

Solar Energy in MIB-Solar

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The Jacob Blaustein Institutes for Desert Research
Ben-Gurion University of the Negev



Ilse Katz Institute for
Nanoscale Science and Technology

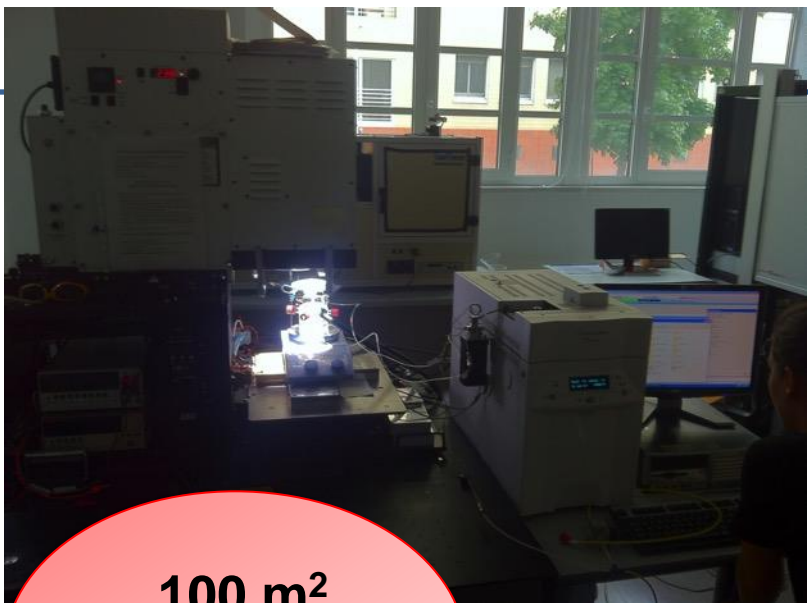


Italian National Agency for New Technologies,
Energy and Sustainable Economic Development



**Ministry of National Infrastructure,
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www.energy.gov.it

MIB-SOLAR clean room



100 m²
ISO 7
clean room



fully equipped
synthesis and
characterization
labs

www.mibsolar.mater.unimib.it



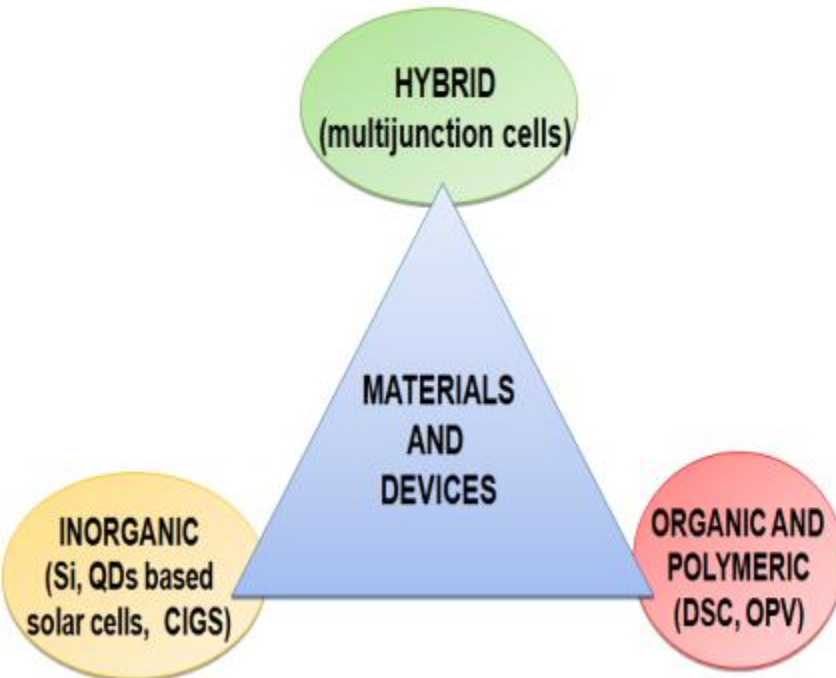
MIB- SOLAR Facilities

- ✓ Main facilities for the preparation of CIGS and DDSC cells and panels (sputtering system, nitrogen and argon filled glove box, laser scribing machine, titanium hotplates, screen printers, UV-ozone cleaners)
- ✓ main facilities for the full characterization of any solar devices (solar simulators up to 6 x 6 inches, I/V, EQE, light soaking chamber for cell ageing, stability studies, electrochemical impedance spectrometer).
- ✓ fully equipped laboratories for organic synthesis and characterization;
- ✓ fully equipped laboratories for optical, structural and electrochemical investigation (PL; PLE, ABS, Raman, XRD, EBIC, Hall set-up ..);



Research lines at MIBSOLAR

- Development of a new deposition procedure to growth Cu(InGa)Se₂ thin film solar cells (M.Acciarri, S. Binetti, L. Miglio)
- Kesterite: a new material for thin film solar cells deposited by sputtering and chemical methods (S. Binetti, M.Acciarri)
- Nanocrystalline silicon solar cells (nc-Si:H) (S. Binetti, M. Acciarri, E. Bonera, M. Guzzi)
- Solar Grade Silicon (S. Binetti, M. Acciarri)
- Thin film Si QDs solar cells (M. Acciarri, S. Binetti)
- Light harvesting to increase the efficiency of silicon solar cells: (S. Binetti, M. Acciarri)
- Dye-Sensitized Solar Cells (DSC): Materials and Devices (A. Abboto)
- Small-molecule and polymeric heterojunction solar cells: materials and devices (A. Abboto, C. M. Mari, R. Ruffo)
- Solar cells of the third generation based thin and individual organic semiconductor crystal film (A. Sassella, A. Papagni, M. Moret, A. Borghesi)
- Panchromatic squaraines for hybrid and organic photovoltaic cells (G. A. Pagani L. Beverina)
- Structure and properties of photoactive materials for catalysis and organic-inorganic solar cells (G. Pacchioni, C. Di Valentin, L. Giordano).
- Computational Science conductivity in nanostructures: ab initio treatment of characteristic processes for the components of organic and hybrid photovoltaic cells (G.P. Brivio).

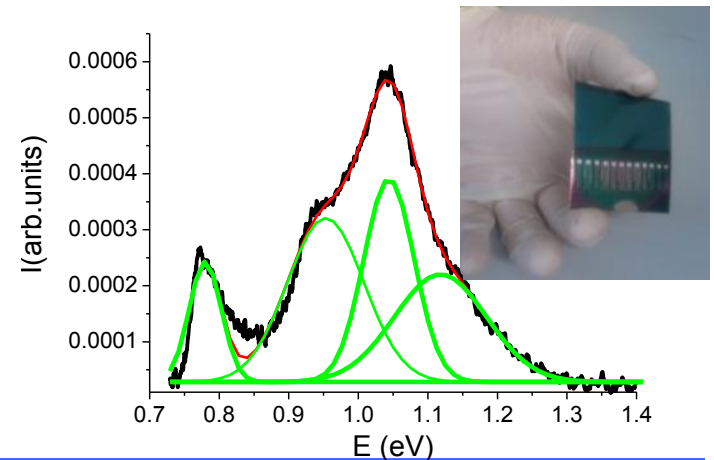
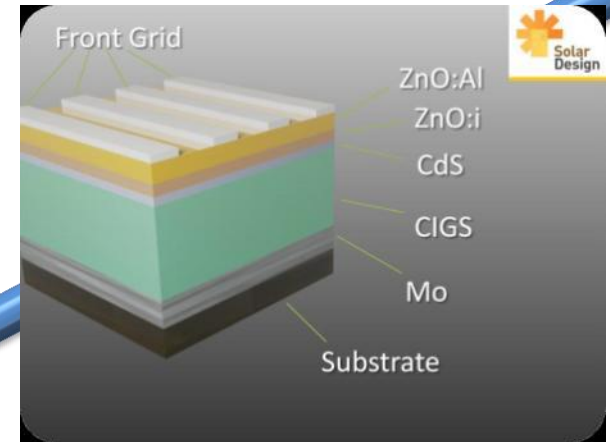


- Silicon solar cells
 - CIGS - CZTS thin film solar cells
 - Triple junction solar cells (InGaP/GaAs/Ge)
 - Light harvesting, spectrum modification
 - Si Quantum dots solar cells
 - Organic solar cells
 - Dye sensitized solar cells
 - Modeling and Theoretical activities
- } M. Acciarri
 } S. Binetti

 } A. Abbotto

The Centre owns its main skills, in the capture and conversion of solar energy from conventional crystalline silicon to new generation inorganic, organic and hybrid thin film devices.

Inorganic Photovoltaic devices



M. Acciarri and S. Binetti group

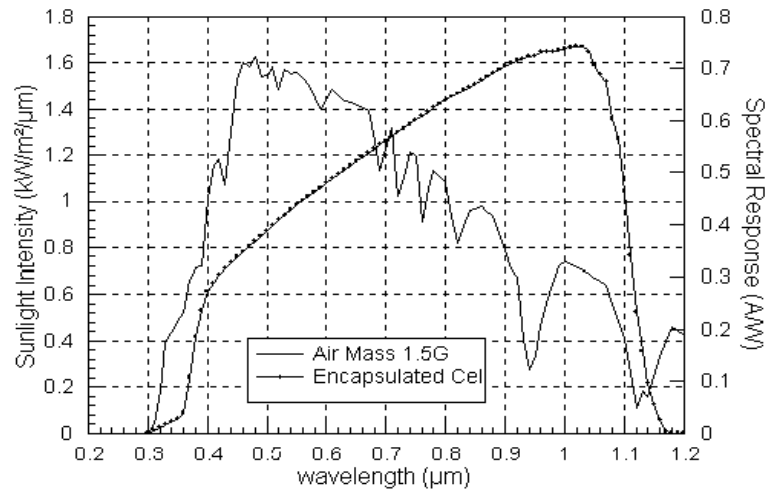
Research lines: Silicon solar cells

Increase the ratio Efficiency / cost

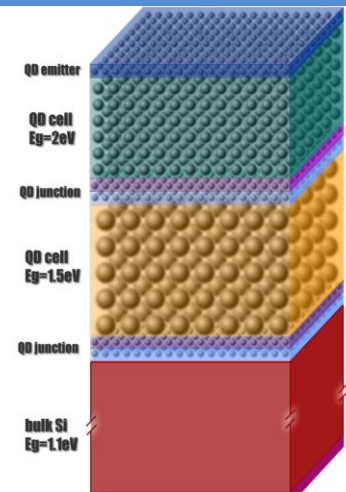
Use UMG Si



Light harvesting



3th generation silicon based solar cells

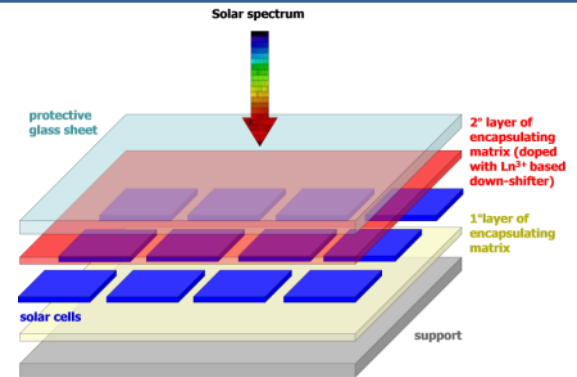


Target 0.20 \$/Wp - $\eta = 40\%$

Inorganic Photovoltaic materials and devices

c-Silicon solar cells

- Since 1990 involved in EU project on silicon solar cells
- mc-Si: role of defects (dislocations, grain boundaries)
- Metallurgical silicon : defect and compensation effect
- Light harvesting, (EVA doped with Eu complexes)
- multilayer quantum dots based material



S. Binetti et al. *Solar Energy Materials & Solar Cells* 130, 696 (2014)

C.Modanese et al. *Prog. Photovolt: Res. Appl.* (2013)

S.Binetti et al. *International Journal of Photoenergy*, ID 249502, 6 pages,(2013)

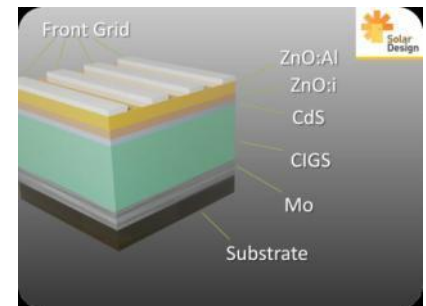
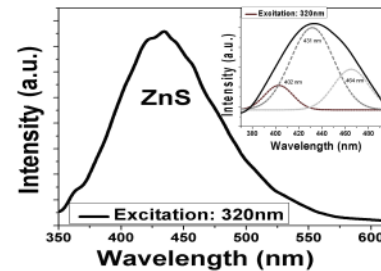
A.Le Donne et al. *J. Appl. Phys.* 113, 014903 (2013)

M.Morgano et al. *Science of Advanced Materials* 3, 388 (2011).

A.Le Donne et al. *Optical Materials* 33, 1012, (2011)

R.Slunjski et al. *Solar Energy Materials & Solar Cells* 95, 559-563 (2011)

M.Tajima et al. *J. Appl. Phys.* 110, 043506 (2011)



Inorganic thin-film technologies

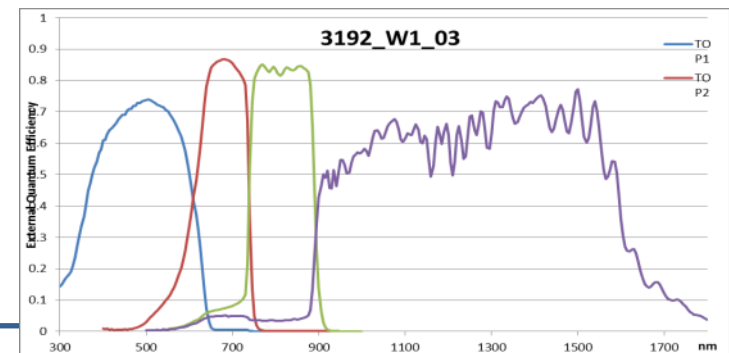
- $\text{Cu}(\text{In,Ga})\text{Se}_2$
- CZTS

III-V based Tandem solar cells

- AlInGaP and AlInGaAs for 32% four junction devices for concentration application (CESI Spa)
- GaAs grown on silicon : chracterization (Pilegrowth s.r.l)

A. Le Donne, et al. *Solar Energy Materials & Solar Cells* 94, 2002 (2011)

R.Campesato, et al. *Proc. EUPVSEC 2013* (2013)



Research lines: Silicon solar cells

Advantages:

- lower cost
- lower energy payback time
- Lower carbon footprint

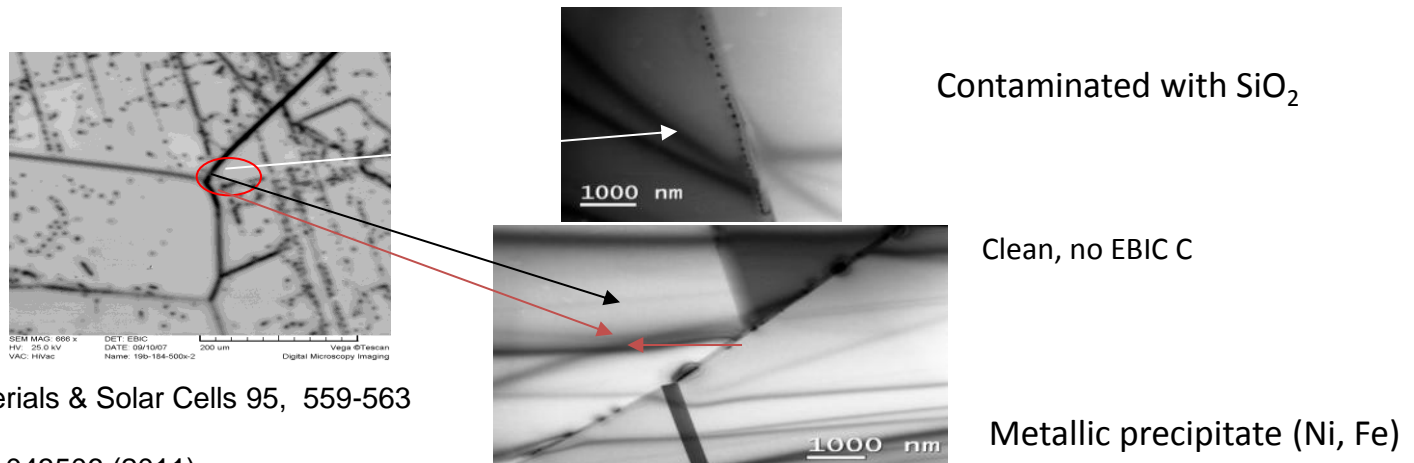
Drawbacks :

- Low purity

Metallic concentration can be reduced by:



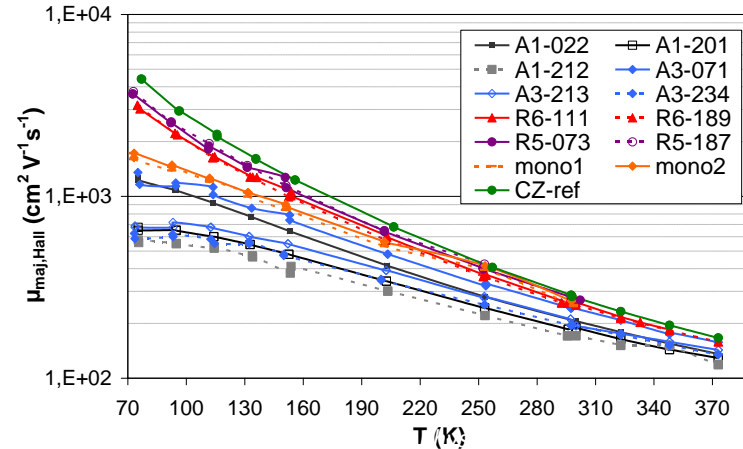
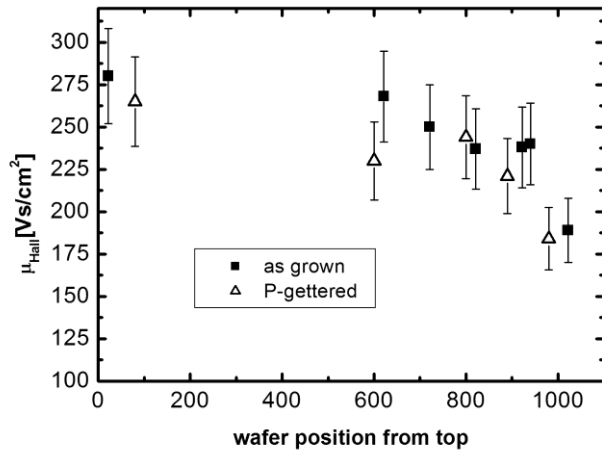
But Internal gettering and metallic precipitates should be avoided



R.Slunjski et al. Solar Energy Materials & Solar Cells 95, 559-563 (2011)

M.Tajima et al. J. Appl. Phys. 110, 043506 (2011)

UMG Silicon solar cells: effect on compensation

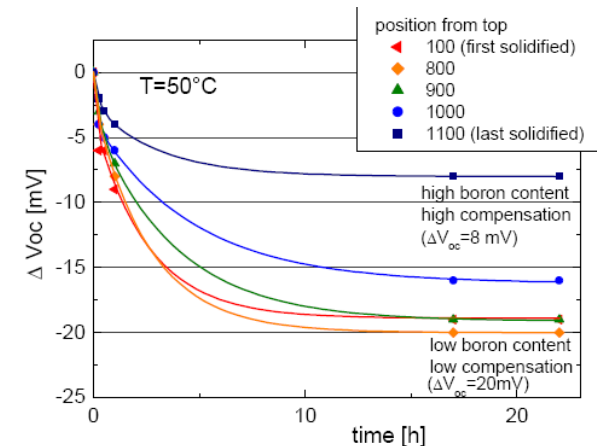


➤ Can lead to carrier lifetime improvements

➤ Reduction the light induced degradation effect (B-O complexes)

R. Kopecek, S. Binetti, M. Acciarri et al., Proc. 23rd PVSEC, Valencia, Spain (2008)

S. Binetti, G. Coletti, M. Acciarri IEEE PV 2014



Silicon sample for PV application grown under reduced melt convection



- Aim is to characterize solar silicon samples grown in microgravity conditions
- (ESA project A0-2009-1051 and Disk Project : a joint Russian- Europe Space Experiments)

Ground-based experiments at University of Freiburg:

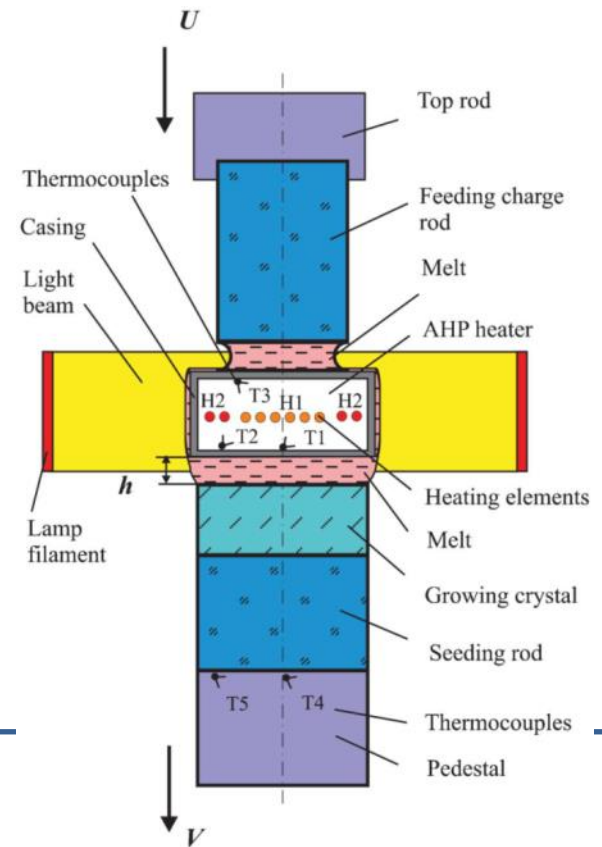
Schematics of crystal growth (modified FZ method) in the crucibleless AHP silicon

Advantages :

- The melt flow has a laminar characteristic
- close to diffuse regime
- flat shape of the crystallization front

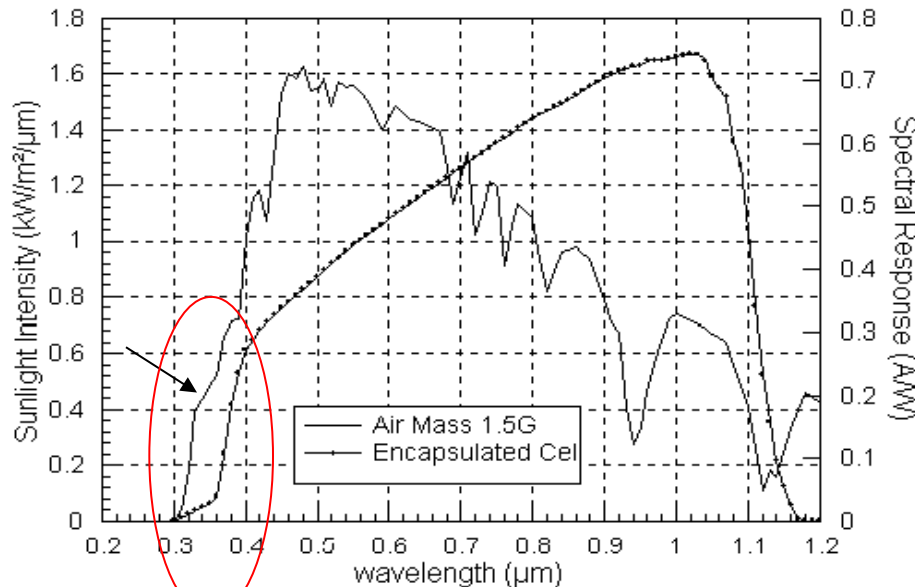
•A. C.Wagner , A.Cröll, M. A.Gonik , H.Hillebrecht, S.Binetti
J. of Crystal Growth Vol.401, 762 (2014)

•S. Binetti et al : J. of Crystal Growth (2015) in press



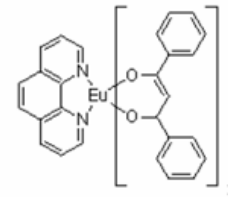
Light harvesting

Modify light spectra down converting photons with $E \gg E_{\text{gap}}$ to photons with energy near the maximum quantum efficiency spectral region on the PV cell

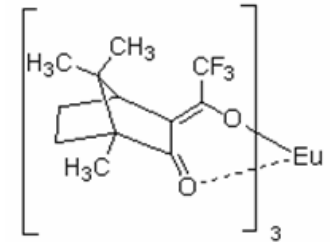


down-shifter dispersed in the encapsulant matrix

Eu (dbm)₃ phen

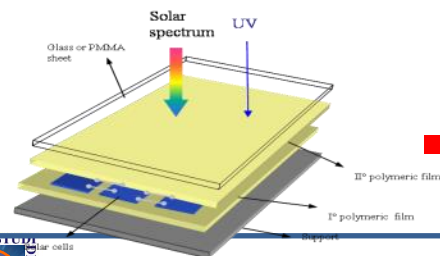


Eu(tfc)₃

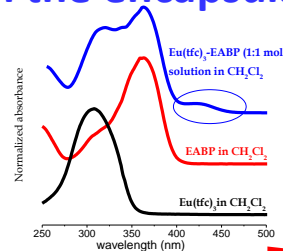


➤ $\Delta I_{\text{sc}} : + 2.7\%$ (relative)

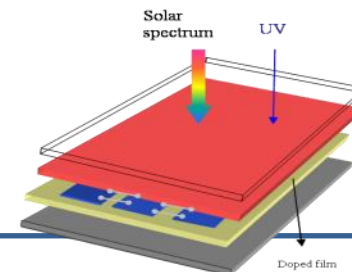
+0,6 % is sufficient to maintain unaffected the Wp price



Commercial encapsulation scheme for solar modules



Eu³⁺ Complex



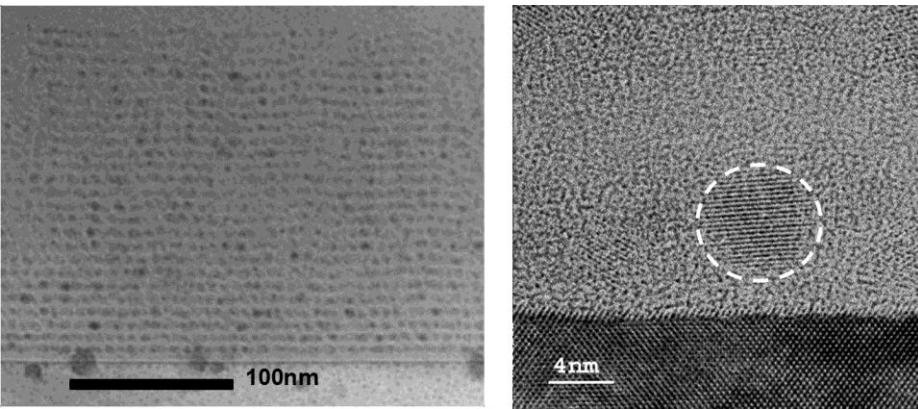
A new material for encapsulation process



Le Donne A, et al. *OPTICAL MATERIALS*, vol. 95 (2011), p.1012-1014,

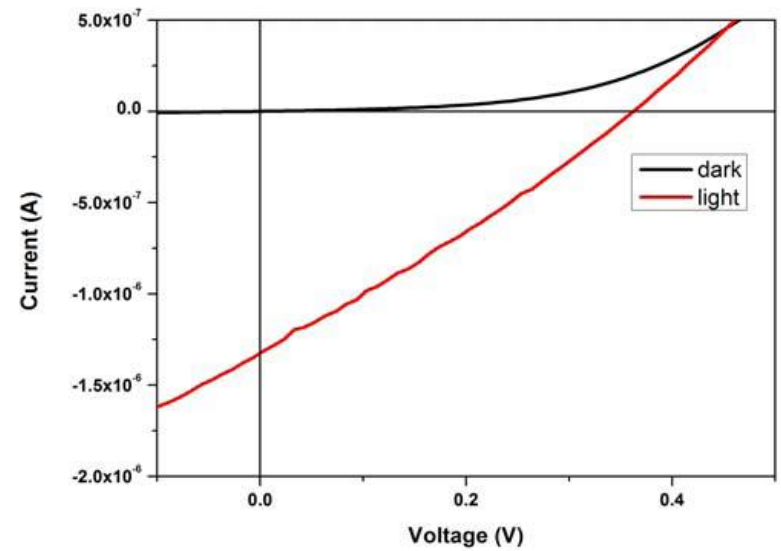
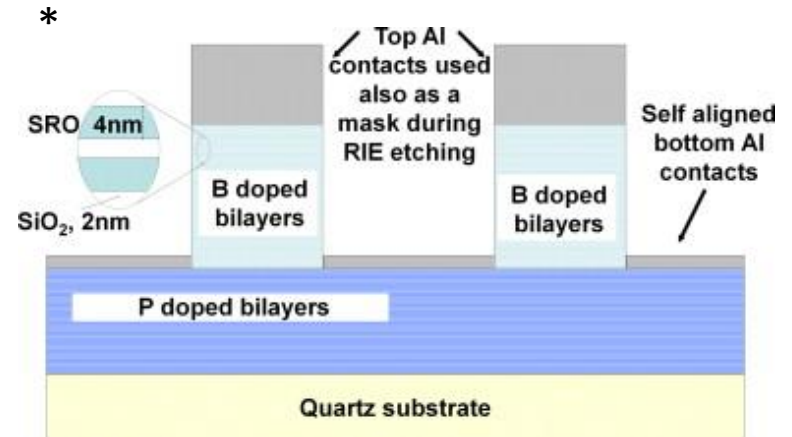
Si QDs solar cells

The Si QDs were formed by alternate deposition of SiO_2 and silicon-rich SiO_x with magnetron co-sputtering, followed by high-temperature annealing.



Transport properties, and doping charge collection are crucial

*in collaboration with UNSW (Sidney)

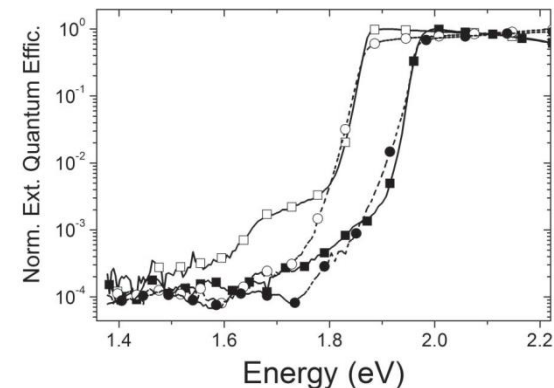
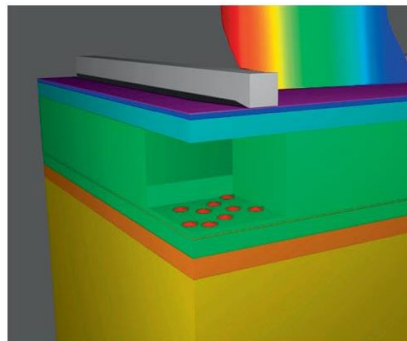
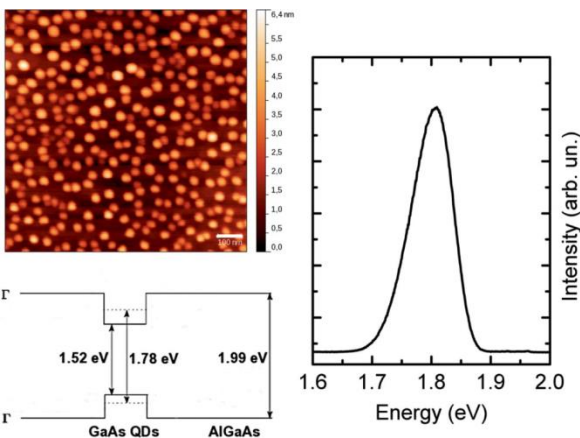


M.Morgano et al. Science of Advanced Materials 3, 388 (2011).

Intermediate band photovoltaic cells

Evidence of two-photon absorption in strain-free quantum dot GaAs/AlGaAs solar cells

Nanostructured materials grown by Droplet epitaxy (DE), a molecular beam epitaxy variant, due to the absence of strain related defects, the high quality of the interfaces, the good confinement, and the capability to grow high density and large aspect ratio QDs, a perfectly suited system for the implementation of QD-IBSCs.



CIGS technology in UNIMIB

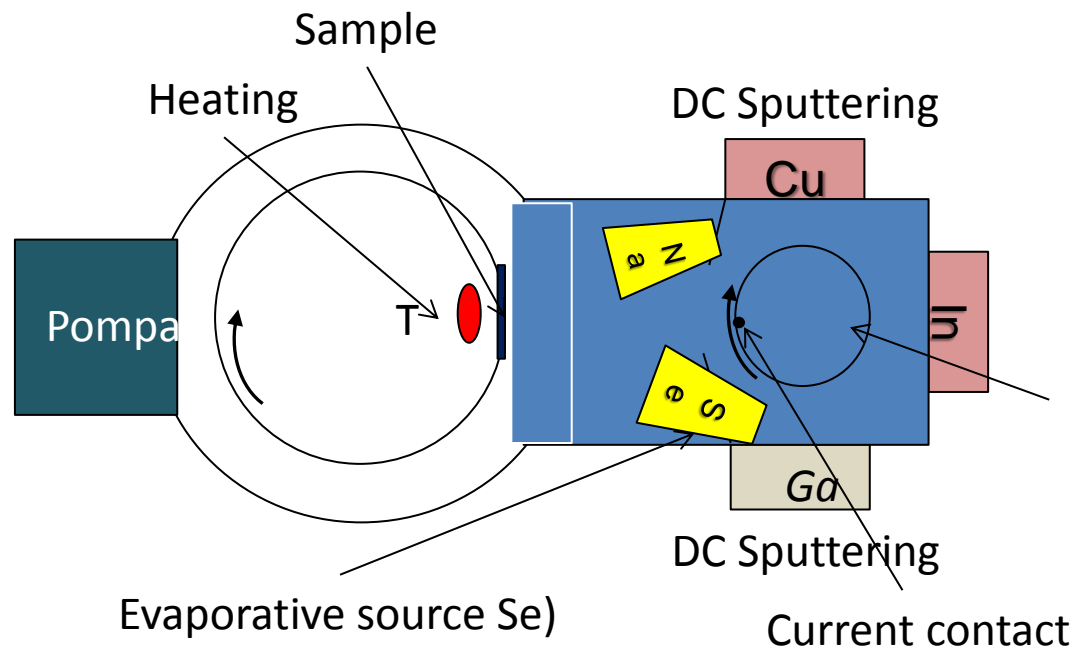


Thanks to the collaboration between the small enterprise Voltasolar S.r.L. e UNIMIB started in 2007, it has been developed an innovative industrial process for the production of the CIGS thin film on flexible substrate

Project SolarDesign (contract no. FP7-NMP-2012-SME-6)
Projects Metadistretti 2008 e 2011 MIUR e Regione Lombardia

CIGS technology in UNIMIB

1. The metal precursors are sputtered on a cylindrical transferring body
2. Metals are then evaporated in Se ambient thanks to a local heating of the graphite elements of the transferring body
3. The process continues since the desiderate thickness is reached.



Cylindrical transferring body

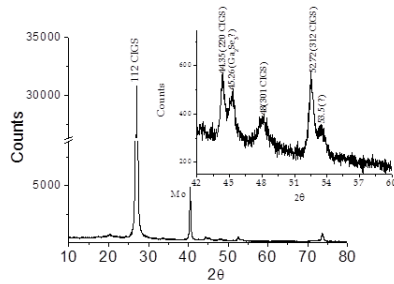


Patent N° [EP 13425019.0](#)

SUBSTRATI:

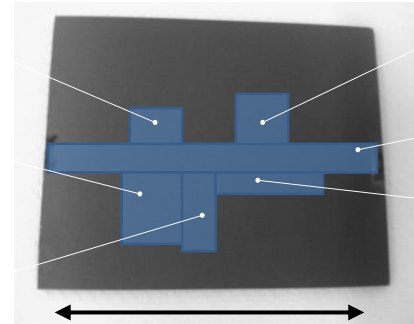
- 14 x 11 cm² soda lime glass 1 mm
- 20 x 10 cm² Cr stainless steel foil 125 μm
- 20 x 10 cm² polyamide 25 μm
- 14 x 11 cm² glass foil 125 μm

CIGS characterizations



Film di CIGS film

XRD



Cell finalization

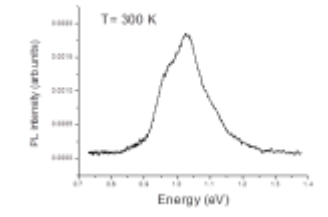
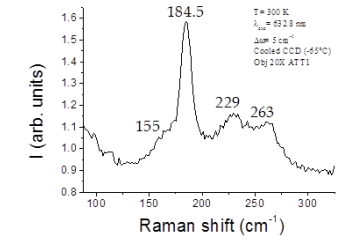
Thickness

Tape-test

SEM / EDX

Section

14 cm

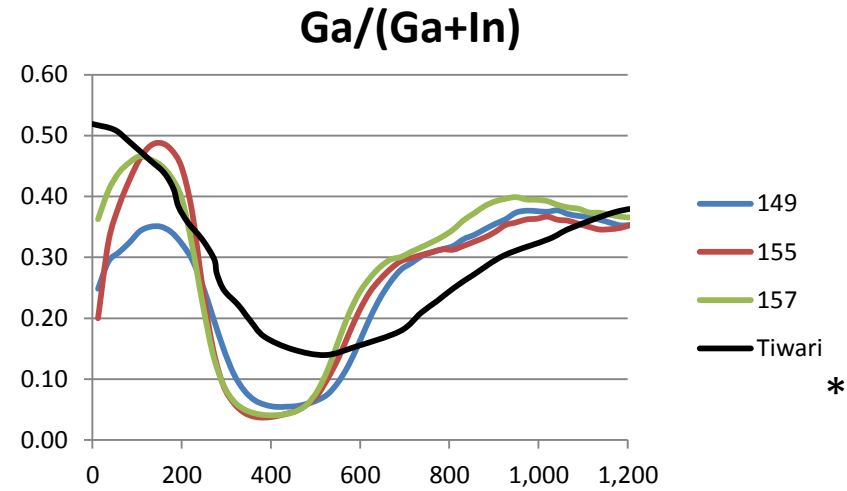
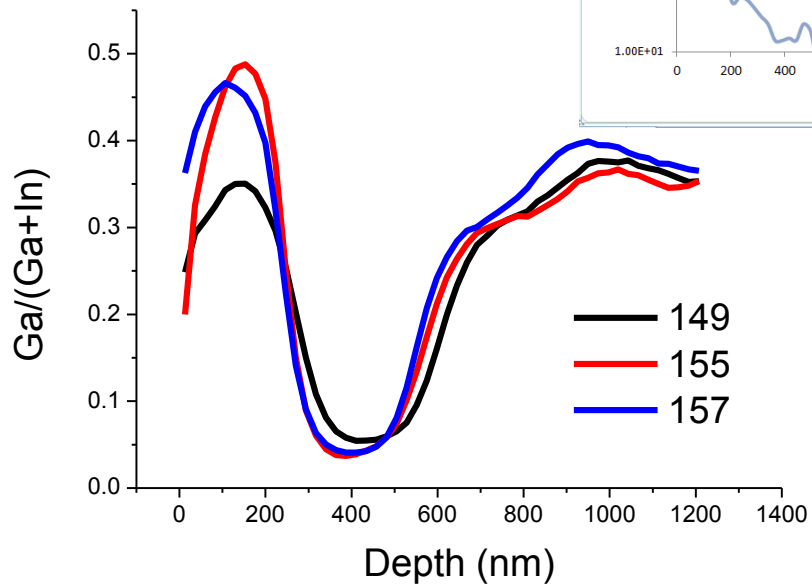
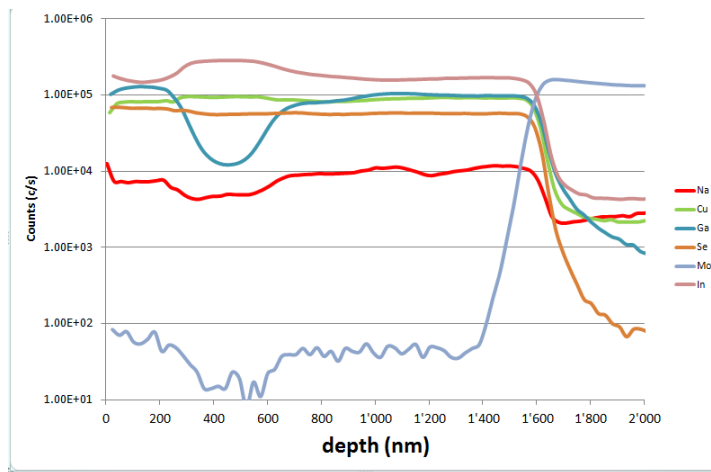


CARATTERIZZAZIONE

- Scanning electron microscope (SEM) with EDX (morphology and composition)
- XRF (composition)
- SIMS (University of Trento) (composition)
- Raman spectroscopy (phase identification)
- Photoluminescence (electrical properties)
- X-ray diffraction (phase identification)
- 4-probes method (resistivity)
- Profilometer (thickness)
- Tape- test (ASTM D 3359-02) (adhesion)

S.I.M.S results *

5.5 keV Cs⁺
sputter beam on
200x 200 μm²



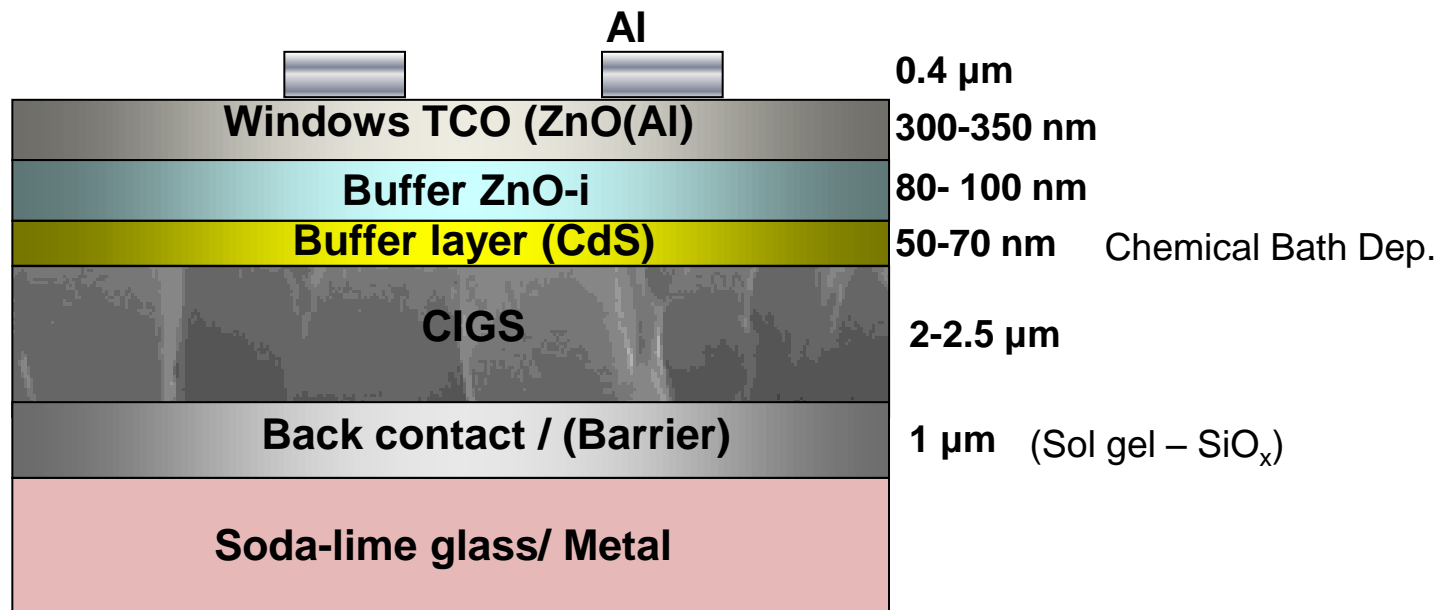
- double grading profile
- The “notch” region is less wide, closer to front contact.
- decrease of CGI ratio close to 200 nm

* Dip di Fisica Università di Padova

Cell finalization

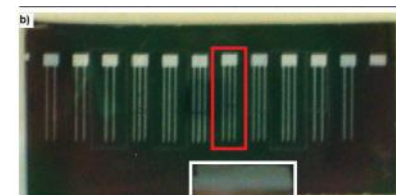
Vacuum

Non vacuum

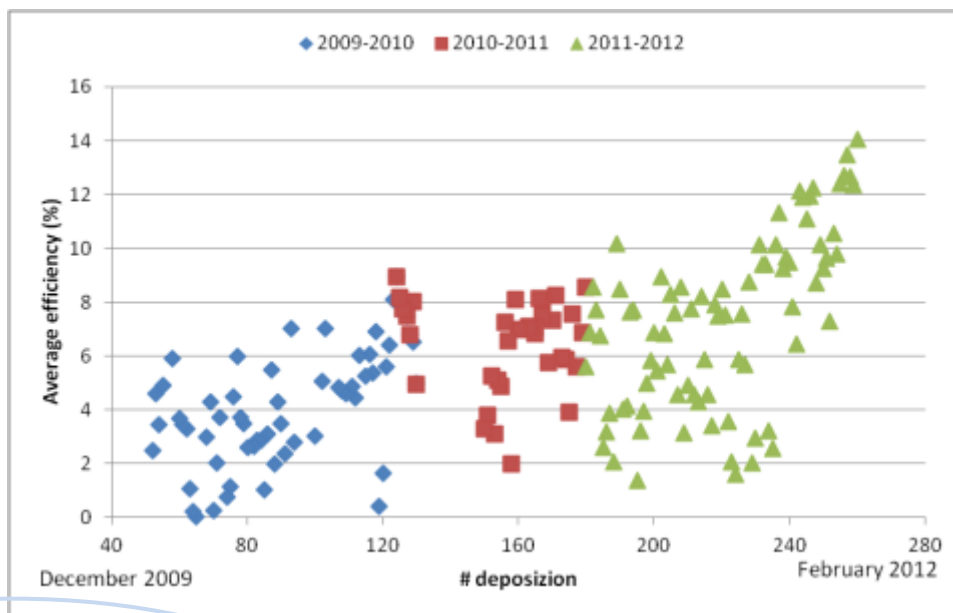
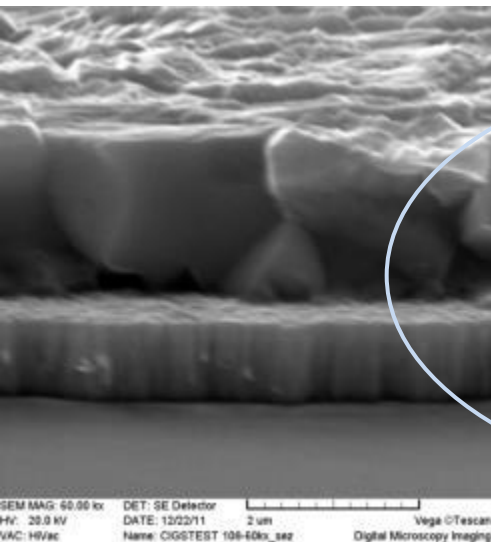
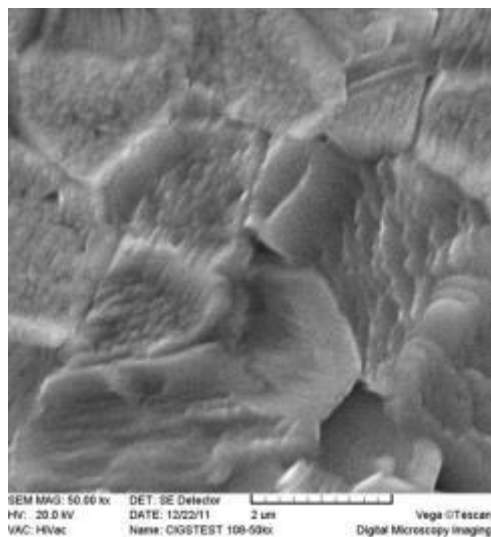


CELL CHARACTERIZATIONS

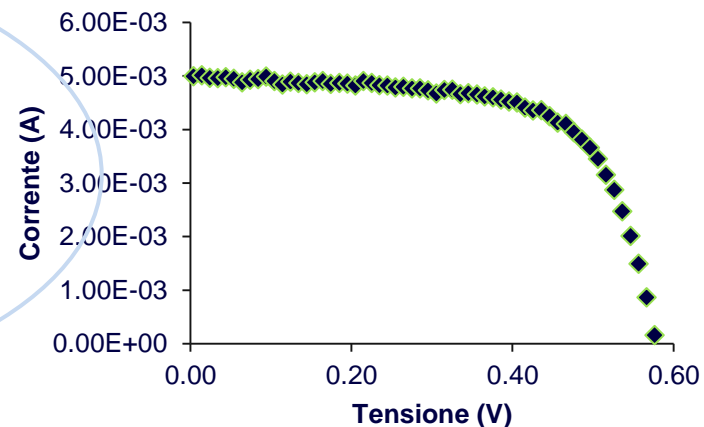
- UV-visible Spectroscopy (CdS,ZnO,ITO optical properties)
- I-V curves (1.5 AM solar simulator) (solar cell properties)
- Scanning electron microscope (section)
- Spectral response (solar cell properties)
- Electron beam induced current (EBIC) maps (solar cell properties)



Best result on glass



η [%]:	14.5
Voc [mV]:	581.71
FF [%]	72.0
Jsc [mA/cm ²]:	34.572
Area [cm ²]:	0.48
Irrad. mW/cm ² :	100



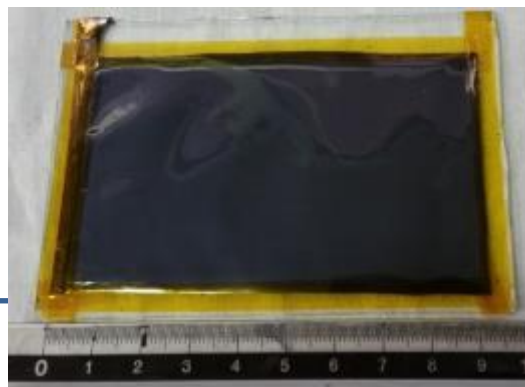
Best results on flexible substrates

Substrate	Eff (%)	Voc (mV)	Jsc (mA/cm ²)	FF (%)	Area cm ²
130um glass	9.2	510	27	66	0.15
Stainless steal	13.1	569	34.1	70	0.15
Polyamide	11.7	512	35.6	64.34	0.15

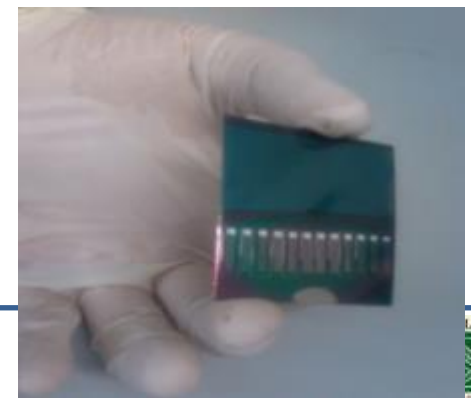
130um glass



Polyamide 25 um



Stainless steal 125 um



From the laboratory to the pilot line

- In 2015, the first pilot line has been installed by Voltasolar in Austria (Sunplugged) and is under testing
- A Roll-to-roll deposition on wide flexible substrates (320 mm) (stainless steel or polyamide)
- Predicted productivity: 1.5-2 MW/y



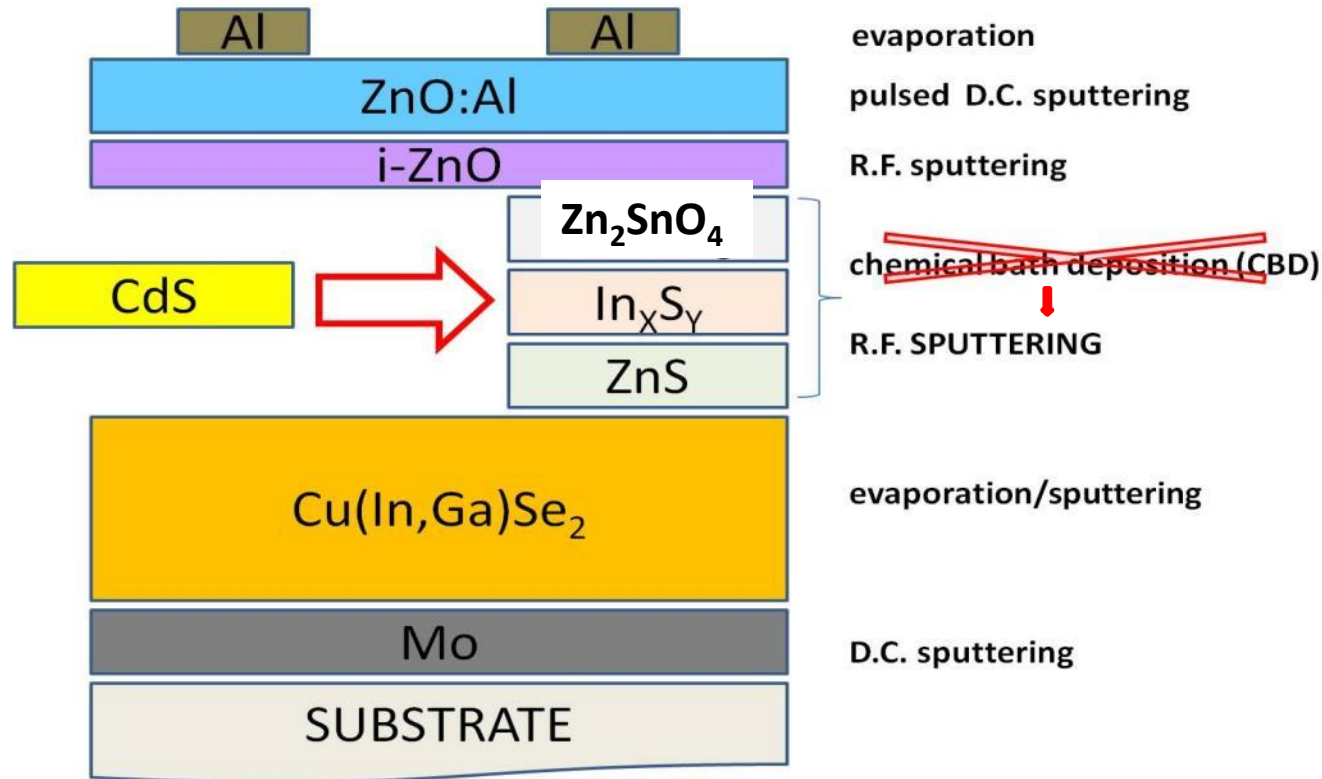
European Union's Seventh
Framework Programme
(FP7/2007-2013)



Beyond CIGS solar cells

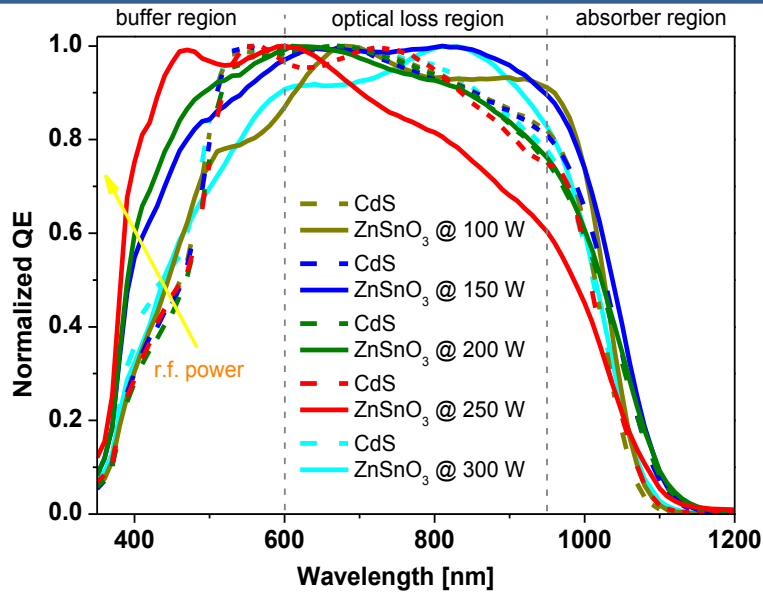
- Problems:
 - Toxicity (CdS as buffer layer)
 - Material shortage
- Solution:
 - Develop new buffer layers
 - Develop efficient thin-film (TF) photovoltaic (PV) absorbers based on earth-abundant elements!
 - $Cu_2M(II)M(IV)S_4$ chalcogenides using same deposition techniques of CIGS
 - Example: Cu_2ZnSnS_4

Cd-free alternative buffer layers for Cu(In,Ga)Se₂ solar cells

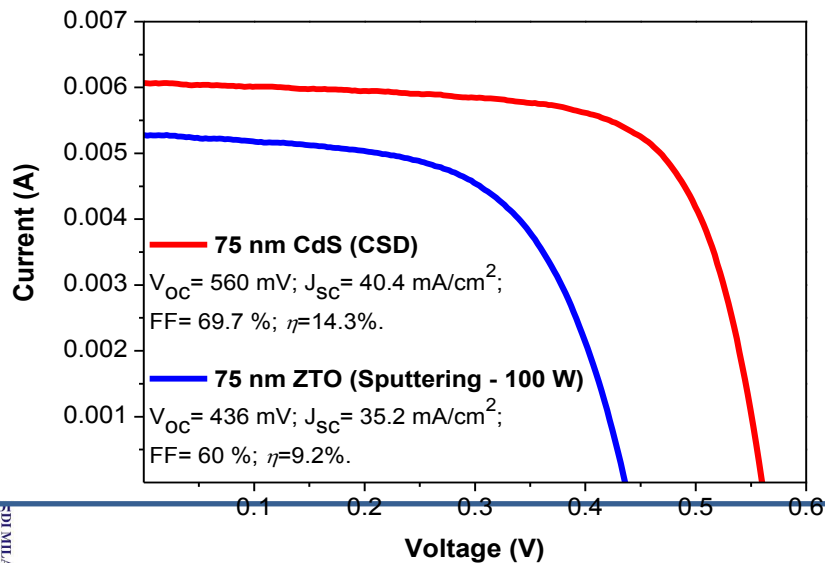


The deposition of the ZTO films was operated both from a ceramic target (75wt% ZnO – 25wt%. SnO₂) and from two metal targets (Zn and Sn) to form a metal bi-layer followed by an oxidation

Buffer layer: Zn₂SnO₄ (c-ZTO)



Size [cm ²]	Power [W]	J _{sc} [mA/cm ²]	I _{sc} [mA]	V _{oc} [mV]	FF [%]	Eta [%]
0.15	100	35.2	5.3	435.7	60.0	9.2
0.15	150	34.7	5.2	391.6	55.7	7.6
0.15	200	34.1	5.1	307.9	48.0	5.0
0.15	250	26.0	3.9	198.4	41.8	2.2
0.15	300	28.1	4.2	367.9	53.4	5.5



• *i*-ZnO and AZO front contacts needs to be re-optimized for each new buffer layer

Cu₂ZnSnS₄ (CZTS) by sputtering

1 . Metal Precursors :

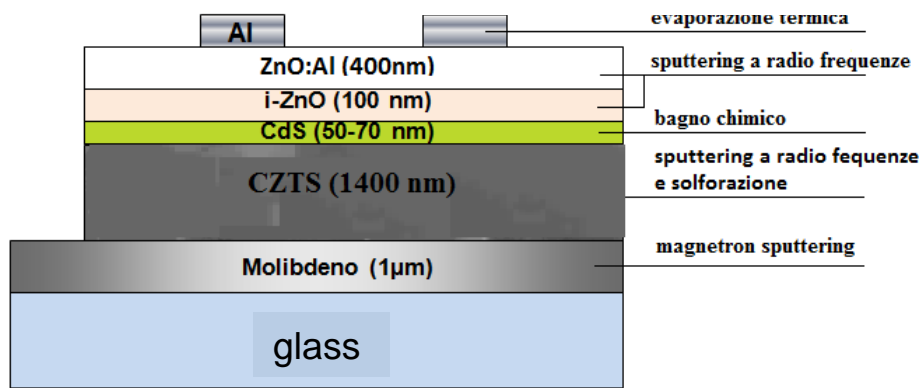
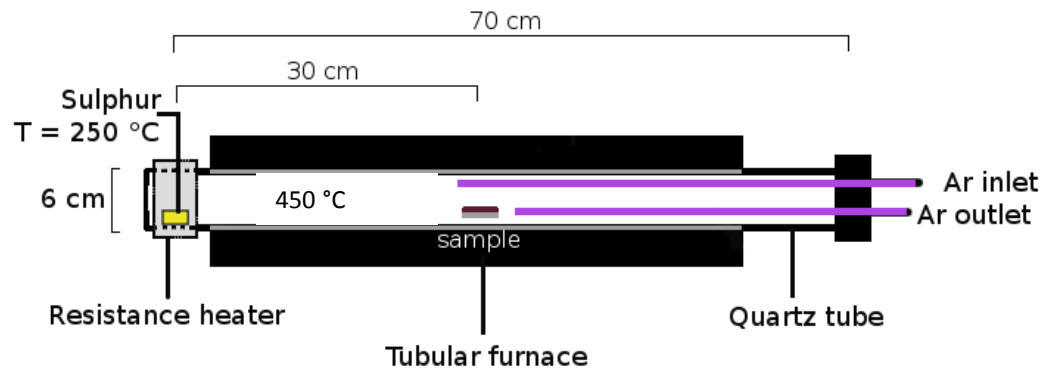
sputtering RF from Cu, Zn, Sn (5N) target on 5x2 cm² Mo coated soda lime glasses (SLG)

Mo back contact deposited by DC magnetron sputtering (1 μm thick)

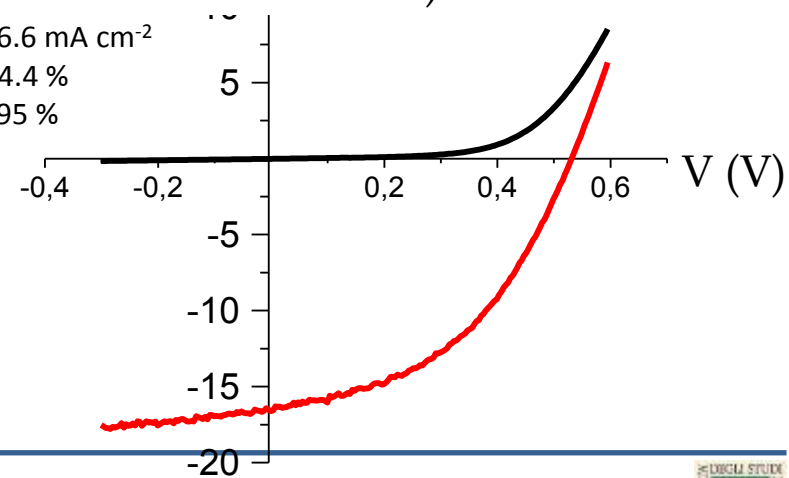
Working pressure

2 . Sulphurization process

- 0.5 – 0.2 g of S in graphite crucible @ 250 °C in
- Ar flow = 30-40 cm³/min
- T= 550 °C



$J_{sc} = 16.6 \text{ mA cm}^{-2}$
 $FF = 44.4 \%$
 $\eta = 3.95 \%$



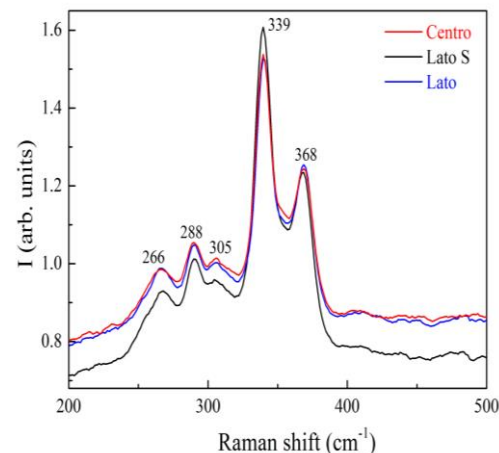
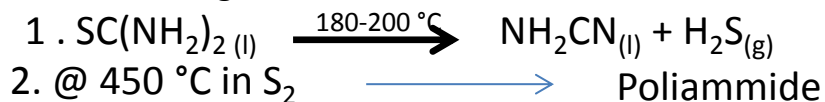
CZTS by chemical method

CZTS absorber layer via drop casting



Reagents	Solvents
$(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O} - 0.05 \text{ M}$	$\text{CH}_3\text{OH} (90\%)$
$(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O} - 0.025 \text{ M}$	$\text{OHCH}_2\text{CH}_2\text{OH} (10\%)$
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O} - 0.025 \text{ M}$	+ PVA (0.50 ml)
$\text{H}_2\text{NCSNH}_2 - 0.11 \text{ M}$	

Annealing



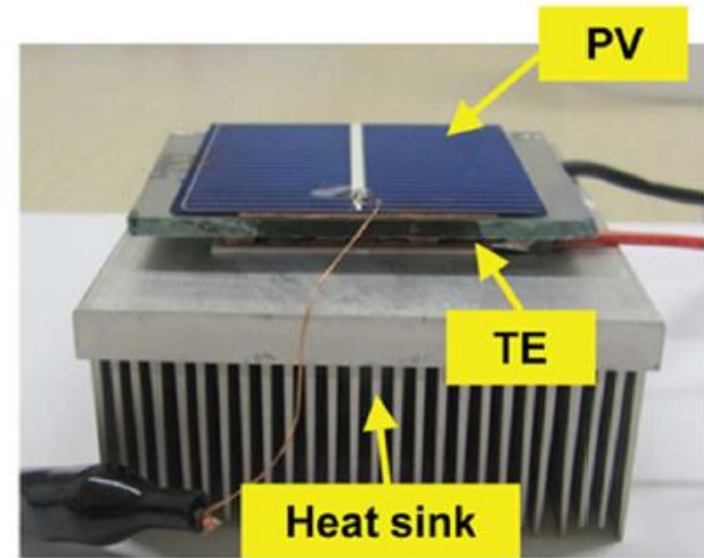
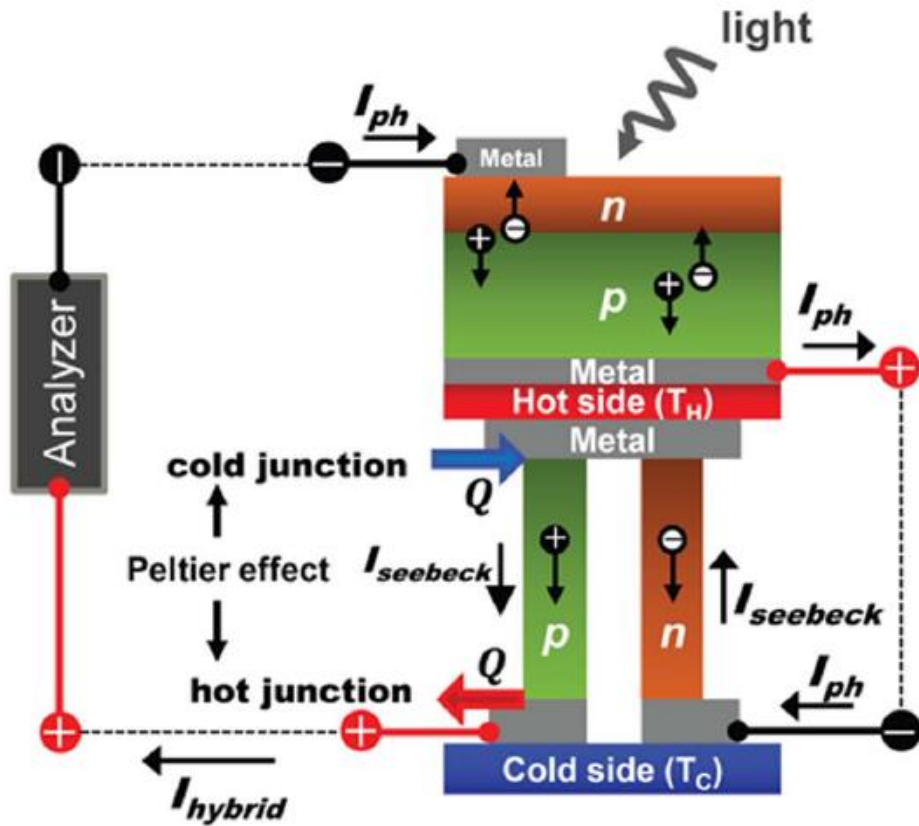
Problems

- Spurious phases
- High rugosity
- $\eta < 1\%$

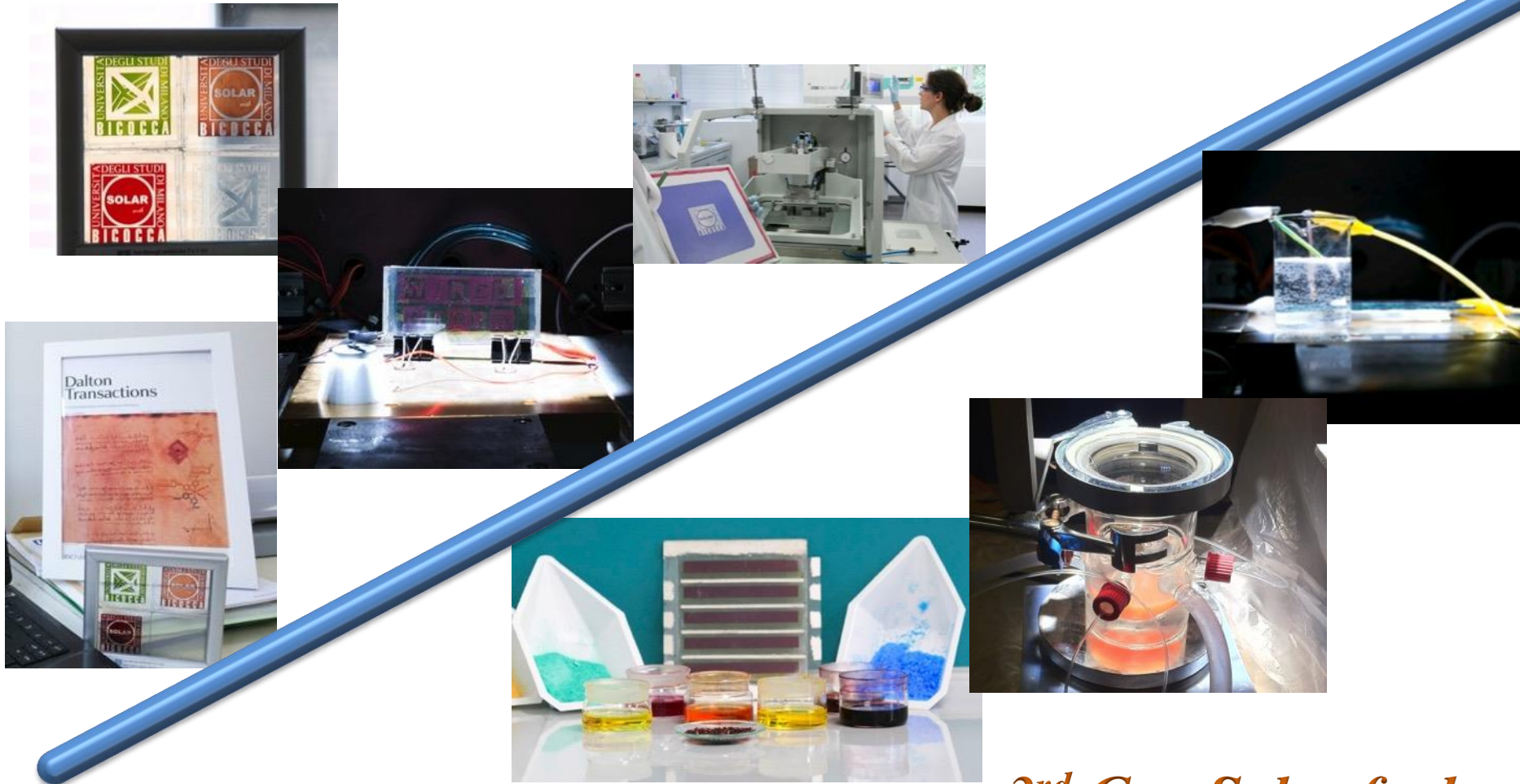
S. Tombolato, et al. Proceedings of 29th EUPSEC pp. 1829-1931 (2014)

Project “Grande Rilevanza -Energy and Environment-
 “Nuovi materiali con basso impatto ambientale per
 la fabbricazione di celle solari a film sottile” –
 Protocollo Esecutivo ITALIA-EGITTO

Thermoelectric Heat Recovery in Single Junction Solar Cells



3rd Gen PV devices (DSSC, OPV, PSC)



3rd Gen Solar fuels

DSSC Overview

PHOTOSENSITIZERS:

- I. Polypyridine and polyquinoline complexes (Ru^{II} , Ir^{III})
- II. Cyclometalated complexes
- III. Porphyrins
- IV. Metal-free organic dyes
- V. p-Type dyes
- VI. Perovskites (PSC)

ELECTROLYTES:

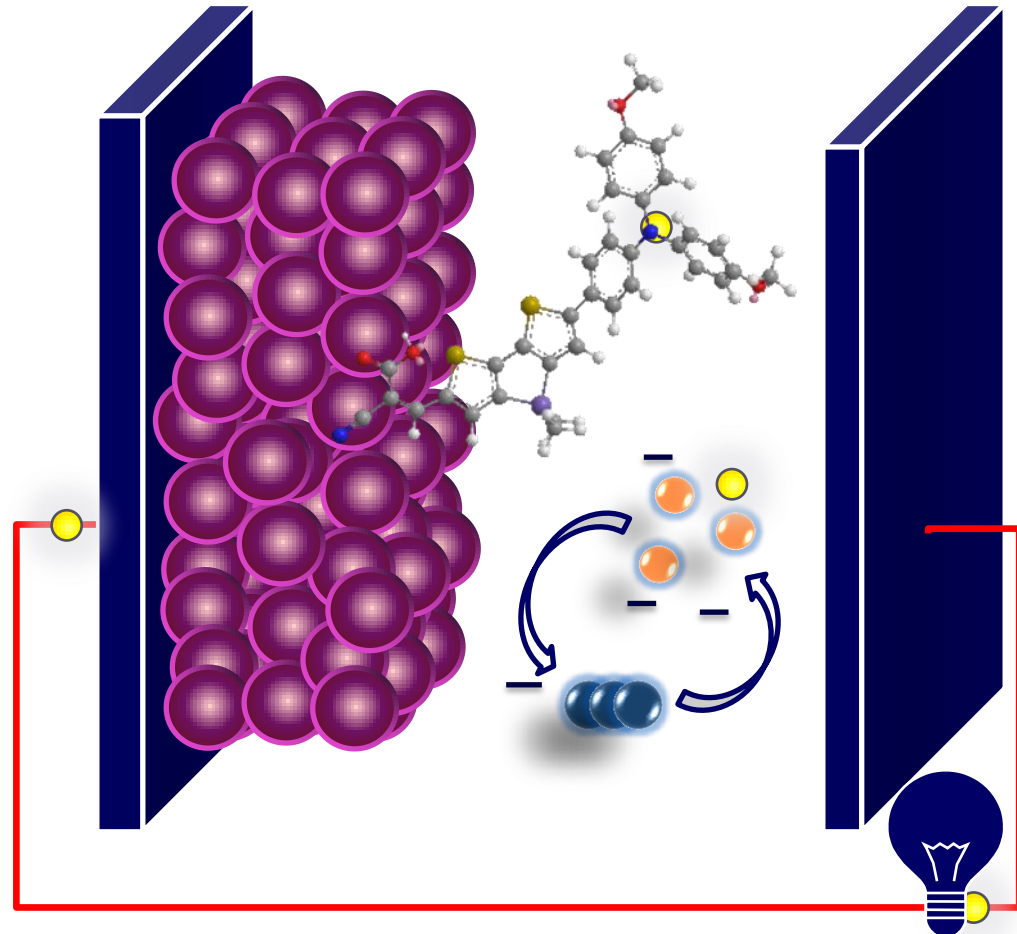
1. Iodine-free electrolytes
2. Quasi solid-state electrolytes

TiO_2 :

1. Hierarchical nanostructures
2. Dye-uptaking

DEVICE

1. Fabrication and Characterization
2. Cells and Modules
3. Hybrid technologies (Si-CIGS-DSSC-perovskites)



MULTIBRANCHED DYES: enhanced photocurrent

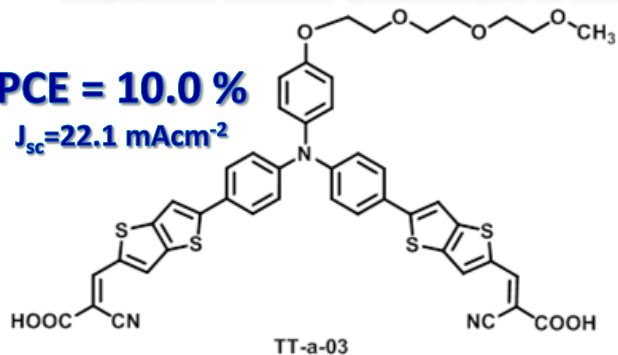
METAL-FREE ORGANIC DYES

In collaboration with



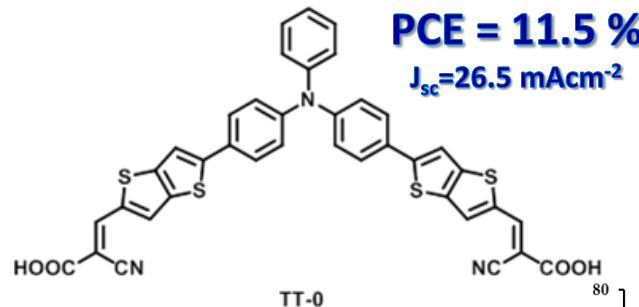
PCE = 10.0 %

$J_{sc} = 22.1 \text{ mA cm}^{-2}$



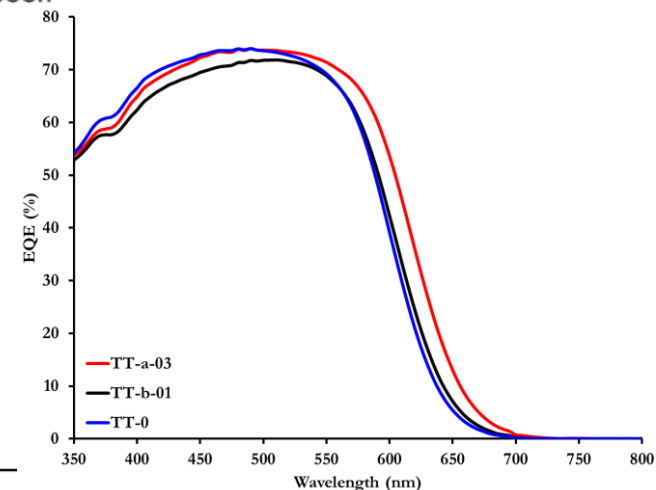
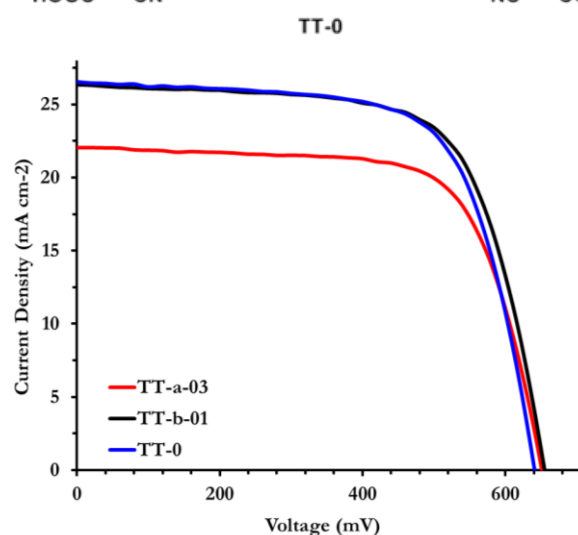
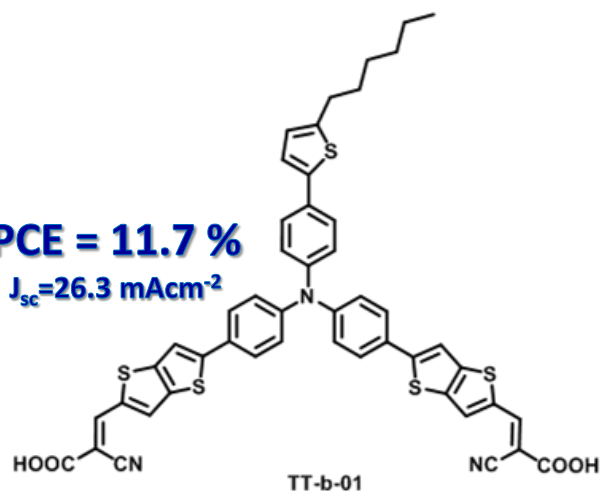
PCE = 11.5 %

$J_{sc} = 26.5 \text{ mA cm}^{-2}$



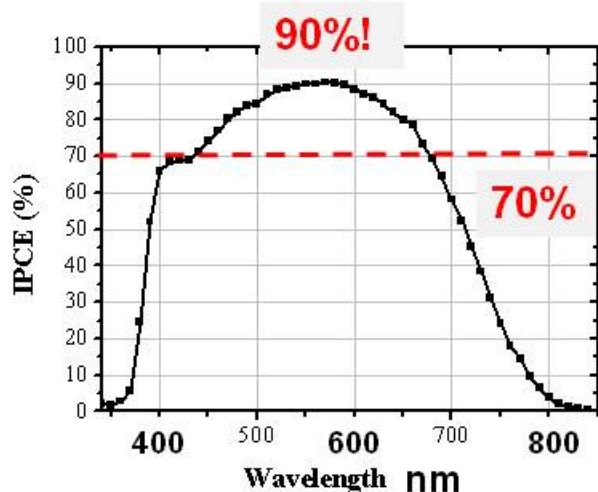
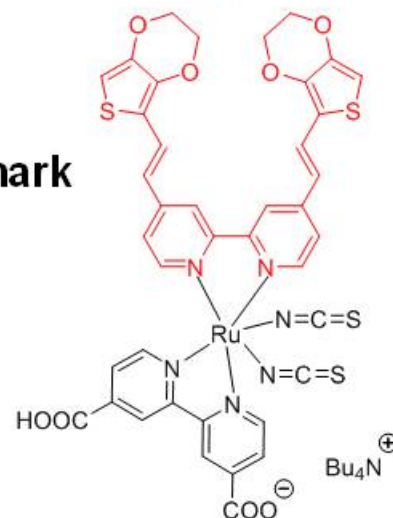
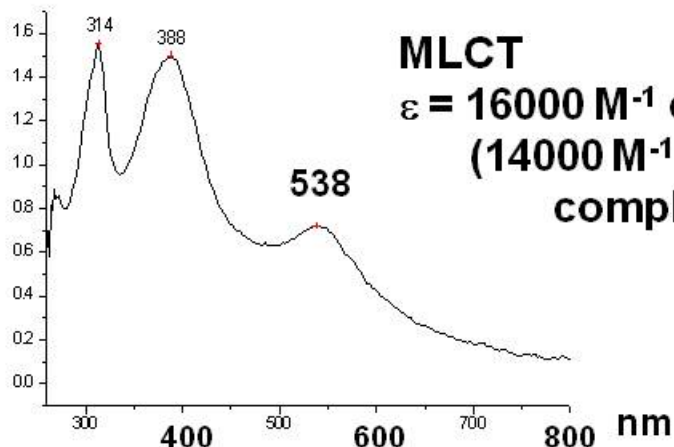
PCE = 11.7 %

$J_{sc} = 26.3 \text{ mA cm}^{-2}$



Abbotto, Acciarri, Biagini, Binetti, *PCT Int. Appl.* **2014**, WO 2014053626 A1 20140410.

DSSC record EQE with Ru(II) dyes



EXTERNAL QUANTUM EFFICIENCY
electrons out
photons in

(benchmark dye: max 87%)

Abbotto et al. *Chem. Commun.* 2008

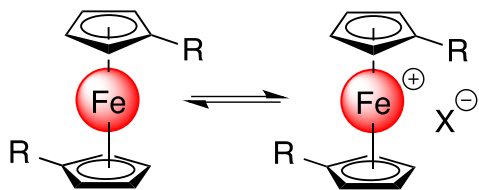
Branched organic dyes: evolution

Multi-Branched Multi-Anchoring Metal-Free Dyes for Dye-Sensitized Solar Cells

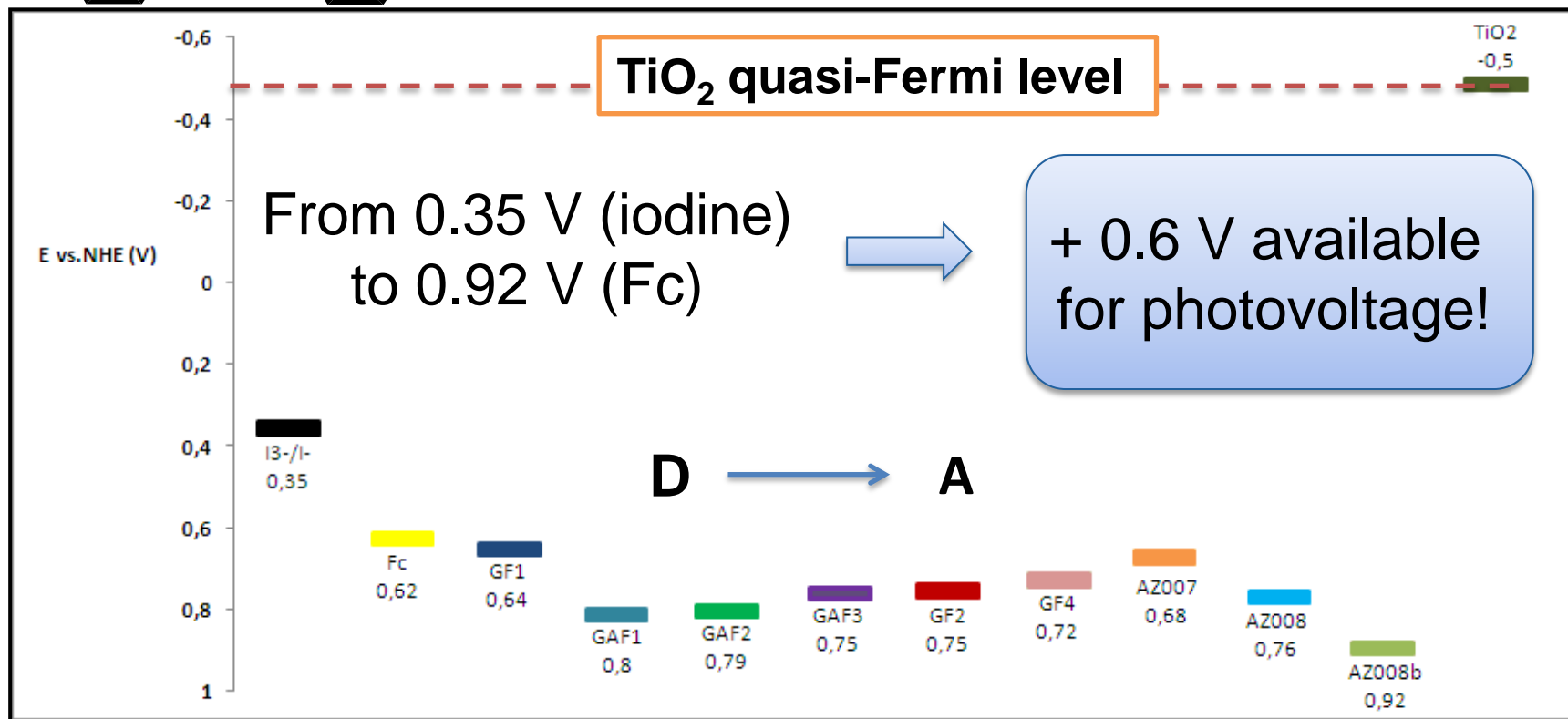
Norberto Manfredi,^{*[a]} Bianca Cecconi,^[a] and Alessandro Abbotto^{*[a]}

Keywords: Solar cells / Dyes/Pigments / Sensitizers / Energy conversion / Photochemistry

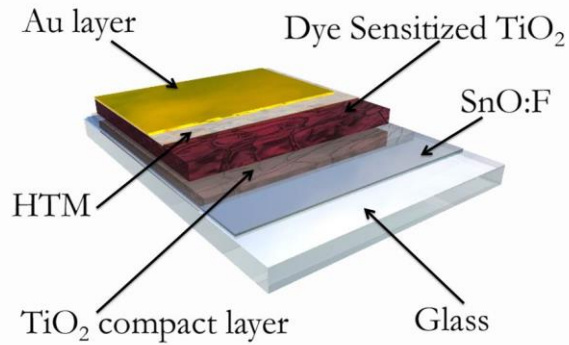
Iodine-free electrolyte



Redox potentials

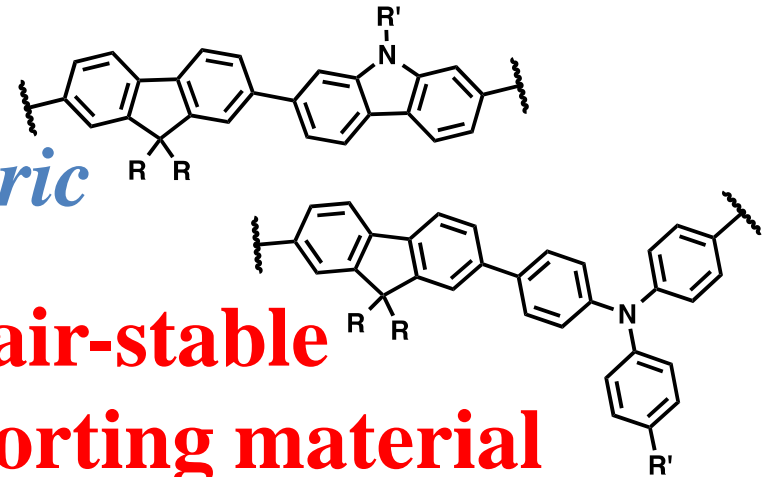


ssDSSC and PSC

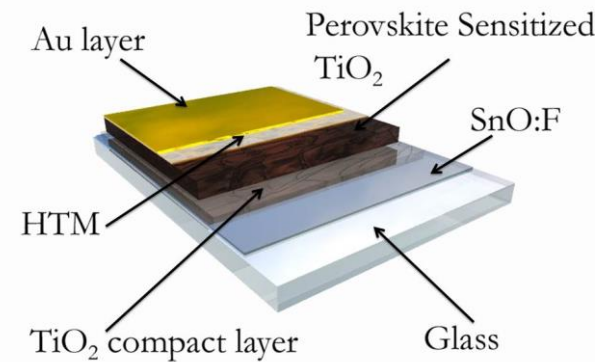
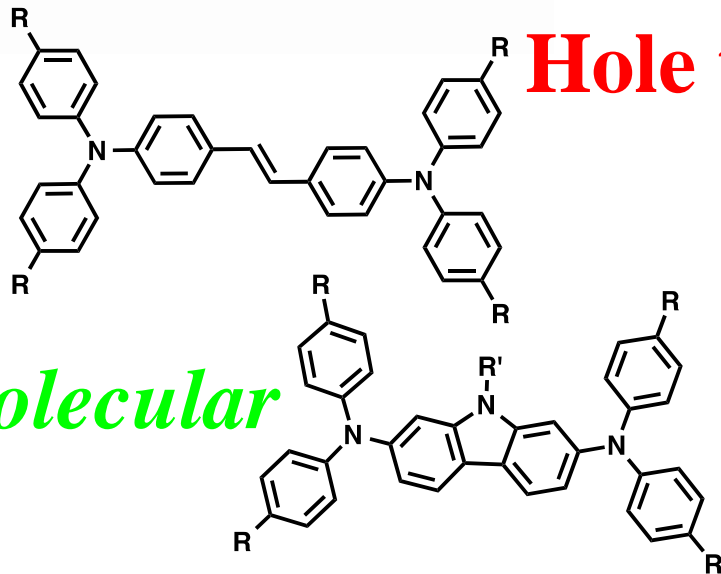


polymeric

**Novel air-stable
Hole transporting material**

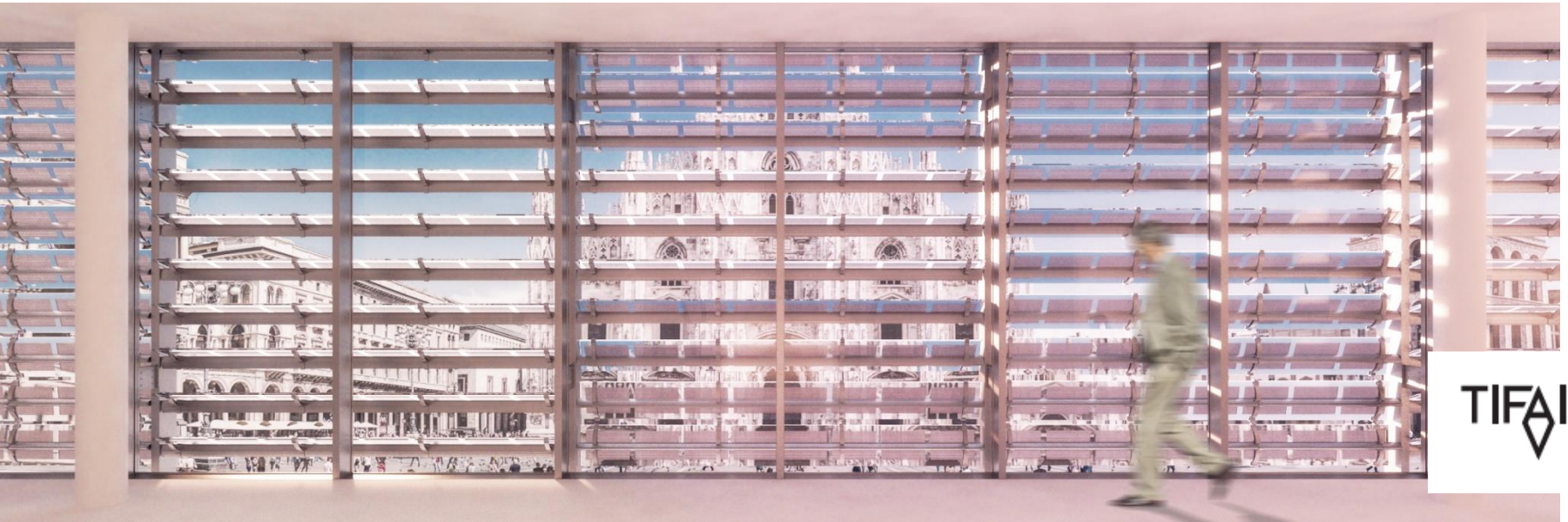


molecular

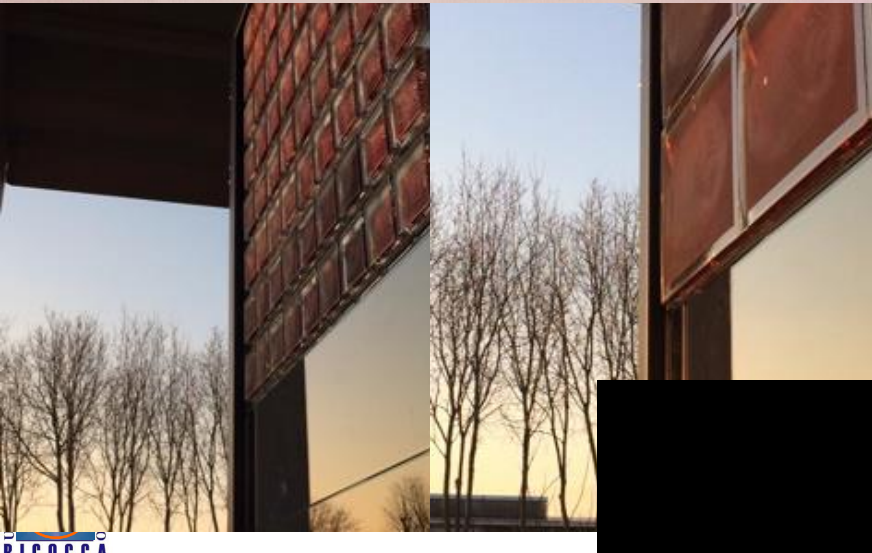


Building-integration PV (BIPV)

Integrated Photovoltaic Glass Tiles for Innovative Architectural Applications



TIFAIN



INDUSTRIA e
INNOVAZIONE

ENERGYGLASS
SOLAR & GLASS ARCHITECTURE

FLAME SPRAY

UNIVERSITÀ DEGLI STUDI
DI MILANO
BICOCCA



iit
ISTITUTO ITALIANO DI
TECNOLOGIA



Ministero dell'Inclusione
dell'Università e della Ricerca

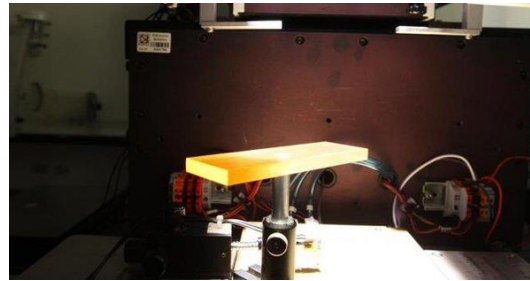
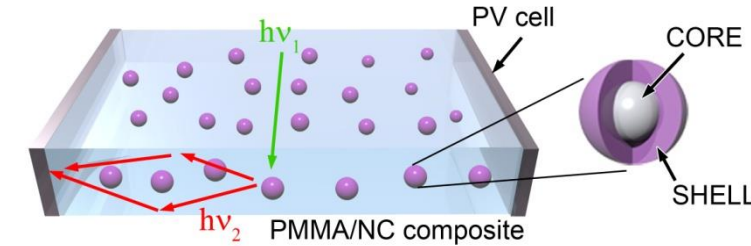
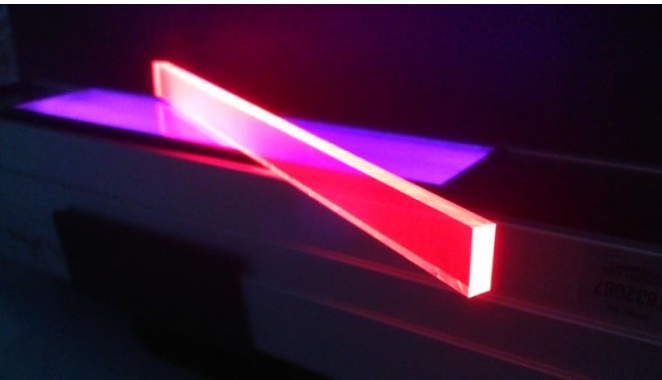
Regione Lombardia



Luminescent solar concentrators

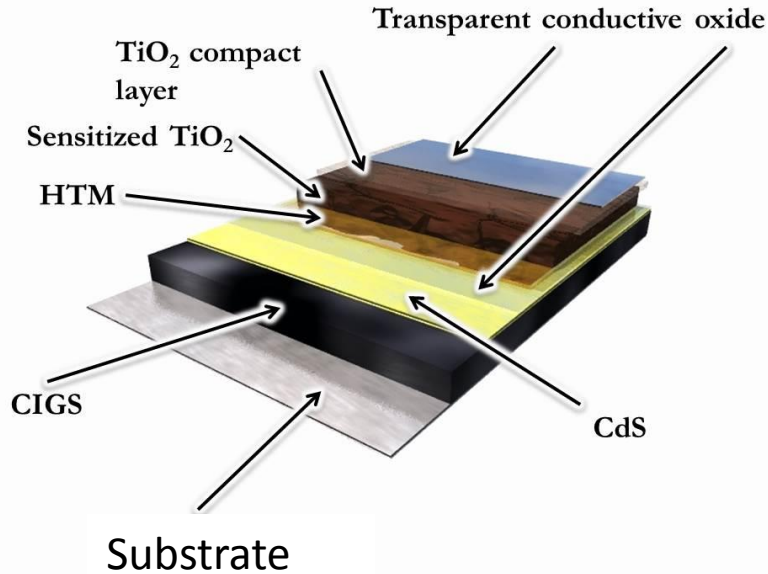
Prof. F. Meinardi and S. Brovelli group.

'Stokes-shift-engineered' CdSe/CdS quantum dots with giant shells (giant quantum dots) were used to realize luminescent solar concentrators without reabsorption losses for device dimensions up to tens of centimetres.

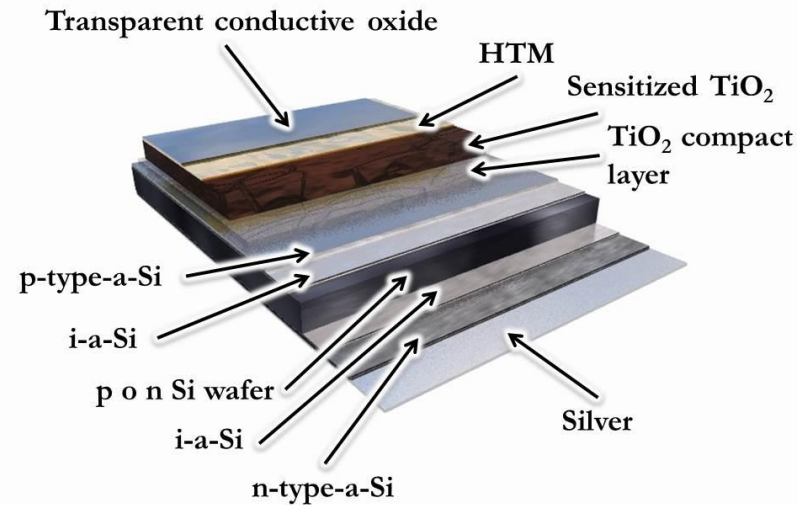


Study of these luminescent solar concentrators yields optical efficiencies $>10\%$ and an effective concentration factor of 4.4. These results demonstrate the significant promise of Stokes-shift-engineered quantum dots for large-area luminescent solar concentrators.

ss-Hybrid technologies



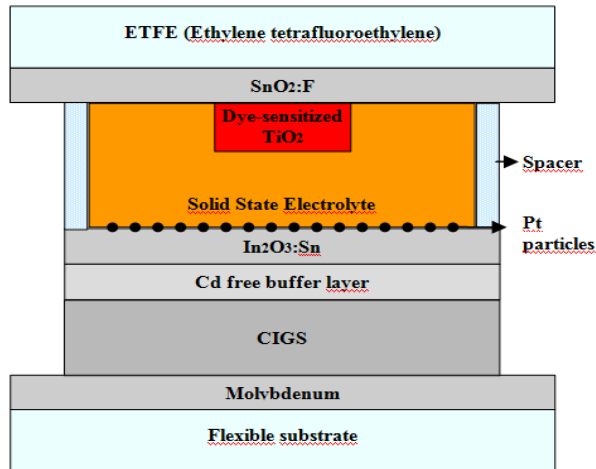
Monolithic solid state devices



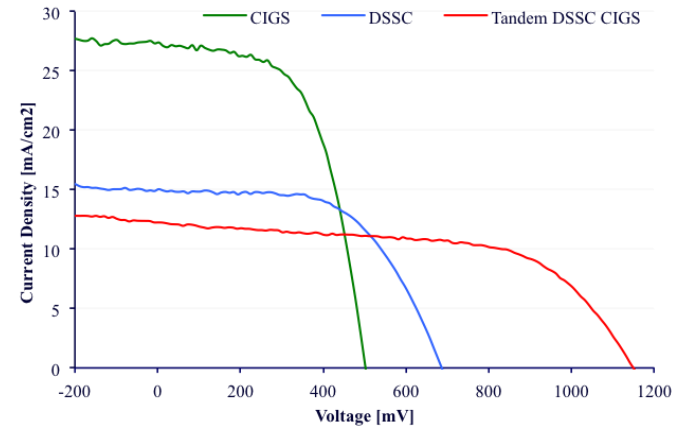
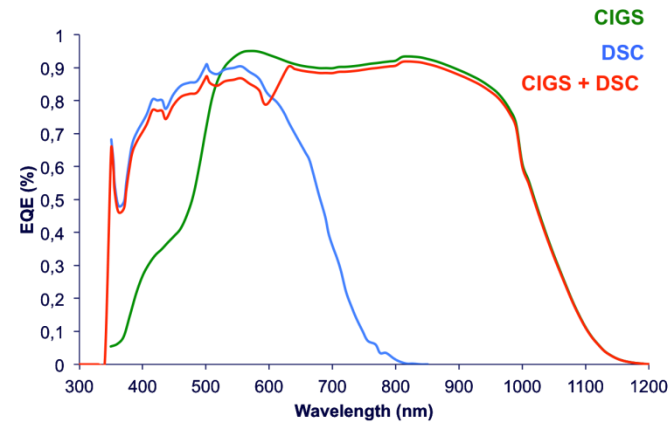
Target

- moderate scenario $\eta=17\%$
- optimistic scenario $\eta=21\%$

Hybrid technologies



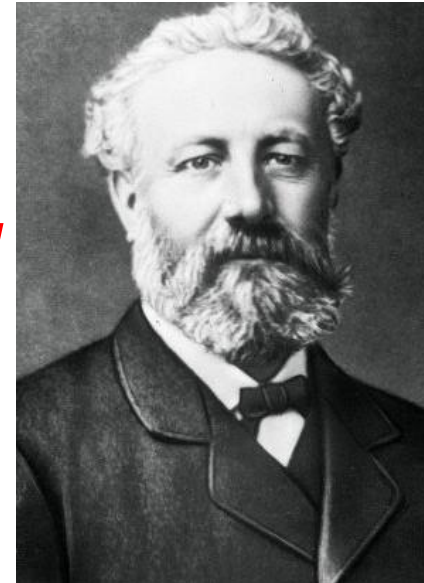
Type	PCE (%)
DSC	6.0
CIGS	7.1
DSC/CIGS	8.4



TOWARD HYDROGEN ECONOMY: SOLAR FUELS (?)

“water will be the coal of the future”

Jules Verne
The Mysterious Island
1874

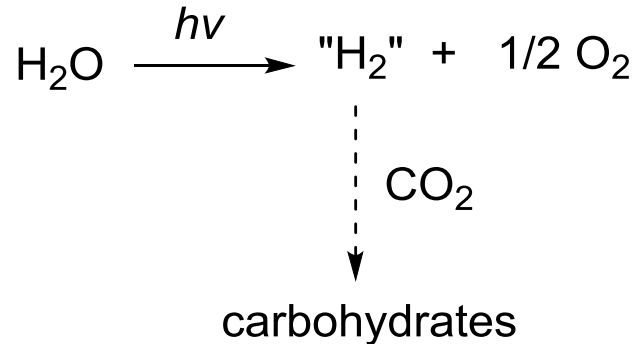


TOWARD A LOW-CARBON SOCIETY

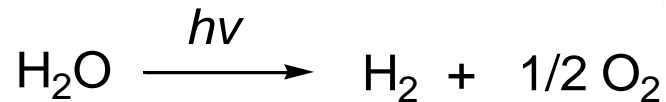


Forward the artificial photosynthesis

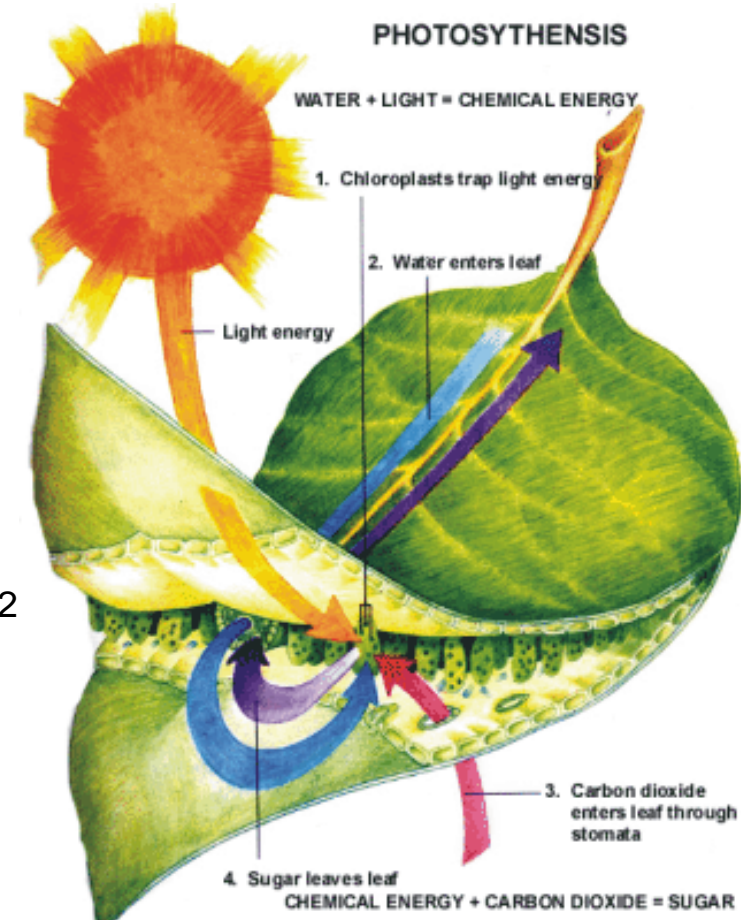
Natural
photosynthesis



Artificial
photosynthesis



The chemical challenge:
High transformation efficiency from electron to
hydrogen



Clean sources of Water Splitting

2-step

1-step



**ARTIFICIAL
PHOTOSYNTHESIS**

electrical power

integrated device
(PEC, photocatalysis)

too
expensive!

PV-driven
electrolysis

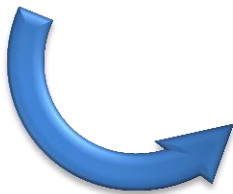
cheaper but low
currents!



Towards artificial photosynthesis



**Dye-Sensitized
Solar Cells**

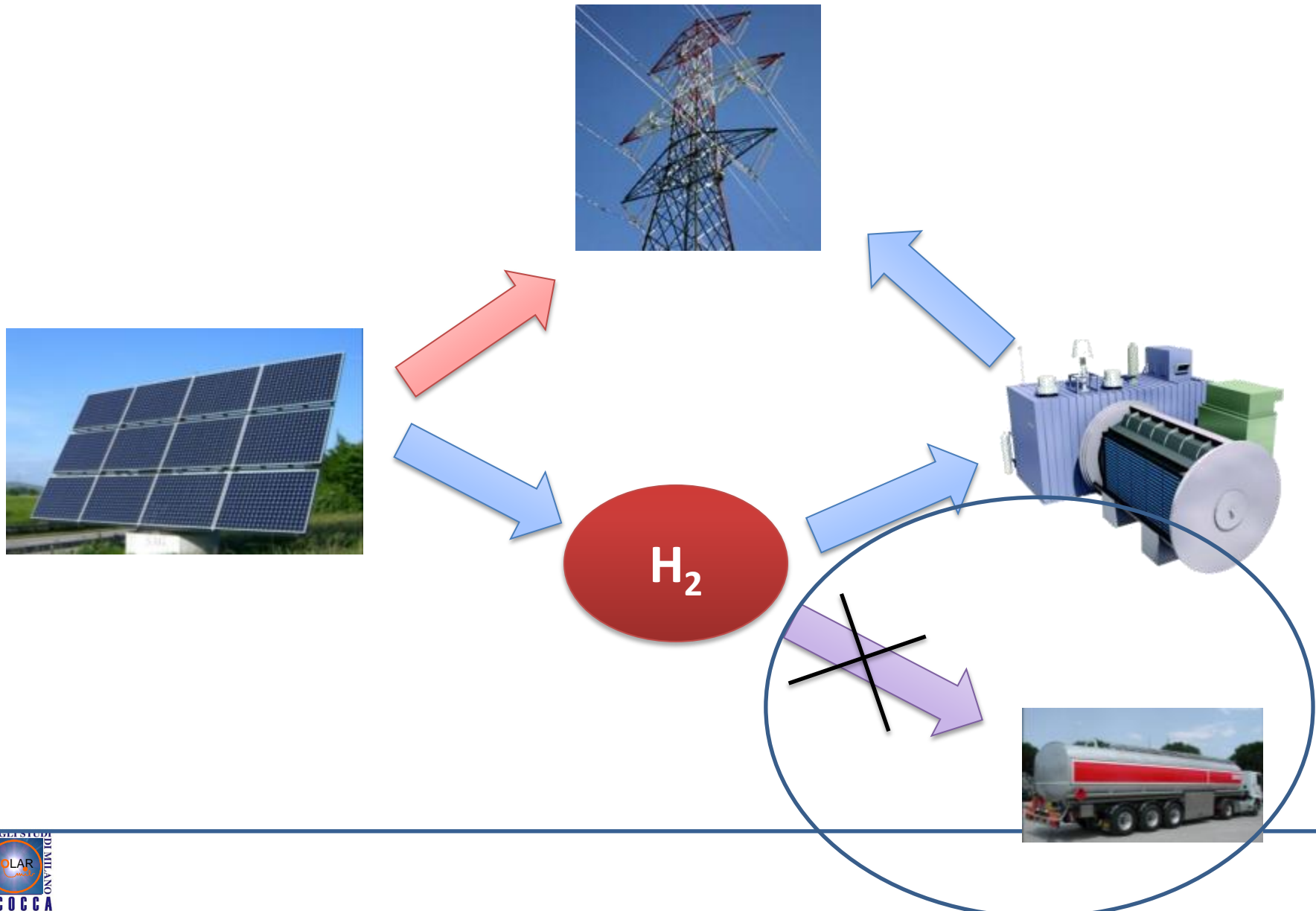


**Water electrolysis
through DSC**

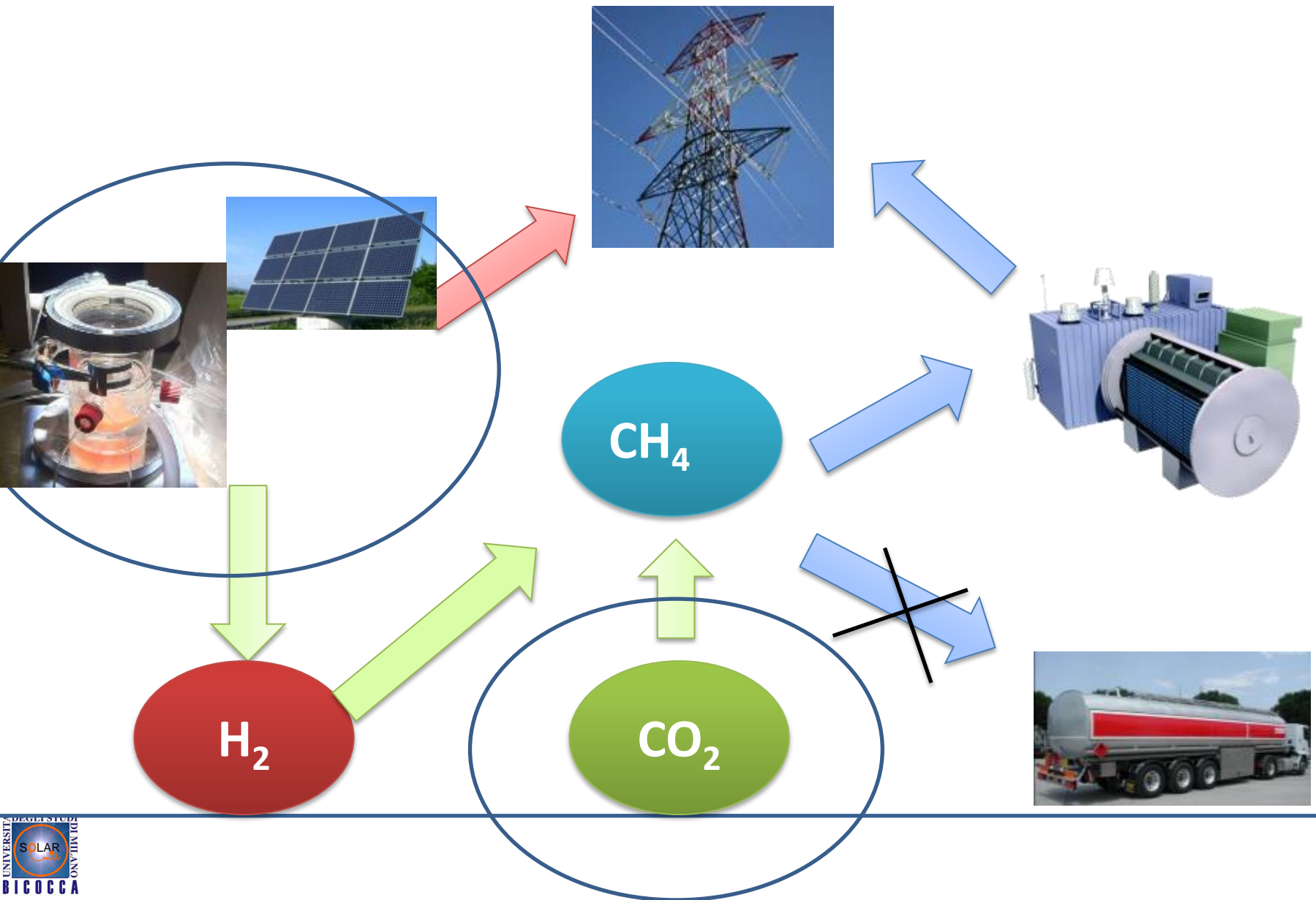


**Water Splitting
with Solar Energy**

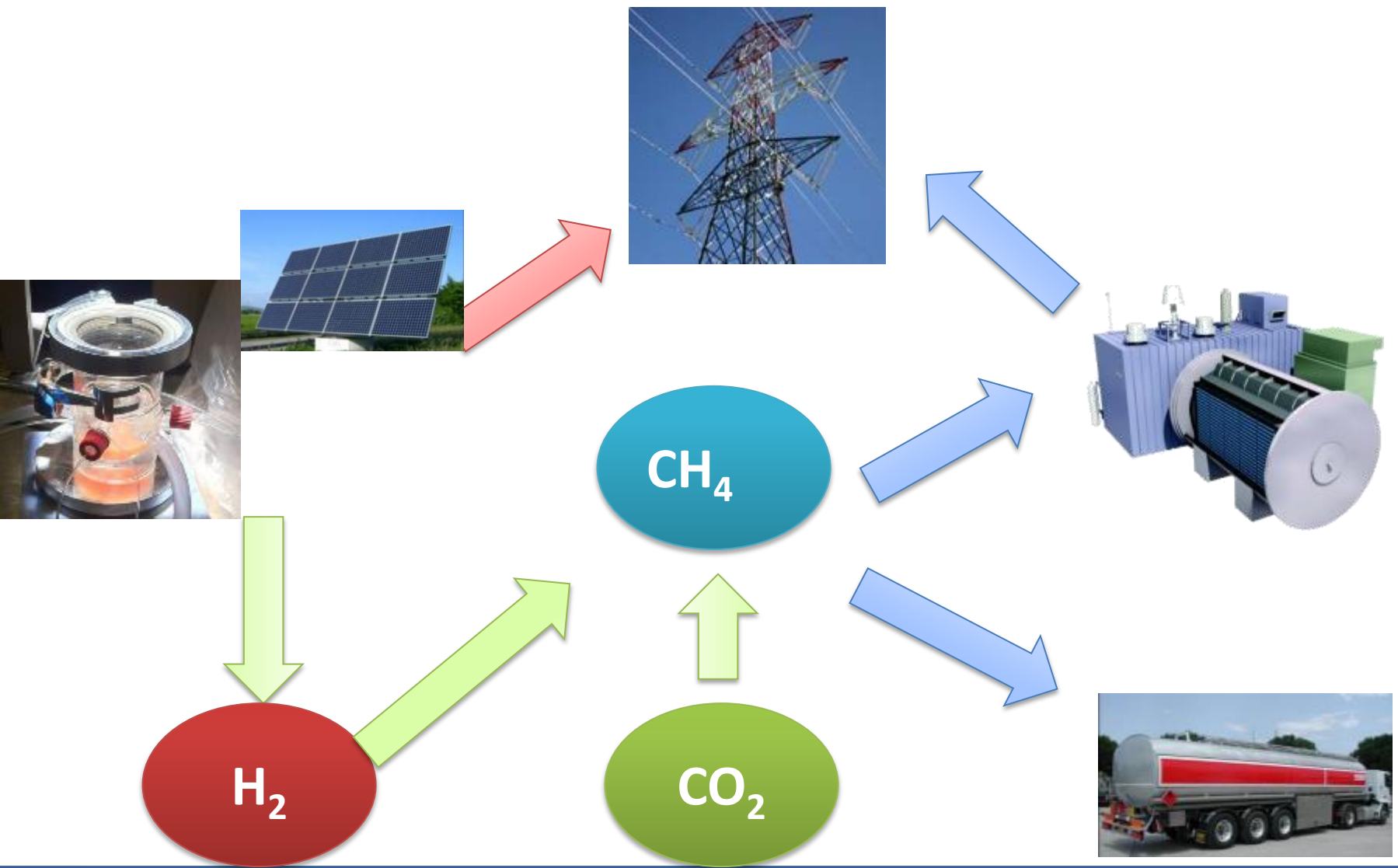
Energy store



Energy store

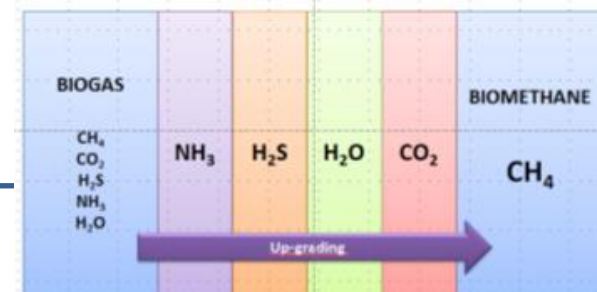


Energy store



Upgrading technologies

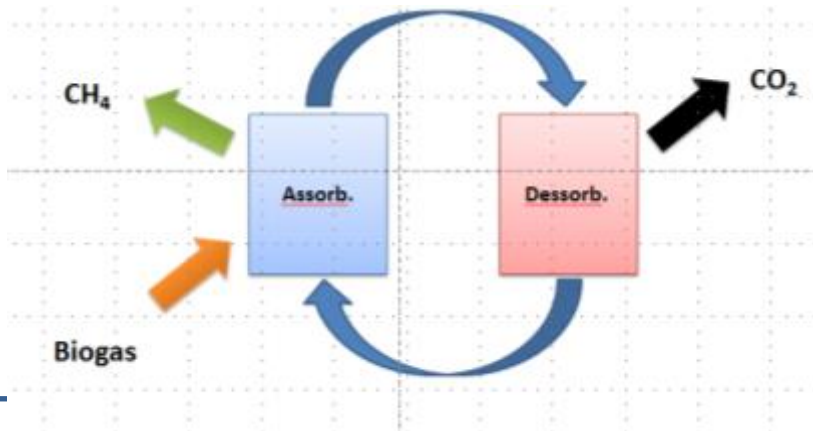
- Upgrading of **biogas** or landfill gas to **biomethane** is defined as removal of carbon dioxide from the biogas.
- This will result in an increased energy density since the concentration of methane is increased to up to 95%.
- Several technologies for biogas upgrading are commercially available and others are at the pilot or demonstration level.



Smart upgrading

Principal phases of our process:

- absorption CO_2 in the **solvent** in the cold column
- Solvent heating for the CO_2 release (temperature below 75°C)
- CO_2 collection and solvent regeneration in the hot stripping
- Solvent cooling
- Solvent reintroduction in the cold absorption column



Solvent based on Ionic liquid

- no toxic
- low cost

2016: Industrial production plant under pianification



Lab scale 1 m³/h
2012

pilot scale 100 m³/h
2014



Pre-Industrial scale
2015

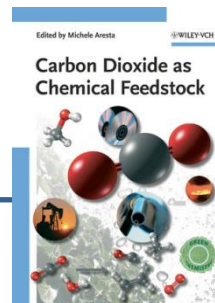


Presso CEM Ambiente Cavenago (MB)

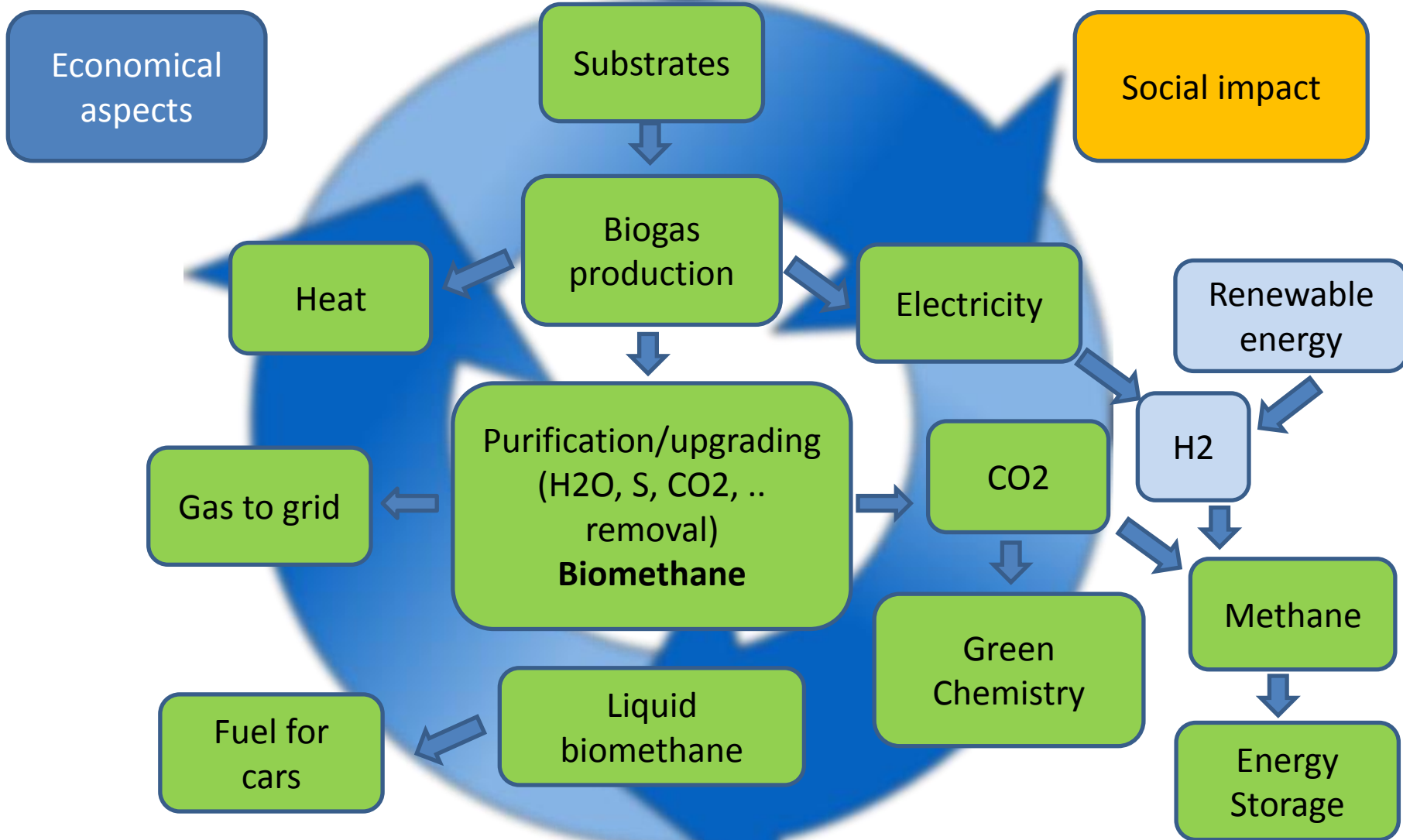
Biomethane and CO₂: energy storage and “sequestration”

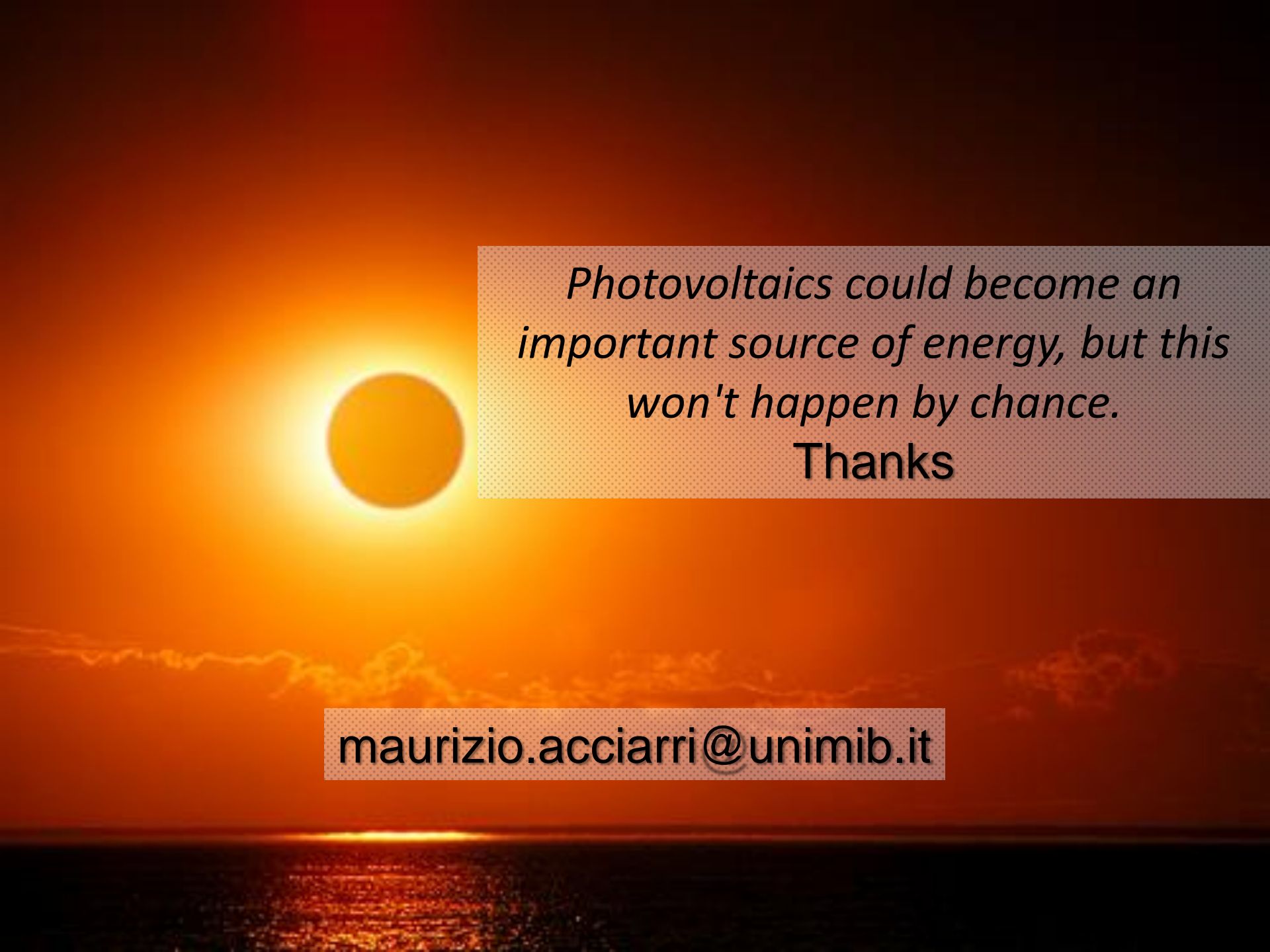


- Biogas produced through anaerobic digestion is often used as a source of combined heat and power (CHP).
- **For use as a transport fuel** as well as **for natural gas grid injection**, biogas must be cleaned and upgraded to typically greater than 97% methane content (then known as biomethane).
- Another advantage is that the biomethane can be used to generate electricity in combined cycle gas turbines that can produce electricity from methane with efficiency above 60%.
- CO₂ can be easily accumulated ... and CO₂ **is ready to go as a fuel and chemical feedstock** (Electrolysis, Artificial leaves, catalytic water splitting, CO₂ reduction, Biotechnology)



Biogas an example of Circular Economy



A sunset scene with a large, bright sun on the left side of the frame. The sky is a gradient of orange and yellow, with some wispy clouds near the horizon. The sun's reflection is visible on the dark water in the foreground. A semi-transparent, light-colored rectangular box with a fine dot pattern is positioned on the right side of the image, containing text.

Photovoltaics could become an important source of energy, but this won't happen by chance.

Thanks

maurizio.acciarri@unimib.it