Faculty of Electrical Engineering and Information Technologies
SKOPJE

Laboratory of Physics

SOLID STATE DYE SENSITIZED SOLAR CELLS

POSSIBLE LOW-COST ALTERNATIVES TO SILICON

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Sustainable Energy: Challenges and Opportunities, Lošinj, Croatia

Outline

1 Introduction – capacities, research activities, SOLTEC Center

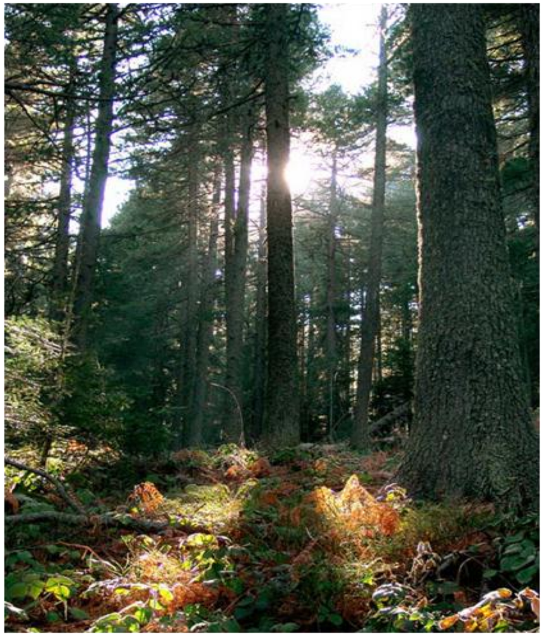
2 Solar PV energy – production grow, efficiency and costs, cost predictions, future exploitation

3 DSSCs – DSSC vs *Si* SC; Why solid state DSSCs?

4 TiO_2/CIS SC –USPD, performances of TiO_2, In_2S_3 & CIS layers

5 Conclusion remarks

Introduction



Introduction

Faculty of Electrical Engineering and Information Technologies

Ss Cyril and Methodius University, Skopje

50 years tradition 1959-2009

11 Institutes
13 Laboratories
15 Faculty Centres and Library
68 Professors
50 Teaching and Research Assistants
29 Administrative and Technical staff
3500 Undergraduate and
550 Postgraduate students

Introduction

CEI
CENTRAL EUROPEAN INITIATIVE

KNOW-HOW EXCHANGE PROGRAMME

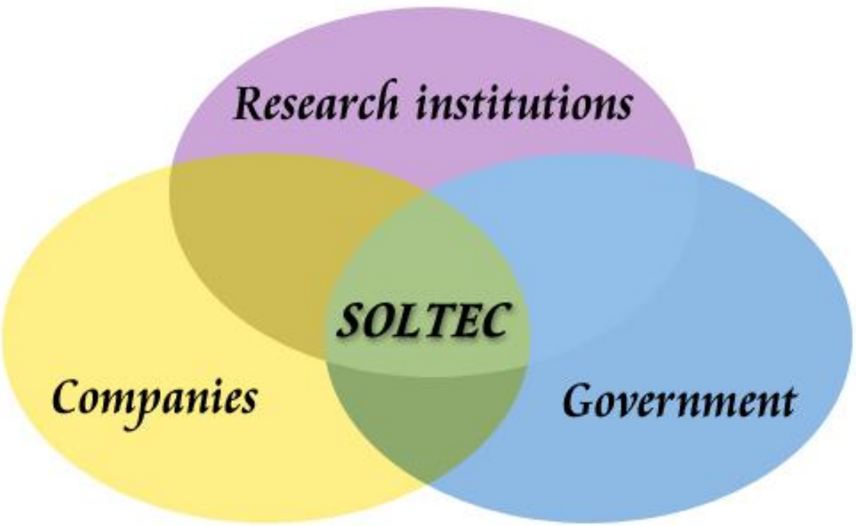
ISMN

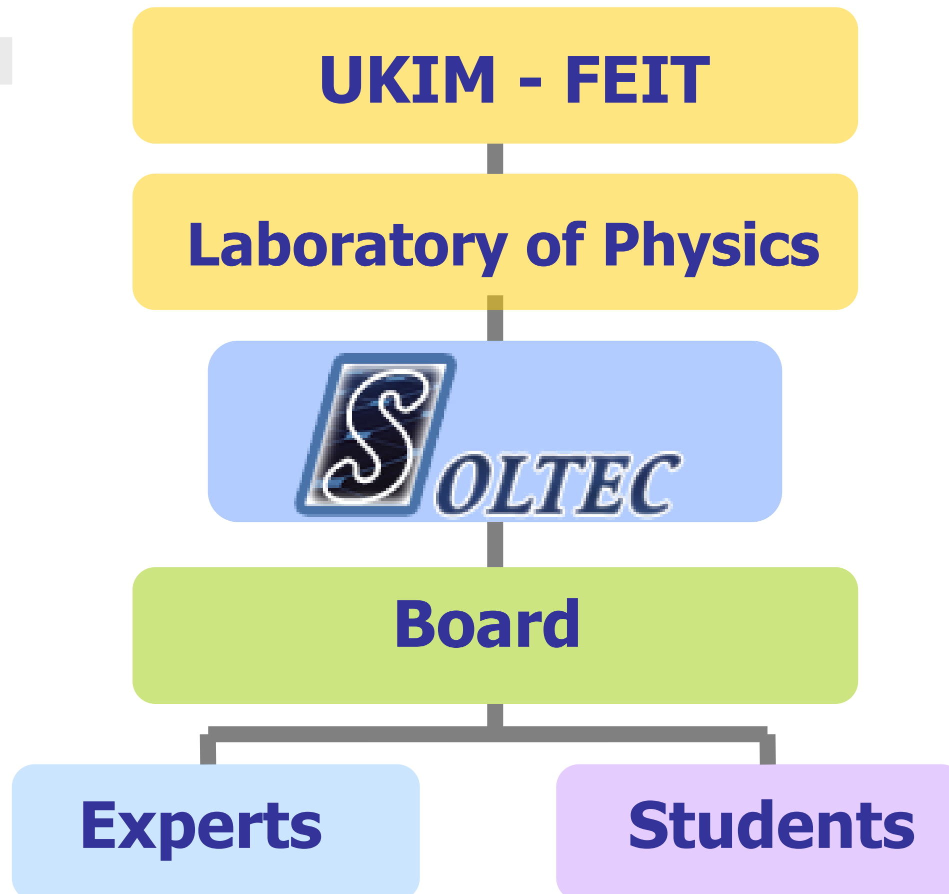
ICTP
The Abdus Salam
International Centre for Theoretical Physics

TRIL Programme

SOLTEC
CENTER FOR LOW-COST SOLAR CELL TECHNOLOGIES

- *Promotion of energy efficiency and renewable energy sources*
  - *Research and development of low-cost technologies for solar cells*





http://soltec.feit.ukim.edu.mk/

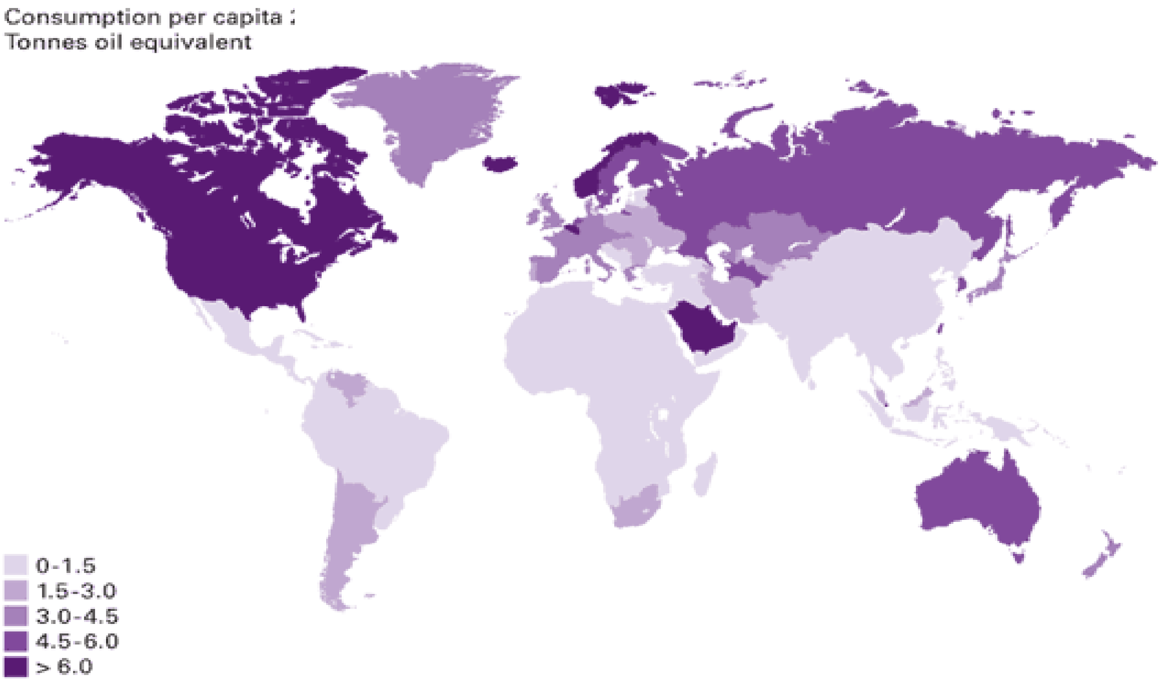
Research interest

1. Investigation of molecular parameters of Polymers and Biopolymers (dimensions, molecular weight, conformation, aggregation and self-assembling)
2. Electrical and electrooptical properties of Liquid Crystals, mixtures with nanomaterials
3. Theoretical analysis and numerical simulations of self-organization in complex systems
4. Electrochemical deposition of thin films
5. Preparation and characterisation (optical and electrical) of Solid State Dye Sensitized Solar Cells

Solar Energy – WHY?

Increasing energy consumption <u>vs</u>
Finite amount of fossil fuels

- **most abundant**
- **most polluting**



Solar Energy – WHY?

Origin of climate changes ➡ ***greenhouse planet***

PV energy

SUN → **clean, infinite energy source**

PVs → **direct conversion of photons in electrons**

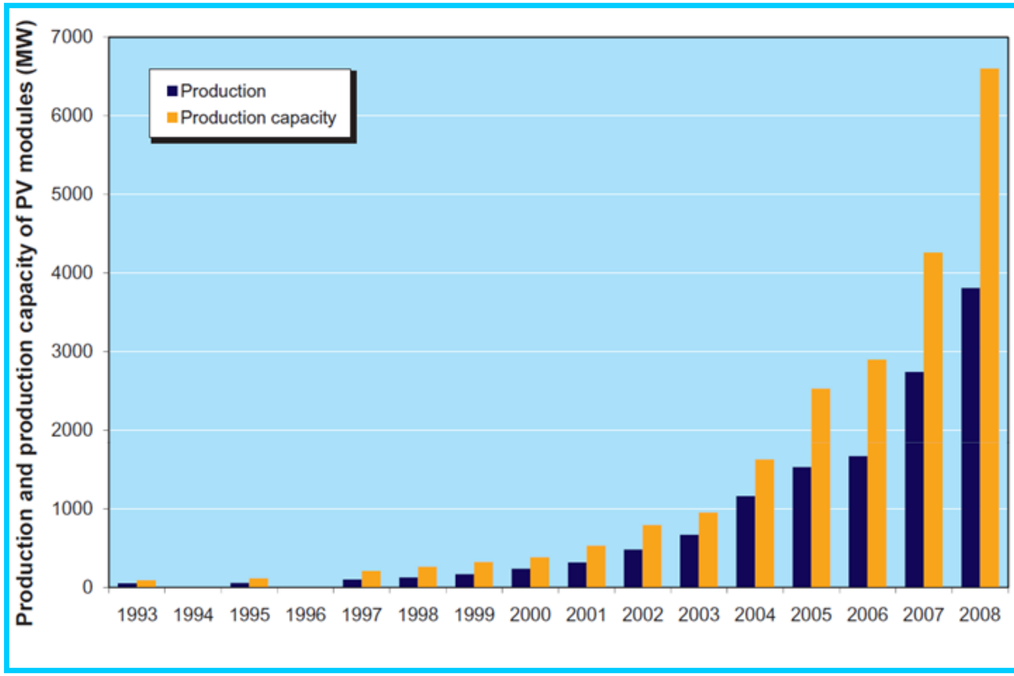
Energy used annually in USA can be produced by 26.000 km^2 of 10% eff. PV panels

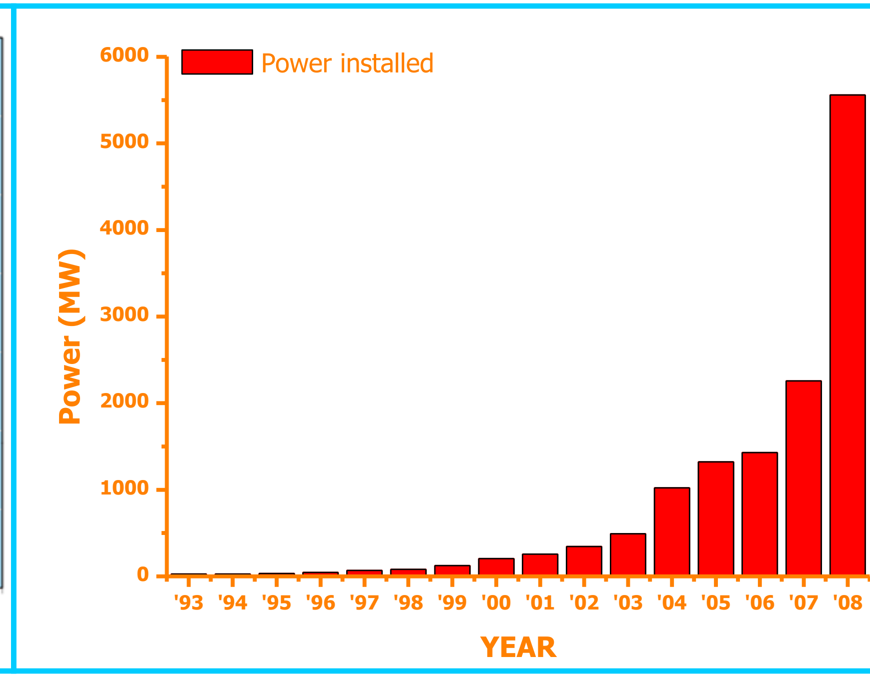
26.000 km^2 →

1/4 of roads total surface or
4 times of the existing rooftops

J. Turner, NREL

PV module production





PV request grow faster than production capacity

Efficiency & costs

Actual cost of PV energy ➡ 0.20 – 0.40 € per KWh

Mean cost of energy from fossil sources ➡ 0.11 €

To be competitive, cost of PV KWh should be smaller than 0.10 €

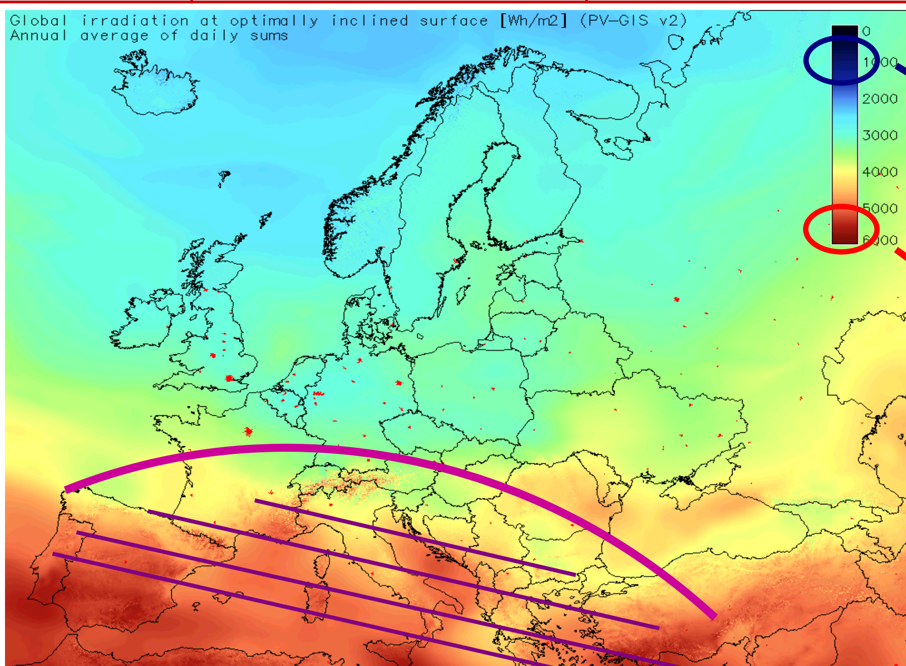
Two strategies

1) Increase efficiency more than costs

2) Decrease costs more than efficiency

PV economic cost prediction

	PV price (€/Wp)	PV electricity costs (€/kWh)	Energy pay-back time (yrs)
1980	>30	>2	>10
2008	5	0.3	>2
2015	2.0/2.5	0.12/0.15 *retail electr.*	1
Long term	1	0.06 *wholesale electr.*	0.5



Grid parity in Europe

Long term:
Competitive with wholesale electricity

2015:
Competitive with retail electricity
Long term :
Competitive with wholesale electricity

Exploatation of PVs to 2030

Off-Grid Industrial: 70 GWp

On-Grid: 150 GWp

Consumers: 20 GWp

Rural Electrification: 60 GWp

Dr. Winfried Hoffman, CEO, RWE, SCHOTT Solar GmbH

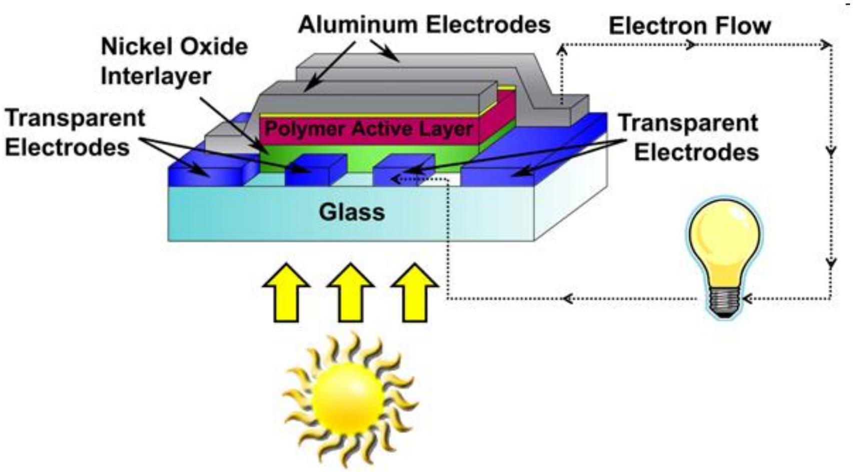
Future 2030

PV Energy: 300 GWp

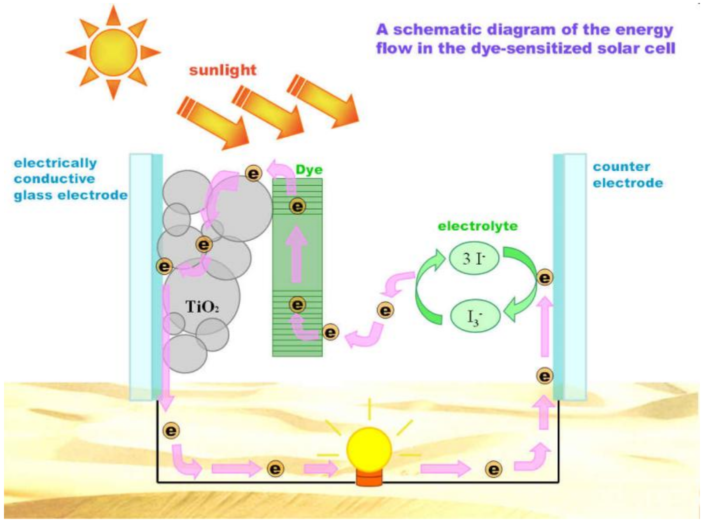
Si PV	→	30 %
Thin film	→	35%

3rd Generation → 35%

All organic PV



Dye sensitized solar cells



Chalenges for exploatation of PVs

Silicone - PVs

Increase efficiency (Crystalline *Si* 15 ➡ 20%)

- large *economic* costs
- large *energetic* costs

3rd Generation PVs

Reduce life-cycle cost

- longer lifetime
- slower degradation

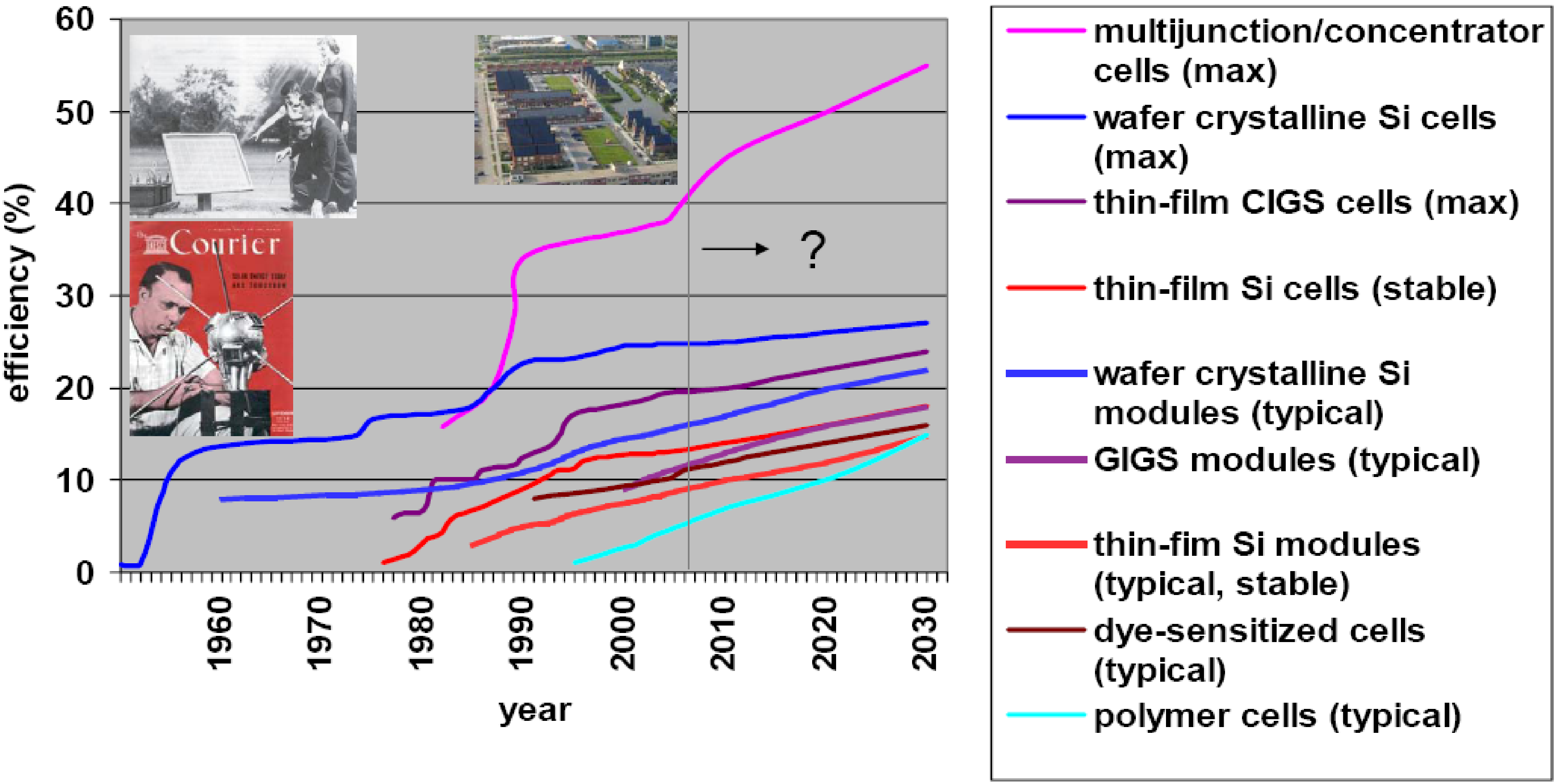
Reduce production cost

- reduce processes cost
- reduce materials cost

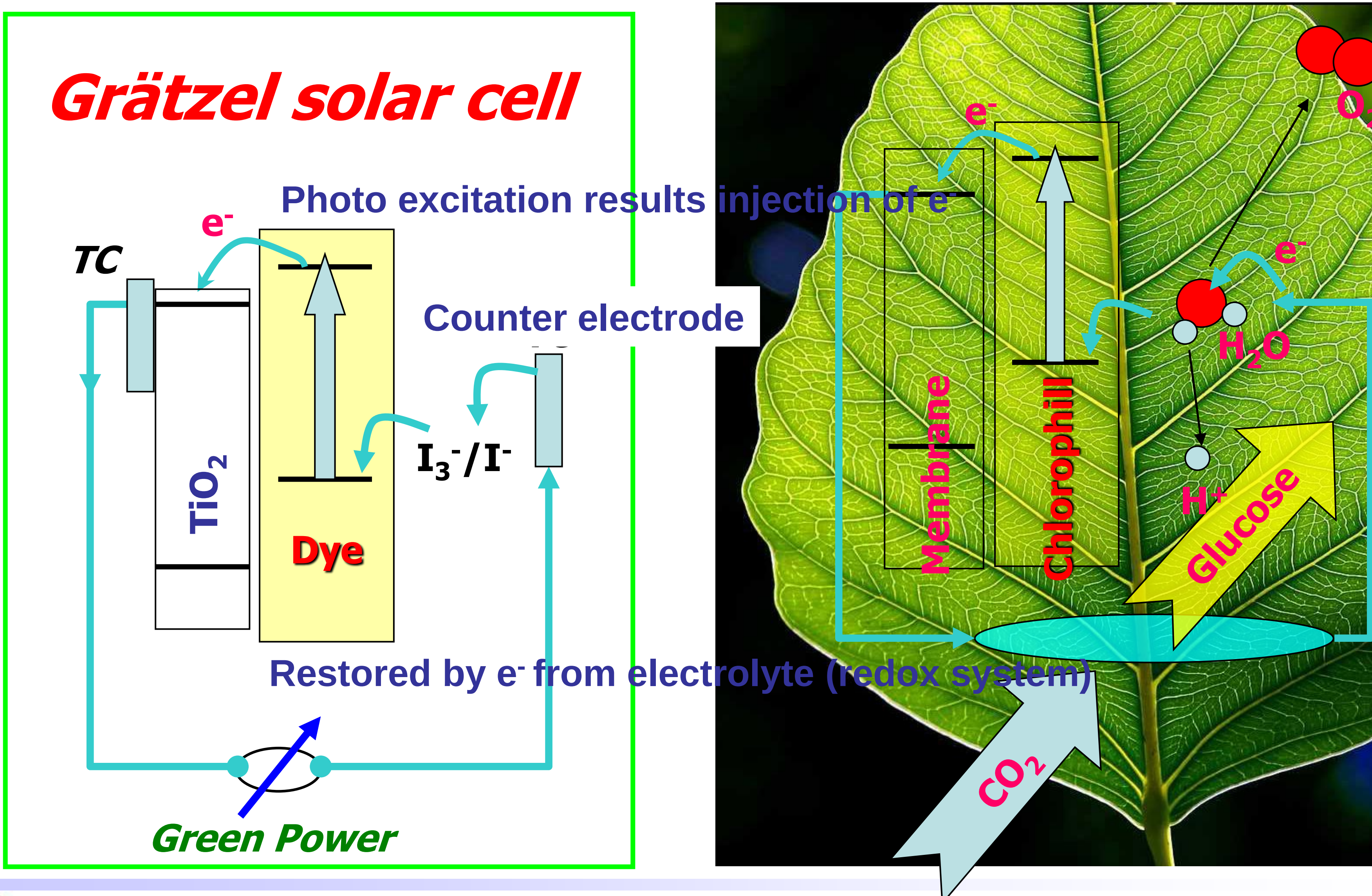
√ **less materials – thin film technologies**

√ **low-cost materials - abundant and raw**

PV technologies

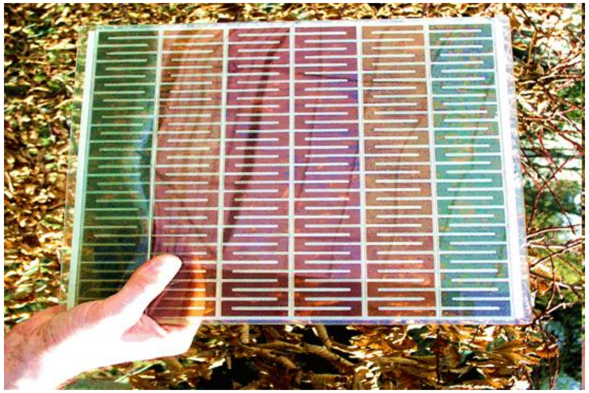


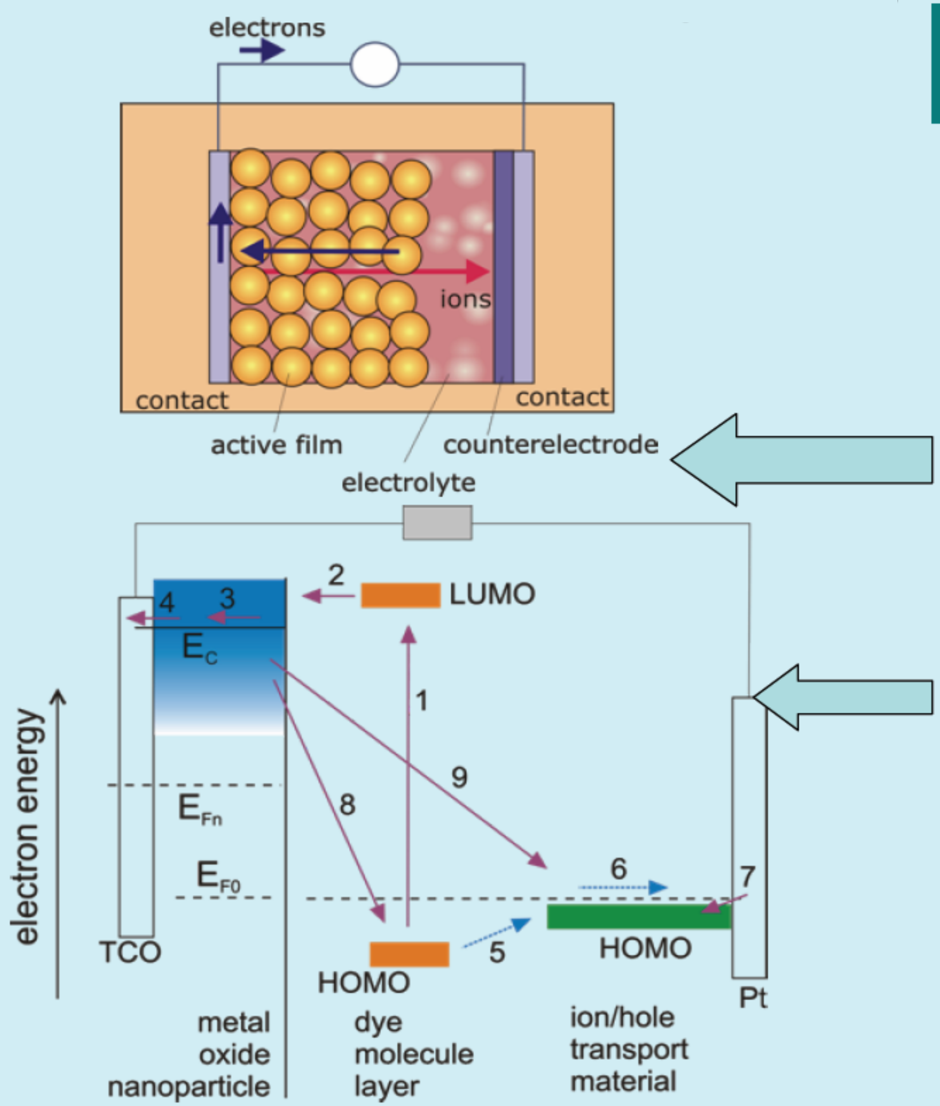
DSSCs - Grätzel solar cells



DSSCs – WHY?

- DSSC's power conversion efficiency (11%)
- Small energy need for fabrication of DSSC's (shorter energy pay-back)
- Low cost fabrication processes (lower costs)
- Use of abundant material (lower costs)
- Good response of DSSC's in non ideal illumination: angle, intensity (efficient use)
- DSSC's can be transparent and colorful (small esthetic impact)





- Light absorption
- Carrier generation
- Electron transport
- Ion/hole transport
- Recombination
- CT at outer contacts
- Series resistance

Stability / Durability

DSSC vs Si PV - Stability

***Si* Pv requirements for outdoor use & international PV standards applied to single crystal silicon**

DSSC

- **UV plus heat (55-60 ^{o}C): 1000 h**
- **Accelerated thermal test at 85 ^{o}C: 1000 h**

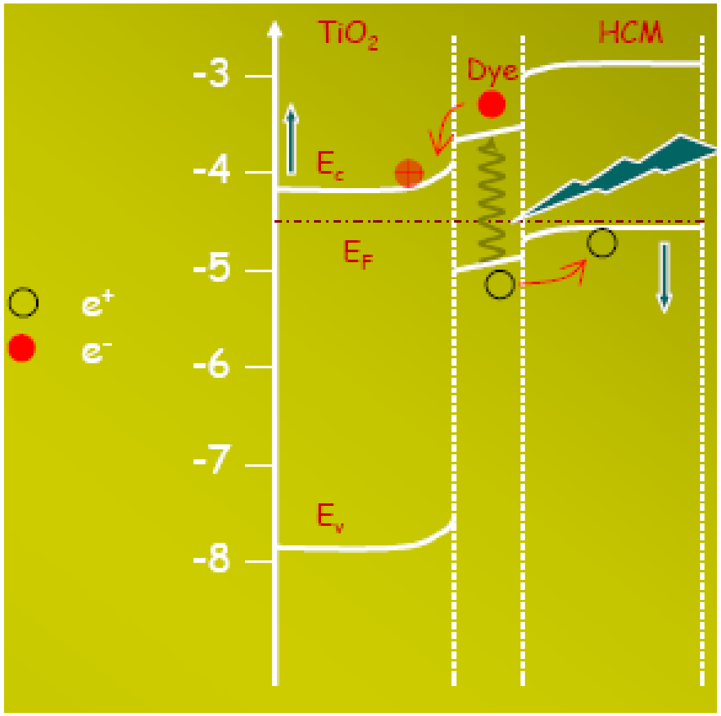
Problems:

- **Solvent (liquid electrolyte) evaporation**
- **Temperature influence on the structure & ions mobility**

Electrolyte is replaced by a Solid State Hole Conducting Material

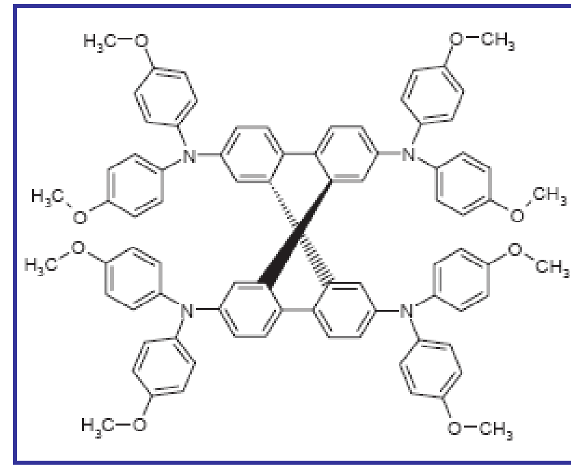
Transformation from LIQUID to SOLID STATE DSSCs

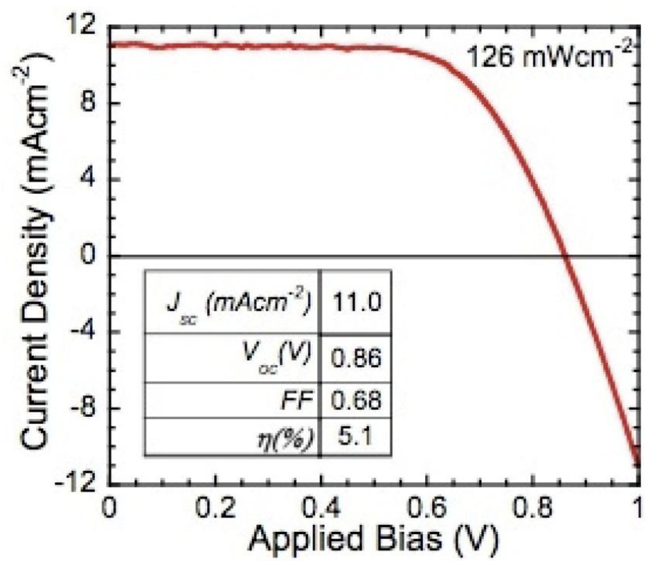
Organic Hole Conducting Materials



HCM: Spiro-OMeTAD

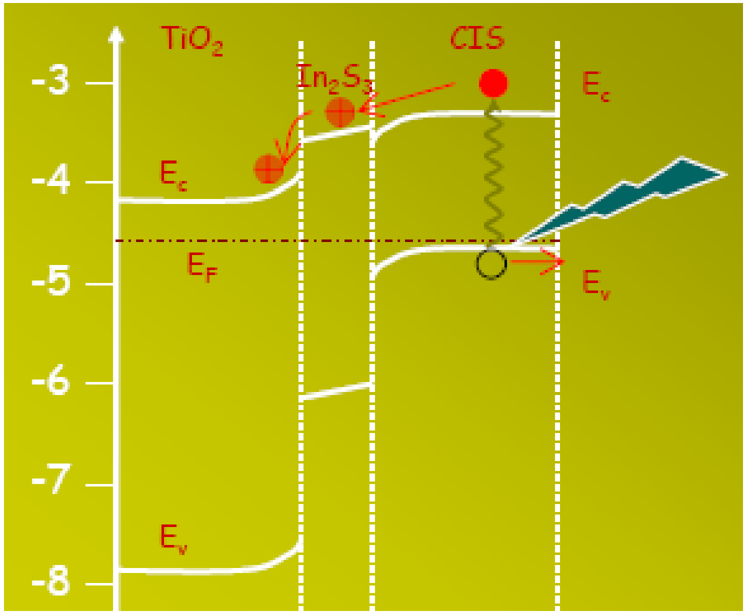
$I_3^-/3I^-$



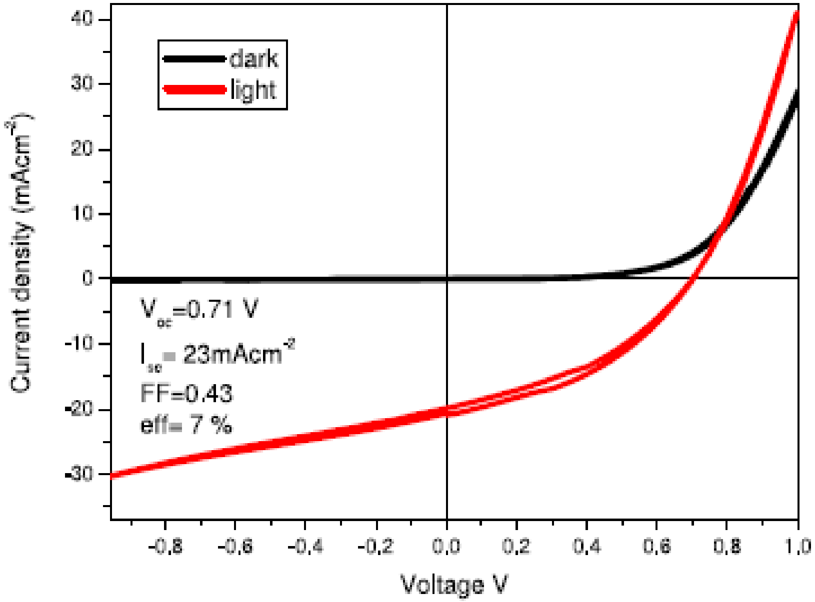


(Grätzel et al. 2005)

Inorganic Hole Conducting Materials

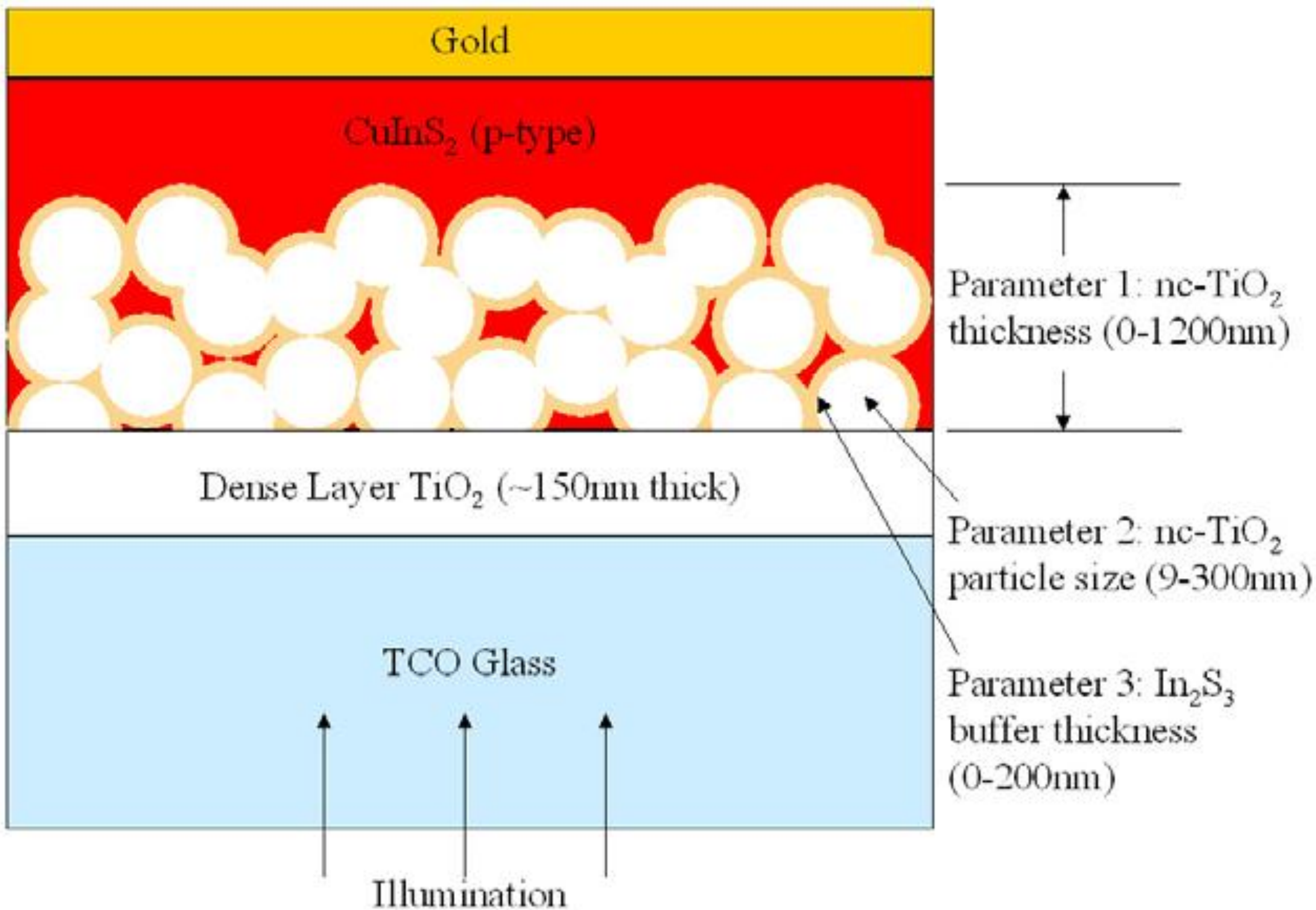


CuInS$_2$ (CIS) acts as Dye and HCM
ONE element only !



Goossens et al. *Nanotechnology* **19** (2008)

TiO_2/CIS 3D nanostructured SC



O'Heyre et al. *Nanotechnology* 18 (2007)

Performance of TiO_2/CIS Solar Cells

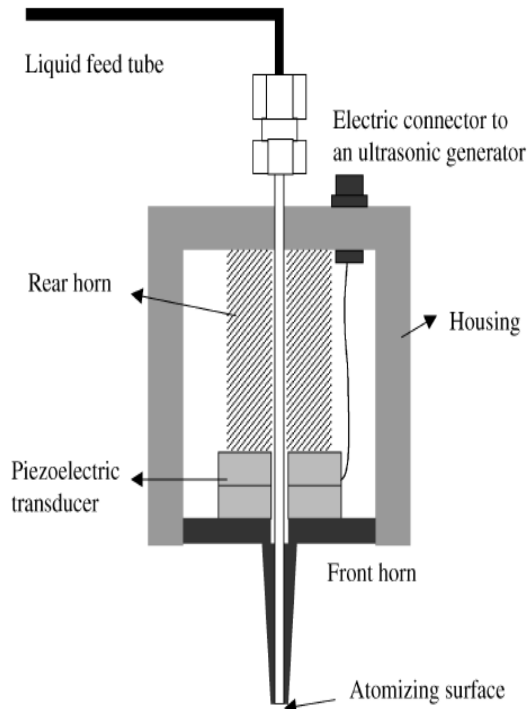
TiO_2/CIS solar cells have achieved grater then
7% energy conversion efficiency

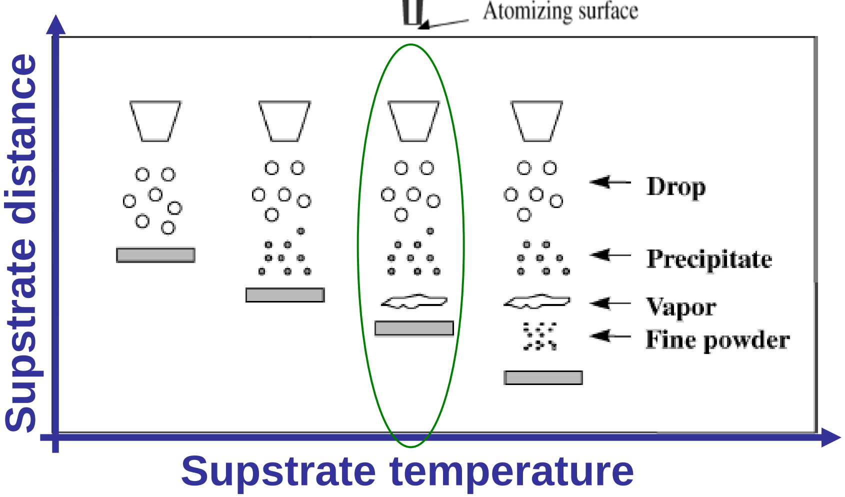
3D hetero-interface increases the structural complexity
of the TiO_2/CIS solar cell system

Performance of TiO_2/CIS solar cell is sensitive
to the **structural factors**

- **size of TiO_2 particles**
- **effectiveness of the buffer In_2S_3 film**
- **thickness of the films**

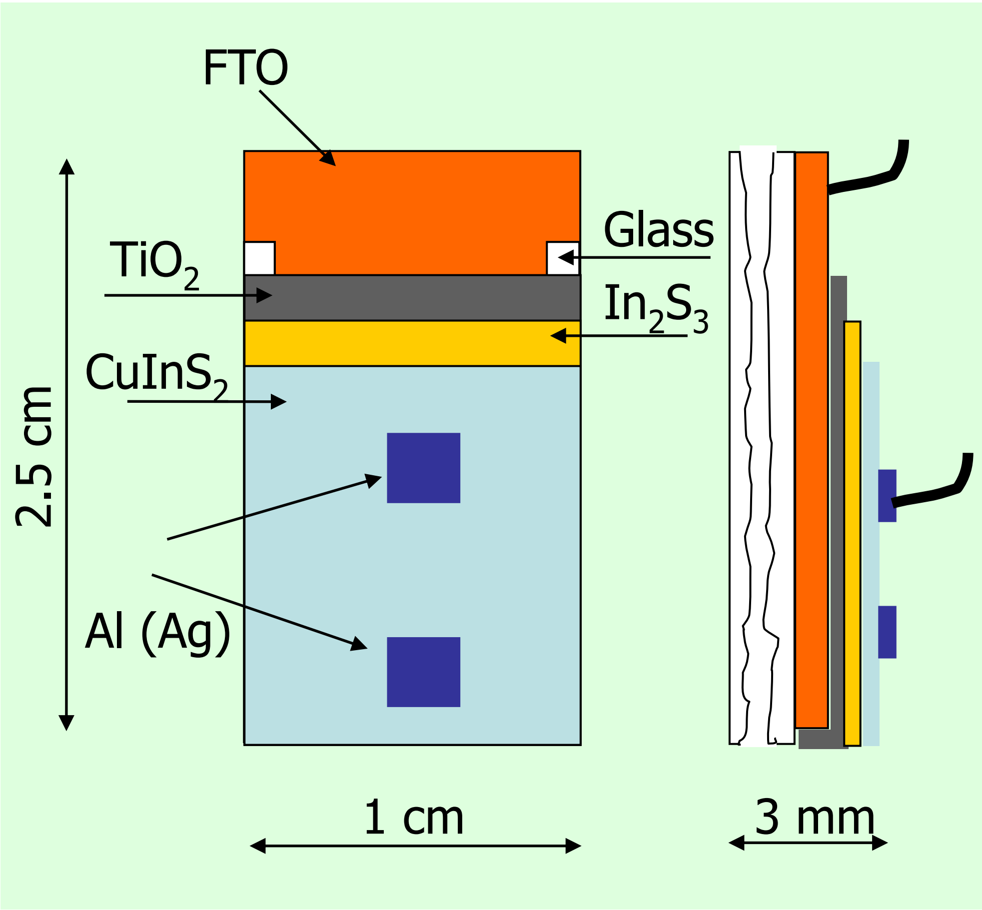
Ultrasonic Spray Pyrolysis Deposition





ISMN-CNR

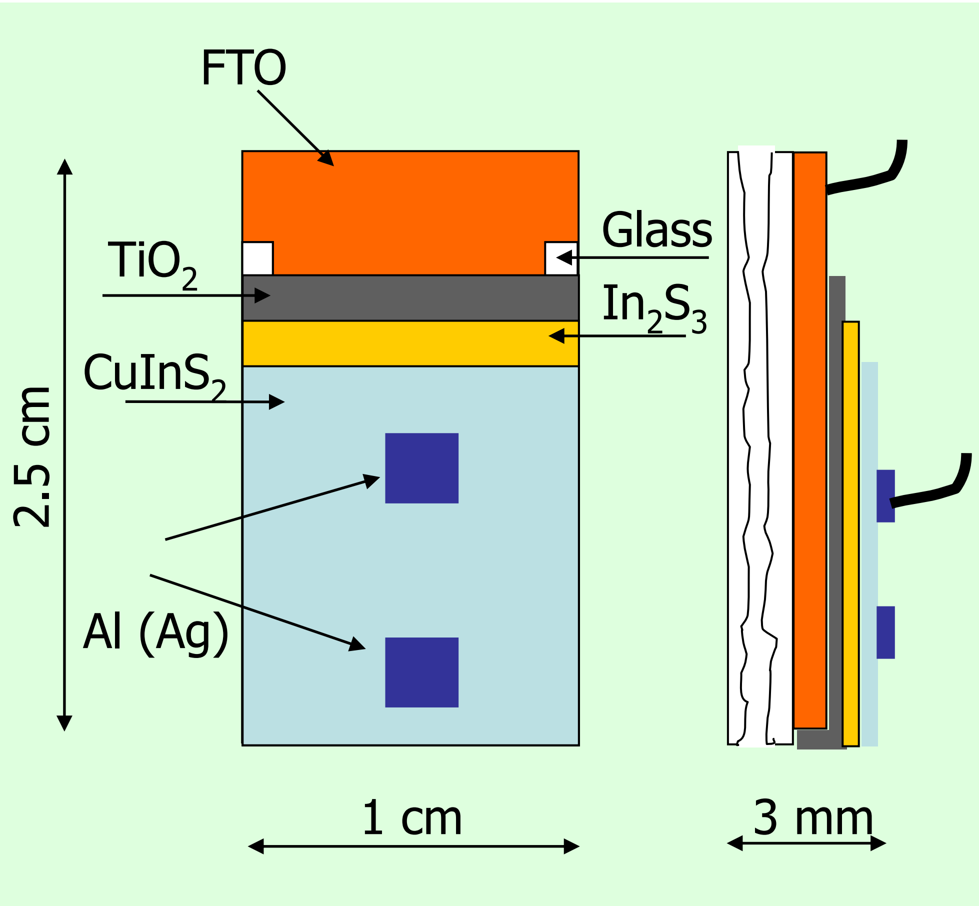
TiO_2/CIS 3D nanostructured SCs



Glass/FTO

Fluorine-doped tin oxide conducting layer
d=150 nm; R(Ω/□)=13 Ω
(commertial supstrate by *Flexitec*)

TiO_2 films preparation



TiO_2

- (50 ÷ 200 nm) anatase compact film
- (1 ÷ 5 μm) mesoporous film

- disordered nanocrystallyne TiO_2 film
  ϕ = 14 nm (commercial *Solaronix* paste)

or

- ordered Inverse Opal TiO_2
  ϕ = 300 nm

Compact TiO_2 Anatase Film

Experimental parameters:

Precursor solution:
0.25M TAA in ethanol
$(CH_3)_2CHO)_2Ti(C_5H_7O_2)_2$

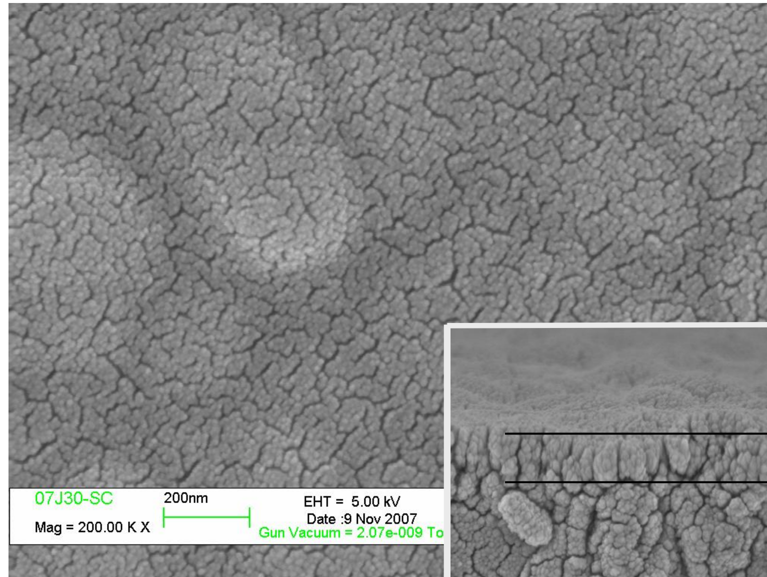
Solution flow rate: 1ml/min

Step I: USPD on Glass/FTO
T deposition = 450 °C

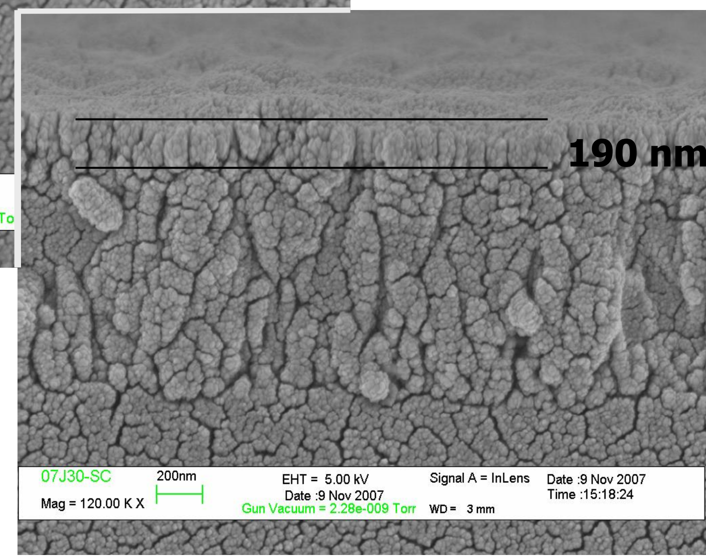
Step II: Spin Coating

Step III: Annealing (1h)
T annealing: 500 °C

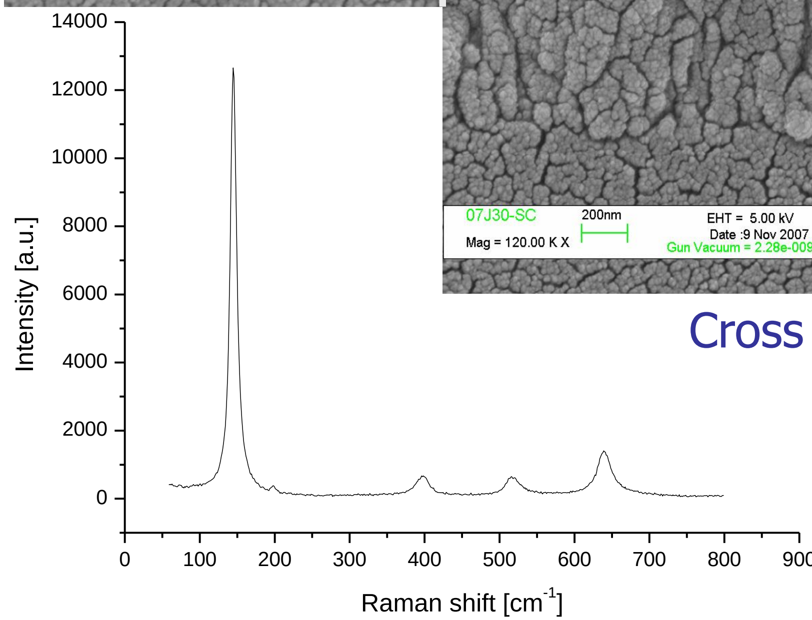
SEM Images



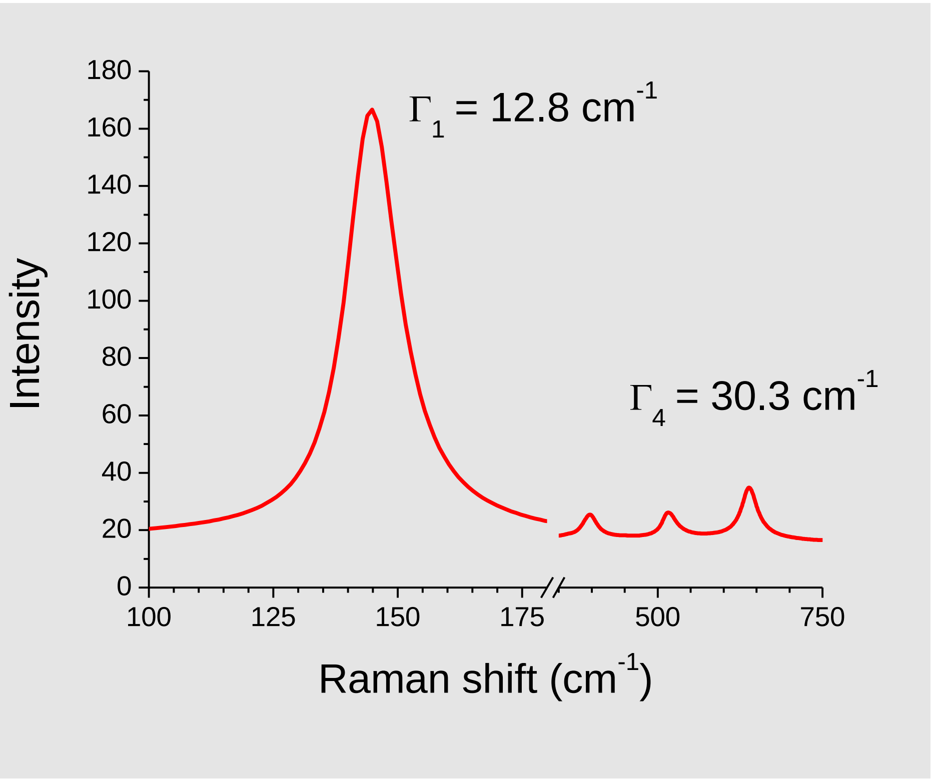
Surface

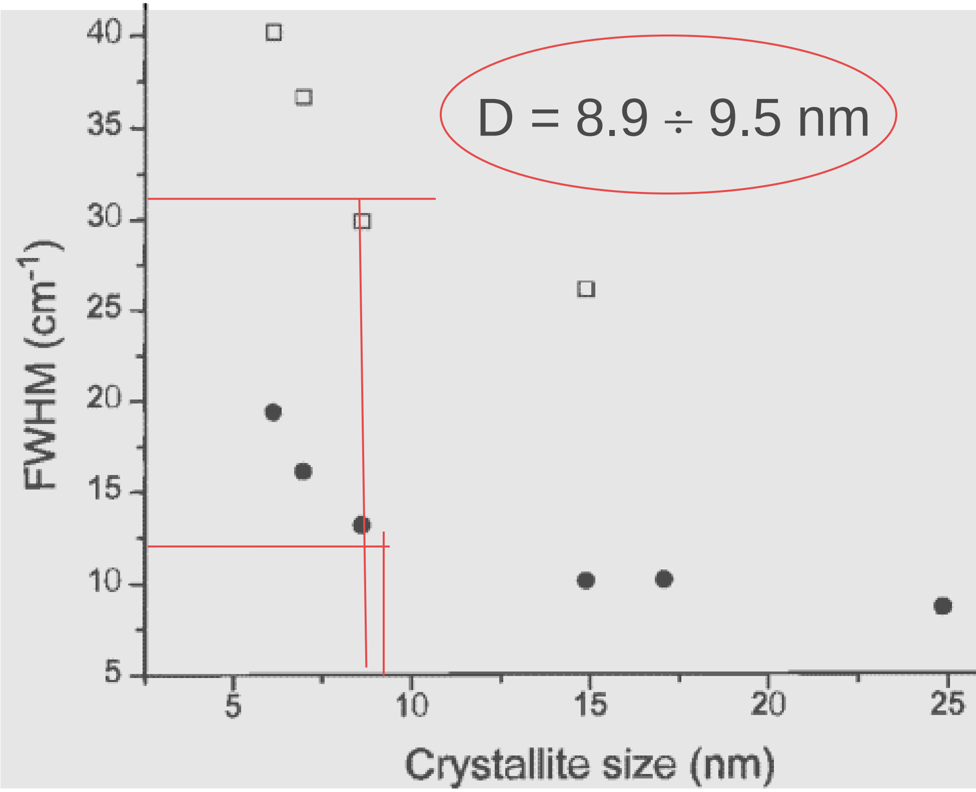


Cross Section



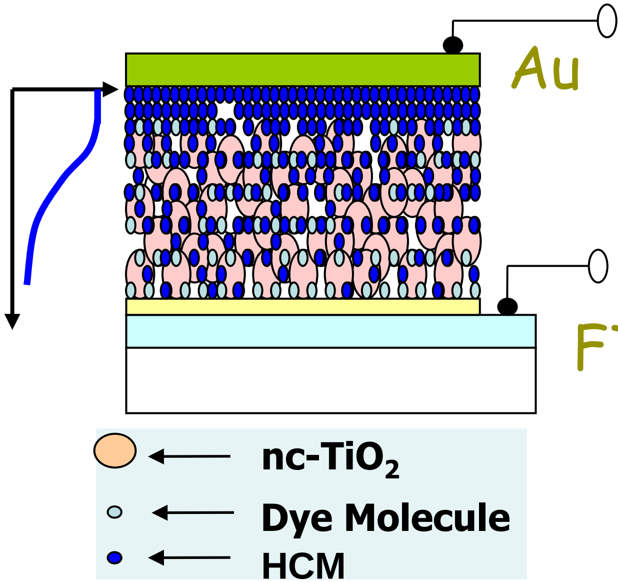
Raman Modes

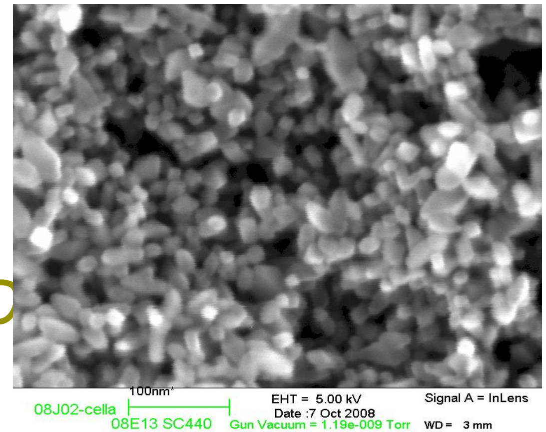




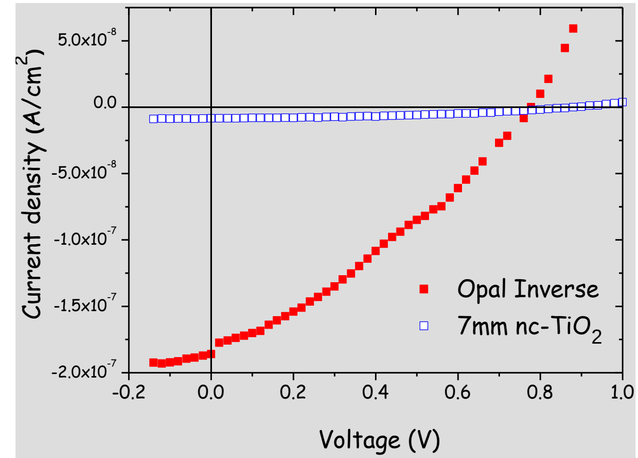
FWHM - **F**ull-**W**idth at **H**alf-**M**aximum

Solid state HCM infiltration

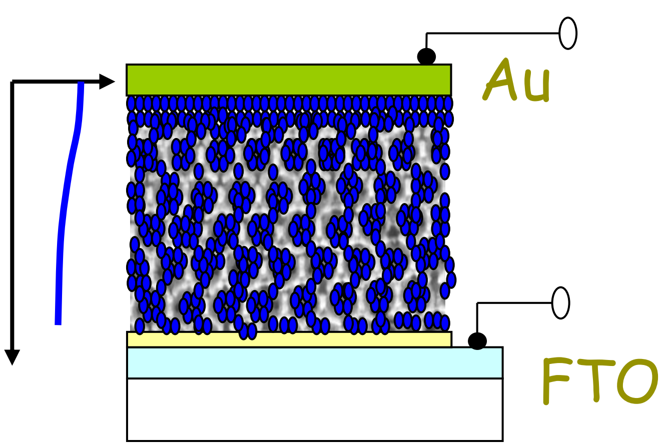


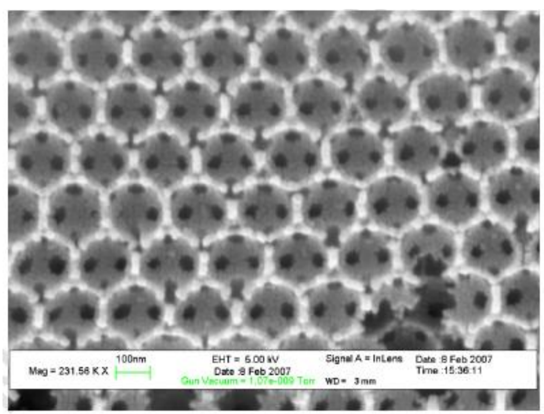


***Solaronix* paste**



P.Somani et al, Sol.En.Mater.Sol.Cells (2005)



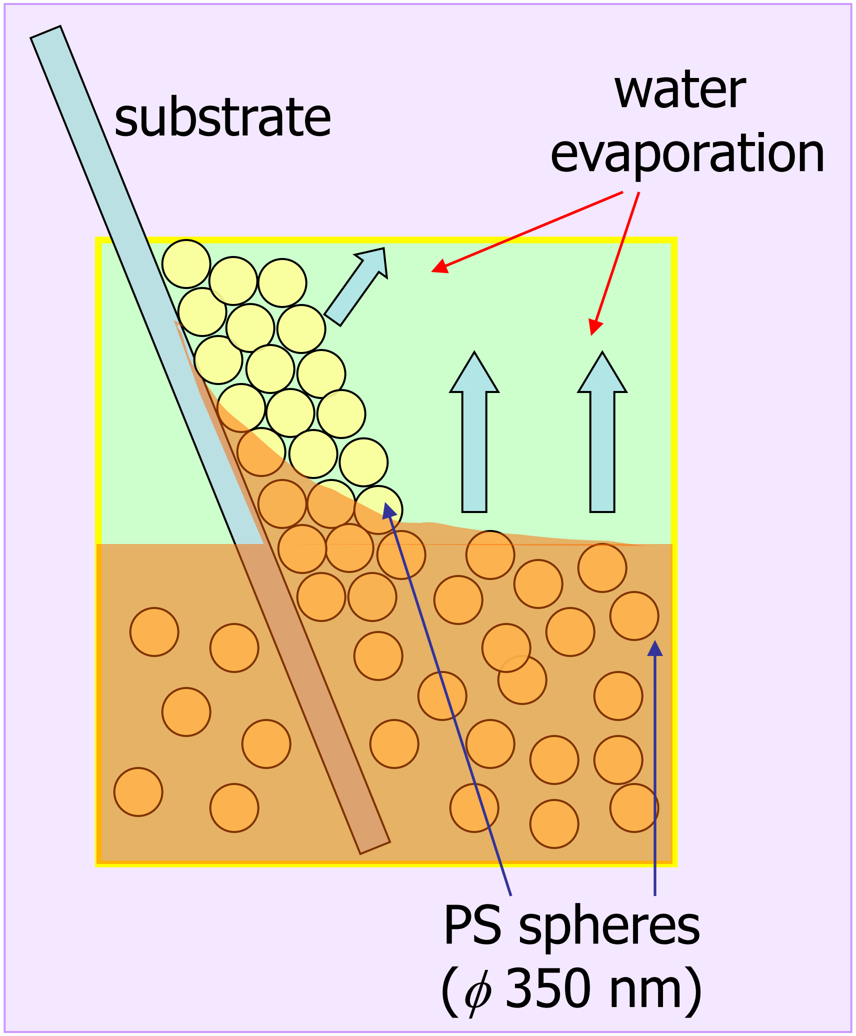


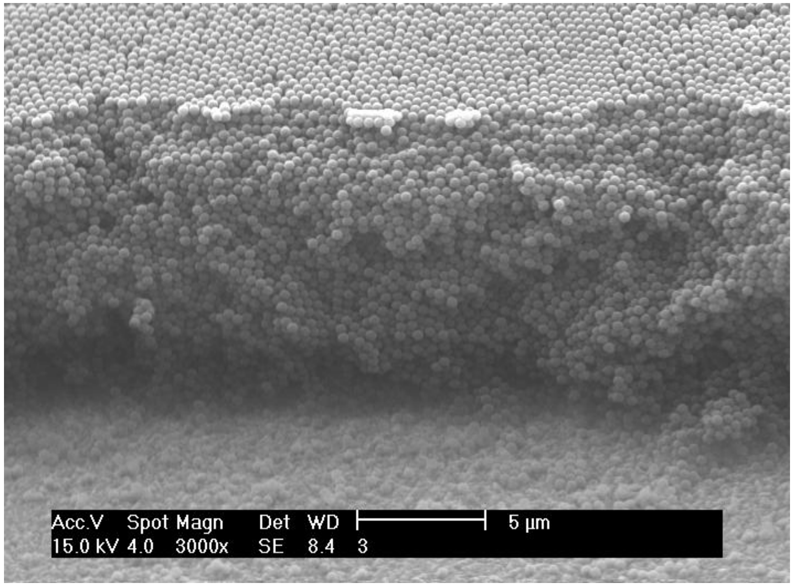
IO structure

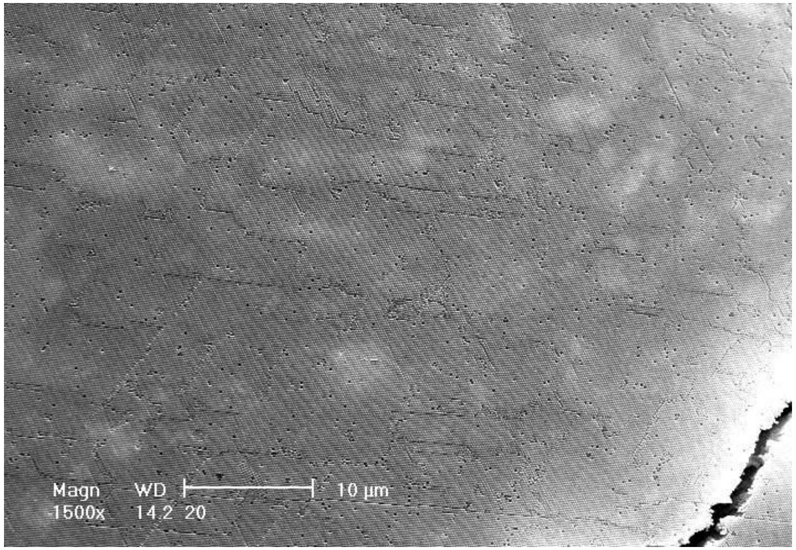
TiO_2 IO structure favor:

- solid state HCM infiltration
- charge carriers percolation

IO film preparation







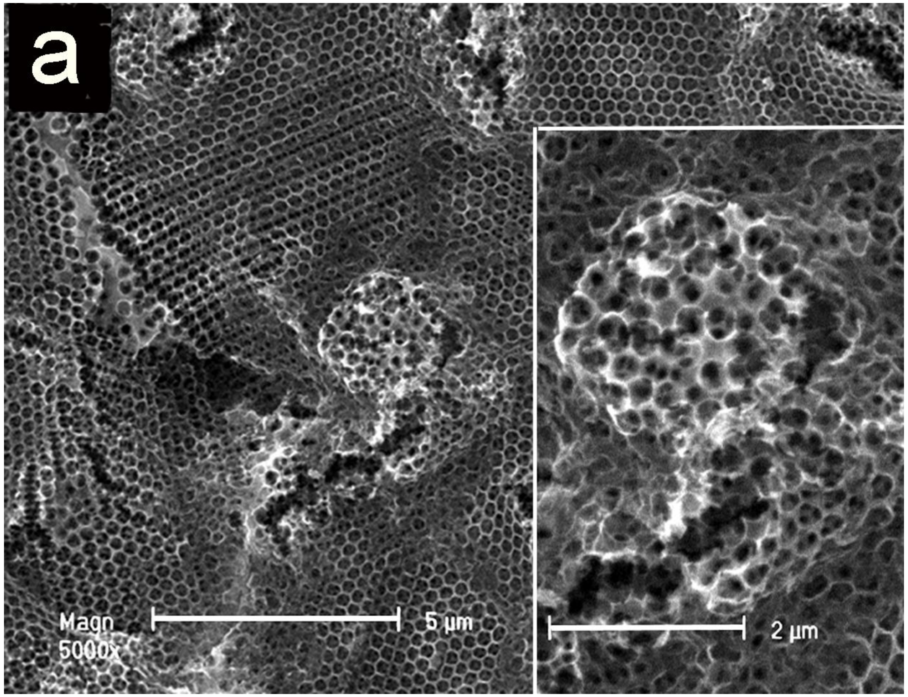
C. Dionigi et al., J. Colloid. Interf.Sci. (2005)

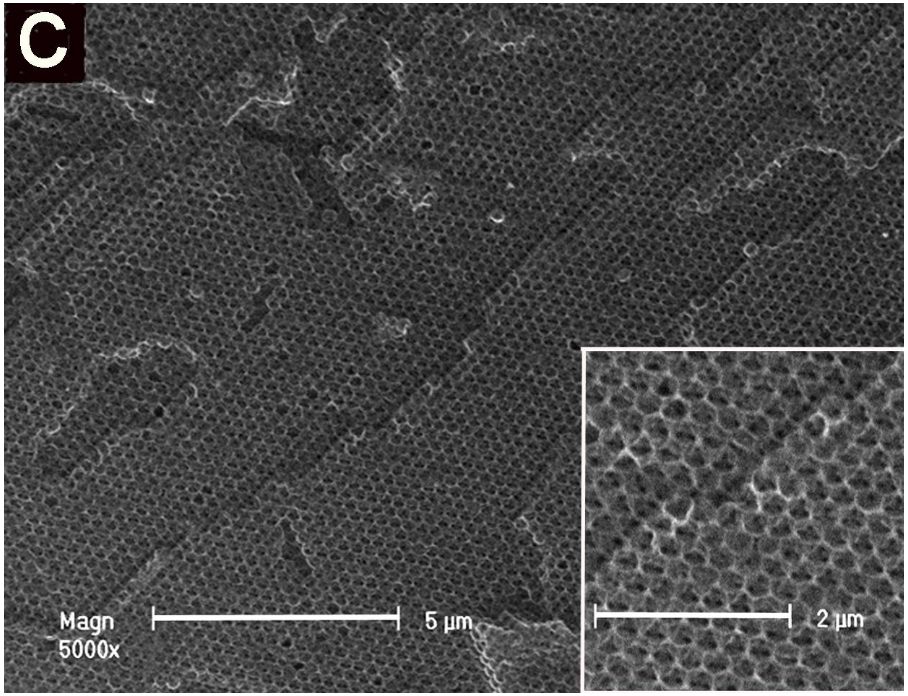
Soaking in Ti-lactate aqueous sol.

T = 55 °C + @ 82 °C

Quality of IO films

Template removal and TiO_2 nanoparticles formation





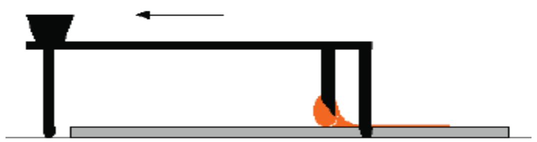
G. Ruani, et al., Sol. En. Mater. Sol. Cells (2008)

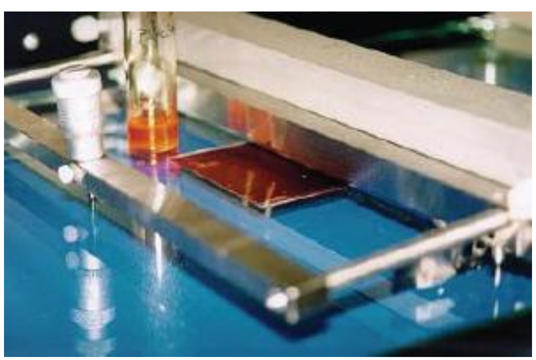
Heated to 450 °C in air
(0.75°C/min)

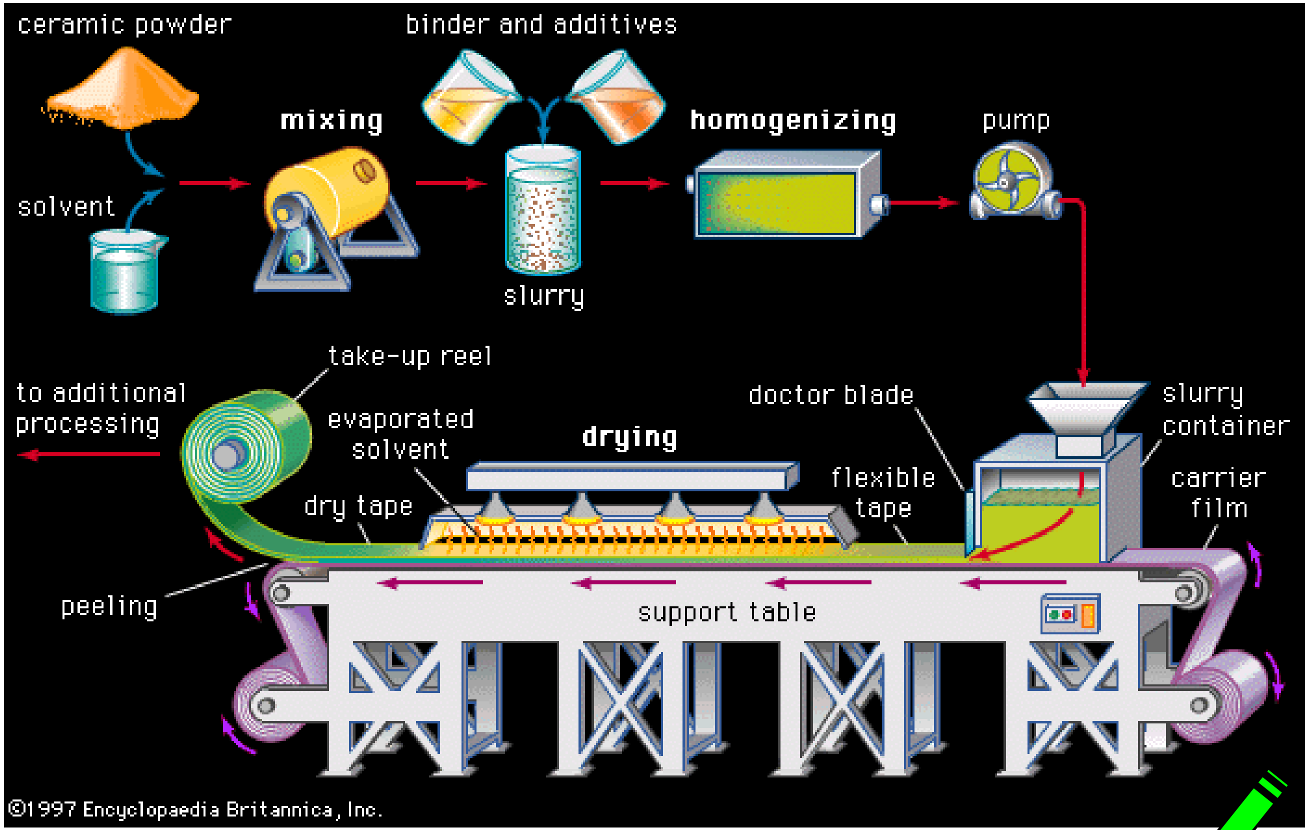
Heated to 450 °C in N_2
(0.75°C/min)

TiO_2 film deposition – faster method

Large area thin film production by using Doctor Blade method



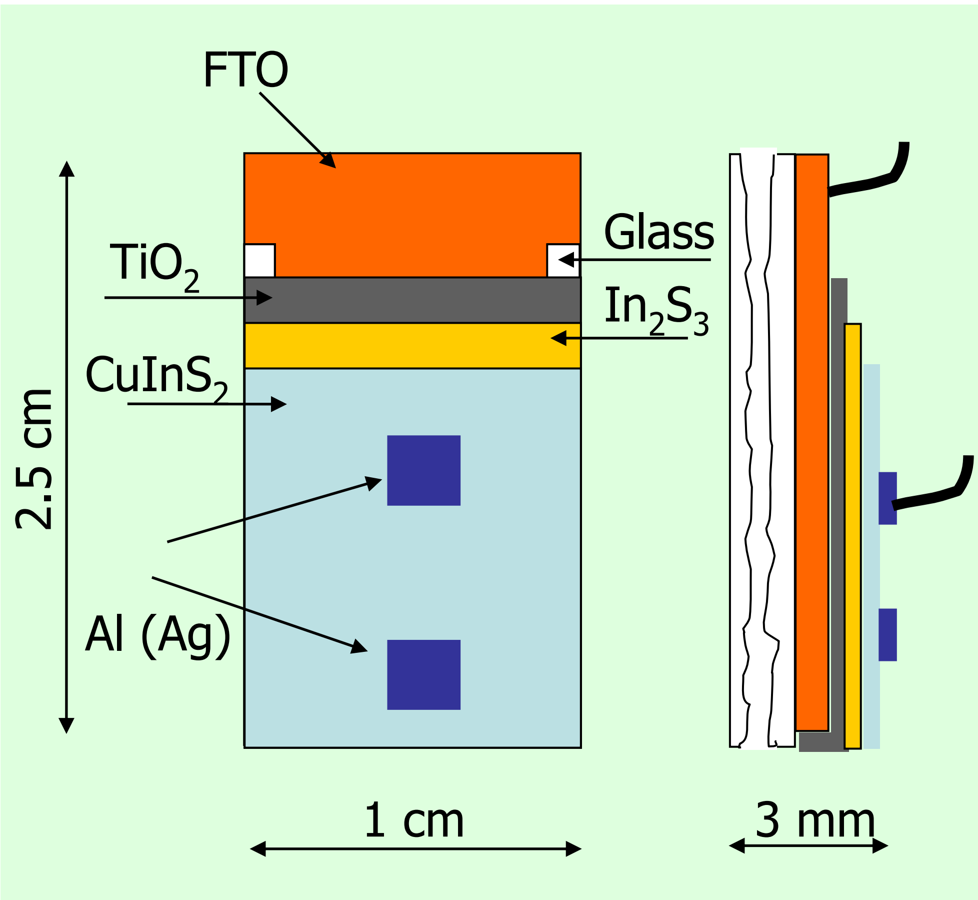




Industry

Laboratory

In_2S_3 film preparation



In_2S_3

intermediate blocking film (buffer layer)
~ 60 nm

In_2S_3 film preparation

Experimental parameters:

Precursor solution:
$InCl_3$ + thiourea

Solution flow rate: 1ml/min

Step I: USPD on substrate

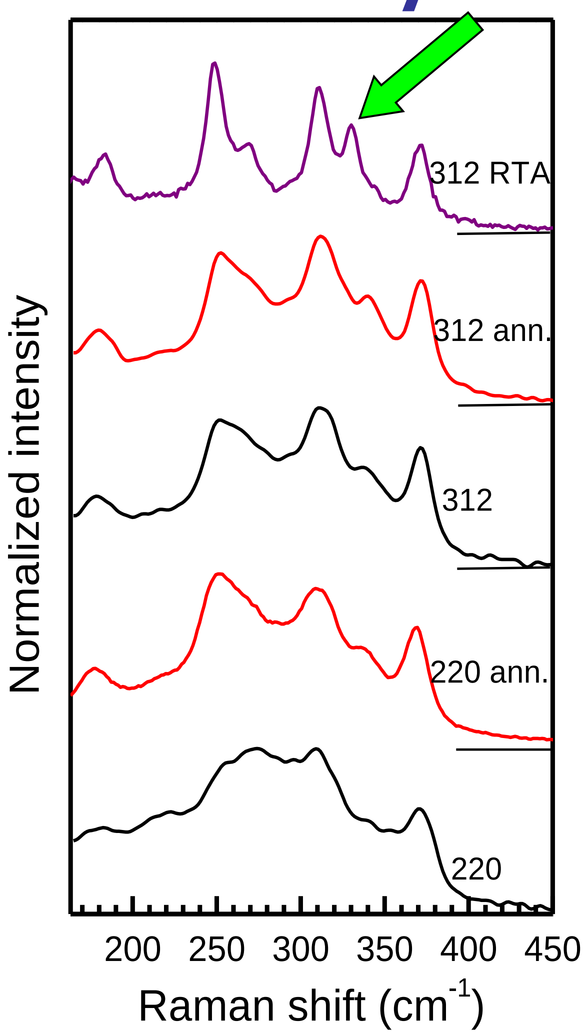
Glass/FTO/c-TiO_2/m-TiO_2

T deposition = 312 °C

Step II: Annealing (1h)

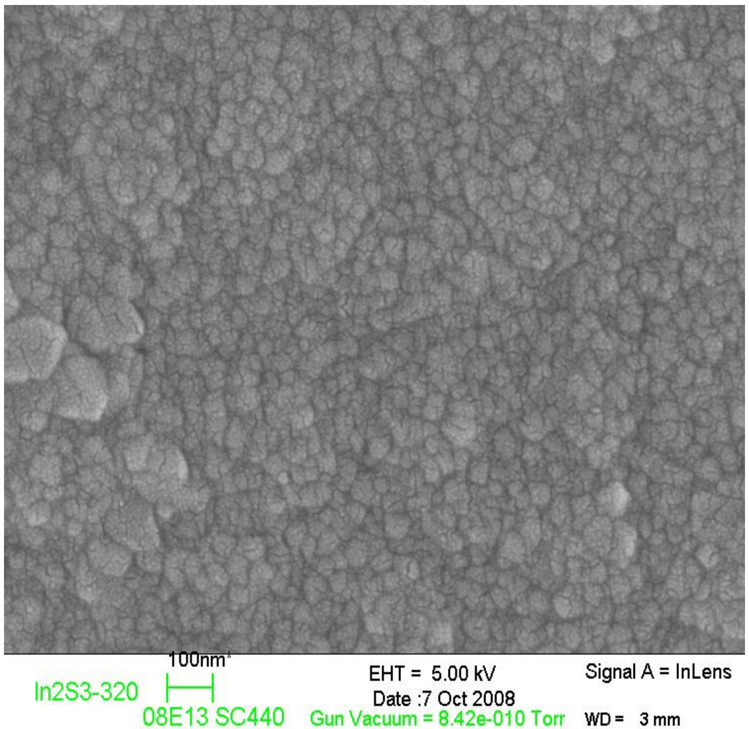
T annealing: 500 °C

Buffer layer



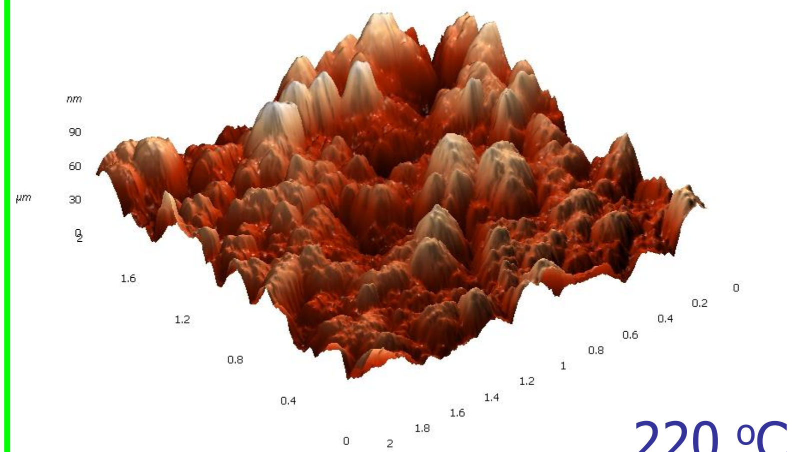
In_2S_3 images

SEM Image

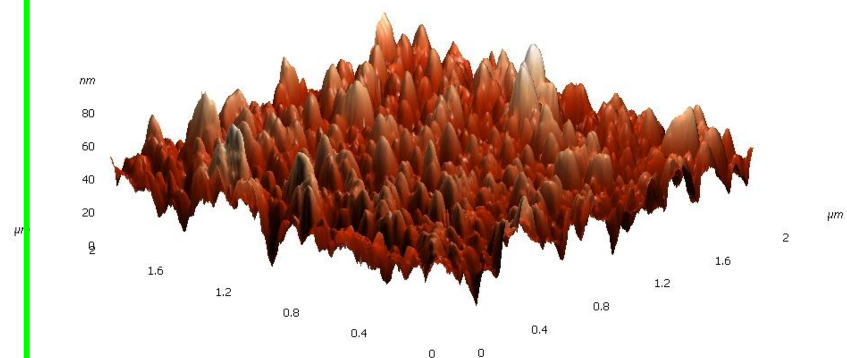


Surface

3D AFM Image (2 X 2 μm)

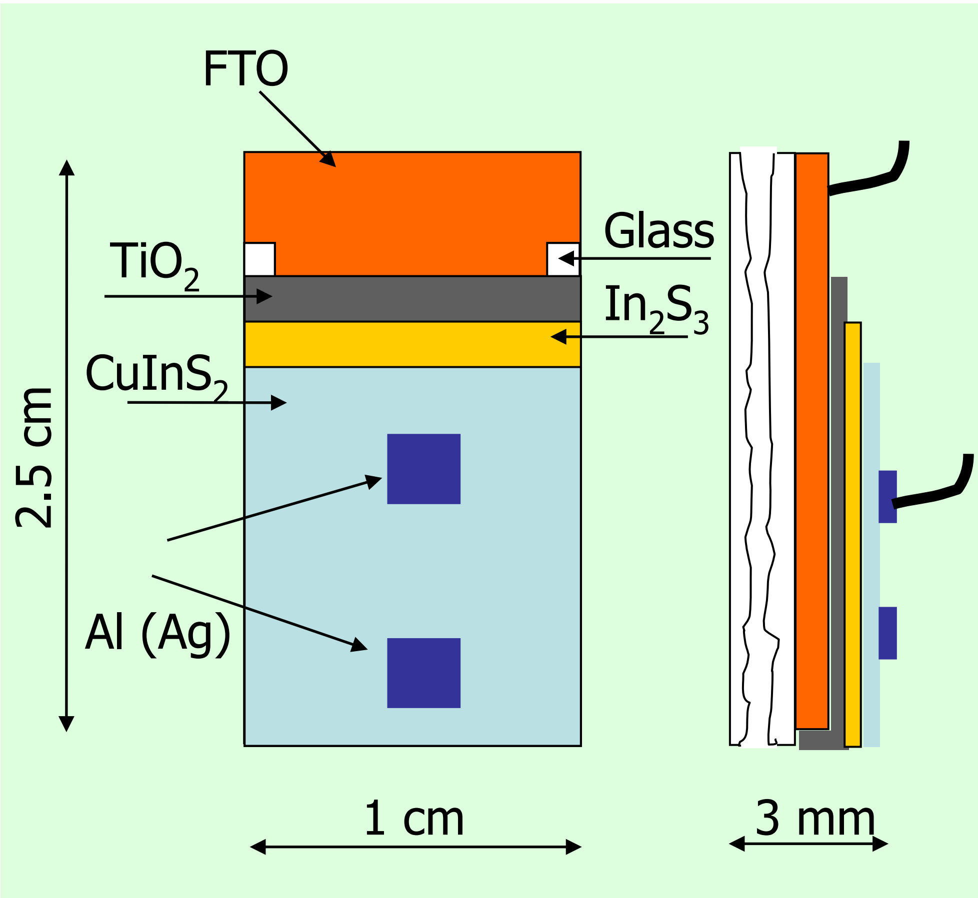


220 °C



340 °C

CIS film preparation



$CuInS_2$ (CIS)

hole conducting film (0.5 ÷ 1.5 μ m)

CIS film preparation

Experimental parameters:

Precursor solution:
$InCl_3$ + thiourea+$CuCl_2$

Solution flow rate: 1ml/min

Step I: **USPD on substrate**

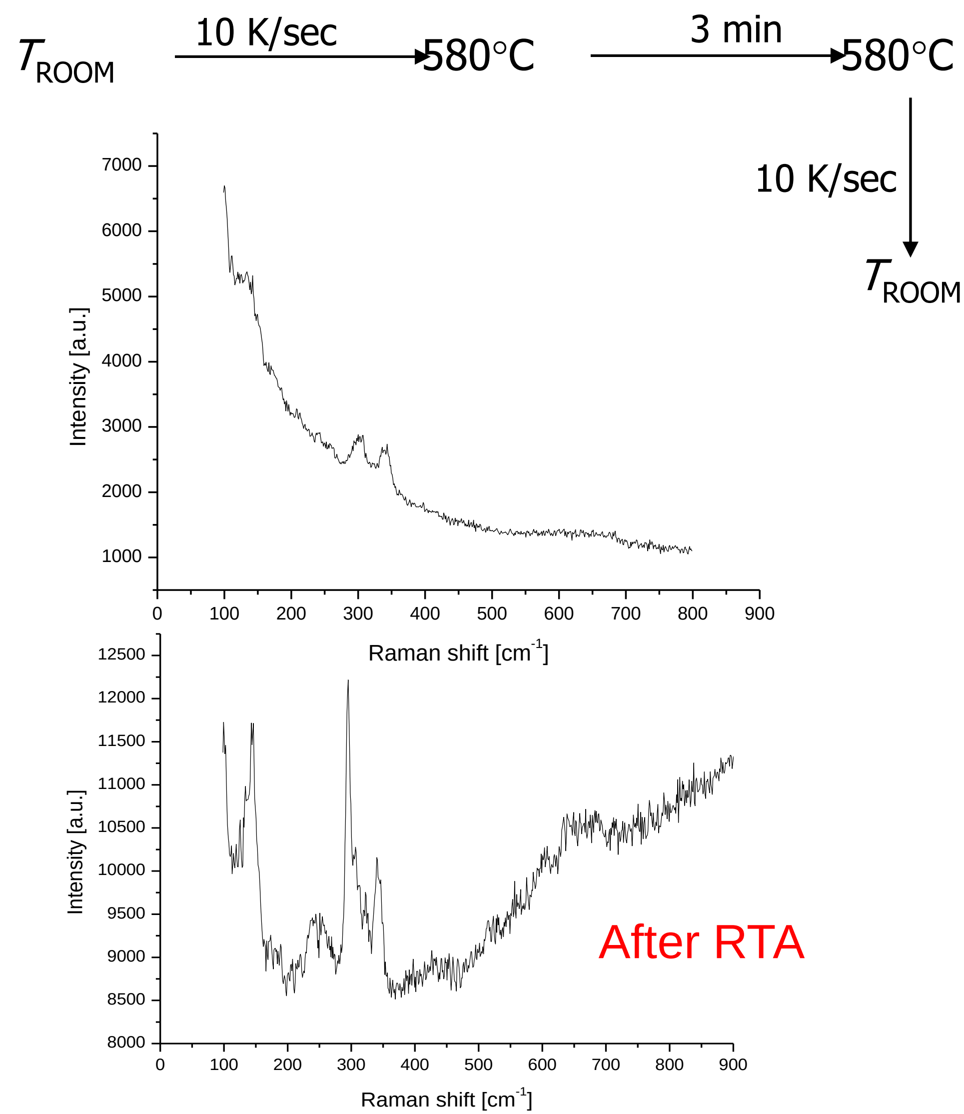
Glass/FTO/c-TiO_2/m-TiO_2/In_2S_3

T deposition = 350 °C

Step II: **Annealing (1h)**

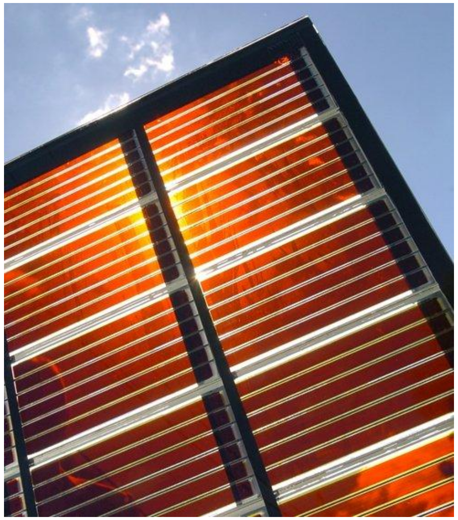
T annealing: 350 °C

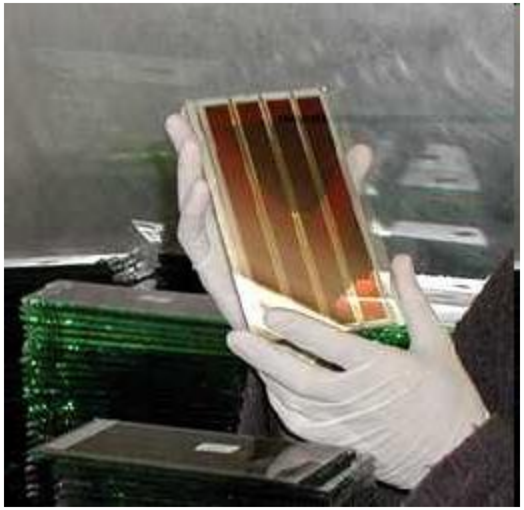
Rapid Thermal Annealing (RTA)



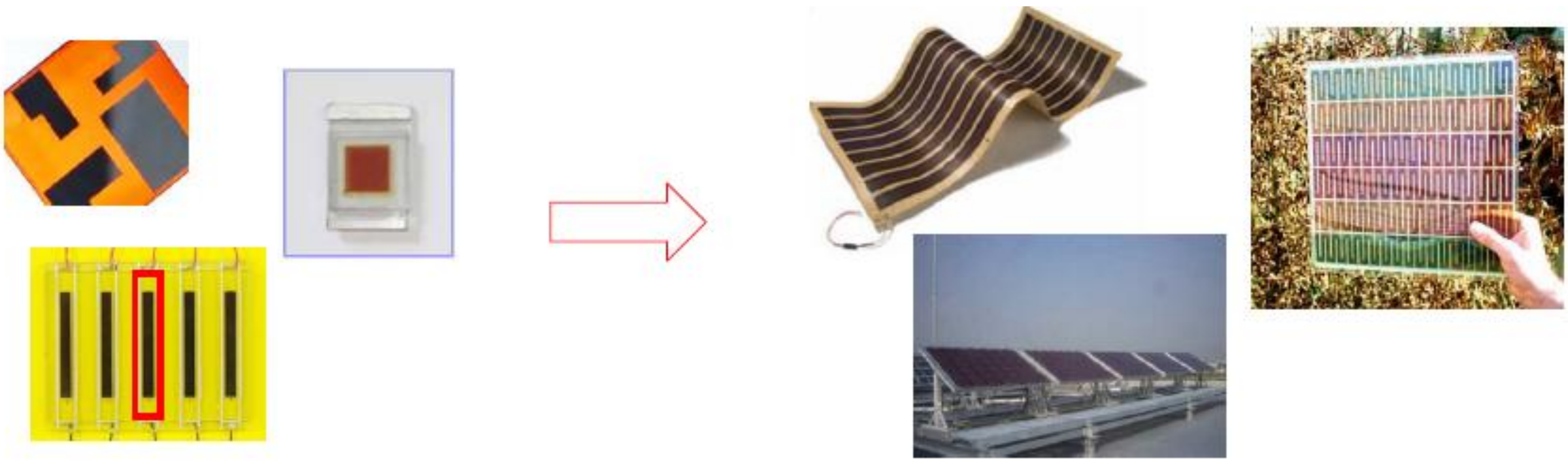
Best rezults in DSSCs

- Liquid electrolyte based cell → 11%
- Liquid electrolyte based panel → 5.6 %
- Solid hole conducting materials → 5%
- All inorganic DSSCs → 5%



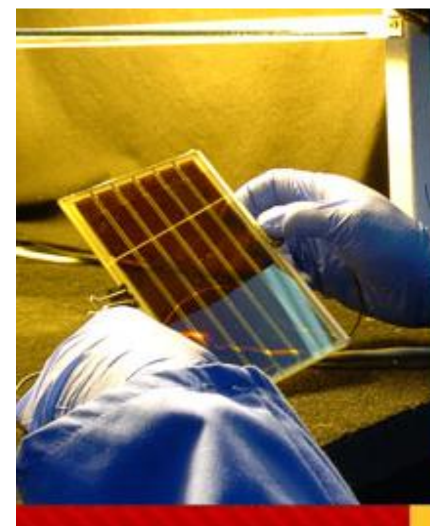


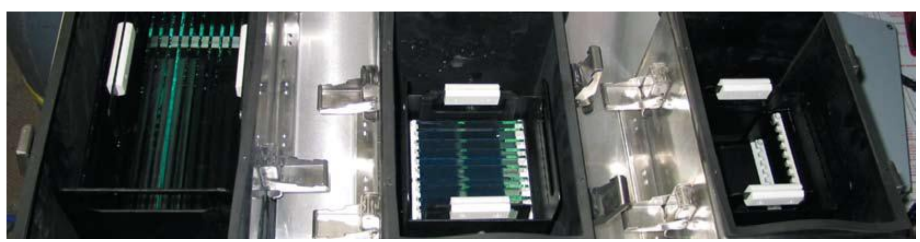
From laboratory...



To pilot plants...

Example ...





Scientific papers on DSSCs

- Before 2000 ⇒ 54% of papers from Europe
- After 2001 ⇒ 32% from Europe
- In 2009 ⇒ 25% China
  60% (Japan, S. Korea, Taiwan)
  32% Europe
- **17** from **20** most cited papers are from European authors

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Gratitude ....

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