

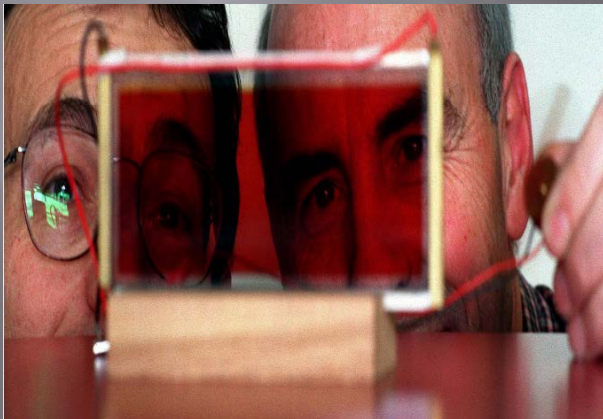


High efficient Dye sensitized and Organic solar cells: A new perspective to the solar energy *A challenge for new market on PV cells*

Prof. Elias Stathatos

Electrical Engineering Dept.

Technological-Educational Institute of Patras, Greece





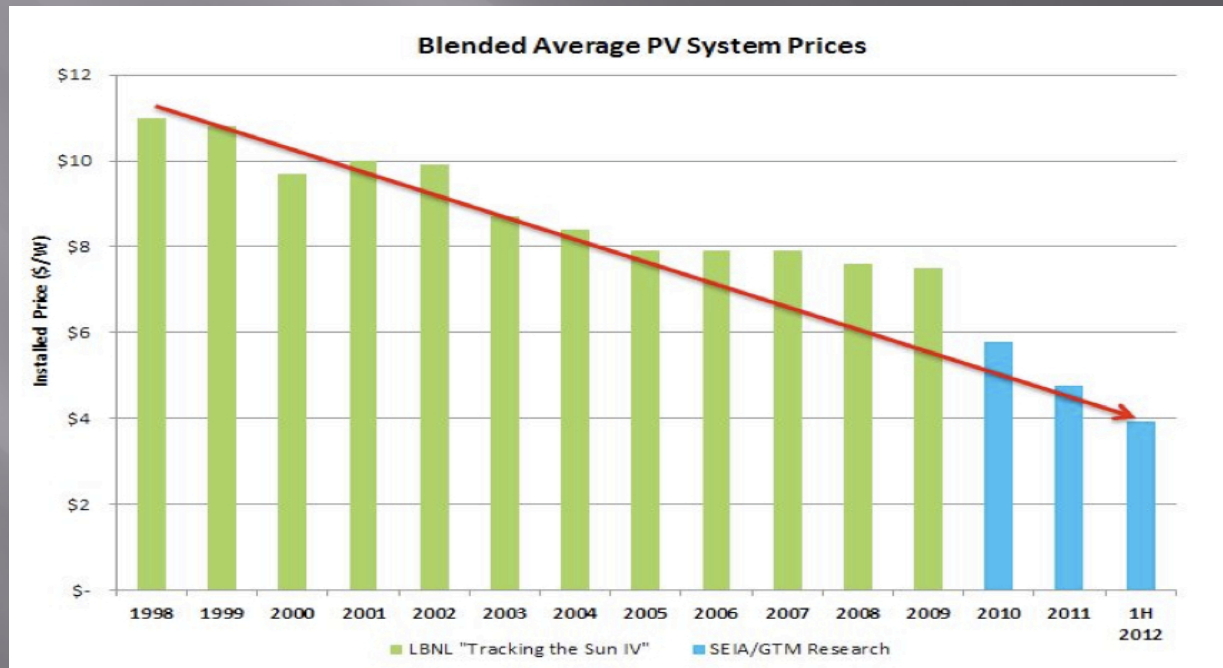
Solar energy

At earth's surface average solar energy is $\sim 4 \times 10^{24}$ J / year

Global energy consumption (2012) was $\sim 5 \times 10^{20}$ J / year (increasing annually $\sim 2\%$)

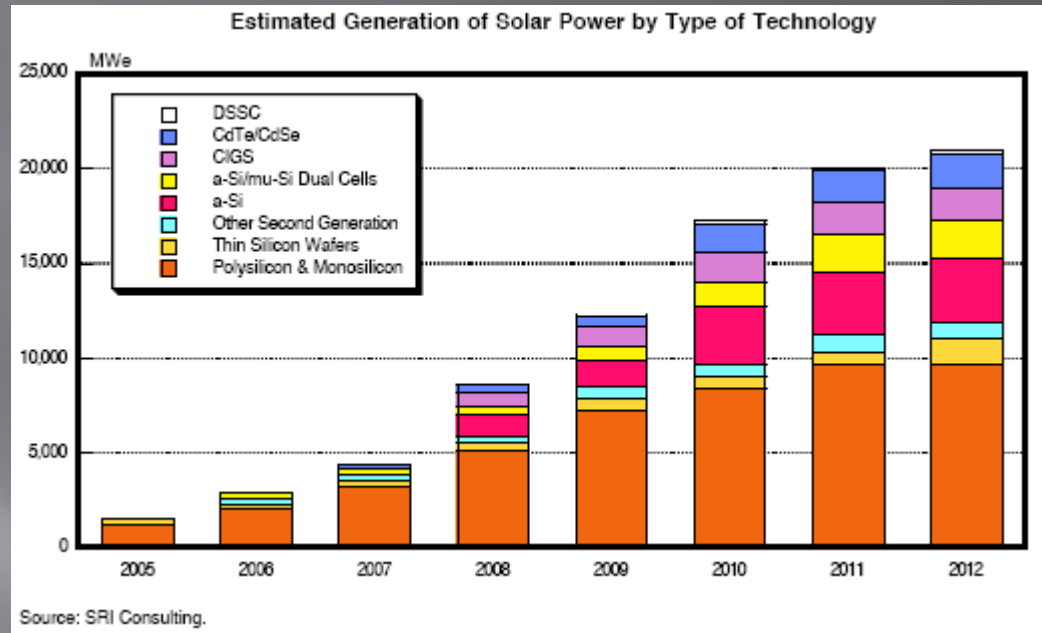
In US, average power requirement is 3.3 TW.

With 10% efficient cells we need 1.7% of land area devoted to PV (\sim area occupied by interstate highways)

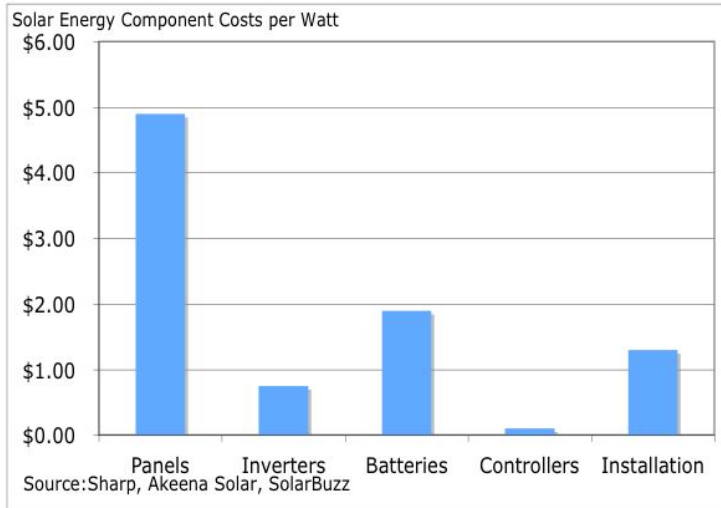




Production and cost of PVs installation



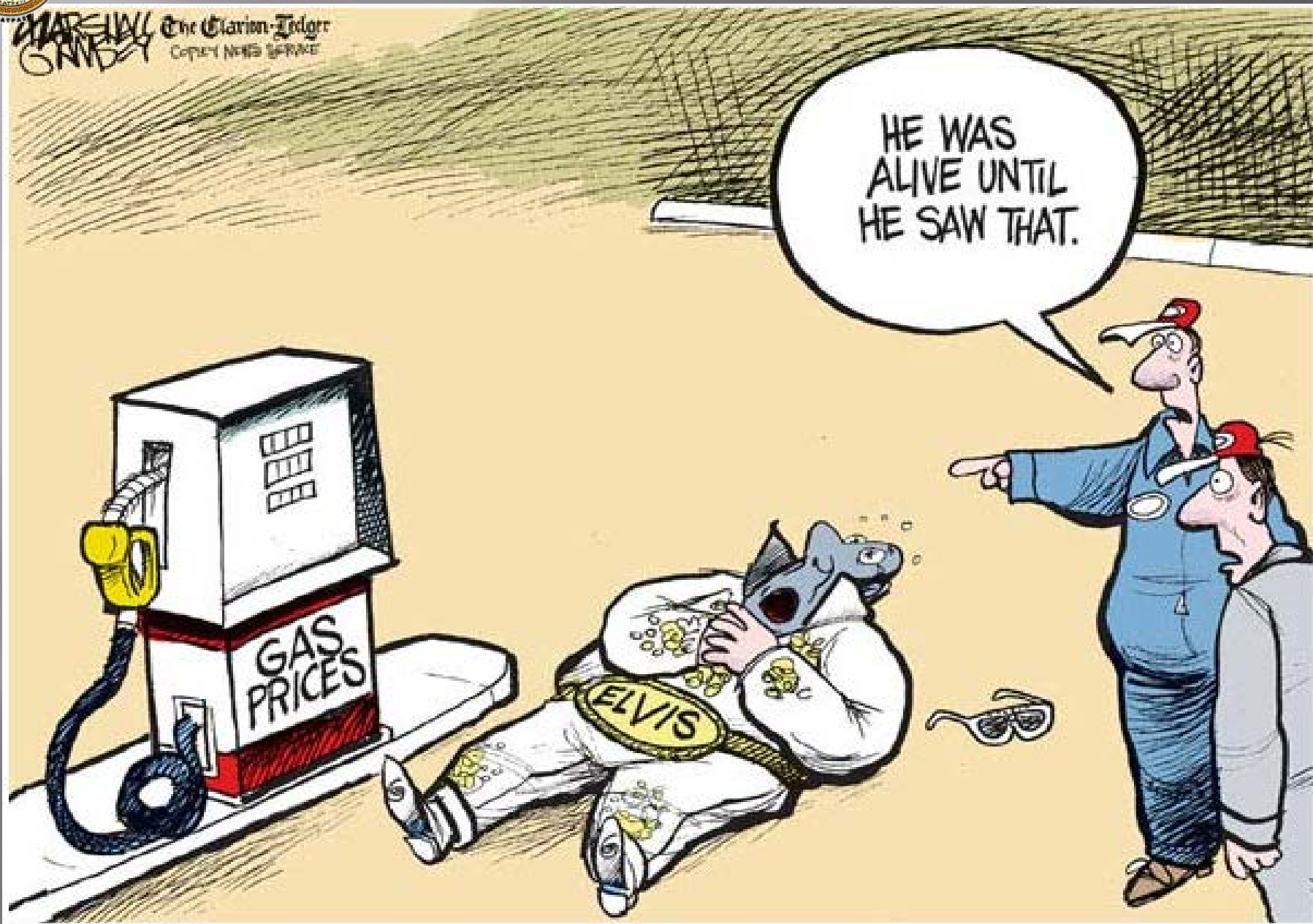
Solar Energy Component Costs





We have to find new technologies in renewable energy sources

MARSHALL
GANDY
The Clarion-Jedger
Copyright © 1998





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 $\text{Cu}_2\text{O}/\text{Cu}$ 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 substrates*

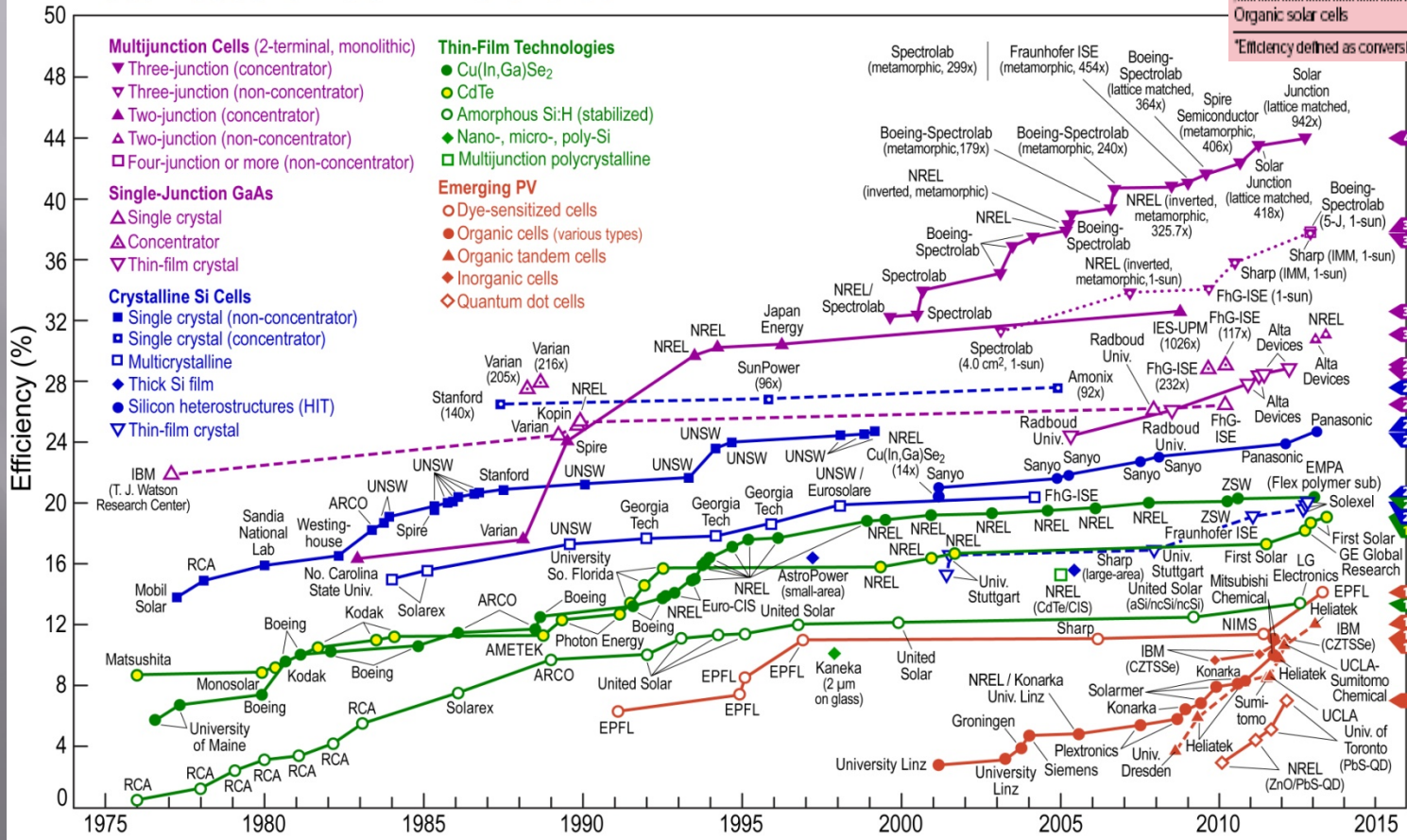


Progress of cell efficiencies

| Type of cell | Efficiency (%)* | | Research and technology needs |
|--|-----------------|--------|--|
| | Cell | Module | |
| Crystalline 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 | 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 |

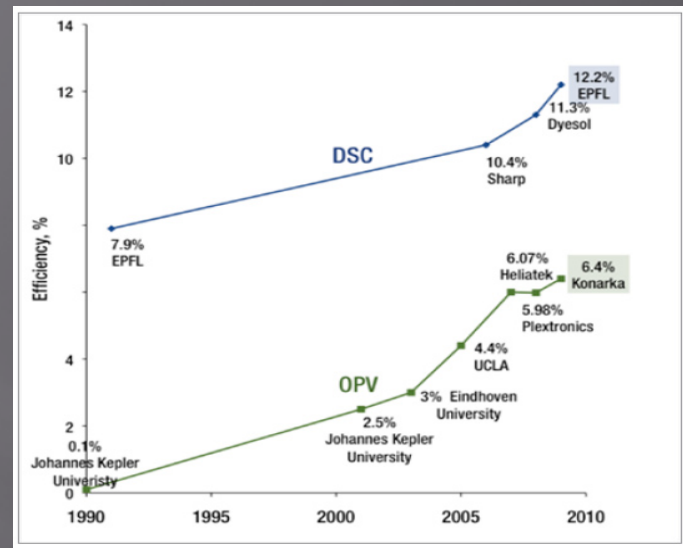
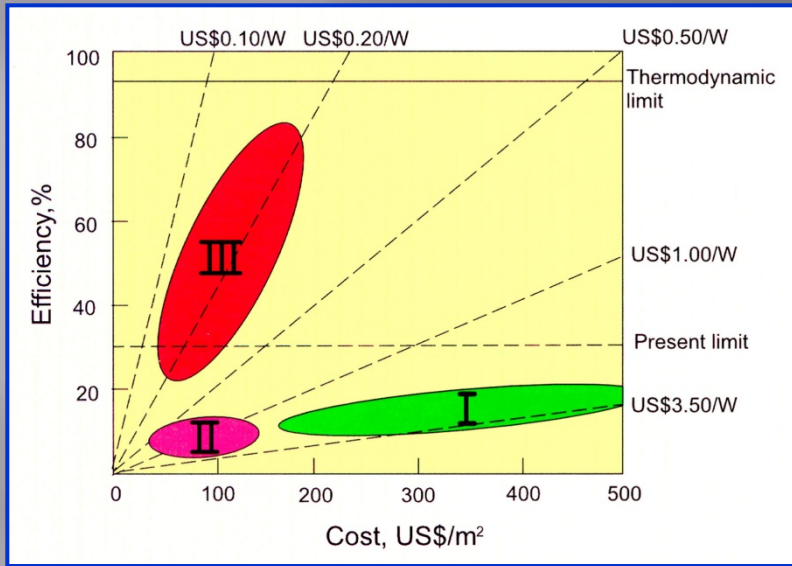
*Efficiency defined as conversion efficiency from solar to electrical power.

Best Research-Cell Efficiencies



Under
AM 1.5G
simulated solar
illumination

(Rev. 06-2013)

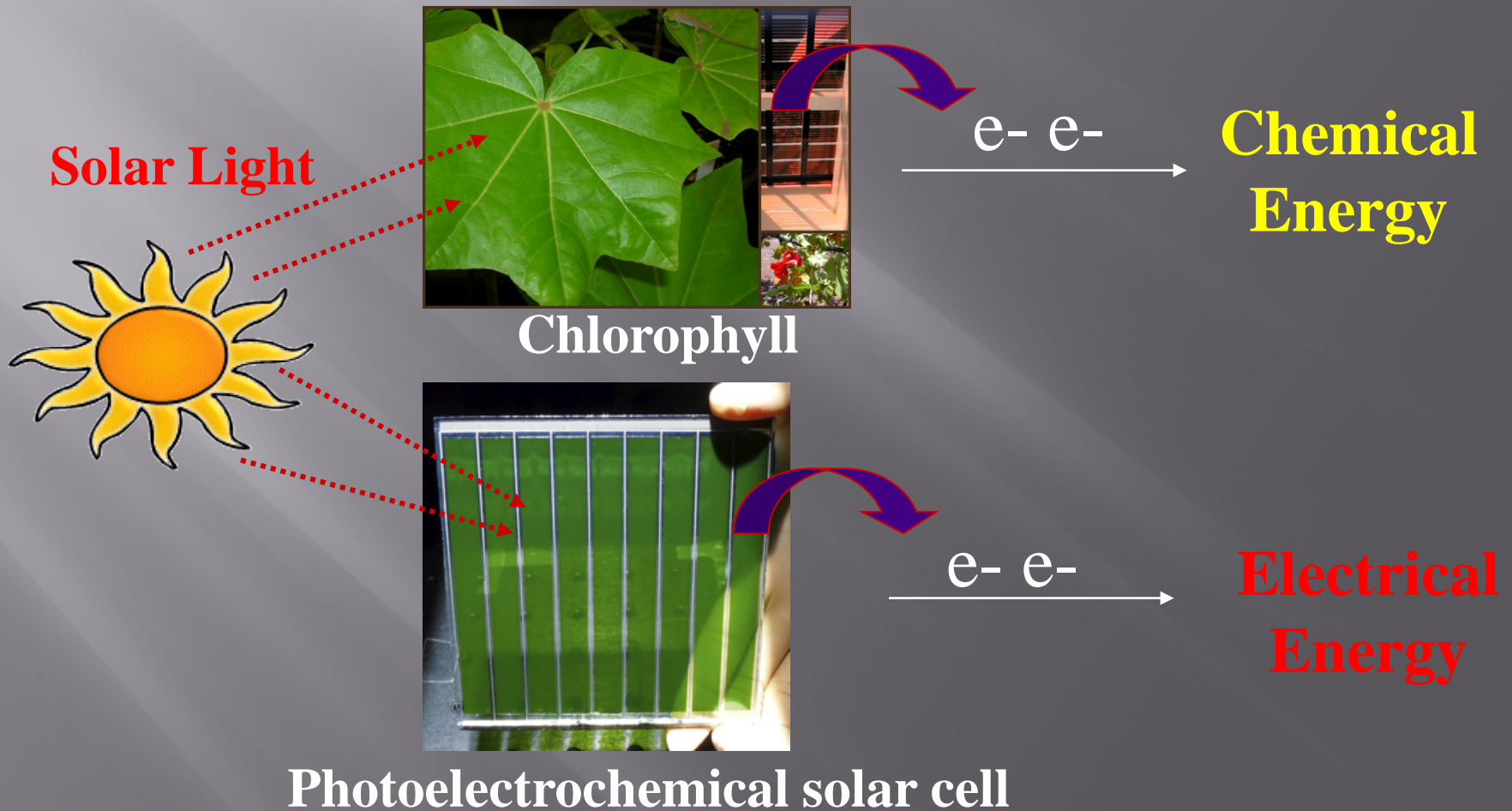


Source: GTM Research

| | 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 | Medium Advantageous | Disadvantageous | Medium Advantageous | Medium Advantageous | Medium Advantageous |
| Crystalline Silicon (1st Gen) | Disadvantageous | Disadvantageous | Disadvantageous | Disadvantageous | Medium Advantageous | Disadvantageous | Disadvantageous | High Advantageous |
| | Disadvantageous | Medium Advantageous | High Advantageous | | | | | |



Photosynthesis and Photoelectrochemical Solar cells





Cell efficiency

Power conversion efficiency (η) 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

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

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



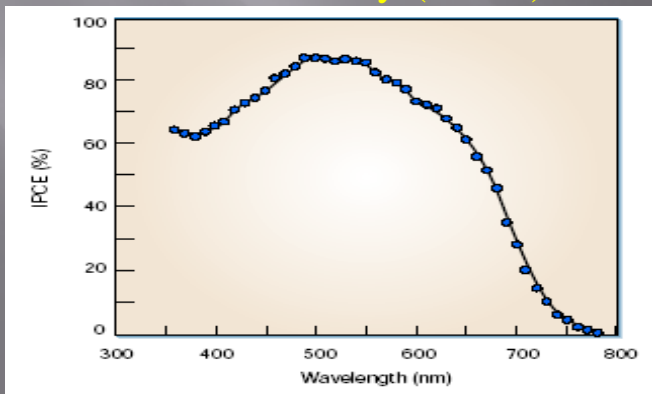
$$\eta = \frac{I_{sc} V_{oc} FF}{P_s} \times 100$$

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

Under **AM 1.5G** simulated solar illumination

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

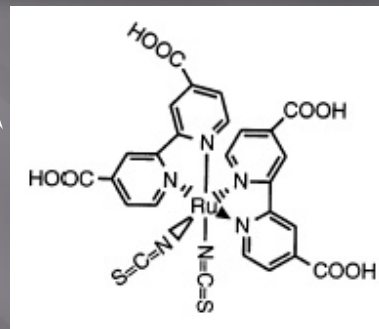
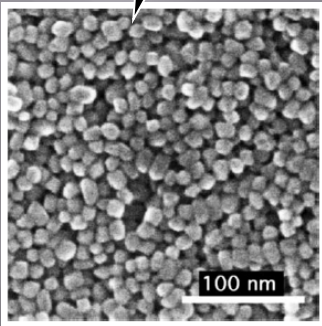
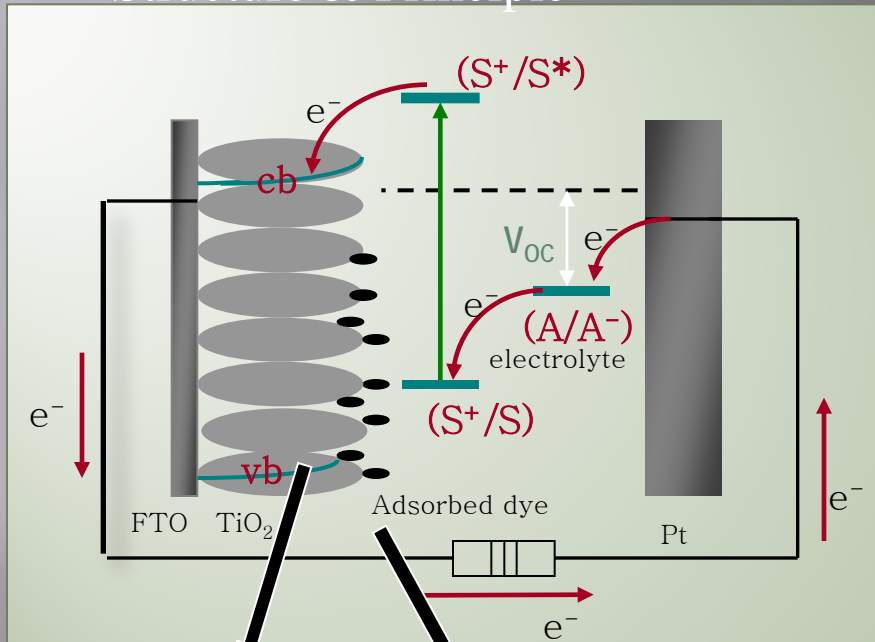
$$= \frac{[1240 \text{ eV nm}][\text{photocurrent density } (\mu\text{A cm}^{-2})]}{[\text{wavelength (nm)}][\text{irradiance (mW cm}^{-2})]}$$





Dye-Sensitized Solar Cell (DSSC)

Structure & Principle



Cell reactions

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

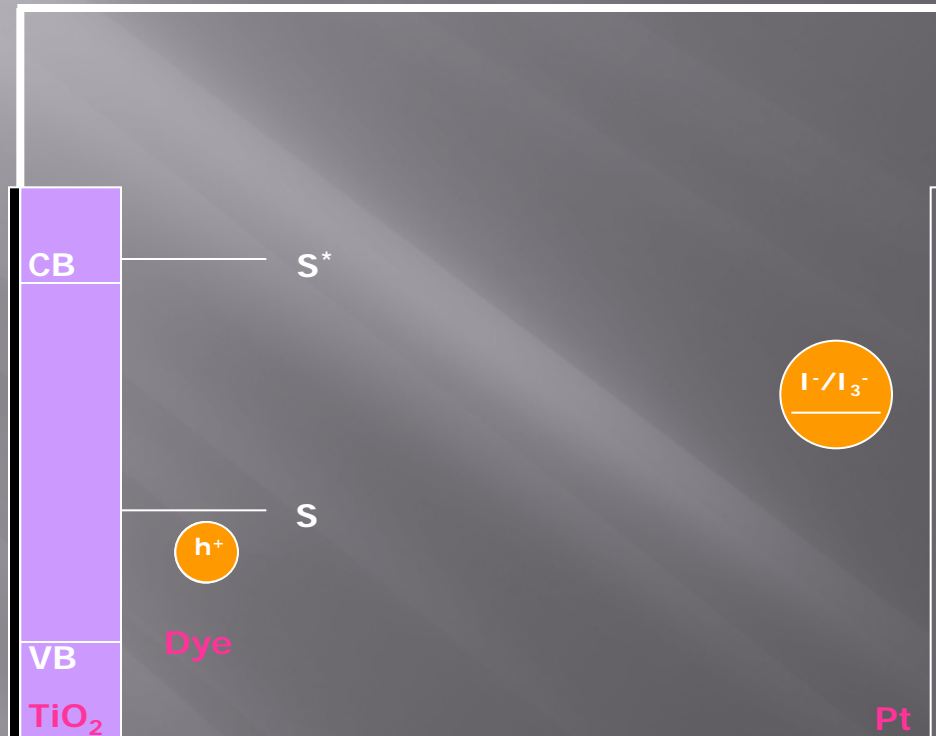
Advantages

- Low cost (<100 euros/m²)
- Utilization of visible range of light
- Simple manufacturing process
- Environmental compatibility
- Transparent solar cell
- Window

Moderate efficiency ~10%



Principle of Operation



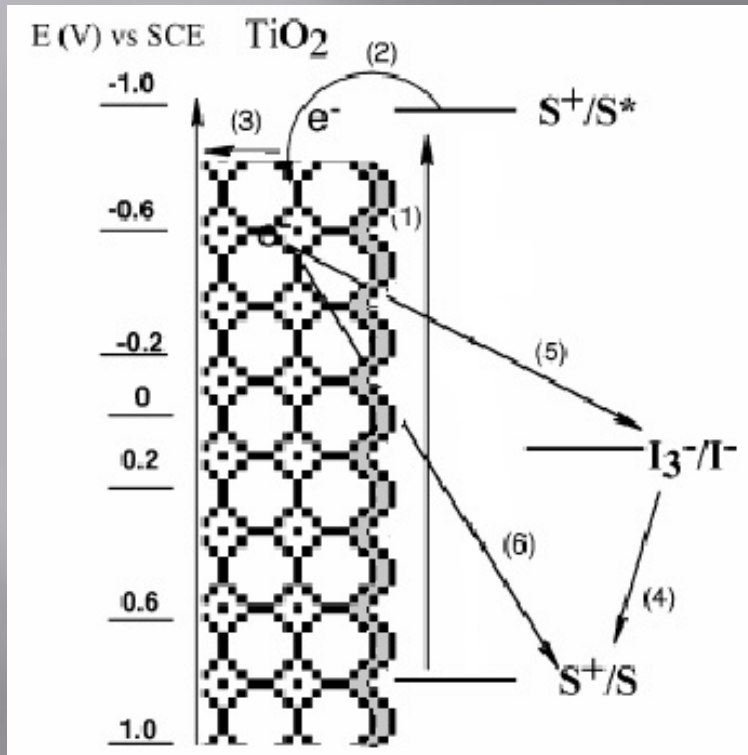


Key Components

- 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

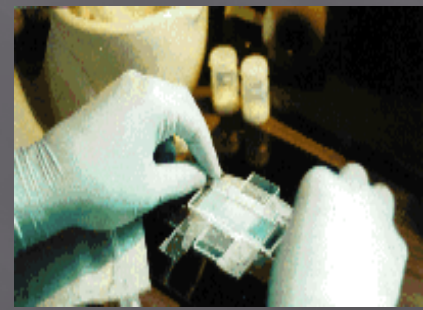
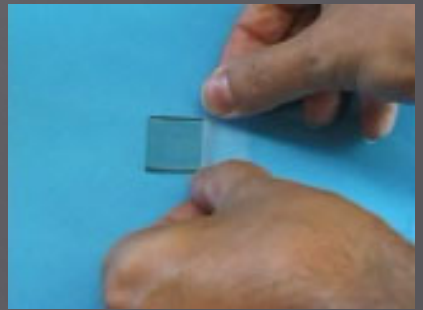
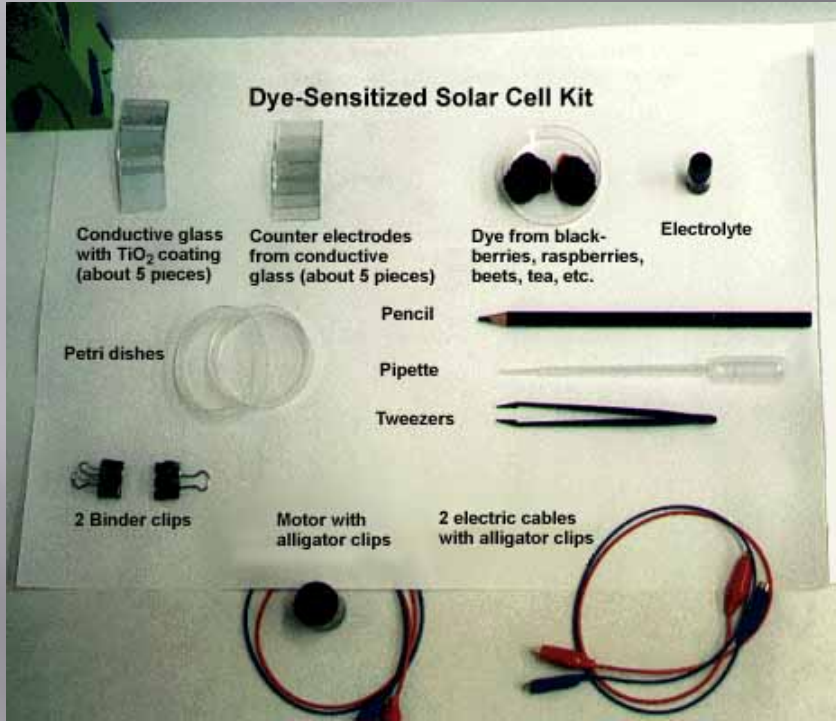


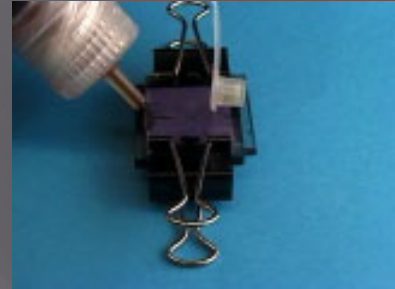
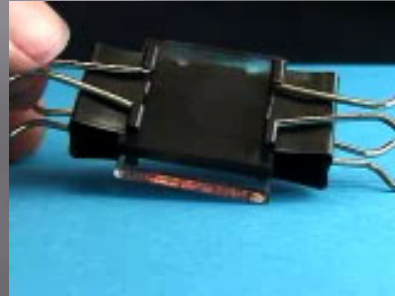
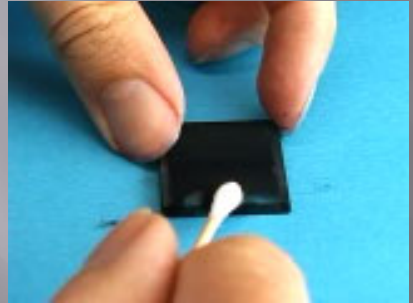
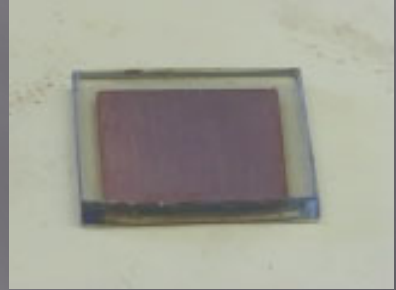
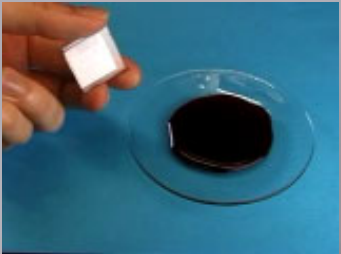
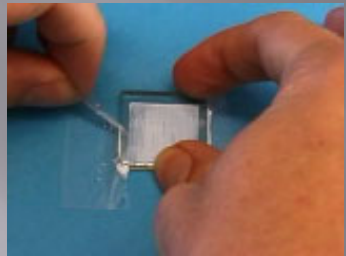
- (1) Excitation of dye under illumination (ns)
- (2) Electron injection (ps)
- (3) Electron transport (ms)
- (4) Regeneration of dye (10 ns)
- (5) Recombination with oxidized redox (ms)
- (6) Recombination with oxidized dye (s)

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



How to easily built a Dye Sensitized Solar cell





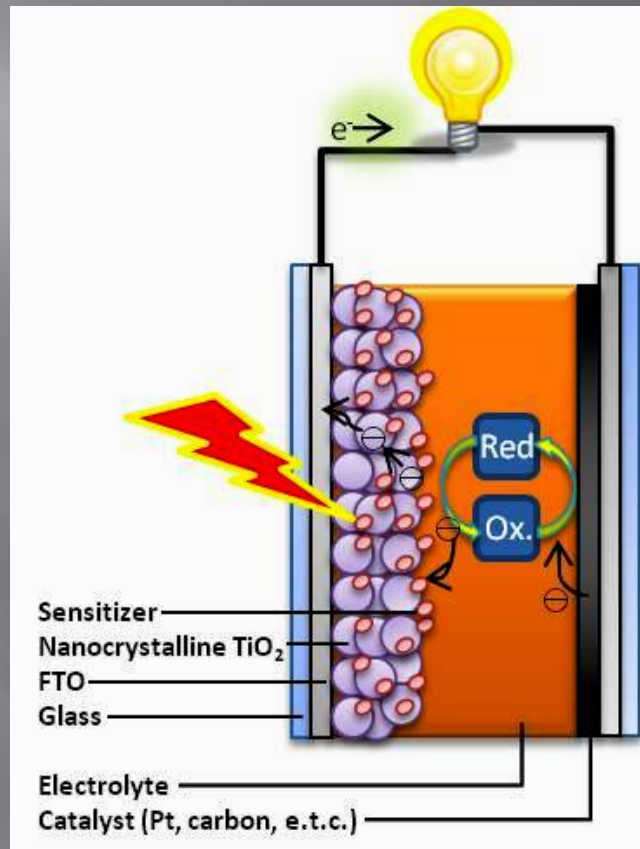


An overview to the Main process steps of Manufacturing a standard nc-DSSCell

- 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°C**
- 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**

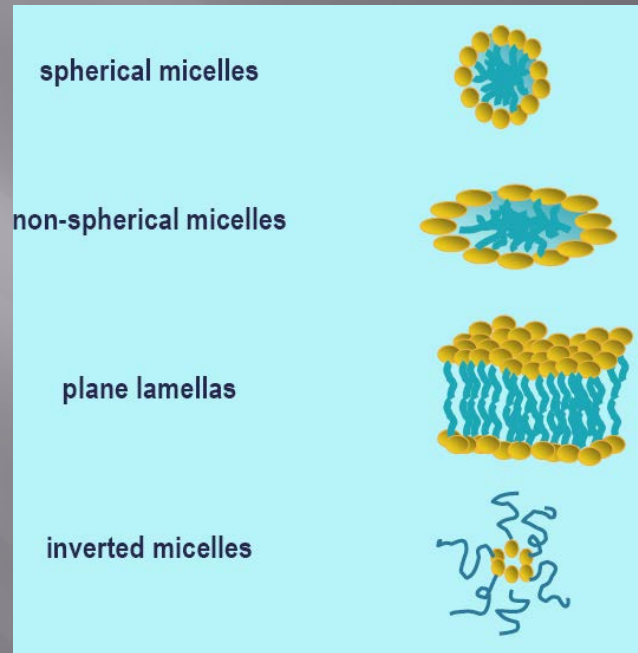


Dye-sensitized Photoelectrochemical Solar Cells based on liquid electrolytes or nanocomposite organic/inorganic gels (solid electrolytes).





Surfactants as templates in the formation of TiO_2 nanostructure



Micelles

of Triton X-100

TiO_2 precursor



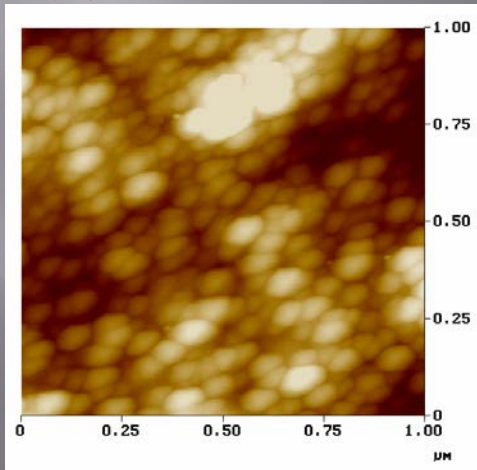


Preparation procedure of TiO_2 powder and films with TTIP precursor.

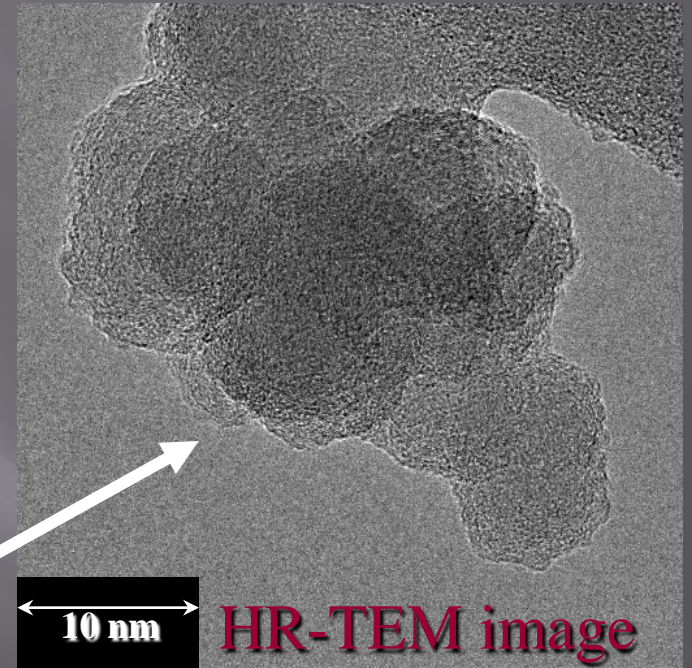
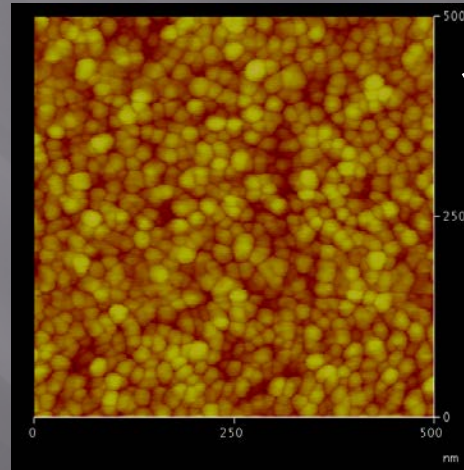
Organic acid solvolysis



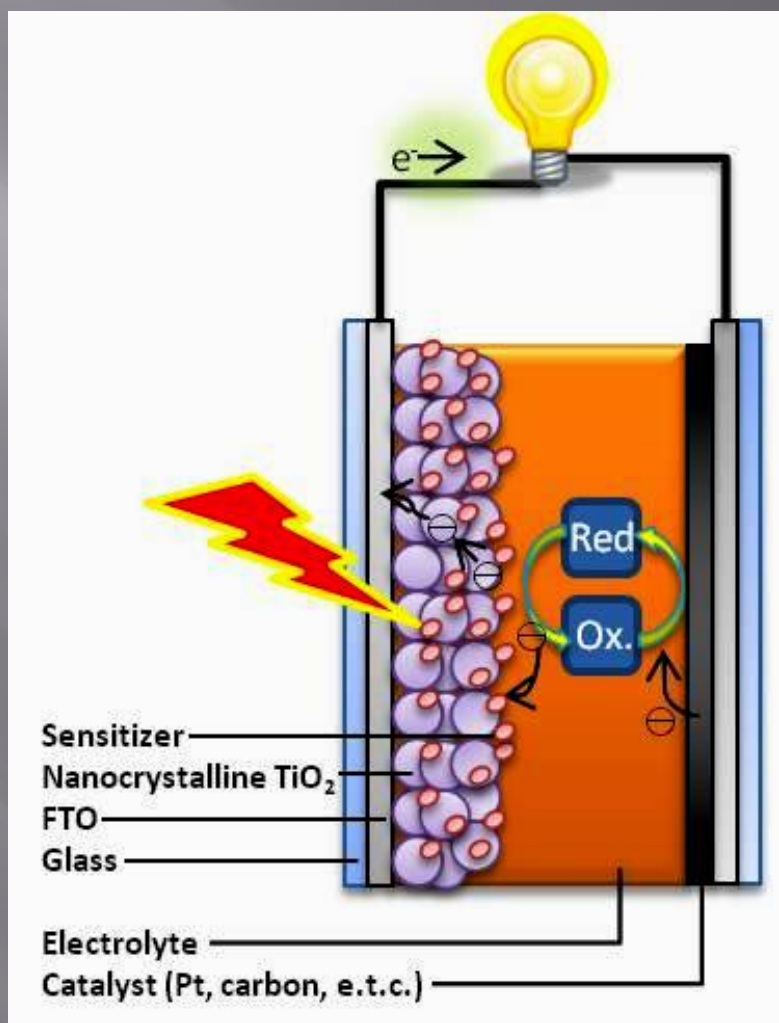
(a) ~ 50 nm



(b) ~ 15 nm

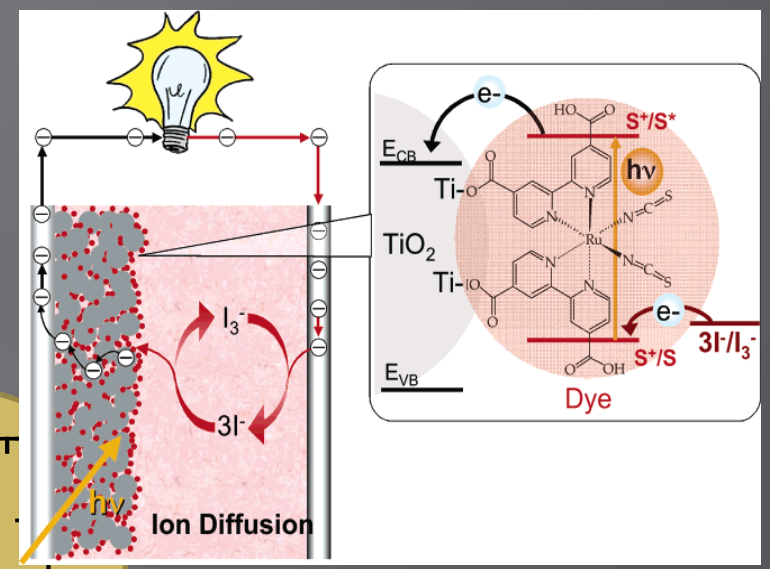
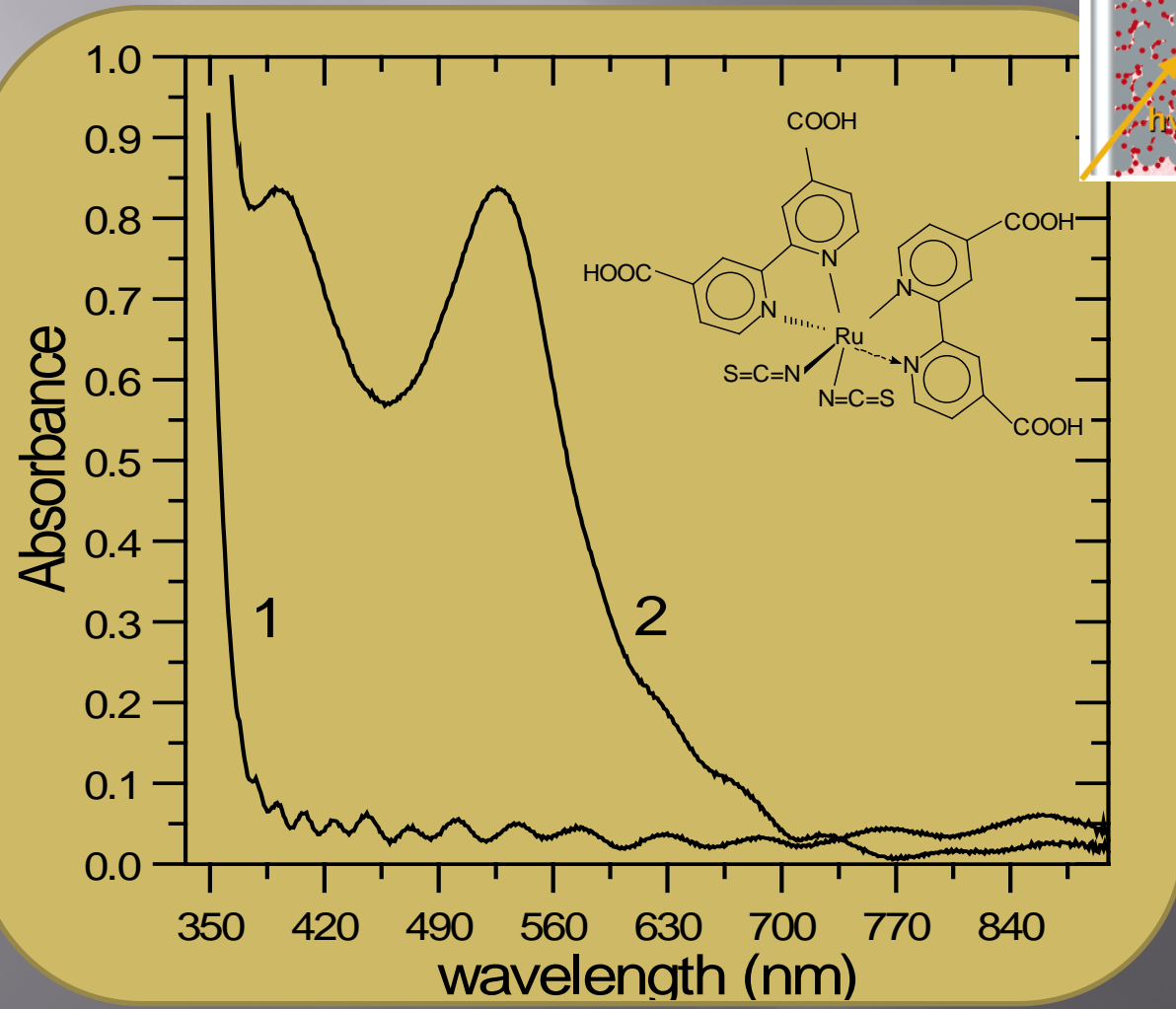


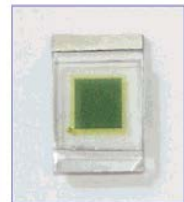
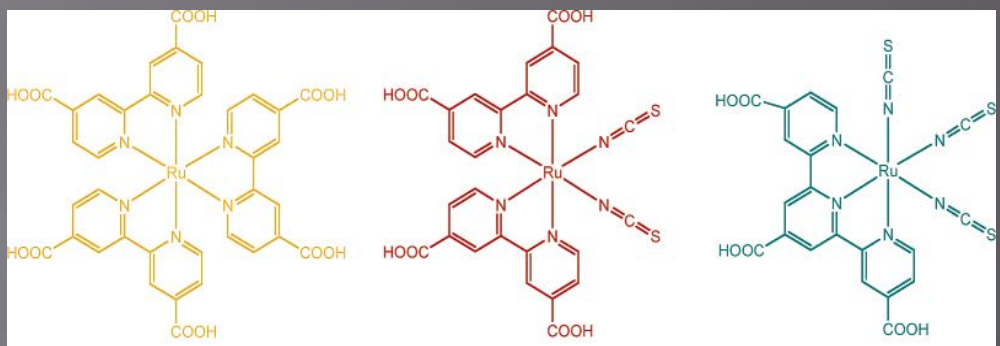
Varying organic Template (a) PEG 2000 and (b) Triton X-100

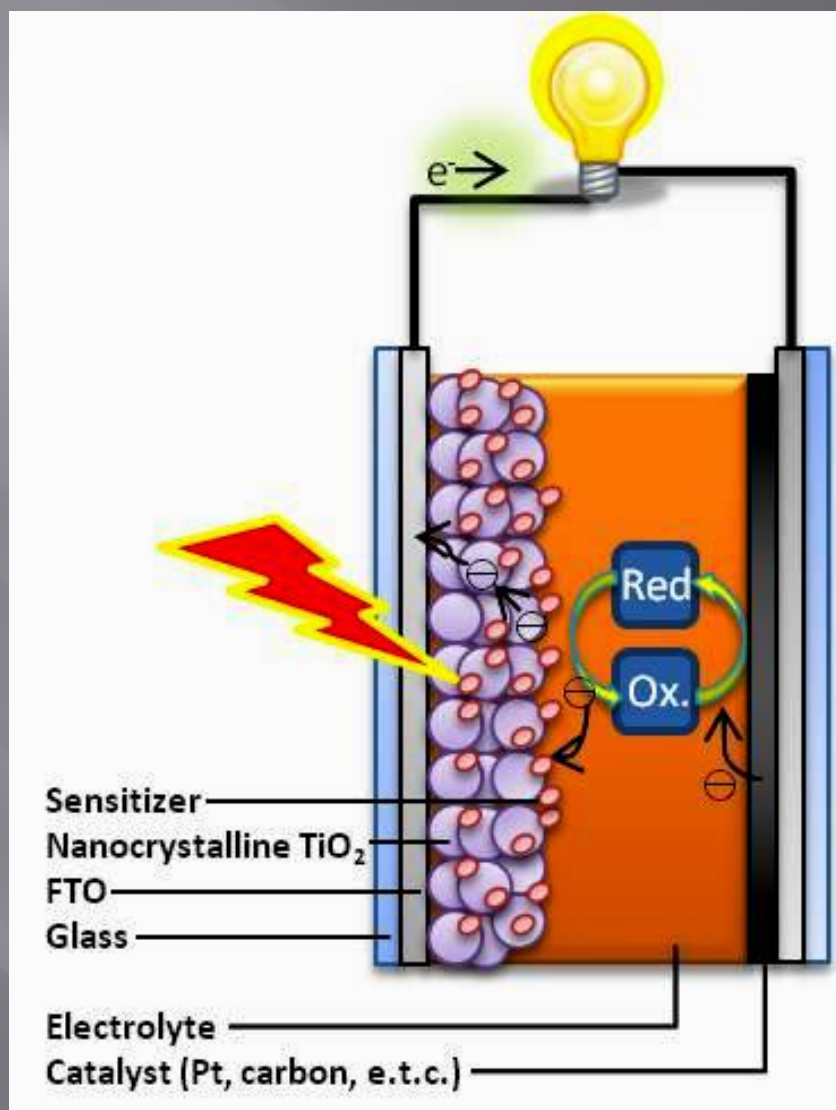




TITANIA FILM AND ADSORBED DYE-SENSITIZER









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

COMPOSITION OF A NANOCOMPOSITE ELECTROLYTE

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

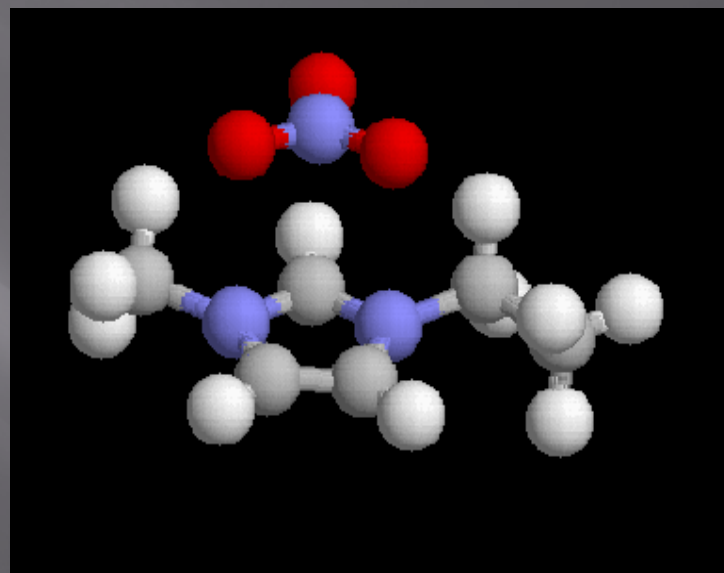
The precursor solution must be sufficiently fluid to fill the pores of the nanostructured semiconductor

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



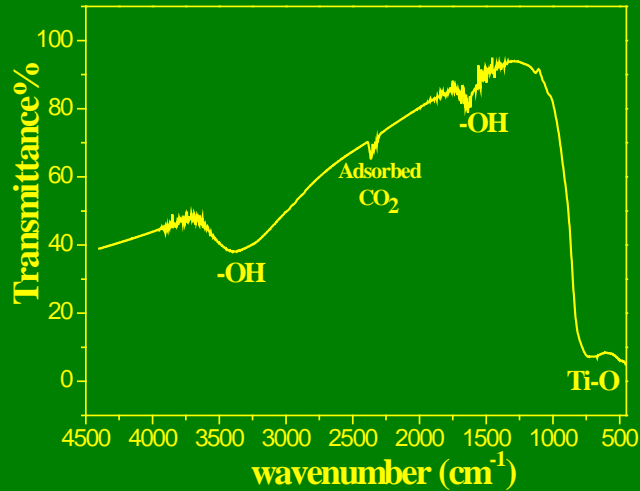
Room Temperature Ionic Liquids (RTILs)

- A RTIL is an ionic material that is liquid at room temperature.
- They are based primarily on asymmetric organic cations paired with inorganic anions.
- By changing the ions, a countless variety of RTILs can be obtained.
- The asymmetric shape of the cations prevents the packing and the formation of solids at room temperature.
- Air and water resistant.
- Can be hydrophilic or hydrophobic.



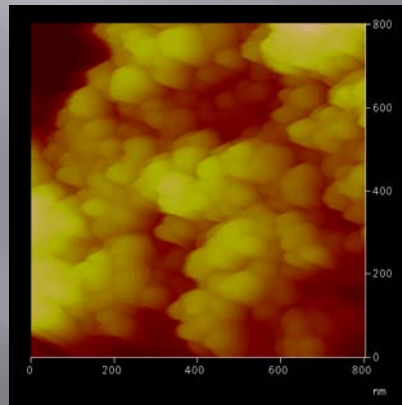
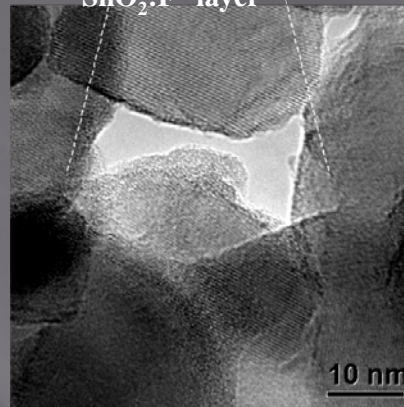
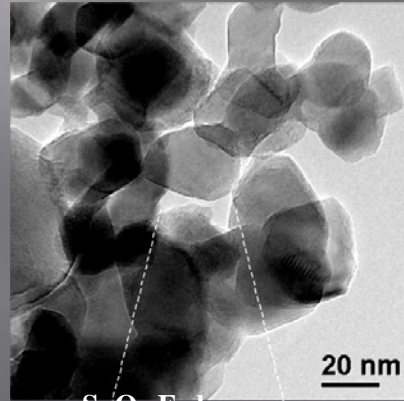
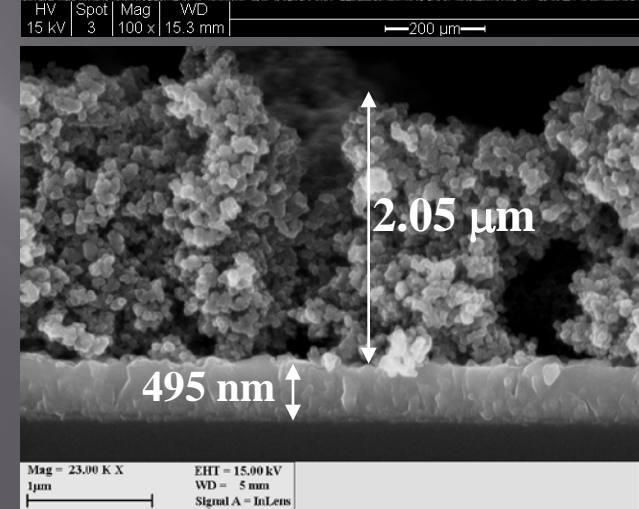
FTIR spectrum of the as-prepared film on silicon wafer rinsed multiple times with water and dried at 100°C.

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



TiO₂ prepared in room temperature

SEM image of the TiO₂ film on FTO glass prepared at room temperature

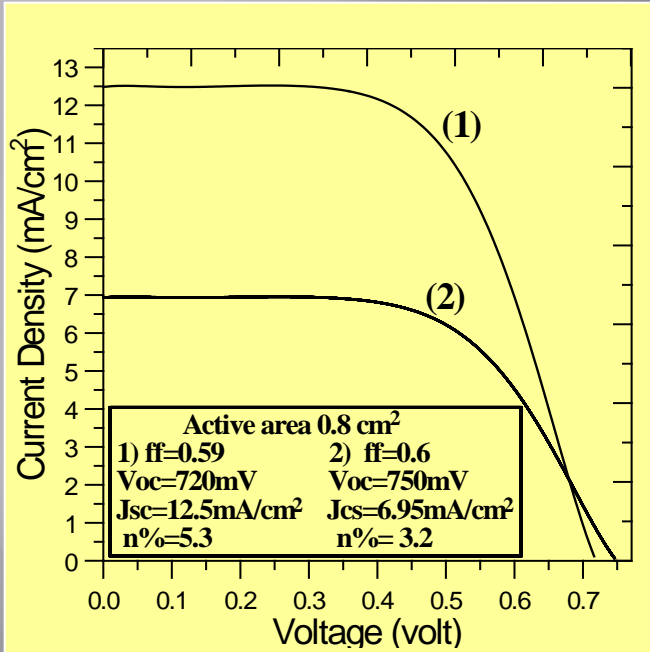


AFM image of the as-prepared TiO₂ film at room temperature

HR-TEM image of TiO₂ film

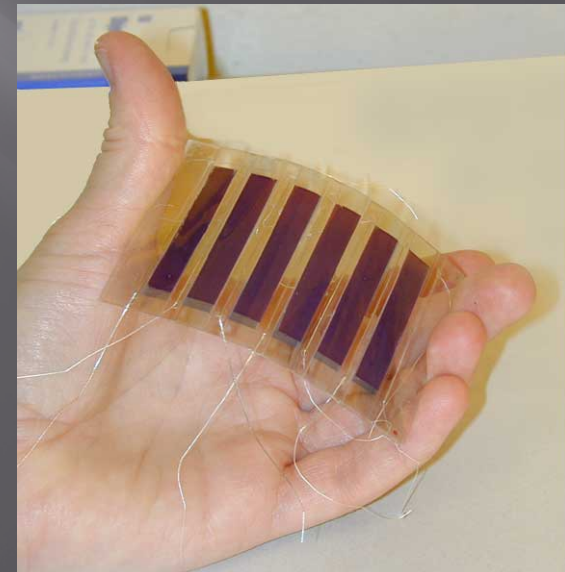
Cross-section SEM image of the as-prepared TiO₂ film.



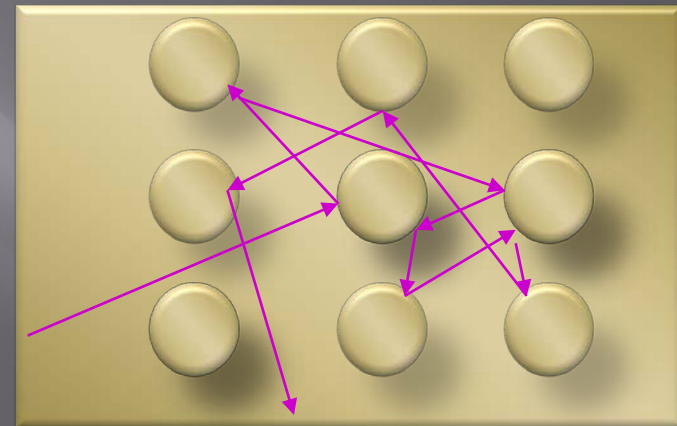
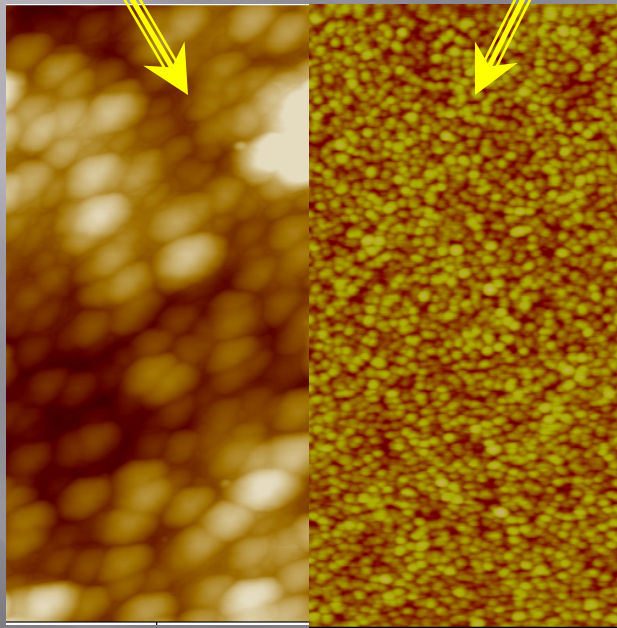
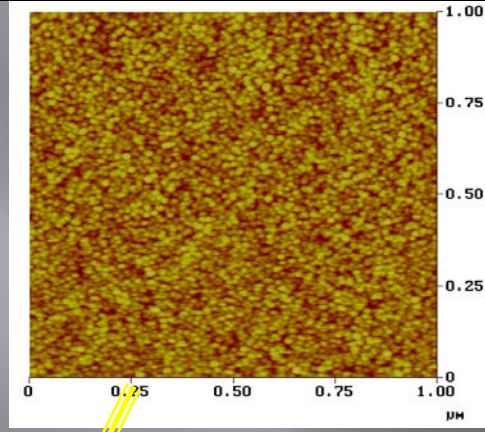
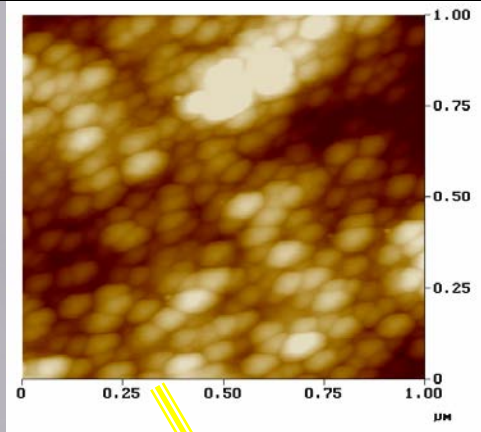


| Substrate | TTIP (M) | TTIP: P25-TiO ₂ (Molar ratio) | Q (%) | IPCE (%) | J_{sc} (mA/cm ²) | V_{oc} (mV) | ff | n (%) |
|-----------------|--------------|--|----------|-----------|--------------------------------|---------------|-------------|------------|
| FTO glass | 0.180 | 0.14 | 0 | 31 | 6.9 | 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 TiO₂ film with quasi-solid state electrolyte employing:
 (1) FTO glass,
 (2) ITO-PET plastic substrate.



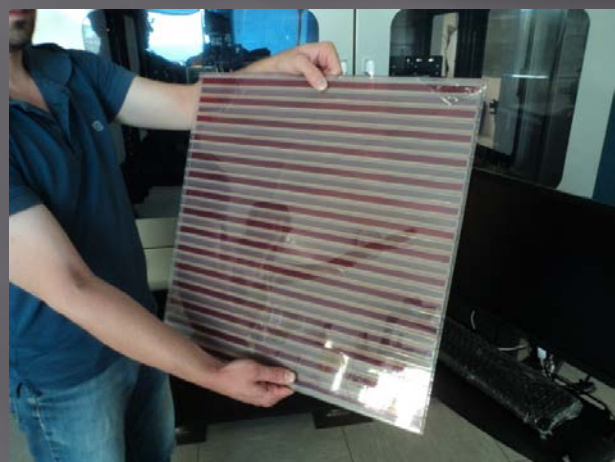
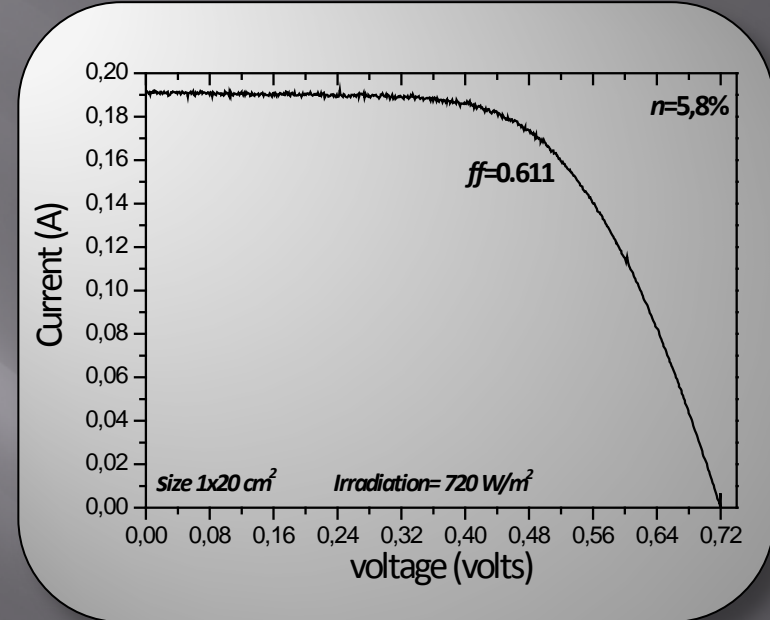
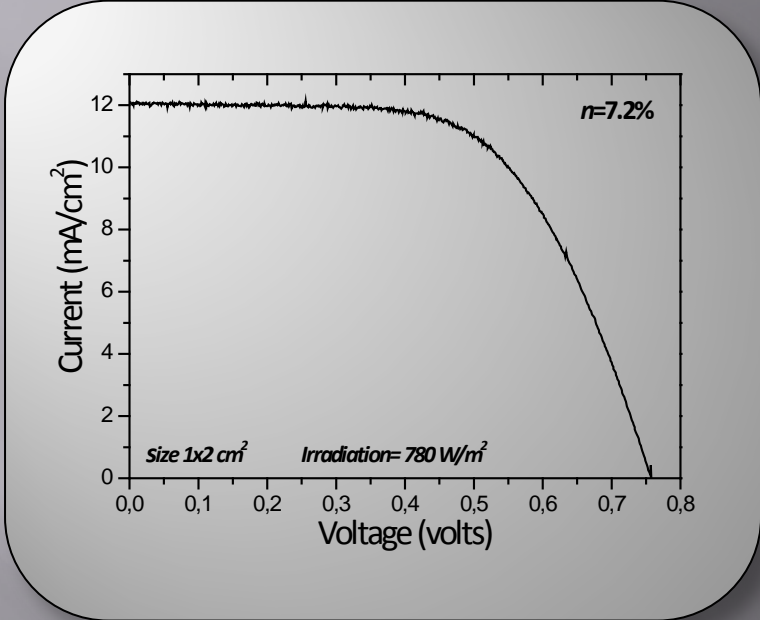
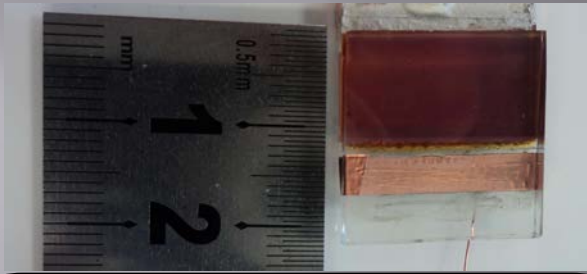
Light entrapment by multiple scattering





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

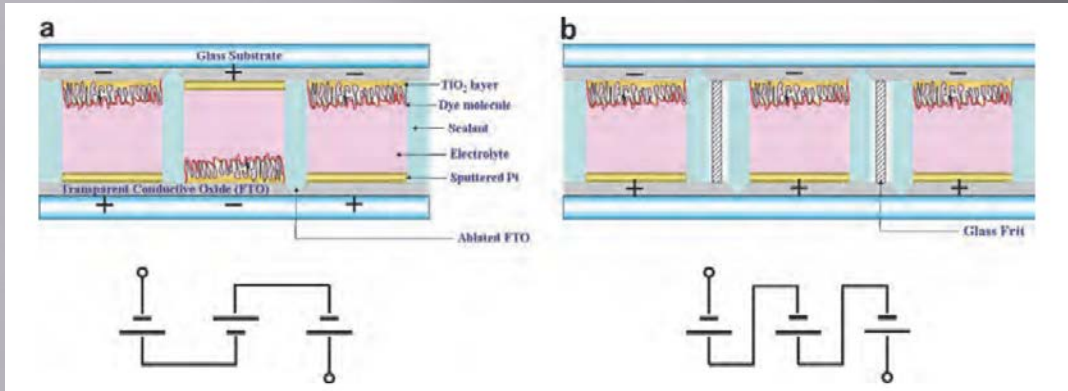
- 1. Large area deposition of uniform TiO₂ layers.**
- 2. Development of methods for dye-staining and electrolyte filling**
- 3. Internal electrical interconnection of individual cells**
- 4. Sealing of modules**
- 5. Long term stability**
- 6. Evaluation of process steps in terms of costs.**



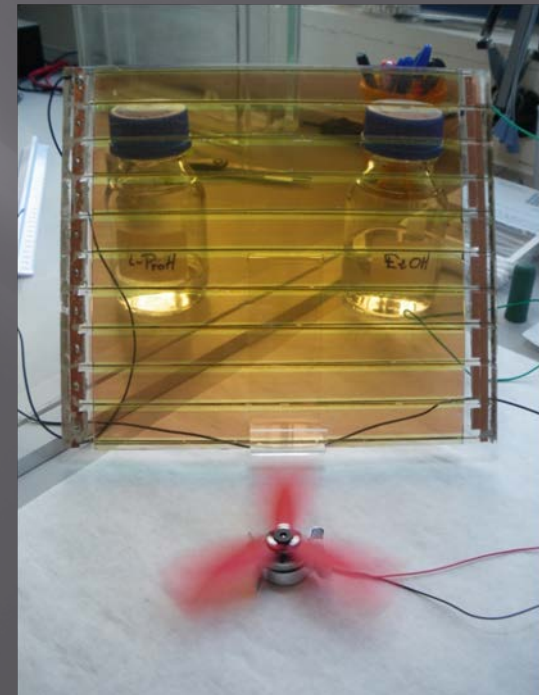
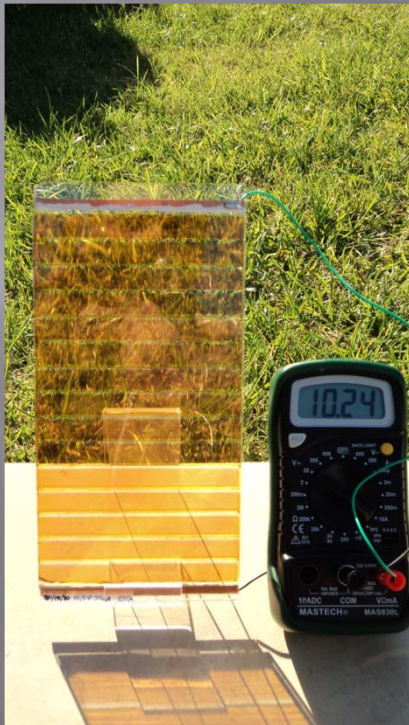
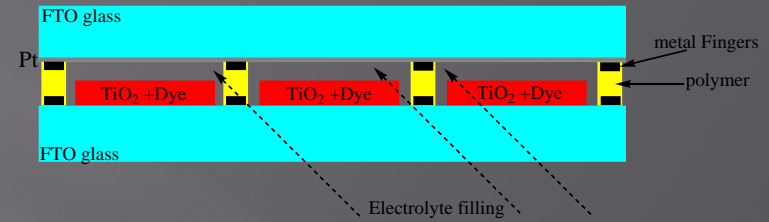


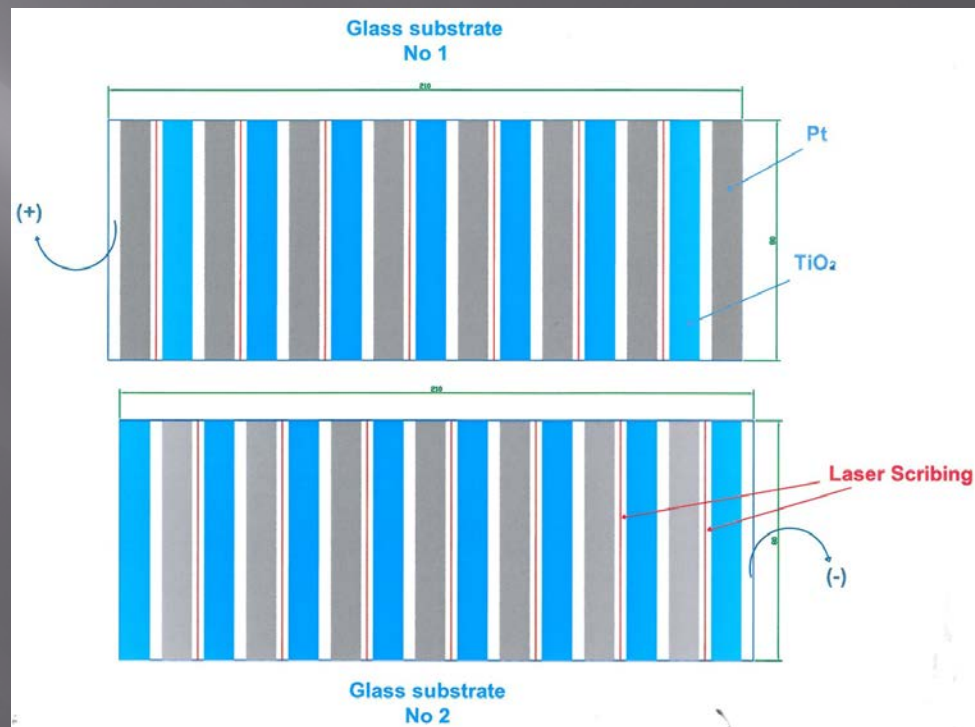
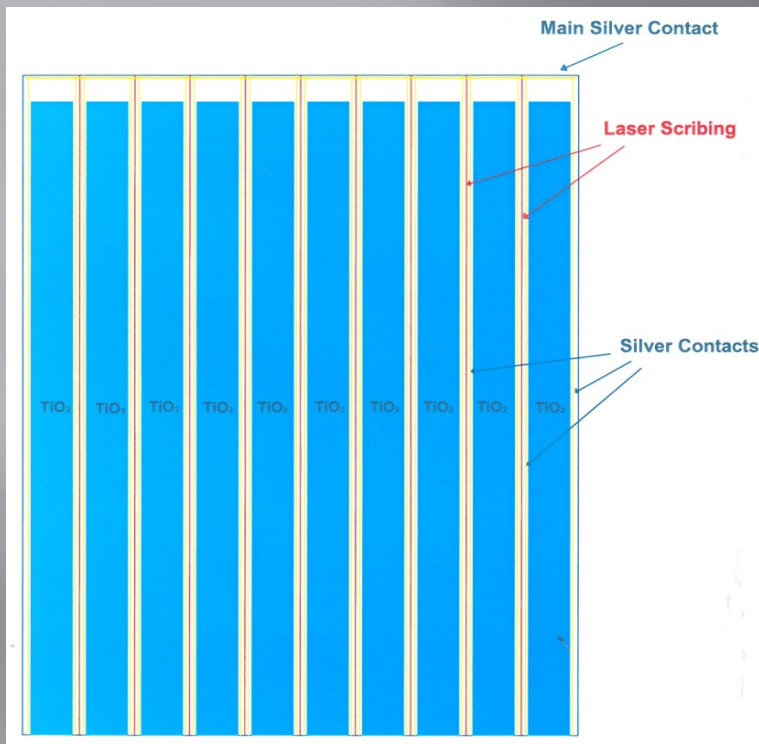
Type of cell connections

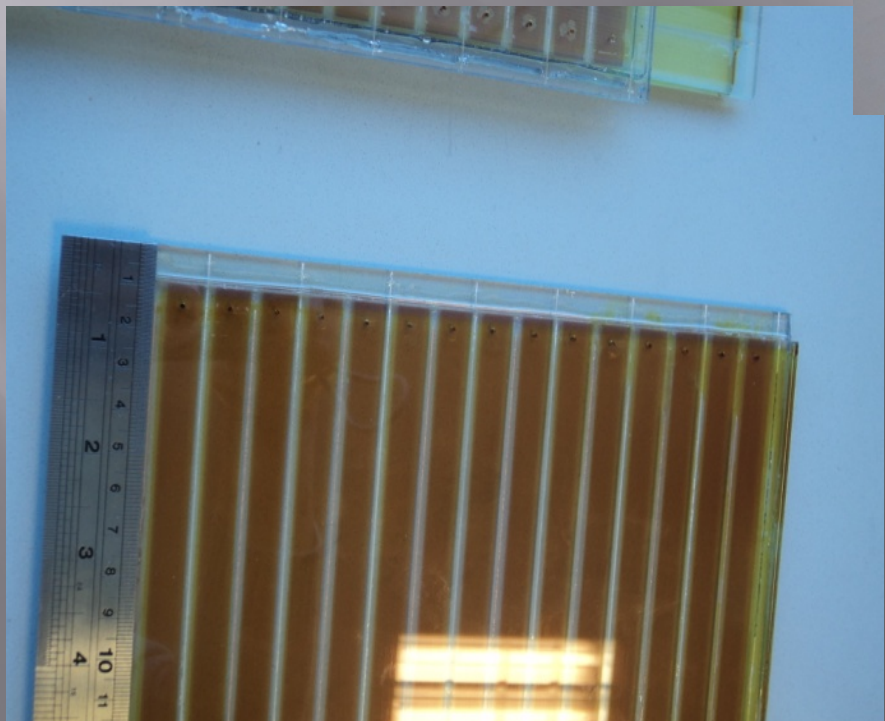
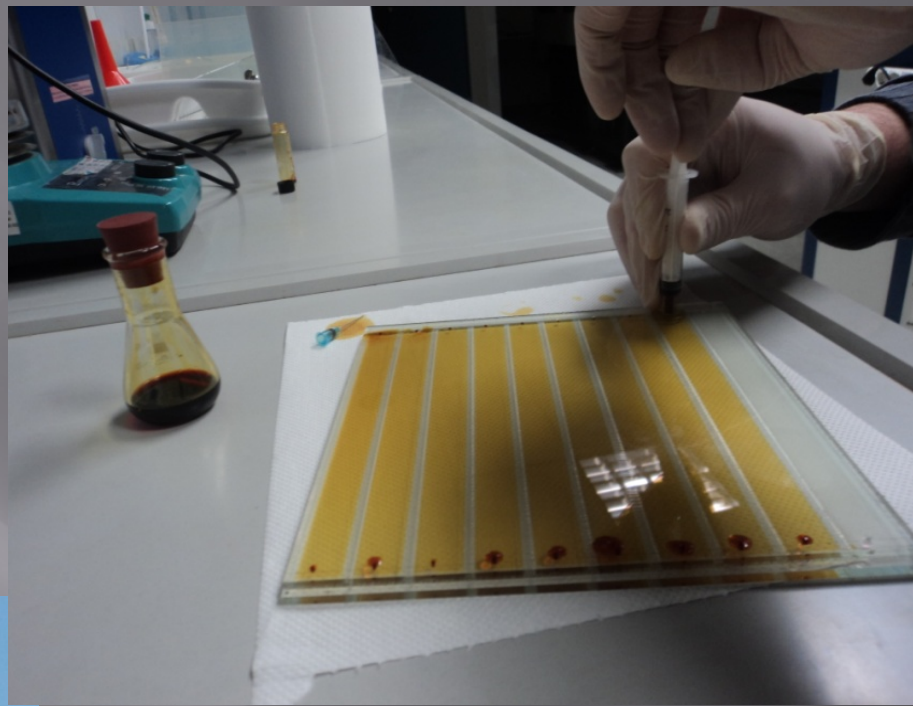
(1) In series

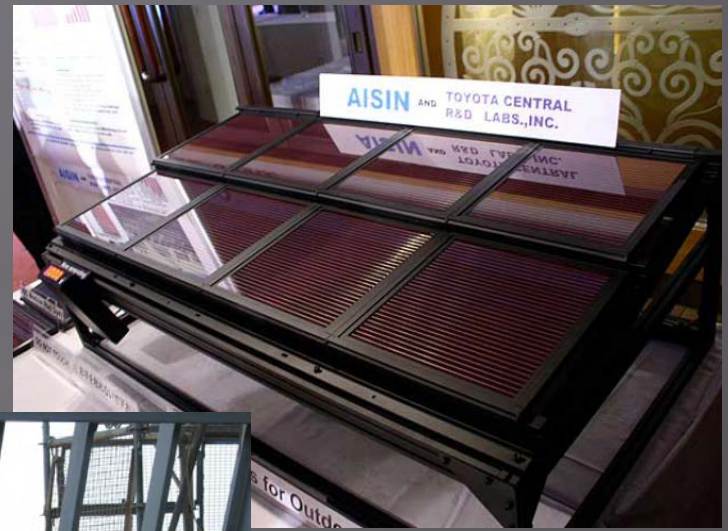


(2) in parallel



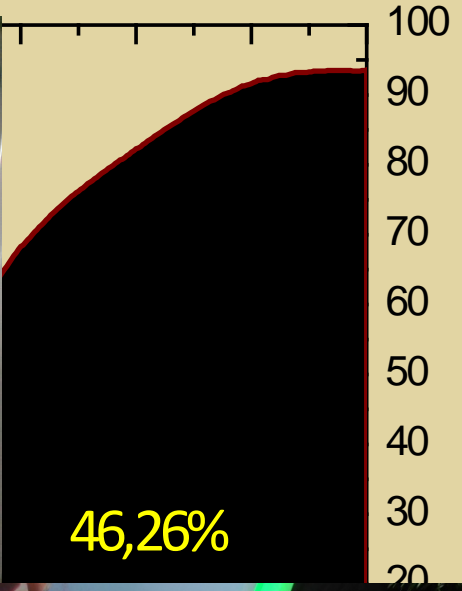
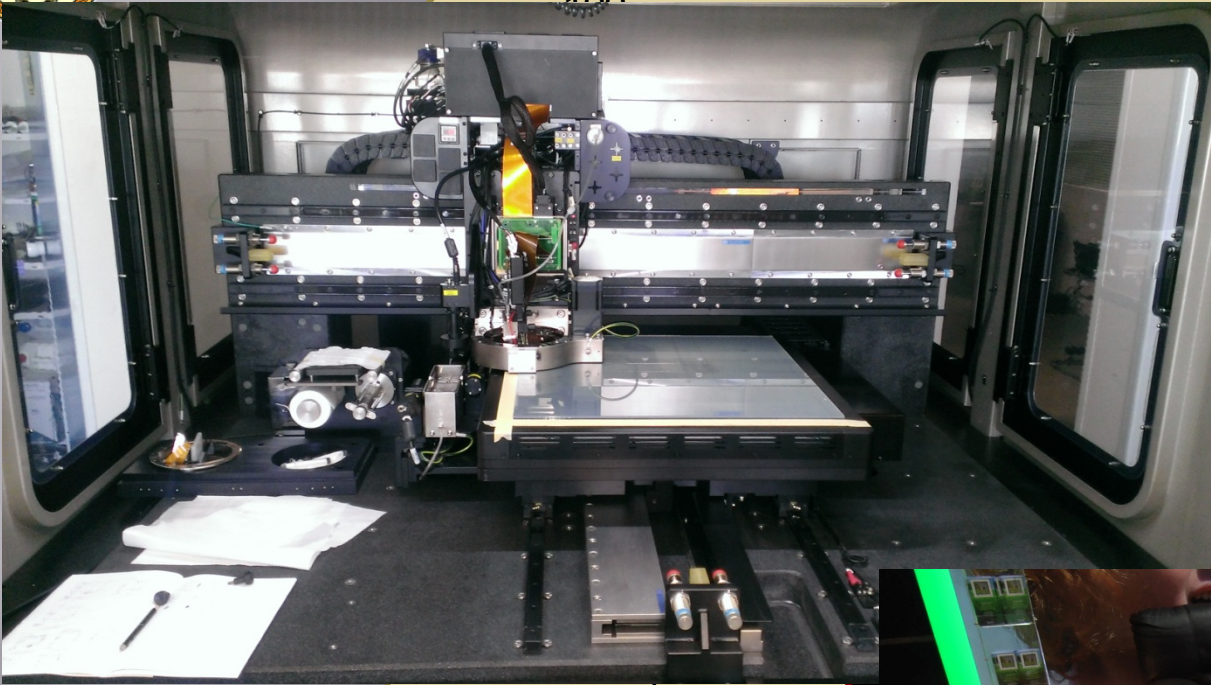




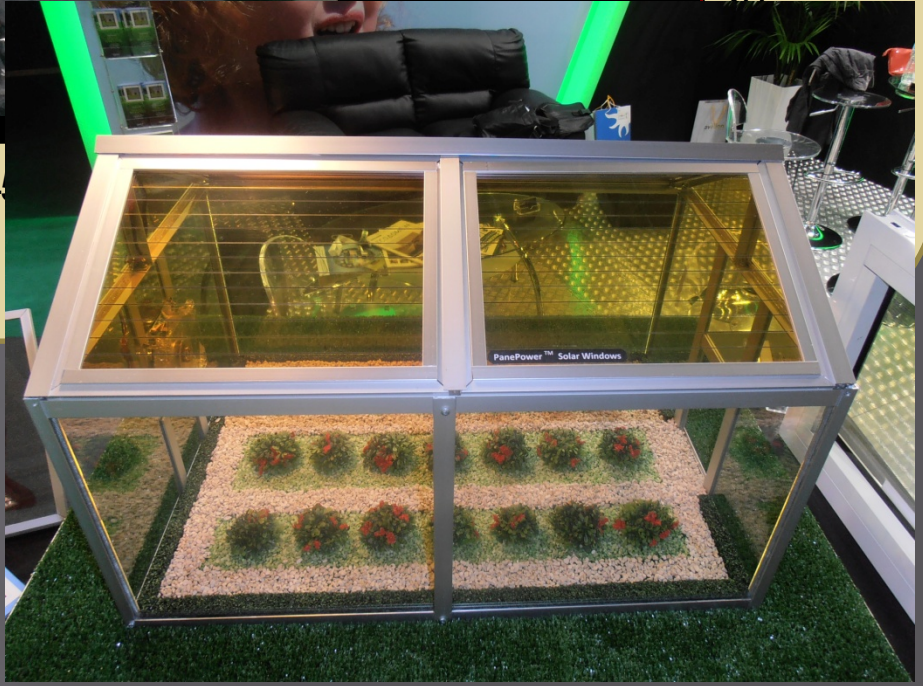


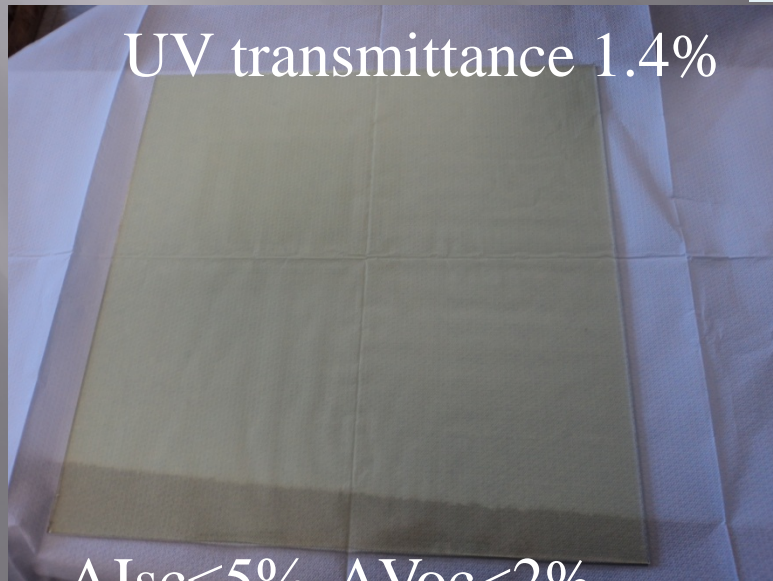
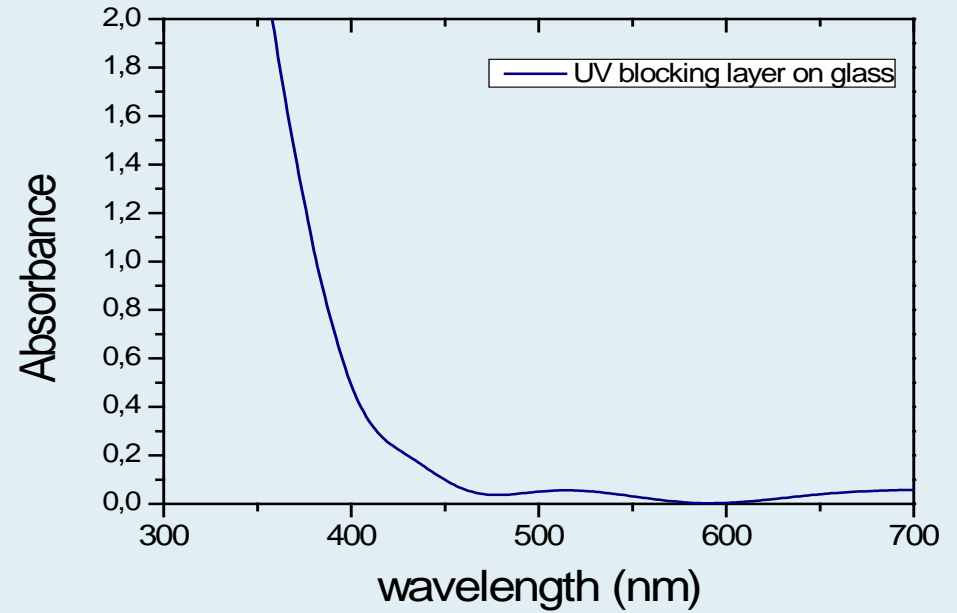


400

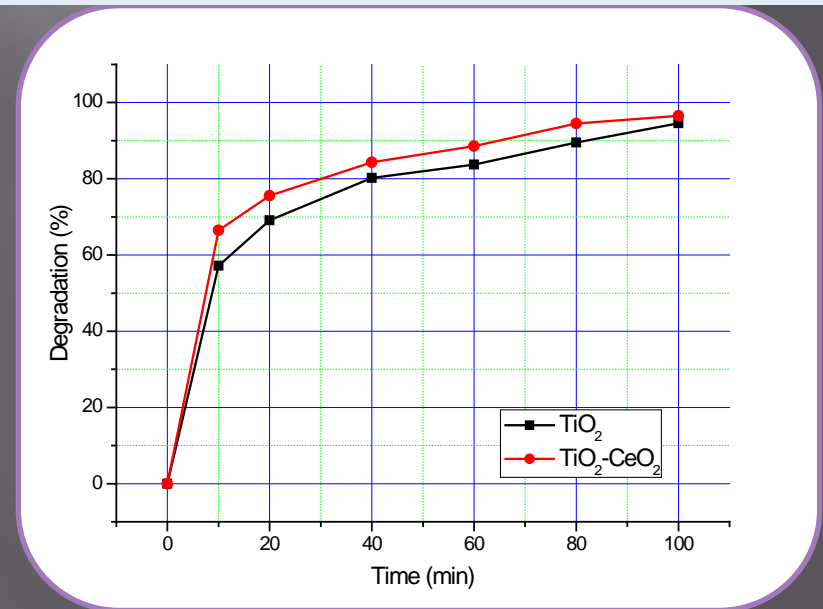


00 4

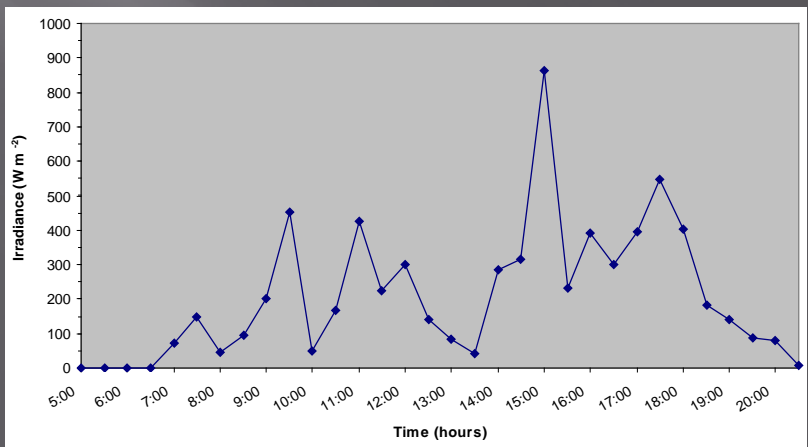
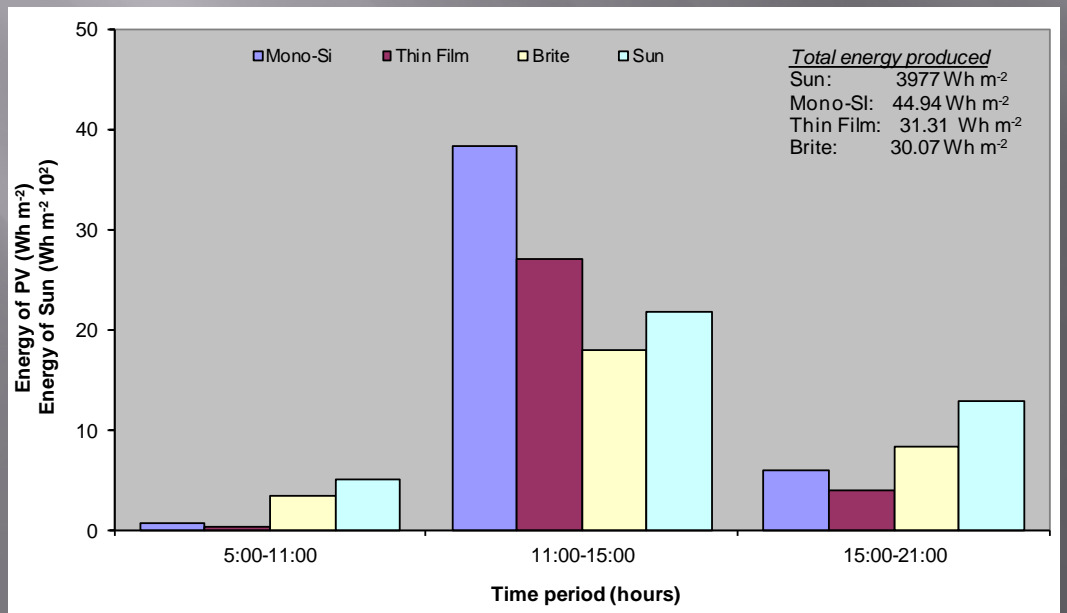
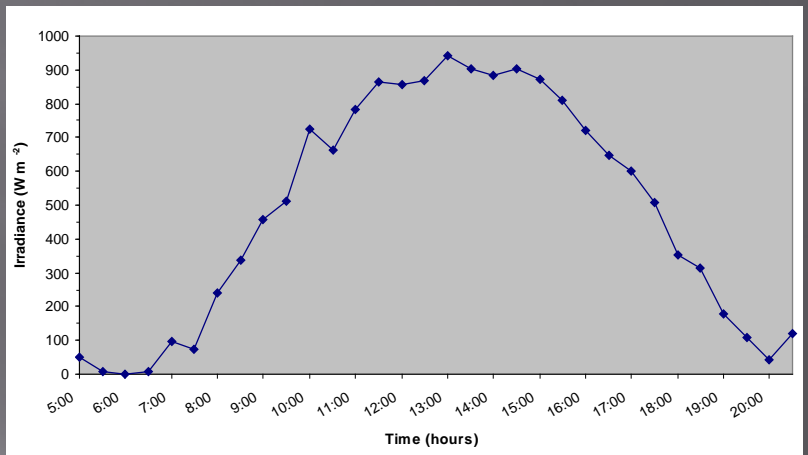
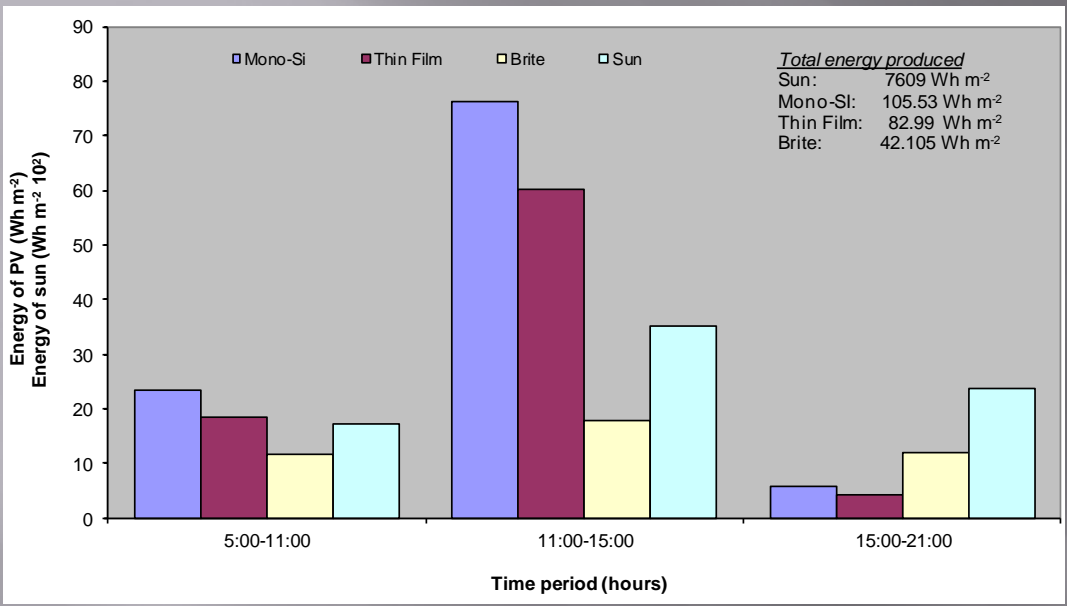


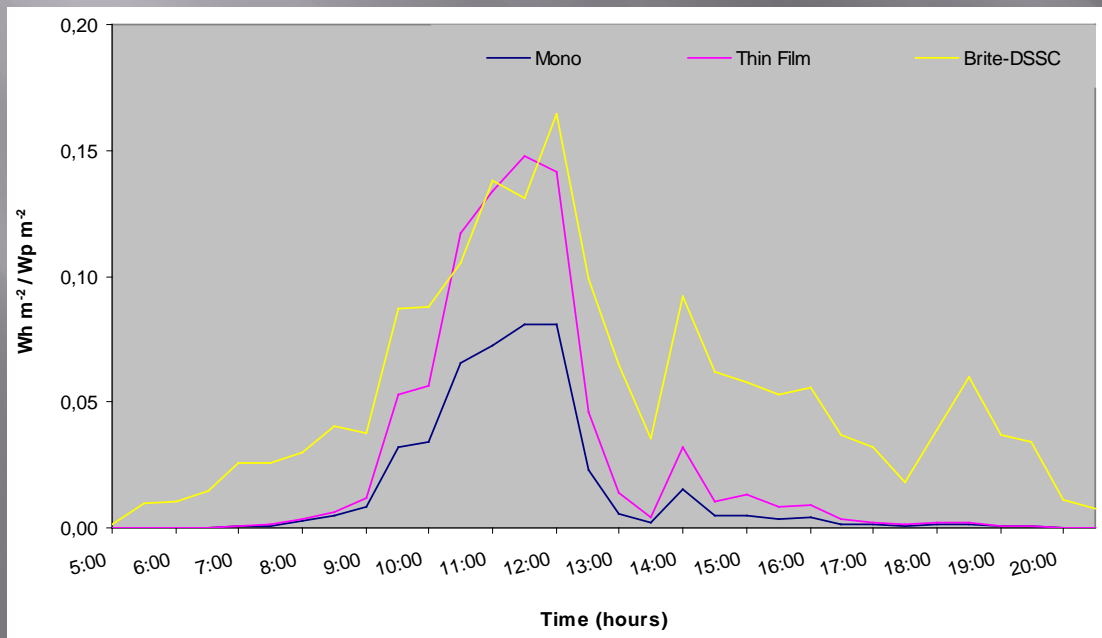
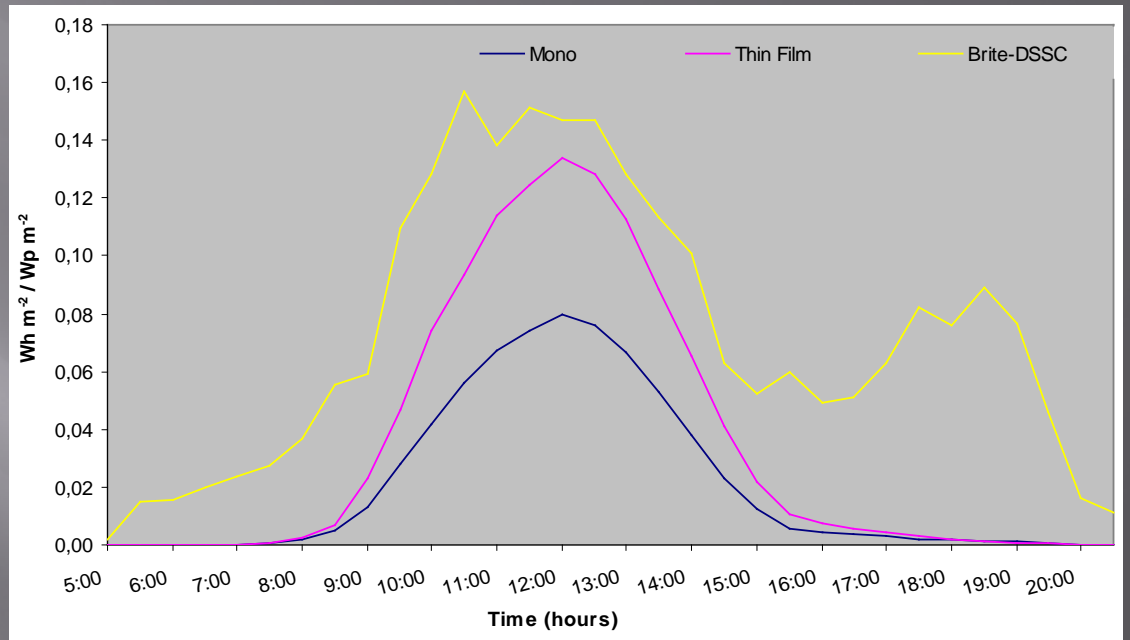


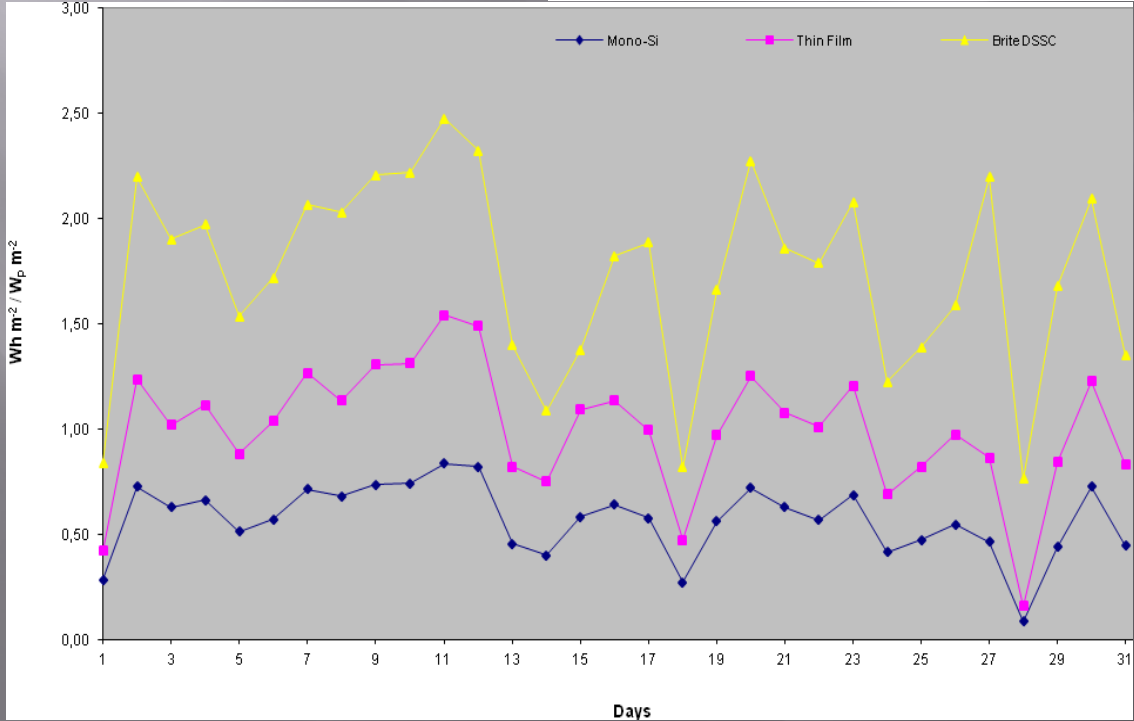
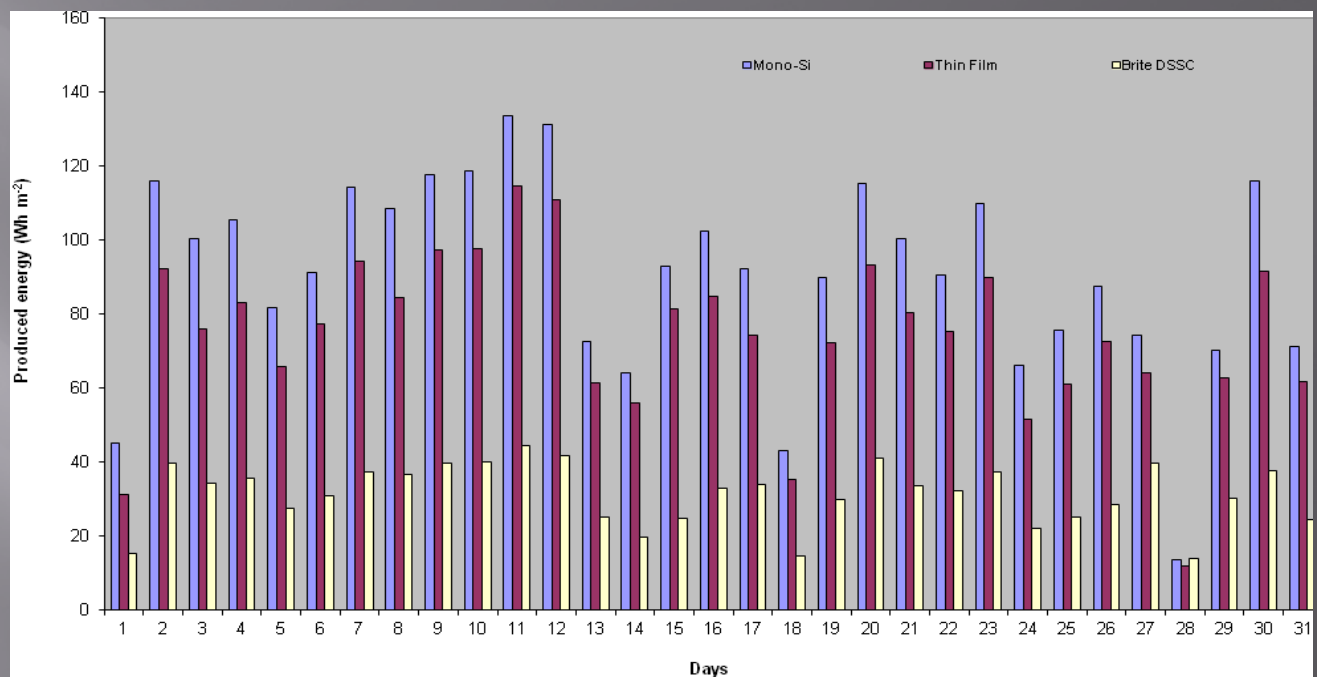
$\Delta J_{sc} < 5\%$, $\Delta V_{oc} < 2\%$

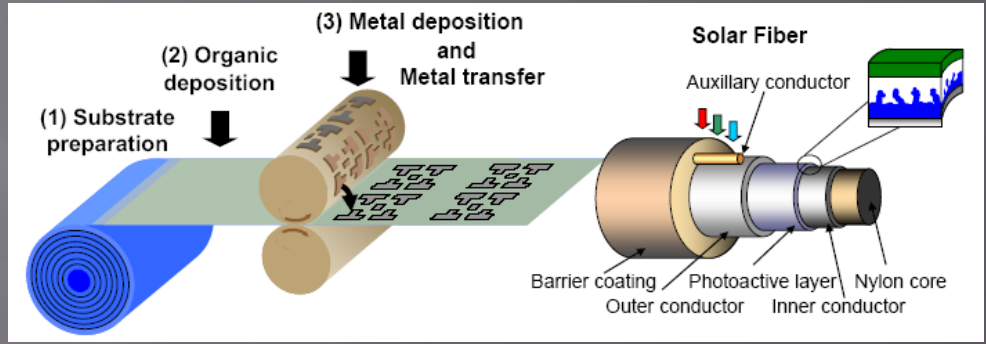
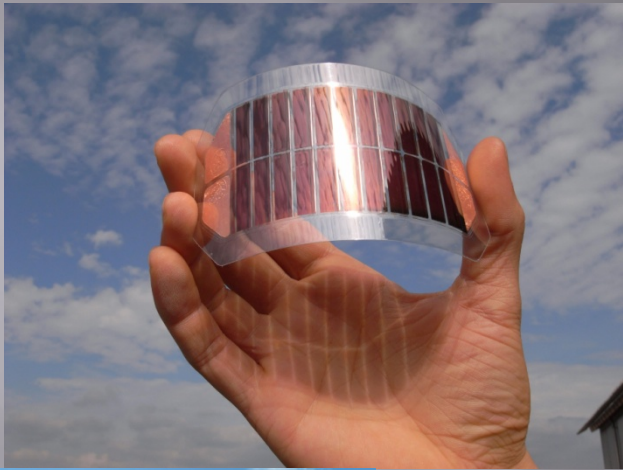






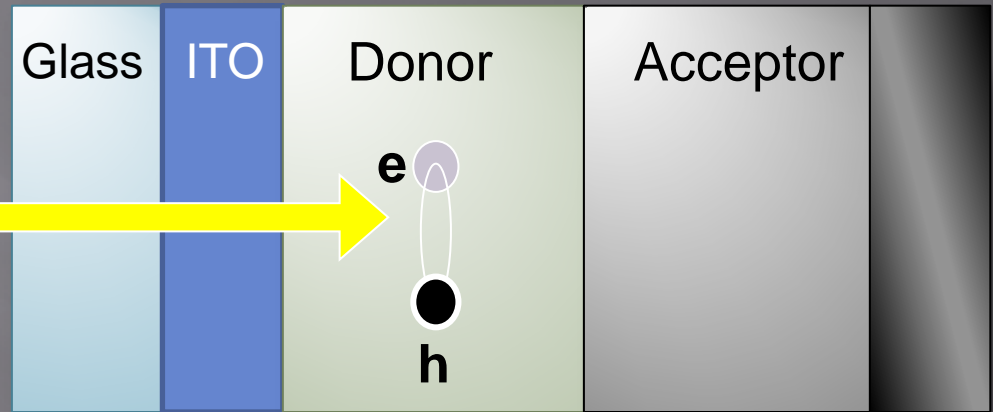




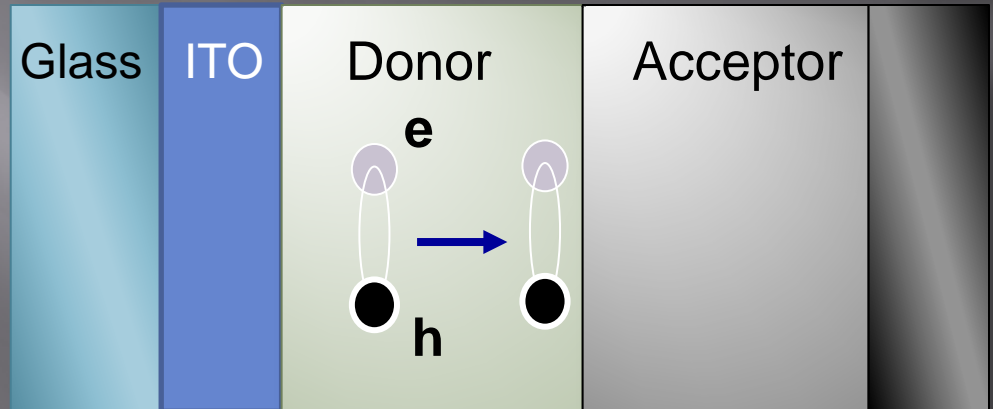




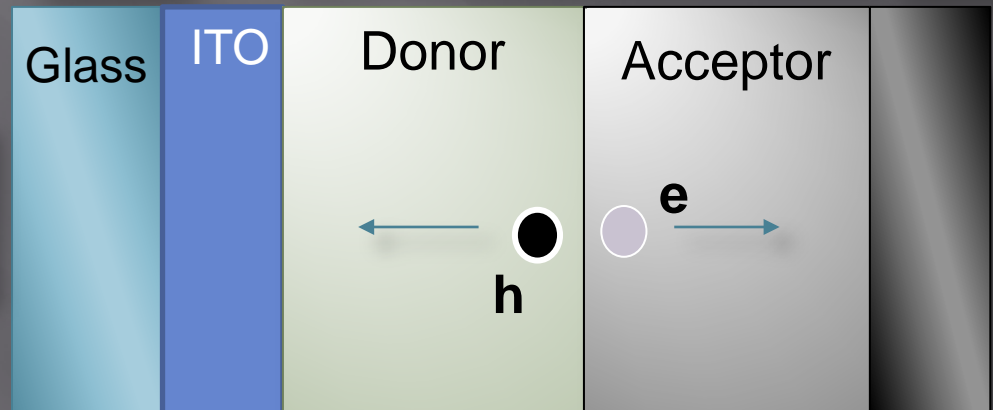
Absorption



Energy Migration
Diffusion length ~ 10 nm !!!!



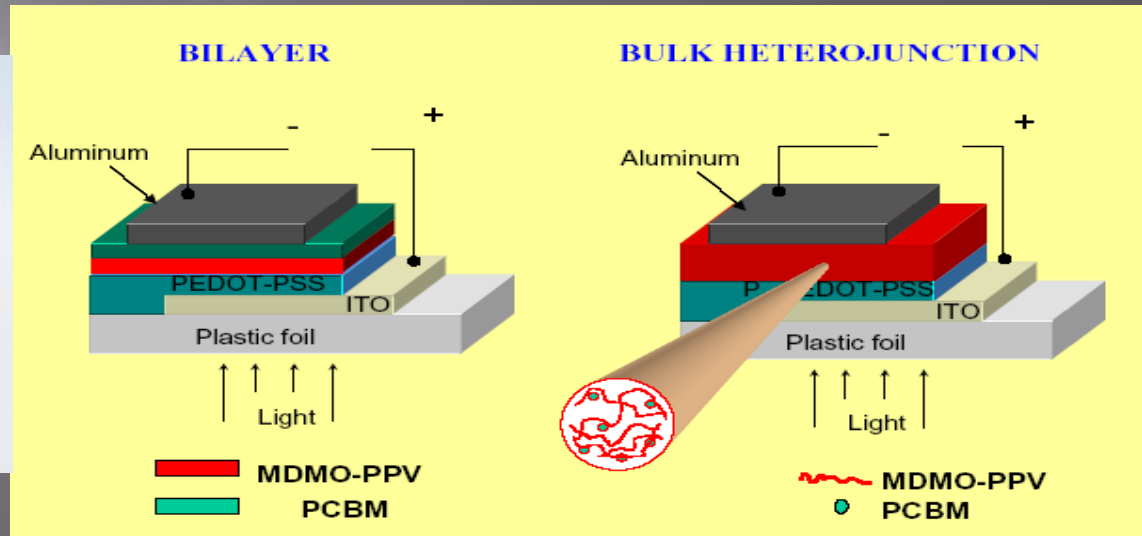
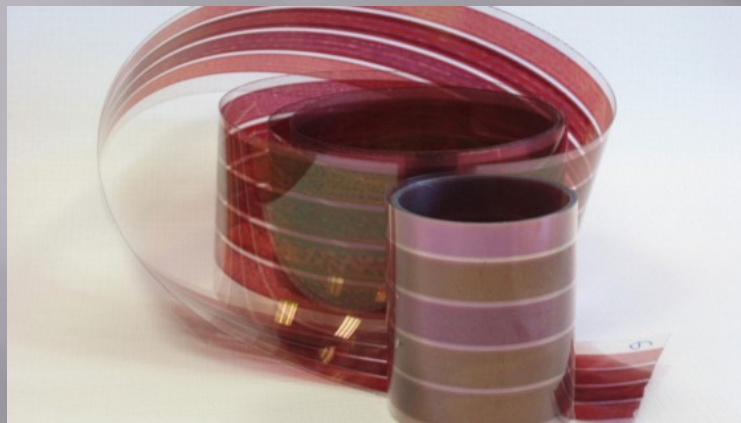
**Photoinduced
Charge Generation**





Critical Steps in organic Photovoltaics

1. Photon Absorption (Band gaps, e.g. 1.3-2.0 eV on earth).
2. Exciton Diffusion (D/A interface within 10-70nm).
3. Charge separation (orbital offsets)
4. Charge transportation (morphology)
5. Charge collection at electrodes.



Key Losses of OPVs

1. Photon loss (light wavelength/spectra vs Band Gap)
2. Exciton Loss (D/A domain size/morphology/Energy Levels)
3. Carrier Loss (Transport Pathway/Morphology/
Molecular Packing/Collection at Electrodes).



Thanks for your attention