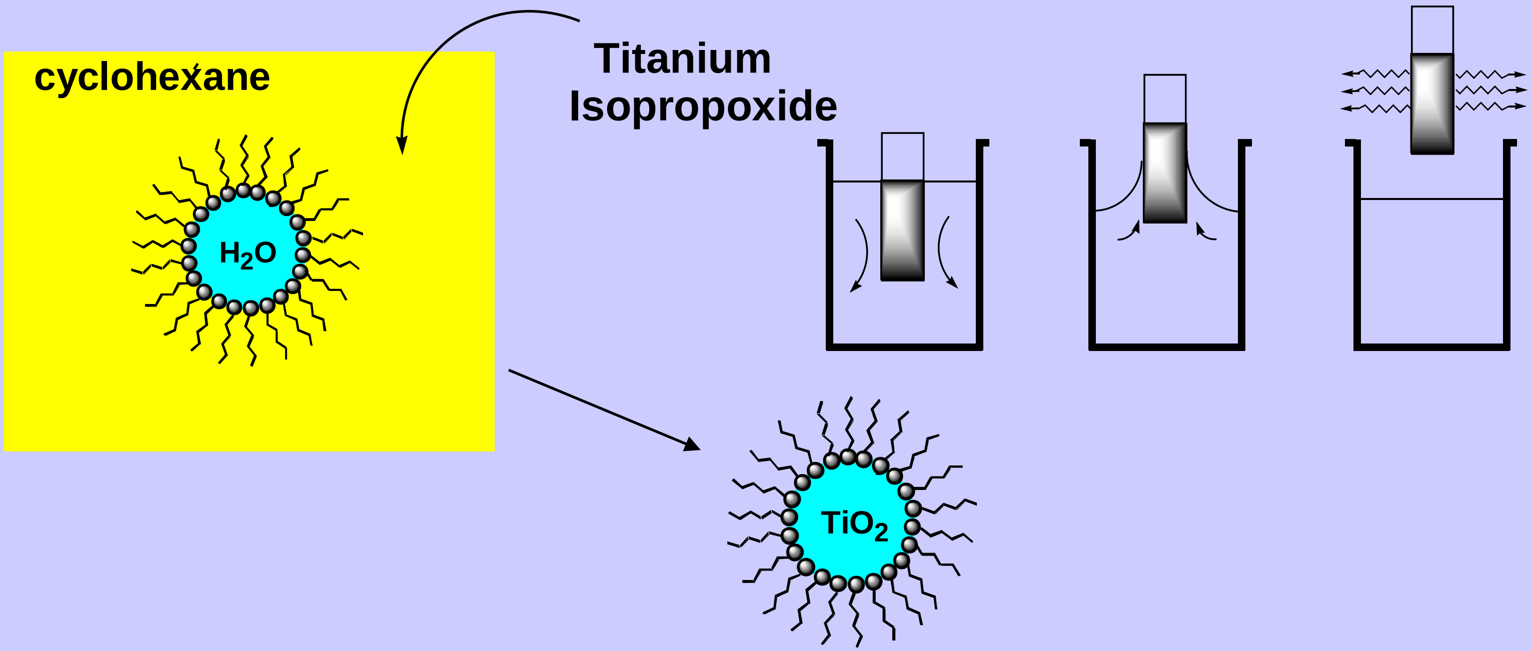


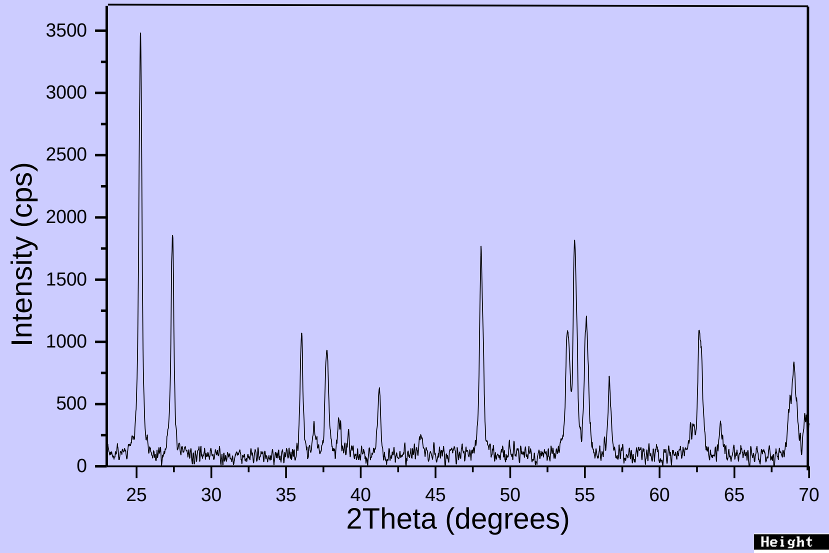
GROWTH OF TiO_2 NANOPARTICLES IN REVERSE MICELLES
FORMATION OF TITANIA NANOCRYSTALLINE FILMS

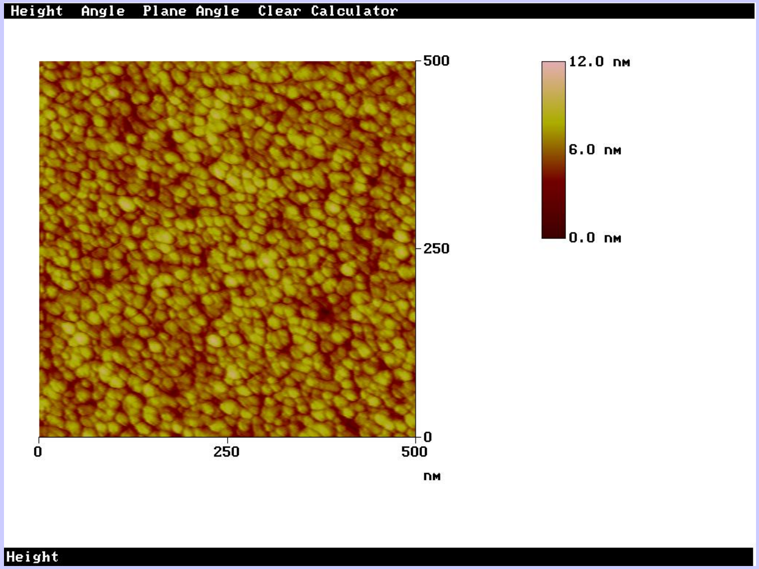
TRITON X-100



TRITON X-100



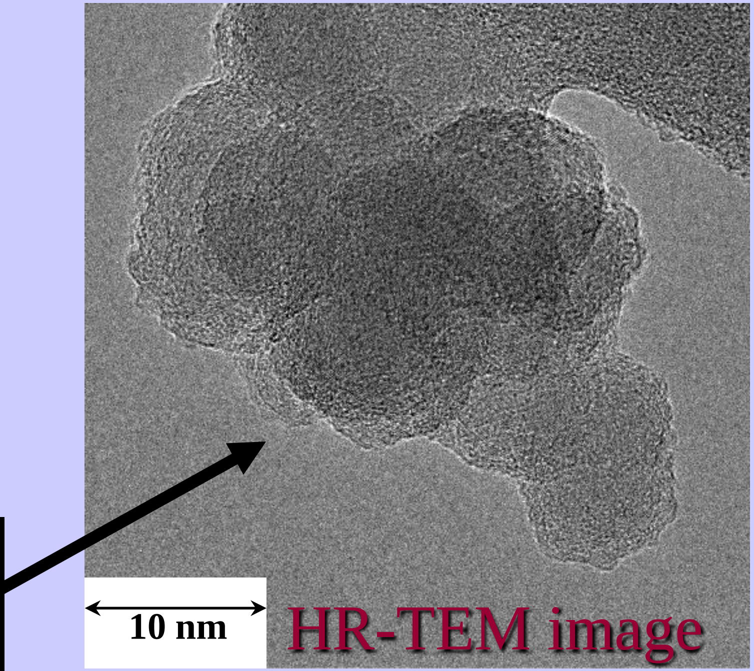

Intensity (cps)
3500
3000
2500
2000
1500
1000
500
0
25
30
35
40
45
50
55
60
65
70
2Theta (degrees)


Height Angle Plane Angle Clear Calculator
500
250
0
0
250
500
nм
12.0 nм
6.0 nм
0.0 nм
Height

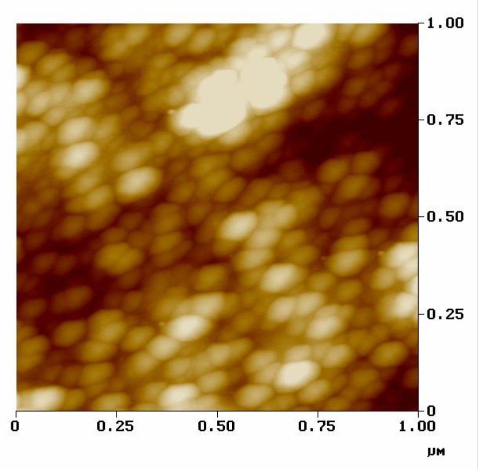
Preparation procedure of TiO_2 powder and films with TTIP precursor.

Organic acid solvolysis

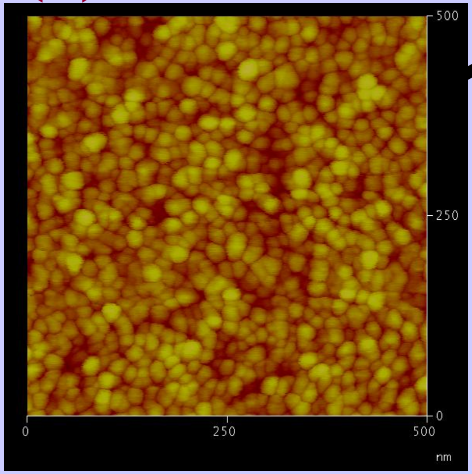
Ti-OR + AcOH $\rightarrow$ Ti-OAc + ROH
ROH + AcOH $\rightarrow$ ROAc + H_2O
Ti-OAc + ROH $\rightarrow$ ROAc + Ti-OH
Ti-OR + Ti-OAc $\rightarrow$ ROAc + Ti-O-Ti



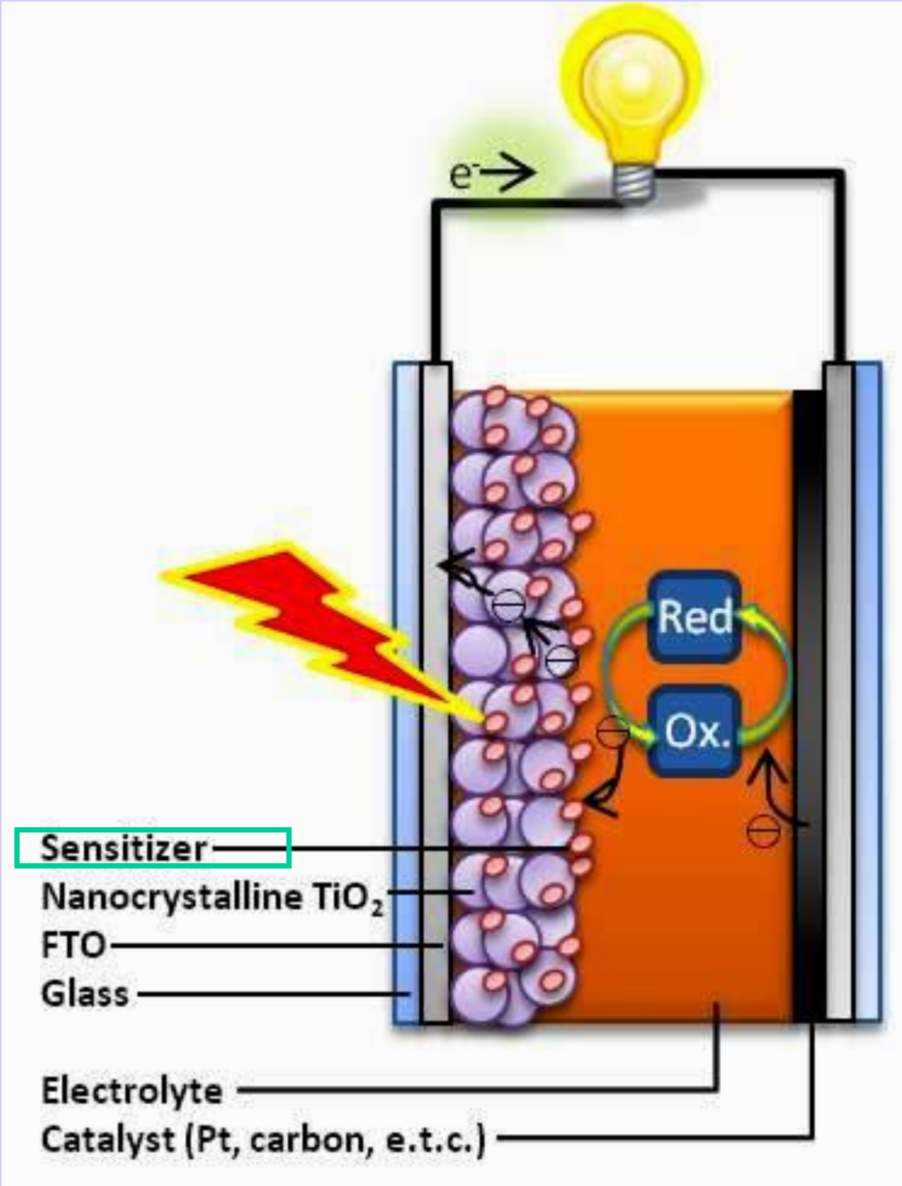
(a) ~ 50 nm



(b) ~ 15 nm

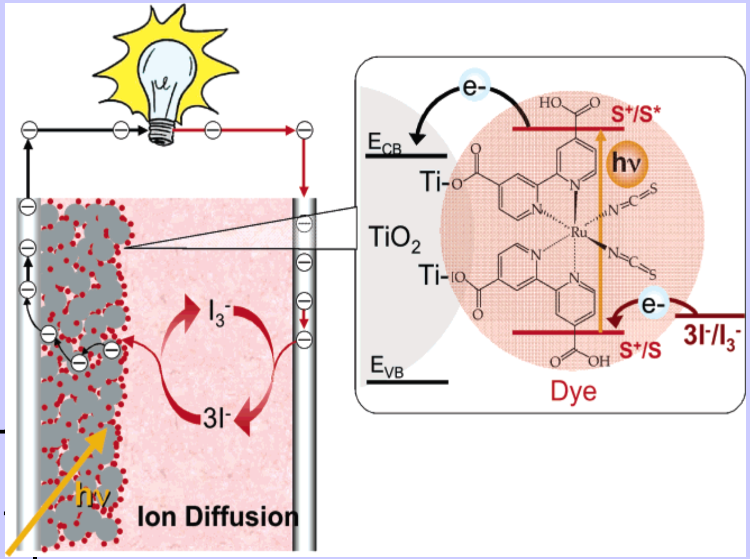


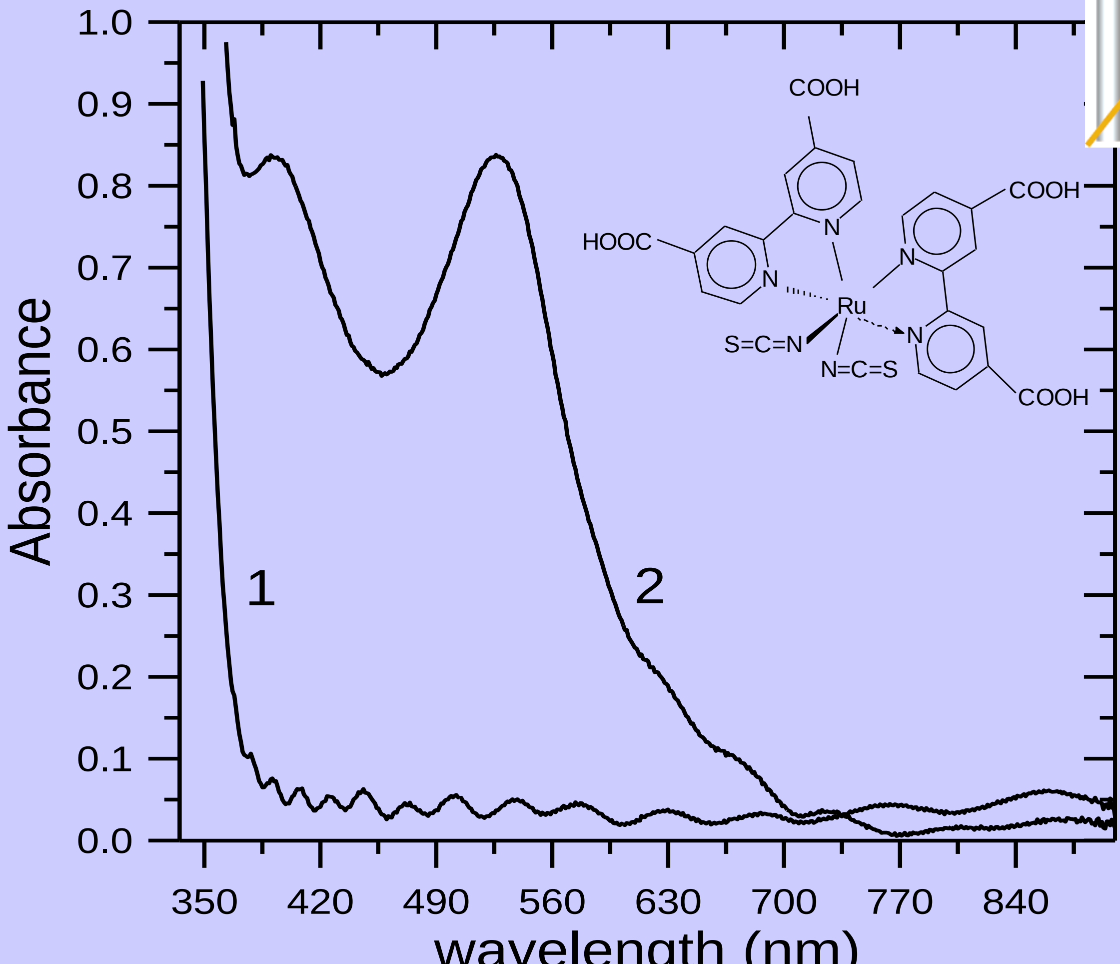
Varying organic Template (a) PEG 2000 and (b) Triton X-100

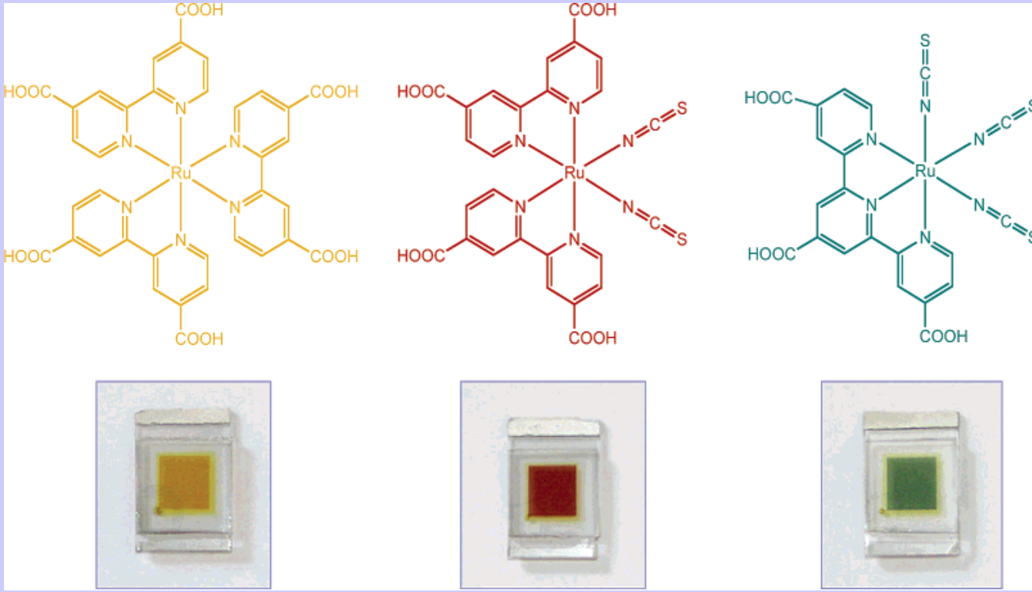


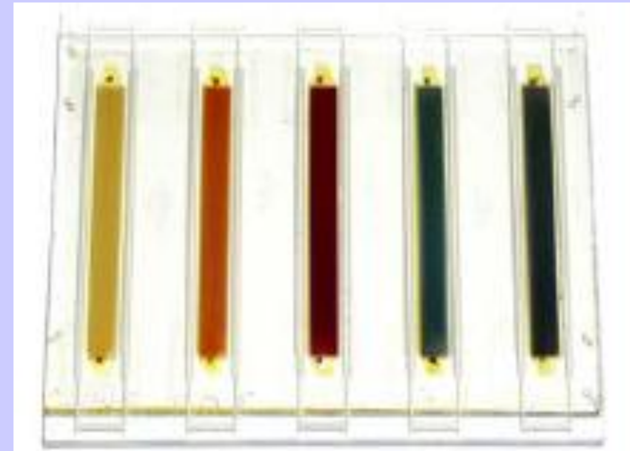
e-
Red
Ox.
Sensitizer
Nanocrystalline TiO2
FTO
Glass
Electrolyte
Catalyst (Pt, carbon, e.t.c.)

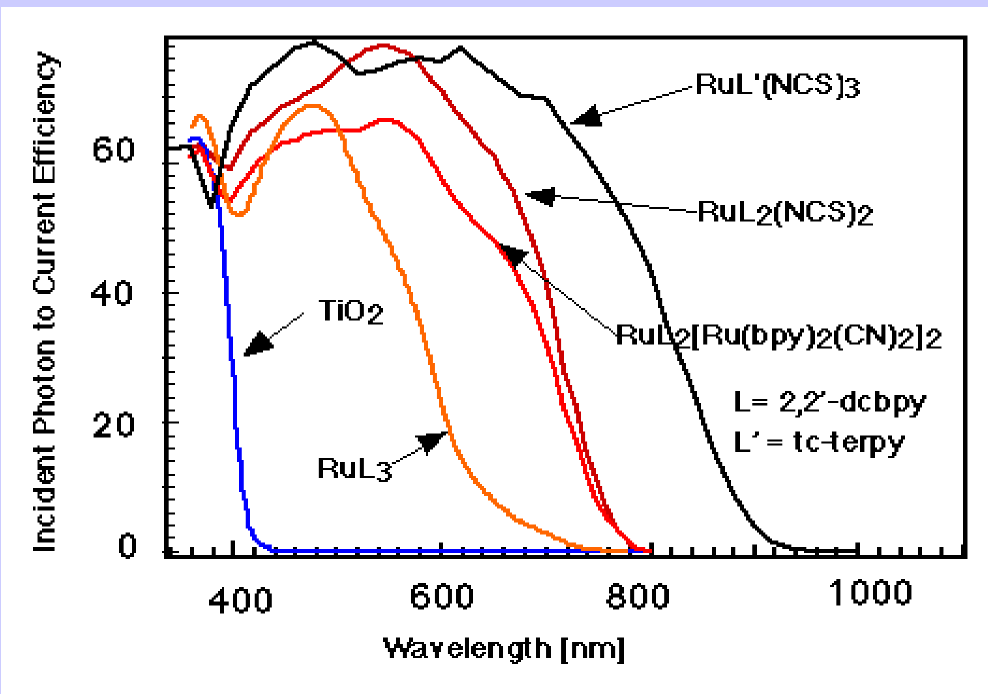
TITANIA FILM AND ADSORBED DYE-SENSITIZER

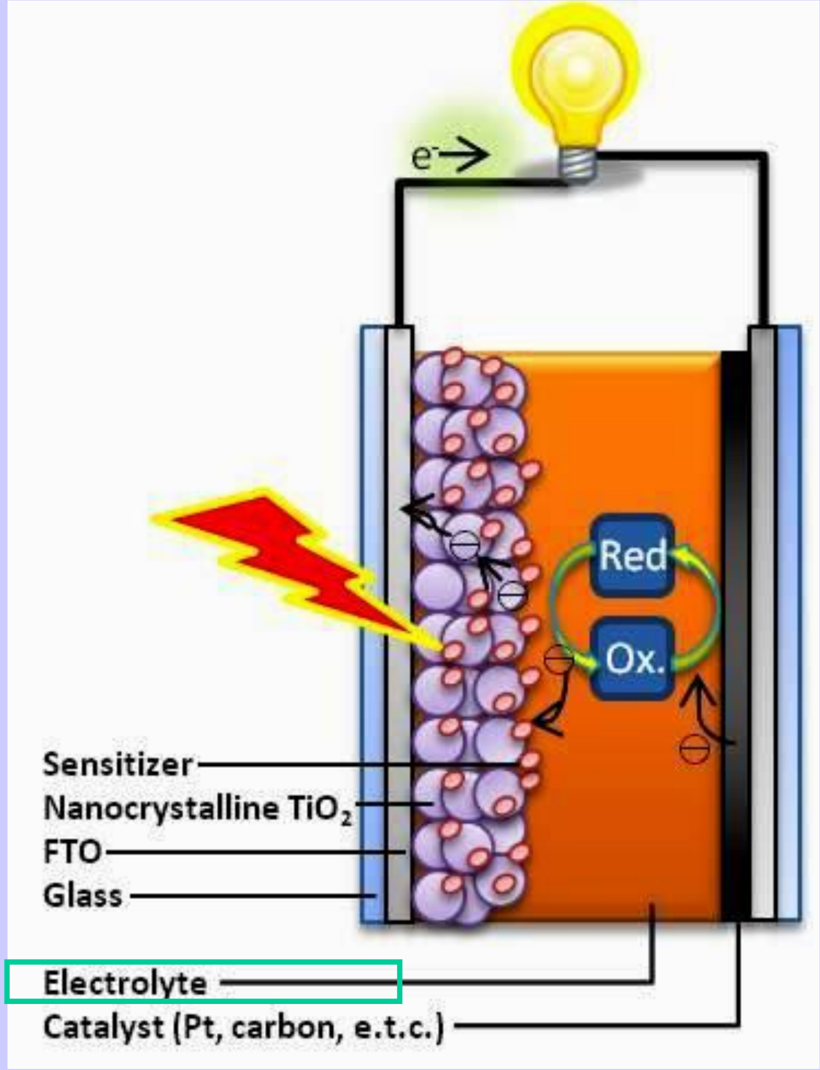





COOH
HOOC
N
Ru
N=C=S
S
C
COOH




Incident Photon to Current Efficiency
60
40
20
0
400
600
800
1000
Wavelength [nm]
RuL'(NCS)3
RuL2(NCS)2
RuL2[Ru(bpy)2(CN)2]2
TiO2
RuL3
L= 2,2'-dcbpy
L' = tc-terpy


e⁻
Red
Ox.
Sensitizer
Nanocrystalline TiO_2
FTO
Glass
Electrolyte
Catalyst (Pt, carbon, e.t.c.)

Liquid electrolyte is usually the redox couple I^-/I^-_3 from a mixture of KI/I_2 in an organic (no viscous) solvent (acetonitrile – sulfolane – propylene carbonate)

More efficient ionic transportation but we have sealing problems

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COMPOSITION OF A NANOCOMPOSITE ELECTROLYTE

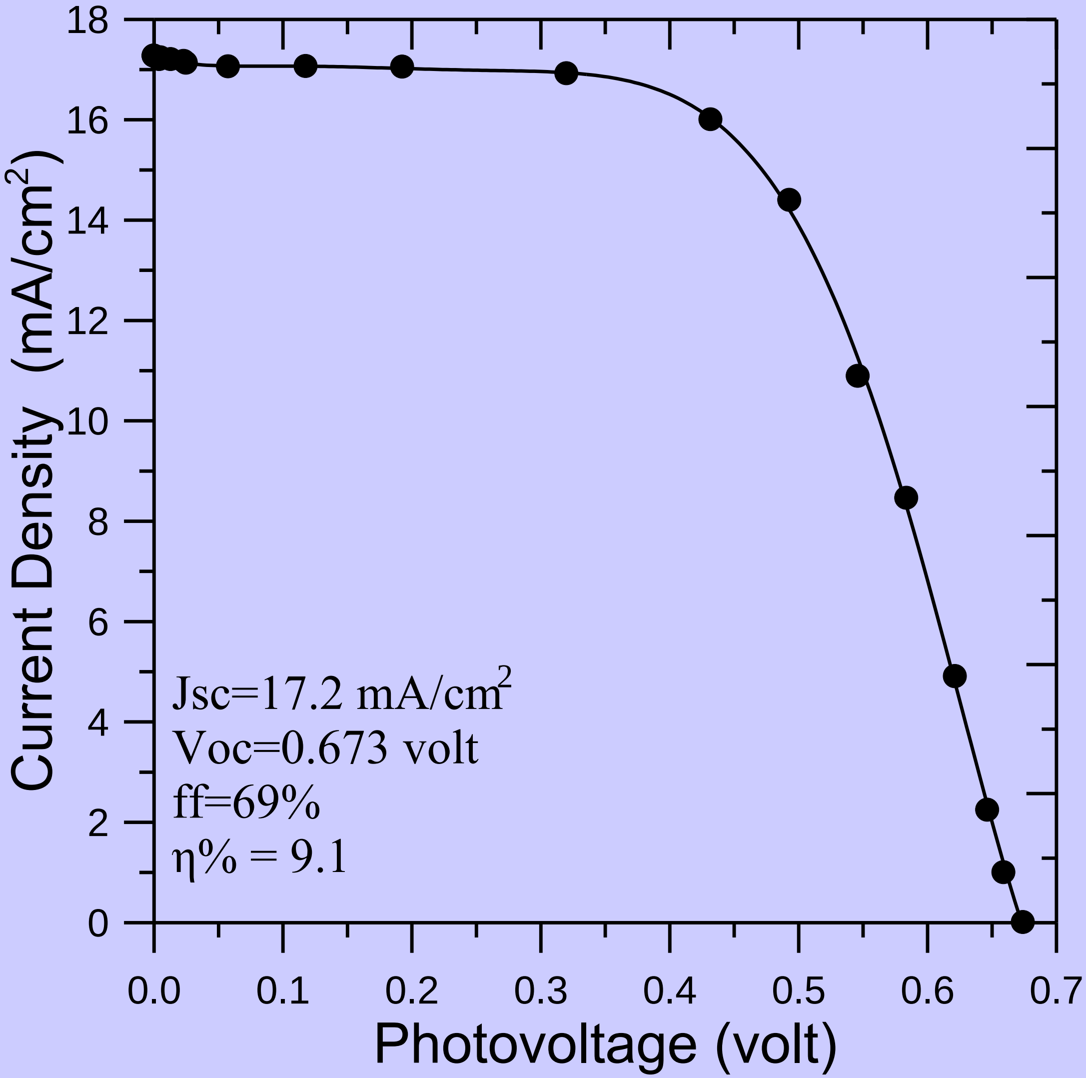
1. **Organic-inorganic matrix**
2. **Solvent**
2. **Redox couple I^-/I_3^-**

The precursor solution must be sufficiently fluid to fill the pores of the nanostructured semiconductor

Nanocomposite organic–inorganic materials prepared through Sol-Gel method give a new type of Solid State Electrolytes with excellent durability and mechanical properties.

Reference: **A High-Performance Solid-State Dye-Sensitized Photoelectrochemical Cell Employing a Nanocomposite Gel Electrolyte Made by the Sol-Gel Route** Advanced Materials Volume 14, Issue 5, Date: March, 2002, Pages: 354-357 E. Stathatos, P. Lianos, U. Lavrencic-Stangar, B. Orel

Cell Performance for a liquid electrolyte system

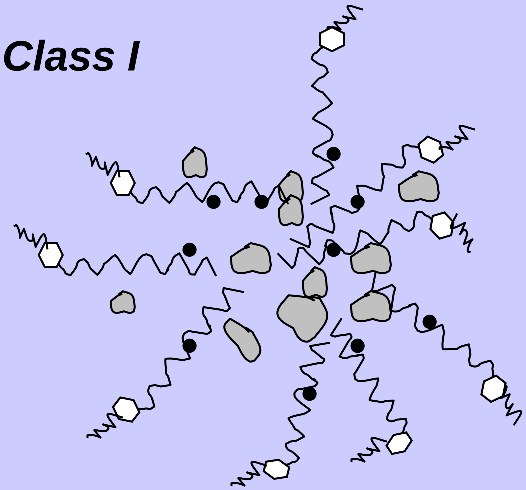


KI & I_2 redox electrolyte

In solvent (acetonitrile)

Two kind of Quasi Solid Electrolytes depending on the different interactions between material blends

Class I



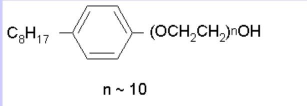
 **PEG** chains

 **Triton X-100**

 **SiO_2 clusters after alkoxides hydrolysis**

- **charge carrier** (I^-/I_3^-)

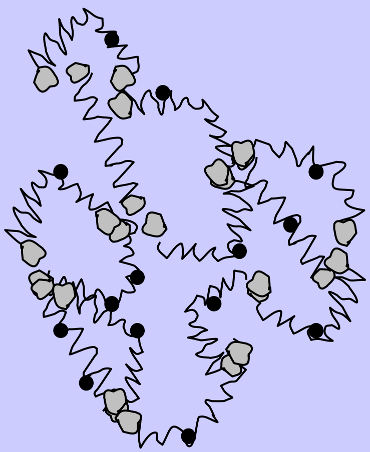
Triton X-100

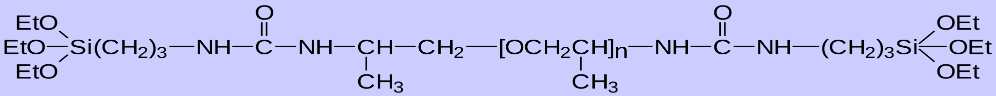


Redox system (I^-/I_3^-)

from KI/I_2

Class II



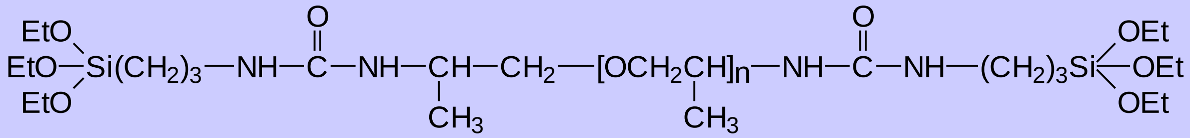


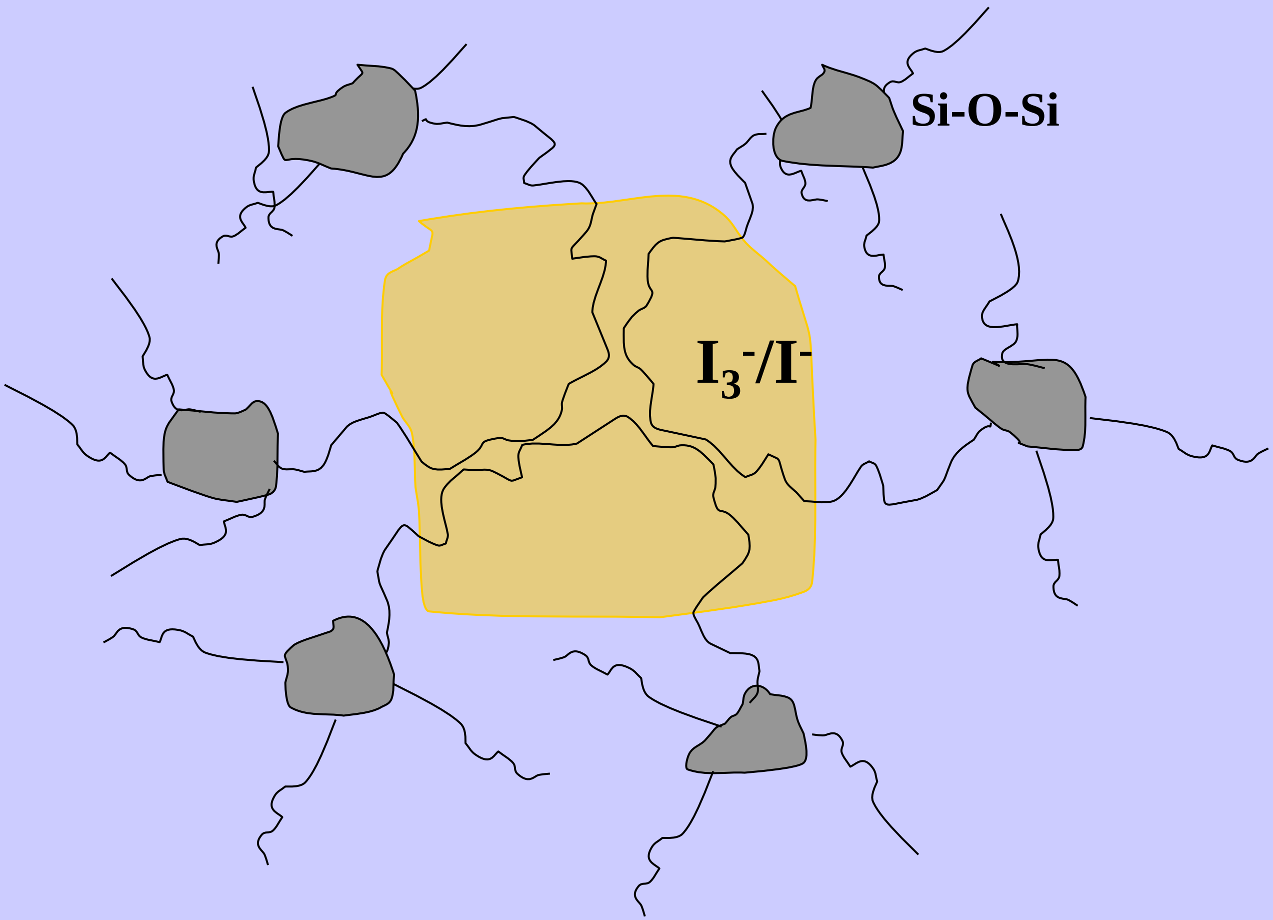
(PPG4000, n~68, PPG230, n~3)

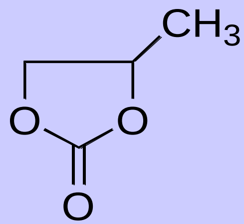
 **Hydrolysed PPG**

 **SiO_2 clusters after alkoxides hydrolysis**

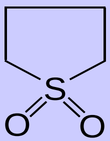
- **Charge carrier** (I^-/I_3^-)



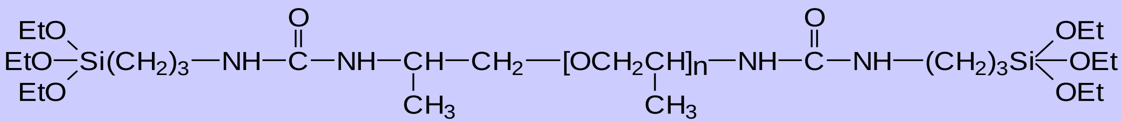

Si-O-Si
I3-/I-



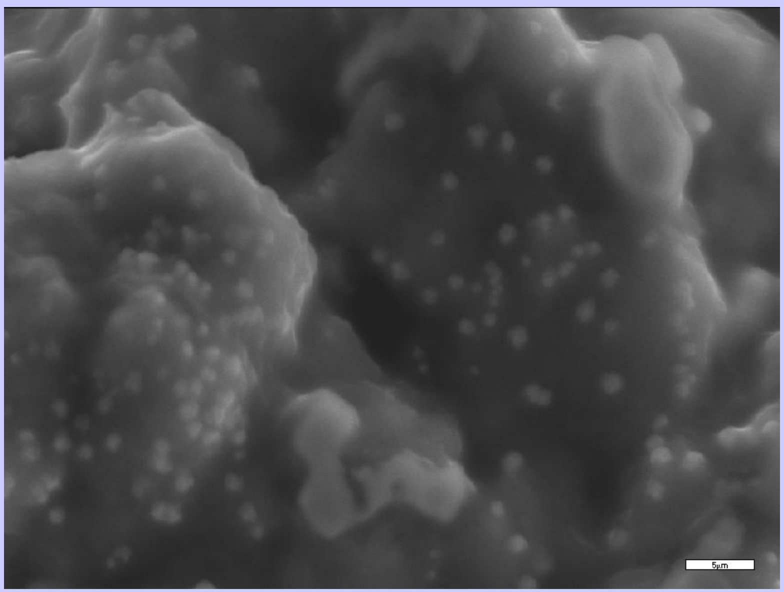
Propylene carbonate



Sulfolane

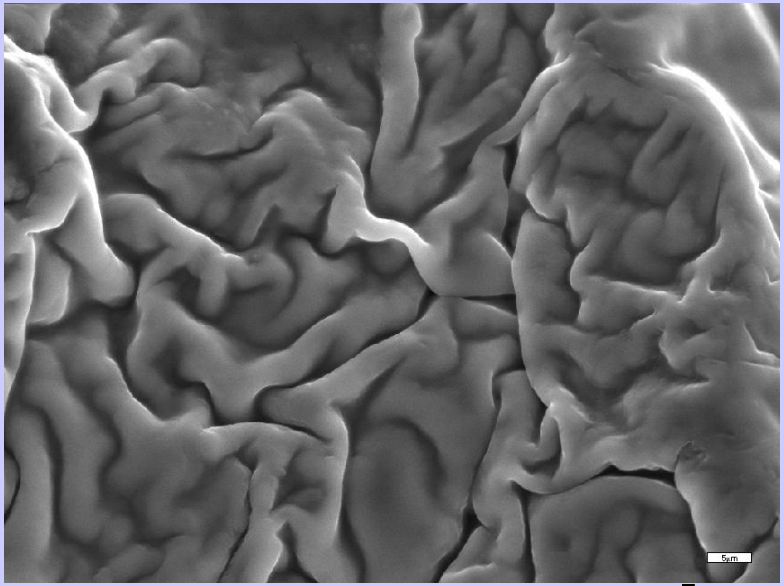


Ureasil PPG 230 (n~3)



5 μm

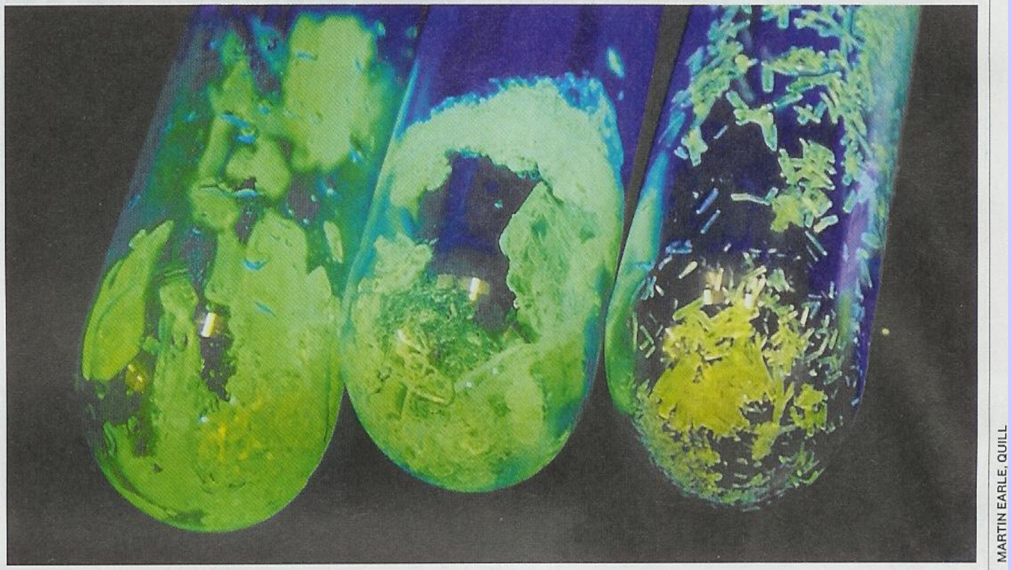
PC



5 μm

Sulfolane

Ionic Liquids in General

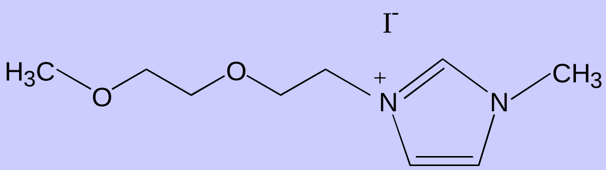


A luminescent green future for ionic liquids

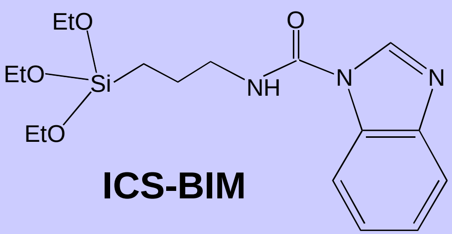
- Ionic liquids are liquids formed only of ions.
- Ionic liquids do not have a solvent component.
- Ionic liquids have a low vapour pressure so they are non-volatile.

Ionic Liquids – An alternative route to the formation of I^-/I^-_3 Redox Couple

Molten iodide salt MEOII as alternative fluid material to alkaline iodides avoiding crystallization problems

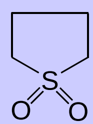


Gelyfing agent and voltage enhancement



ICS-BIM

Sulfolane



Ionic Liquids offer low melting points (approx. –45°C) and great stability in high temperatures

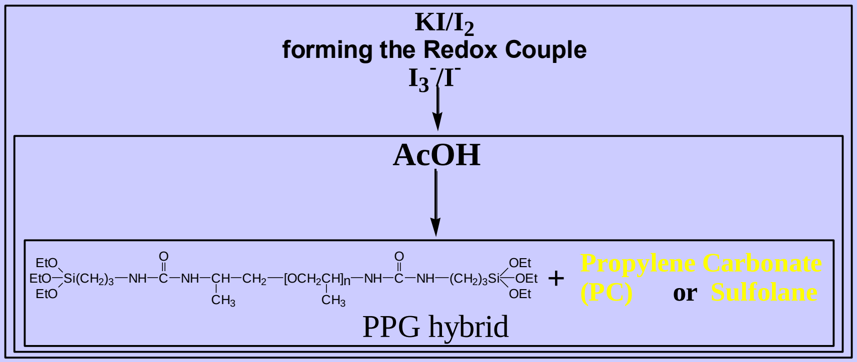
Efficiency data of DSSC at various electrolyte compositions

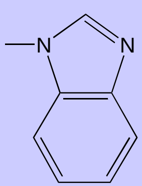
Electrolyte composition	V_{oc} (volt)	J_{sc} (mA/cm^2)	ff	η%
(1) MEOII+NMBI(0.5M)+I_2(0.5M)	0.76	10.02	0.68	4.8
(2) 1ml ICS-BIM+2ml Sulfolane + 0.7 ml AcOH + 0.6M MEOII + 0.06M I_{2-}	0.78	12.60	0.69	6.0
(3) 1ml ICS-BIM + 0.15ml TMOS+ 2ml Sulfolane 0.7+ ml AcOH+ 0.6M MEOII + 0.06M I_{2-}	0.79	10.92	0.68	5.4

Dye-sensitized solar cells with electrolyte based on a trimethoxysilane-derivatized ionic liquid *Thin Solid Films*, *Volumes 511-512*, *26 July 2006*, *Pages 634-637* Vasko Jovanovski, Elias Stathatos, Boris Orel, Panagiotis Lianos

I-V characteristics of DSS cells employing organic-inorganic solid materials

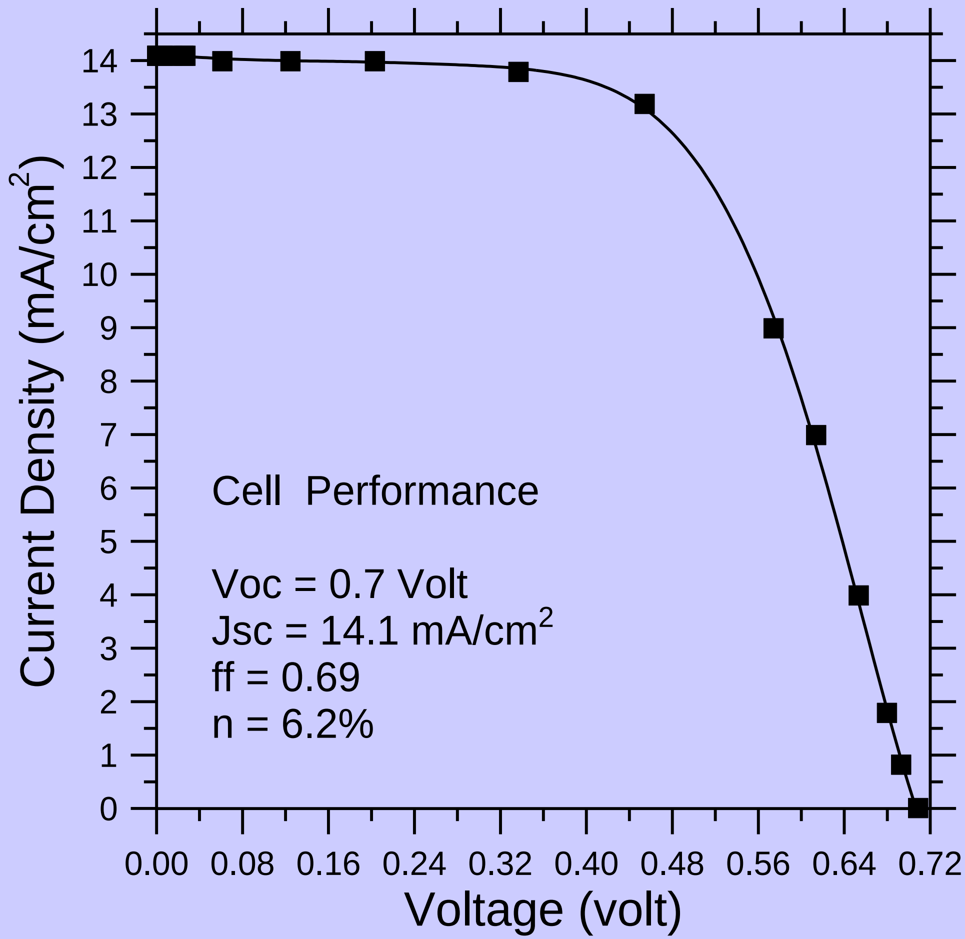
Typical electrolyte composition





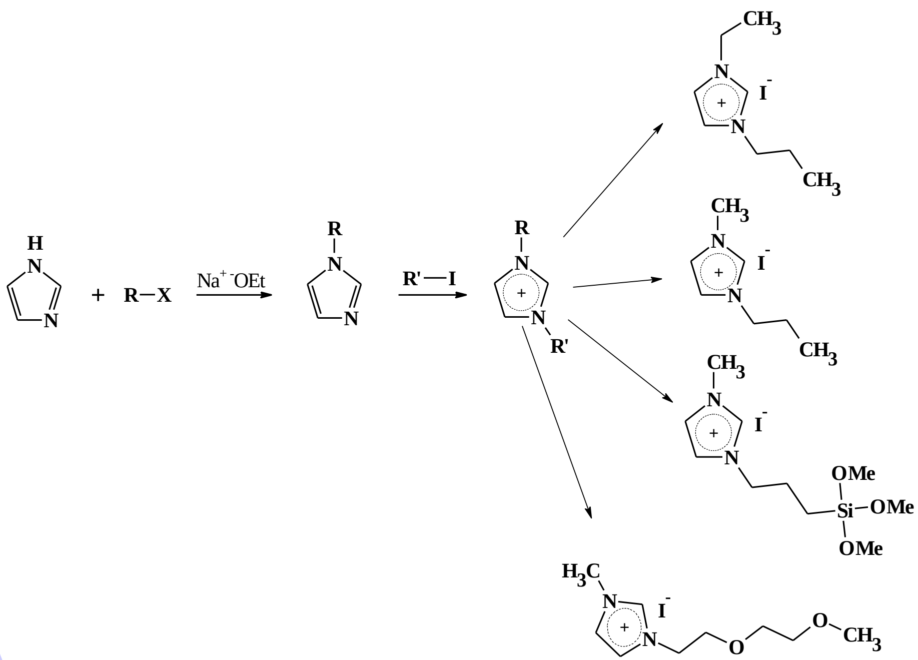
Methylbenzylimidazole additive

for Voltage enhancement



Ionic liquids + sol-gel precursors

Synthesis of iodide containing ionic liquids



1-ethyl-3-propylimidazolium iodide

EtPrImI

1-methyl-3-propylimidazolium iodide

MePrImI

1-methyl-3-[3-(trimethoxy-λ4-silyl)propyl]imidazolium iodide

MeTMSPrImI

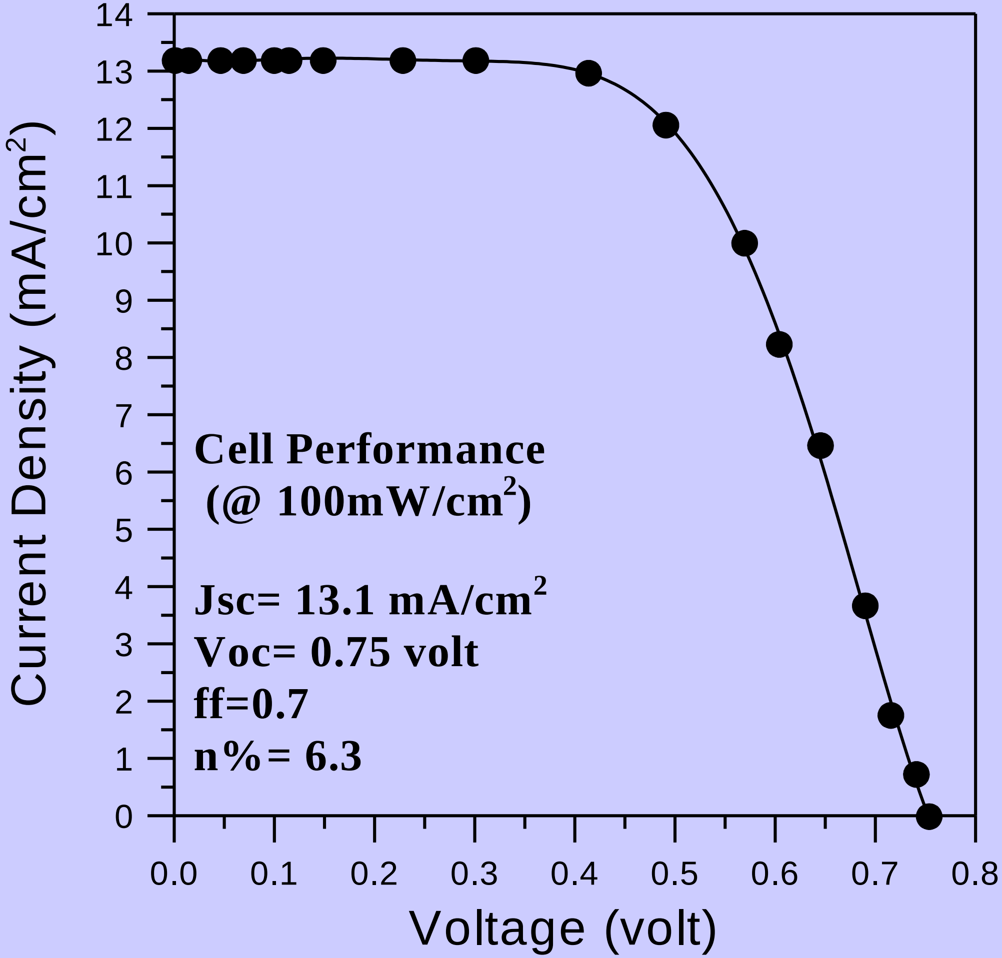
3-[2-(2-methoxyethoxy)ethyl]-1-methylimidazolium iodide

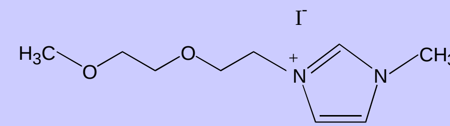
MeMEEImI

Dye-Sensitized Solar Cells Made by Using a Polysilsesquioxane Polymeric Ionic Fluid as Redox Electrolyte

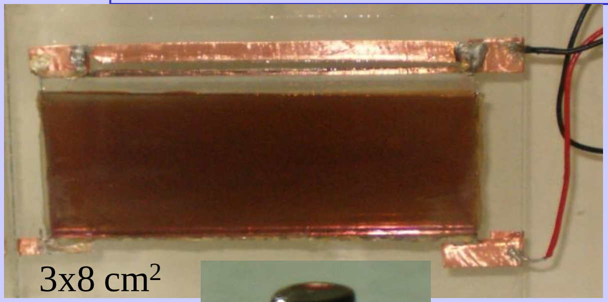
Stathatos, E.; Jovanovski, V.; Orel, B.; Jerman, I.; Lianos, P. J. Phys. Chem. C.; 2007; 111(17); 6528-6532.

DSSCell made of Solid electrolyte with ionic liquid and I_2 redox couple in a sol-gel matrice





& I_2 redox electrolyte

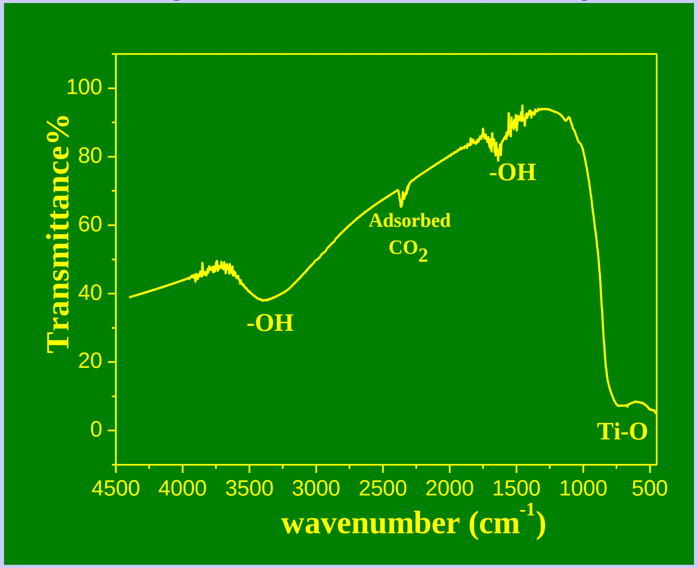


A Quasi-Solid-State Dye-Sensitized Solar Cell Based on a Sol-Gel Nanocomposite Electrolyte Containing Ionic Liquid Stathatos, E.; Lianos, P.; Zakeeruddin, S. M.; Liska, P.; Gratzel, M. *Chem. Mater.; (Article); 2003; 15(9);*

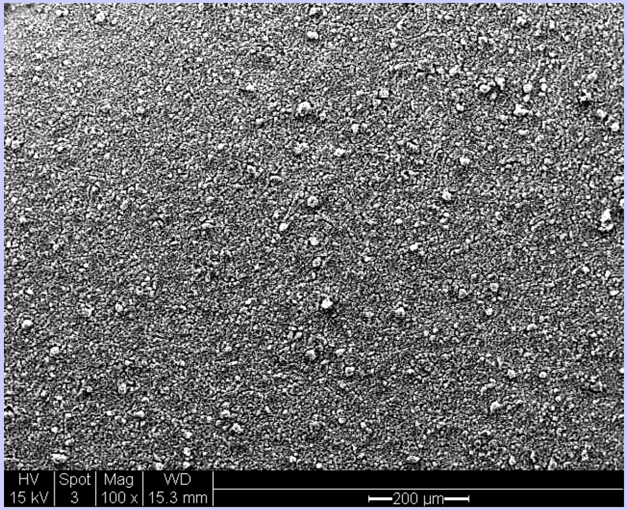
TiO_2 prepared in room temperature

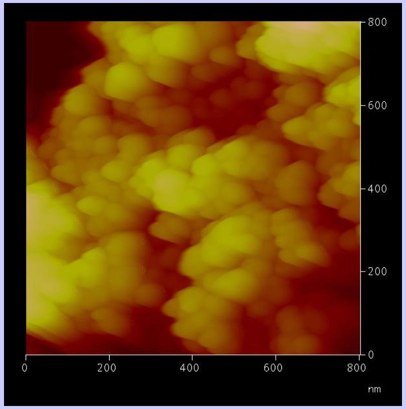
FTIR spectrum of the as-prepared film on silicon wafer rinsed multiple times with water and dried at 100°C.

No organics are detected (area of 1500-1000 cm^{-1})

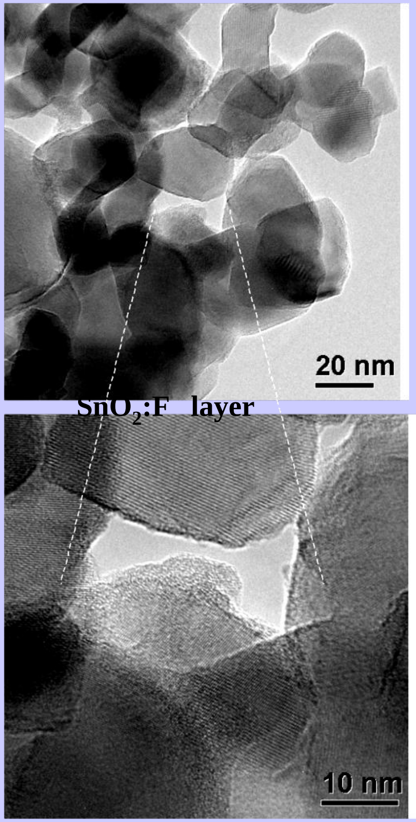


SEM image of the TiO_2 film on FTO glass prepared at room temperature

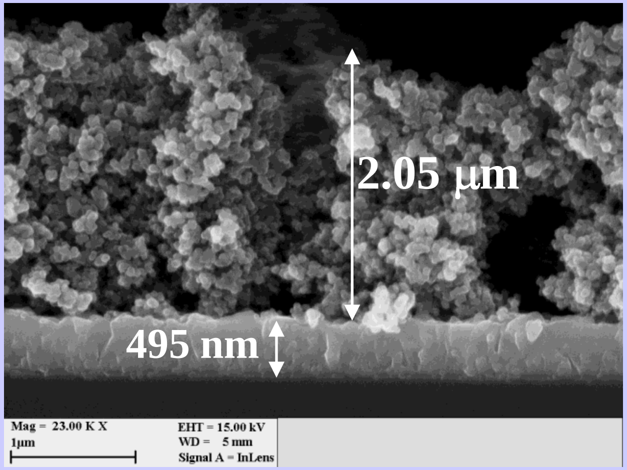




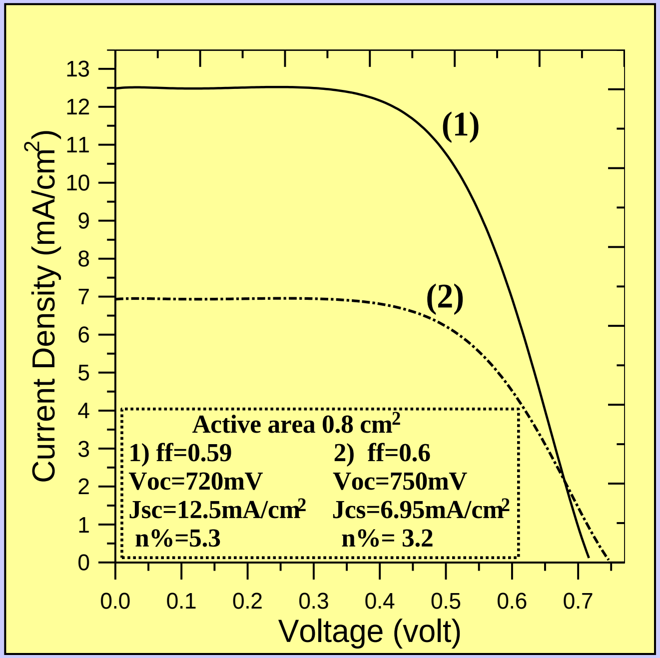
AFM image of the as-prepared TiO_2 film at room temperature



HR-TEM image of TiO_2 film

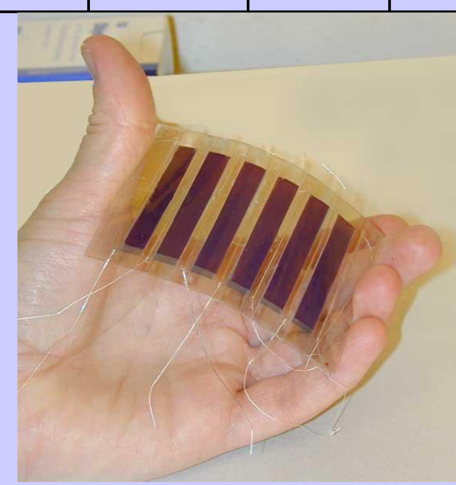


Cross-section SEM image of the as-prepared TiO_2 film.



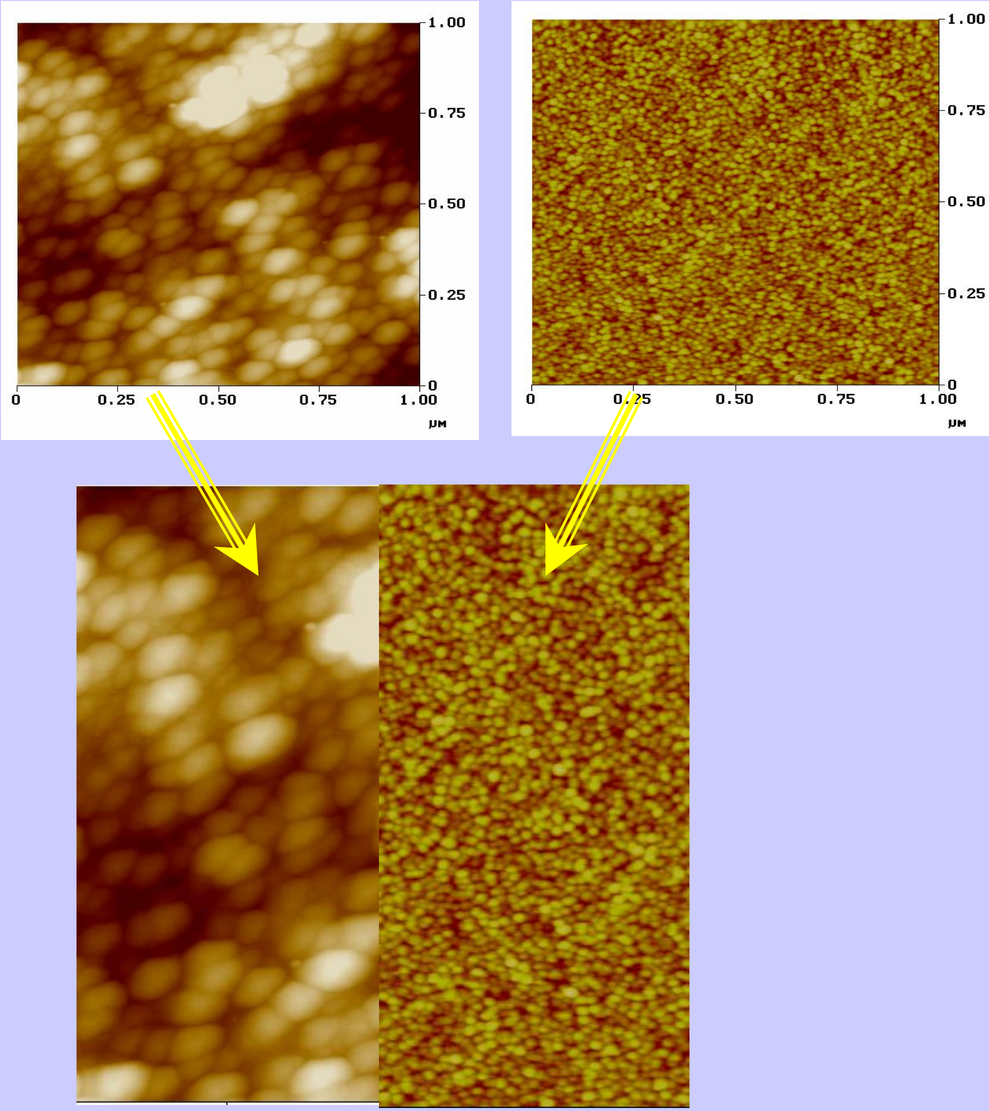
Substrate	TTIP (M)	TTIP: P25-TiO_2 (Molar ratio)	Q (%)	IPCE (%)	J_{sc} (mA/cm^2)	V_{oc} (mV)	*ff*	n (%)
FTO glass	0.180	0.14	0	31	6.9	673	0.58	2.7
	0.110	0.084	0	46	11.2	711	0.59	4.7
	0.070	0.056	0	58	11.7	720	0.59	5.0
	0.053	0.042	0	62	12.5	720	0.59	5.3
	0.035	0.028	2.5	59	9.7	700	0.60	4.1
	0.017	0.014	4.0	48	8.4	688	0.59	3.4
ITO-PET plastic	0.180	0.14	0	20	4.6	697	0.59	1.9
	0.110	0.084	0	27	5.9	736	0.59	2.6
	0.070	0.056	0	34	6.7	741	0.60	3.0
	0.053	0.042	0	41	6.9	750	0.60	3.2
	0.035	0.028	2.4	37	6.8	722	0.61	3.0
	0.017	0.014	5.3	32	5.5	694	0.60	2.3

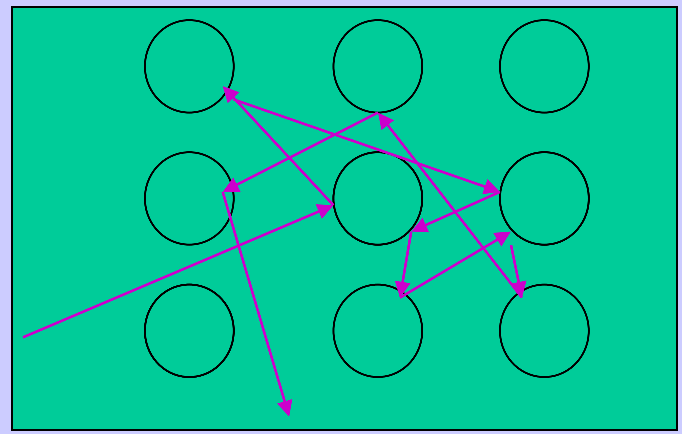
J-V curves at 1 sun for the DSSCs containing the as-prepared room temperature nanocrystalline TiO_2 film with quasi-solid state electrolyte employing:
(1) FTO glass,
(2) ITO-PET plastic substrate.

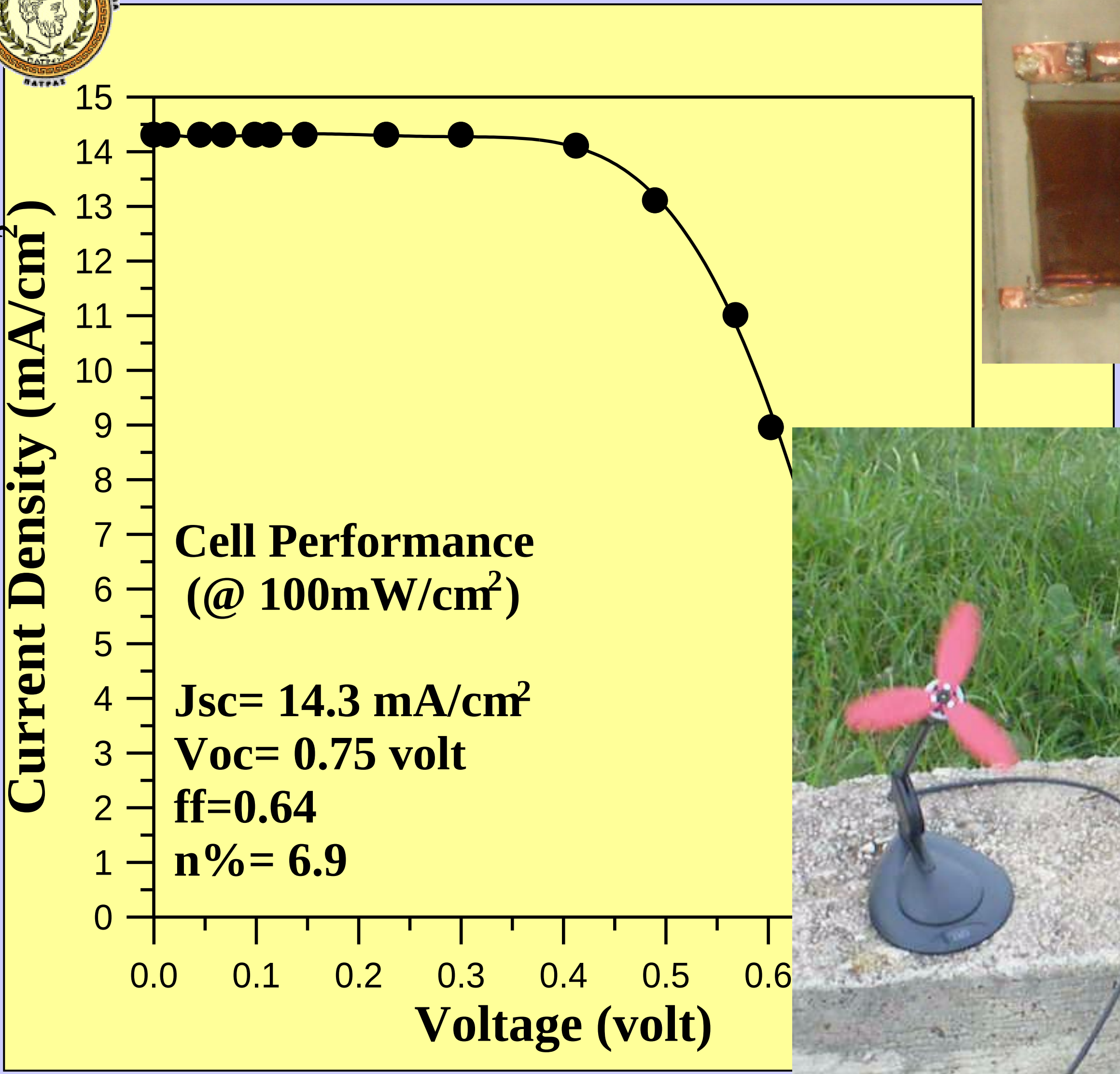


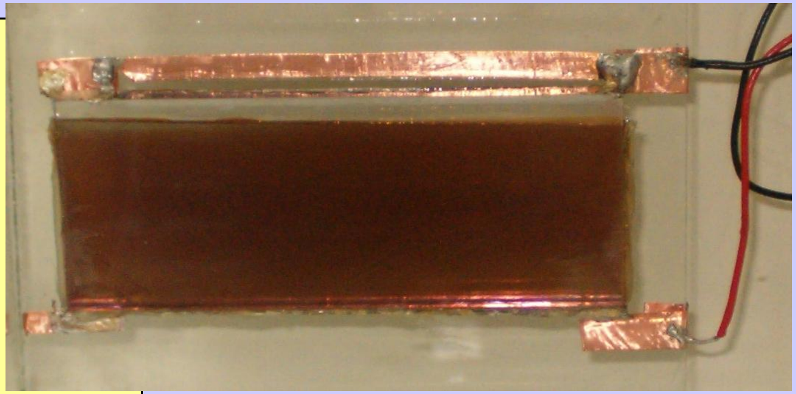
Quasi solid state dye sensitized solar cells employing nanocrystalline TiO_2 films made at low temperature ***Solar Energy Materials and Solar Cells***, *In Press*, Elias Stathatos, Yongjun Chen, Dionysios D. Dionysiou

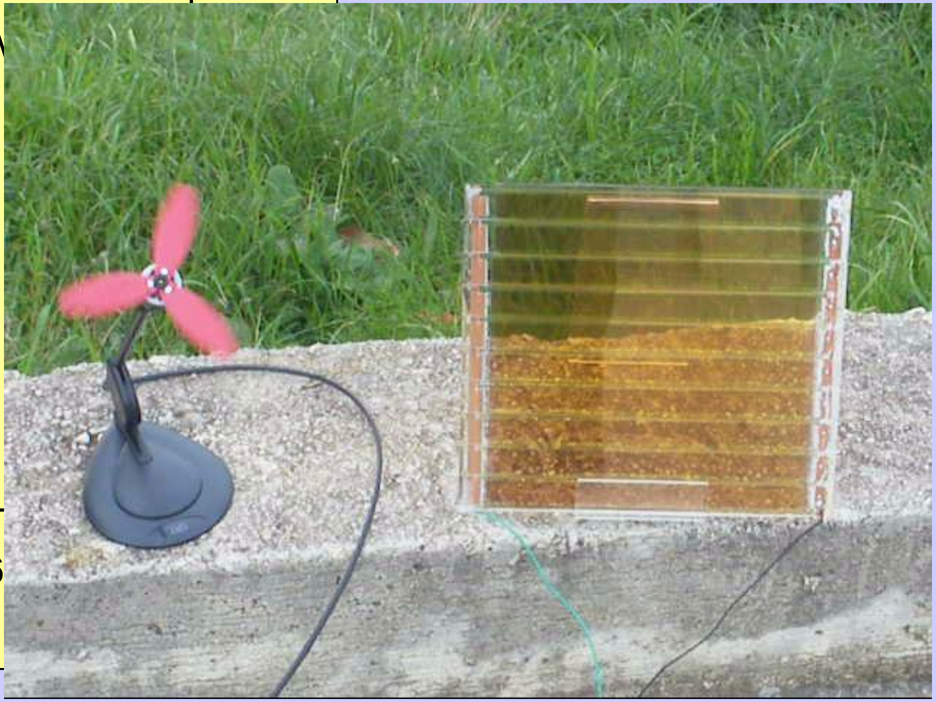
Light entrapment by multiple scattering











REFERENCE: Increase of the Efficiency of Quasi-Solid State Dye-Sensitized Solar Cells by a Synergy between Titania Nanocrystallites of Two Distinct Nanoparticle Sizes Advanced Materials Volume 19, Issue 20, 2007, Pages: 3338-3341 E. Stathatos, P. Lianos

Conclusions in Dye sensitized solar cells employing solid state nanocomposite electrolytes

1. Quasi Solid electrolytes as an essential alternative to liquid phase electrolytes overcoming the obvious problems of leaching and sealing.
2. Quasi Solid State Dye sensitized solar cells can be effectively prepared from sol-gel nanocomposite materials with maximum overall efficiency n>6.9%.
3. The stability of that type of cells may be further improved by using ionic liquids which may in excellence cooperate with the rest of the materials in the Solid Electrolyte.

Summary: optimization

There is enormous potential for future photovoltaic applications of DSSCells:

(1) Reduction of production costs: amounts and required purity of organic materials are low (<100 euro/m^2) and large scale production is considered to be relatively easy compared with most inorganic materials, involving low temperature processing at atmospheric pressure, cheap materials and flexibility.

(2) They can in principle be tailored to all needs due to the infinite variability of glass substrates and this makes them widely applicable.

(3) They are mostly transparent increasing this way the number of their applications (semi transparent windows for energy production)

Summary: optimization

Materials

• Up to now, Ru-based dyes have proved to be more efficient than other organic dyes. The efficiency of the DSSCells could be higher if the dye could also sensitize in the Near –IR.

• TiO_2 nanocrystalline semiconductor is the best choice so far. The surface area and nanoporosity are the crucial parameters for the high efficiency of the cells. The optimum thickness of the nanocrystalline semiconductor film is approx. 10 microns

• Electrolyte with high ionic conductivity values could increase the efficiency of the cells

LiI/I_2

KI/I_2

Ionic liquids /I_2

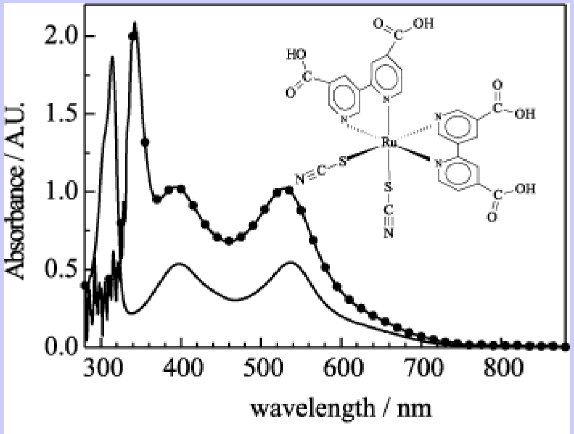
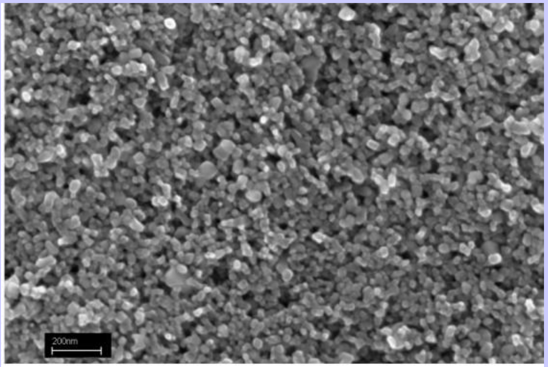


Figure 4. Absorption spectrum of the N3 dye in ethanol solution (—) and of a N3 dye-sensitized nanocrystalline TiO_2 electrode (-•-).



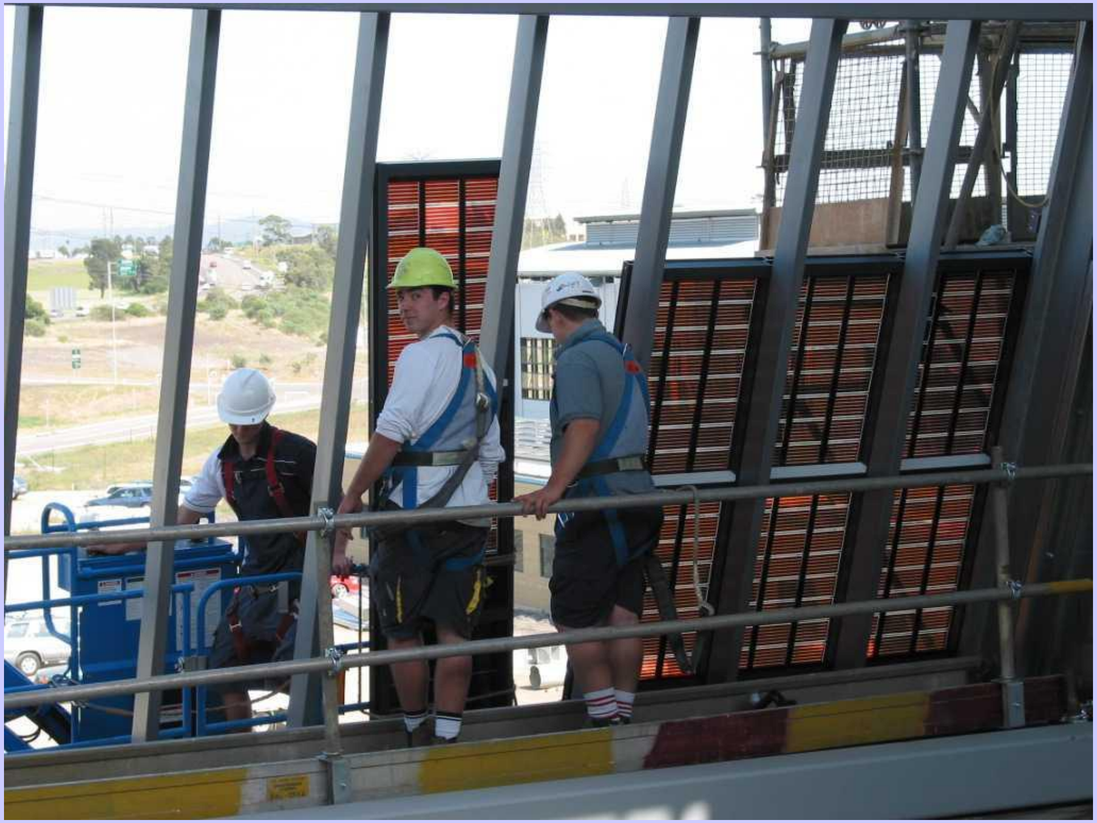
Which are the topics that are essential for reliable and cheap production technology?

1. Large area deposition of uniform TiO_2 layers.
2. Development of methods for dye-staining and electrolyte filling
3. Internal electrical interconnection of individual cells
4. Sealing of modules
5. Long term stability
6. Evaluation of process steps in terms of costs.

Suggested Literature on DSSCells

1. *Titanium dioxide dye-sensitized polyaniline solar cells by Hooi-Sung Kim*
2. *Solar energy conversion at dye sensitized nanostructured electrodes fabricated by sol-gel processing by Peter C Searson*
3. *Optoelectronics of solar cells (SPIE Press Monograph vol. PM115) by Greg P. Smestag*
4. *Third Generation Photovoltaics : Advanced Solar Energy Conversion (Springer Series in Photonics) by Martin A. Green*


ETRI

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