



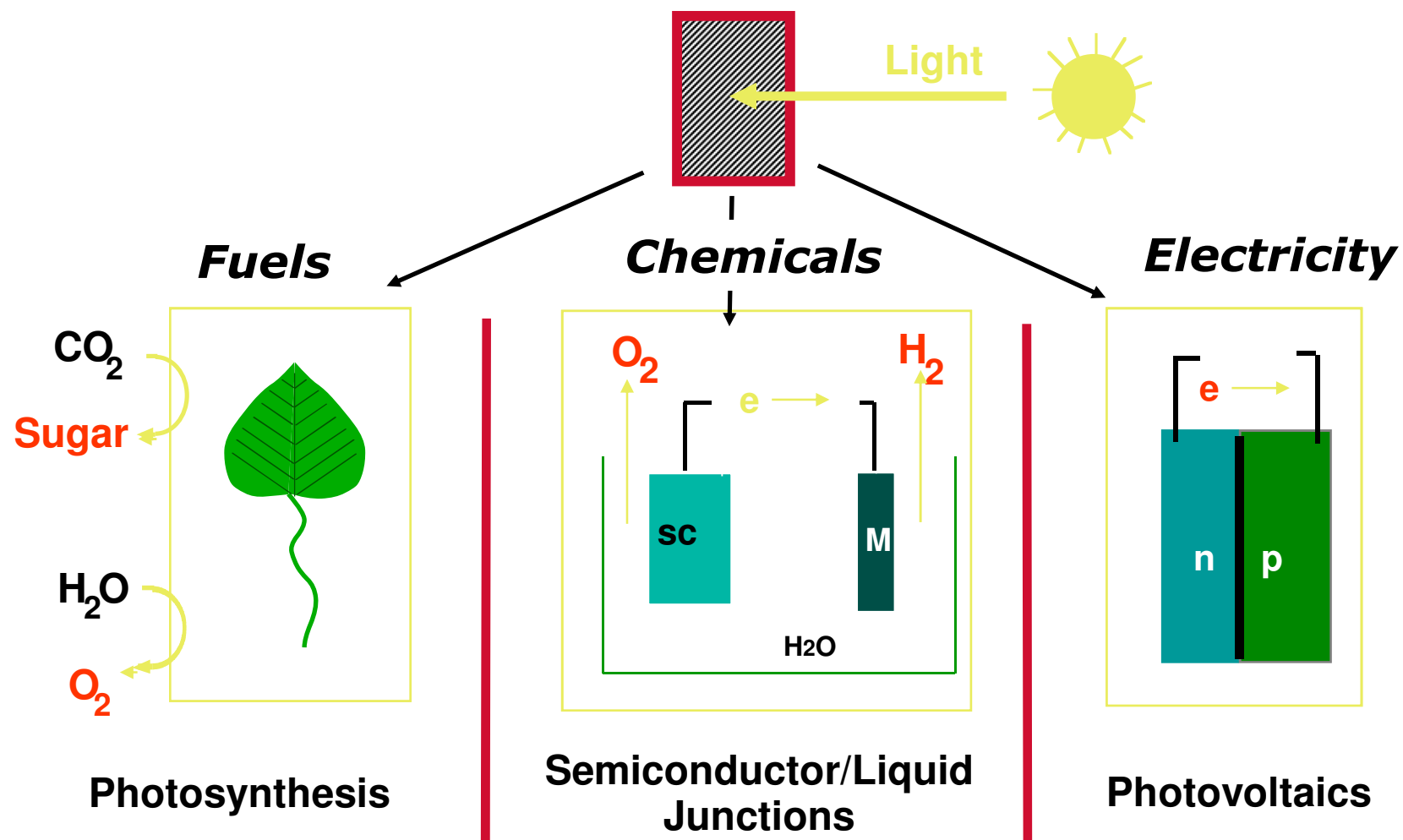
Solar Hydrogen Generation For Energy Storage

Fabio Oldani
Istituto eni-Donegani
Via Fauser 4, Novara
fabio.oldani@eni.com

www.eni.it

Roma, 24 Aprile 2013

Solar Energy Conversion Strategies



eni

[N.S. Lewis, D.G. Nocera, *Powering the Planet*, Proc. Nat. Acad. Sci. USA 103 (43) 2006, 15729]

Possible applications of photosplitting technology

- **Electricity** : solar H_2 in fuel cell to generate electricity off-grid
- **Environment** : photo-redox reactions of wastewater
- **Fuels** : reaction of H_2 with CO_2 to fuels
- **Automotive** : addition of H_2 to CH_4 in vehicles to decrease emissions

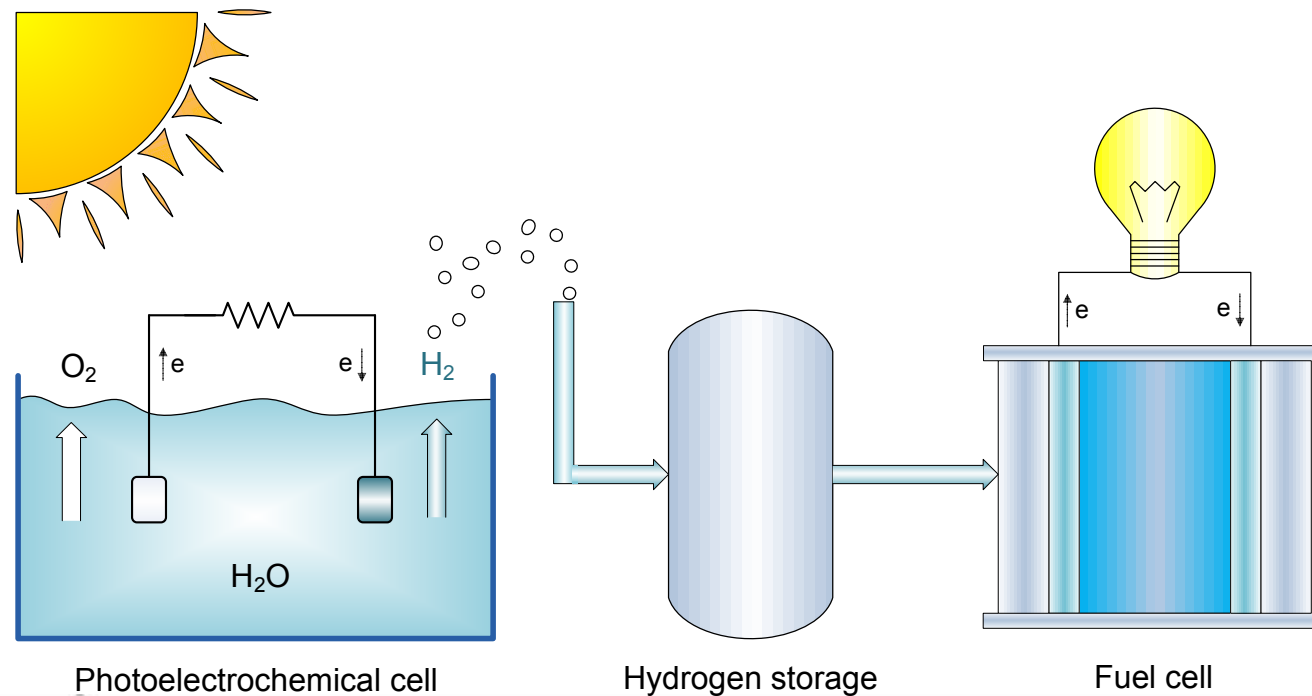


eni

Solar Hydrogen in a PEC cell

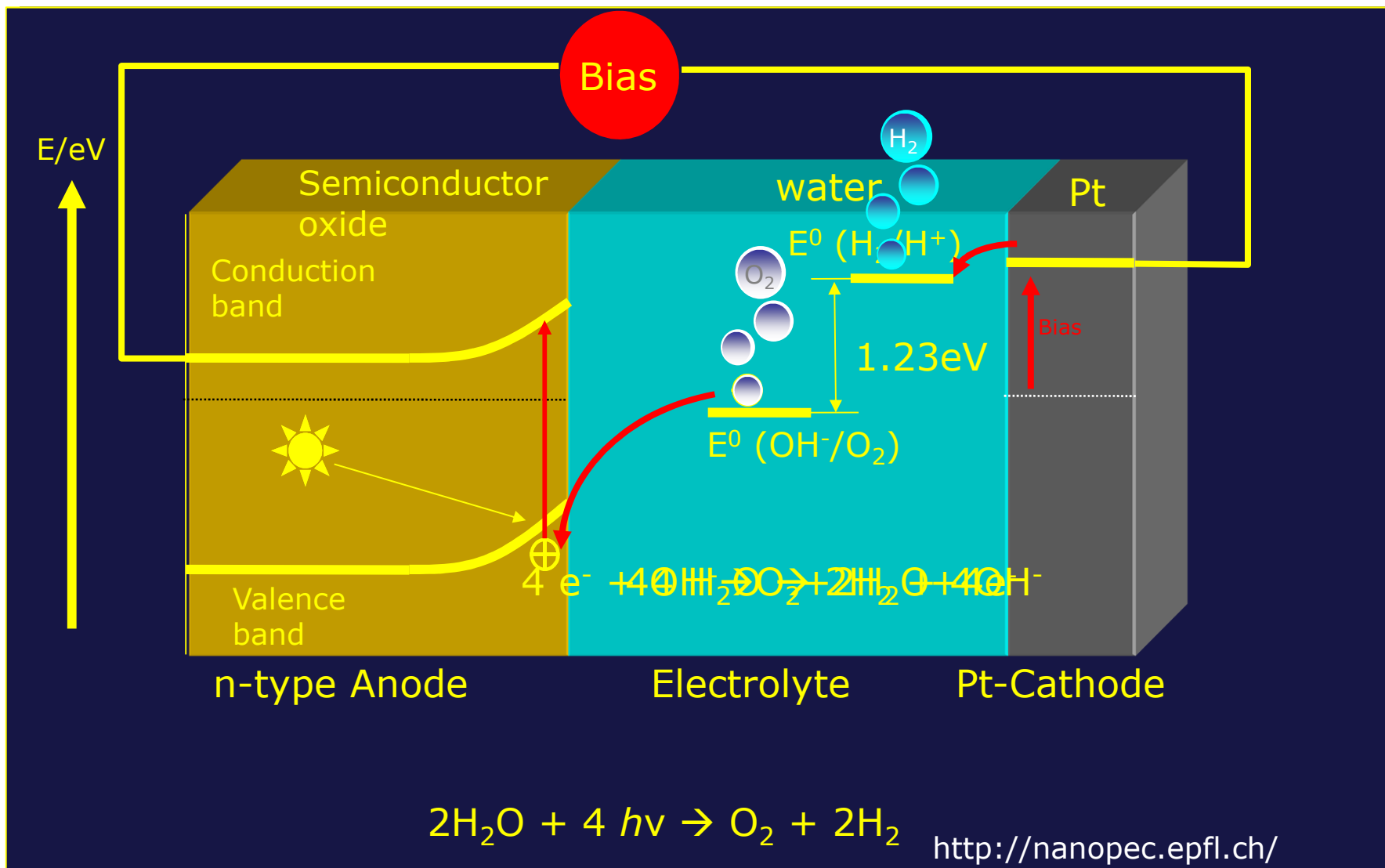
*Solar Hydrogen can store energy and react with CO₂ to produce fuels.
Solar Oxygen can be used for oxidative reactions.*

*Aim of this research are **lower production cost** and **improved efficiency**.*



eni

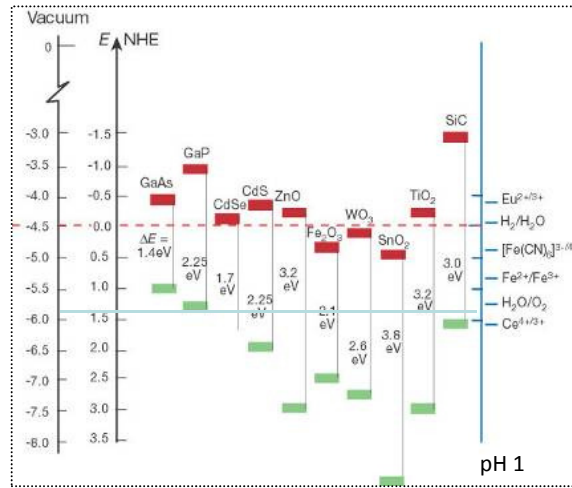
Energetic diagrams



eni

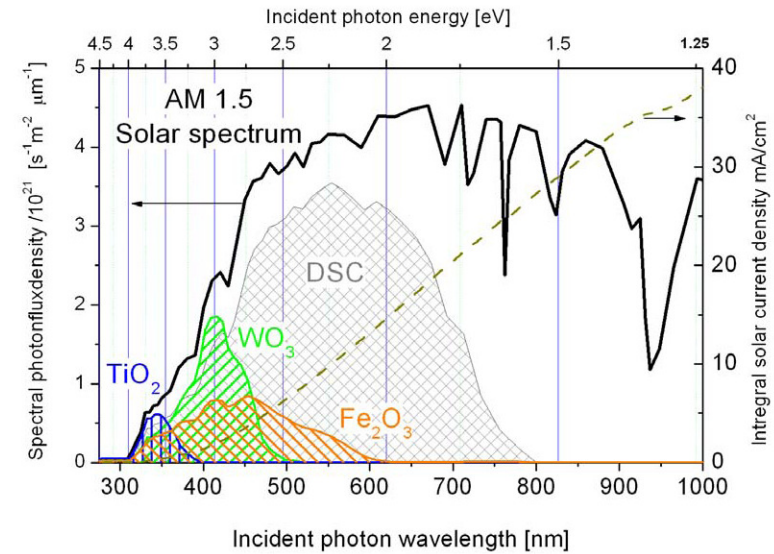
Semiconductor Candidates

[M. Gratzel, Nature 414 (2001) 338]



Low bandgap
 → Good harvesting;
 → Scarce stability

High bandgap
 → Scarce harvesting;
 → Good stability



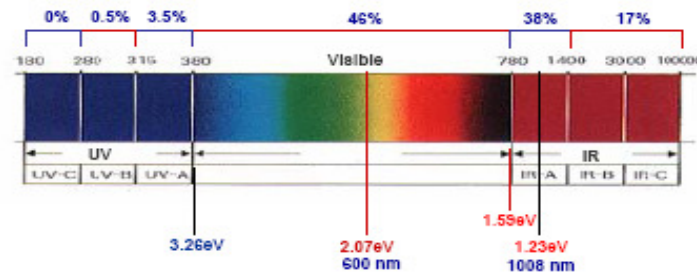
Thermodynamic request

1.23 eV

Kinetic losses & overpotentials

$E_g > 2 \text{ eV}$

Solar Light Spectrum



[K. Rajeshwar, J. Appl. Electrochem.37 (2007) 765]

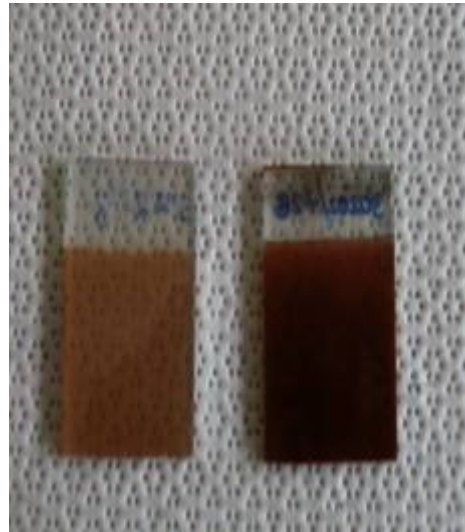
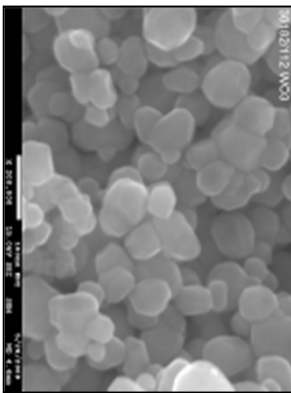


eni

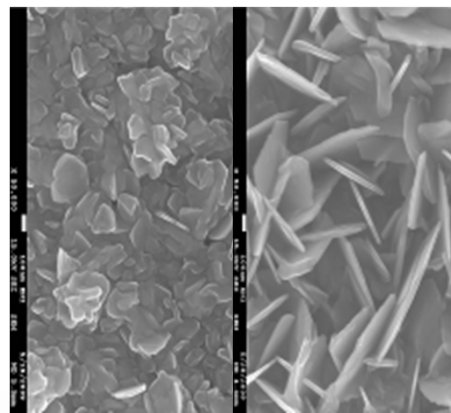
Nanostructured Photo-electrodes



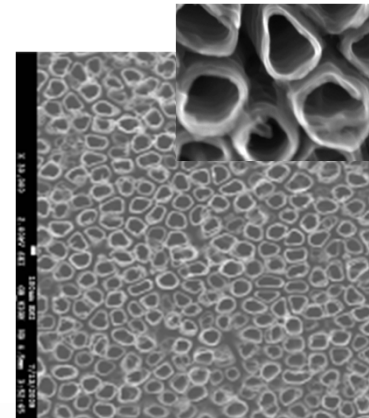
WO₃ – solgel
Xstal domains 20-80 nm
Area max. 100 cm²



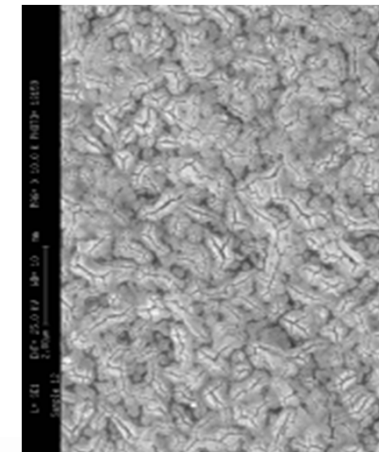
Fe₂O₃ + Ti –spray
Xstal domains 20-60 nm
Area max. 100 cm²



TiO₂ -anodic
Xstal domains 20-80 nm
Area max. 150 cm²



WO₃ -anodic
Xstal domains 20-100 nm
Area max. 150 cm²

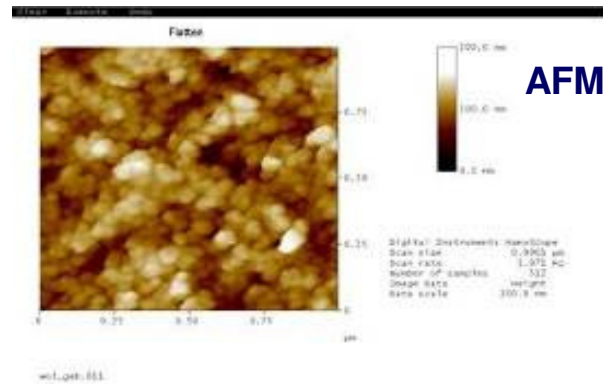
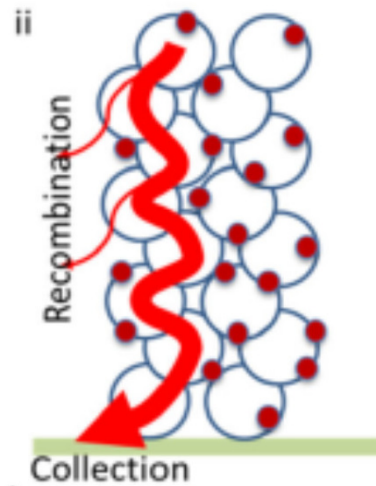


eni

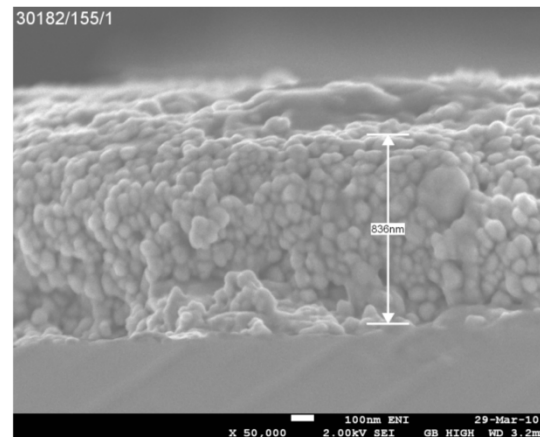
Sol-gel nanostructures



10 x 10 cm²

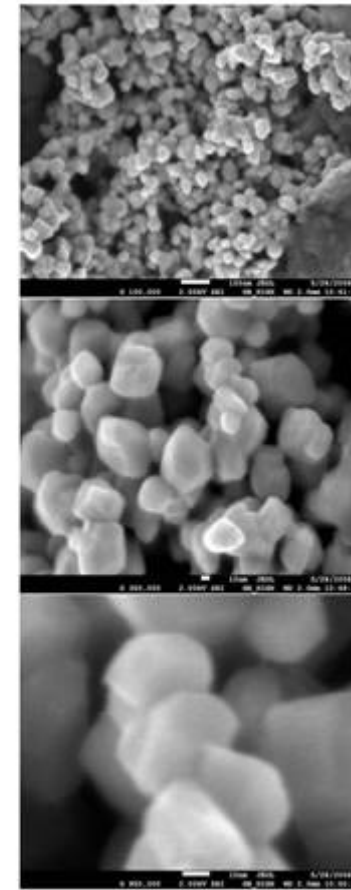


AFM



*From tungstate salts to acidic solution
+ colloidal dispersion and gelification
+ blade deposition on conductive glass (FTO)
+ final calcination (450 ° C – 650 ° C)*

SEM

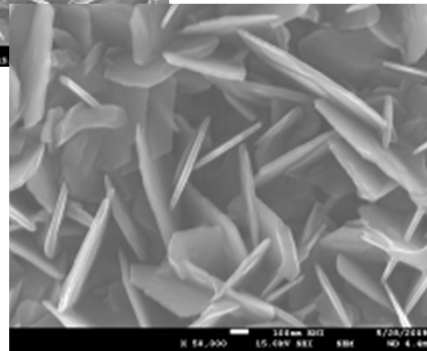
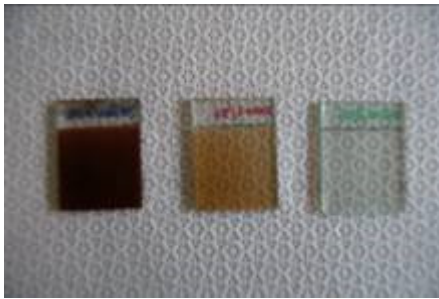
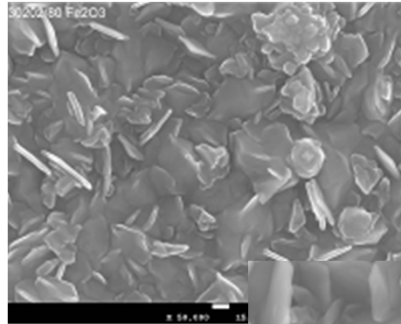


eni

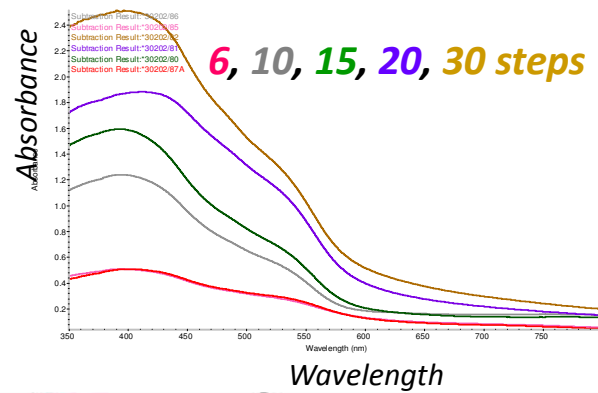
[L. Meda, G. Tozzola, A. Tacca, G. Marra, et al, SOLMAT 94 (2010) 788]

Spray deposited Nanostructures

Fe₂O₃ + Ti 5%



***Solutions sprayed on FTO
at high temperature (> 400 ° C)***

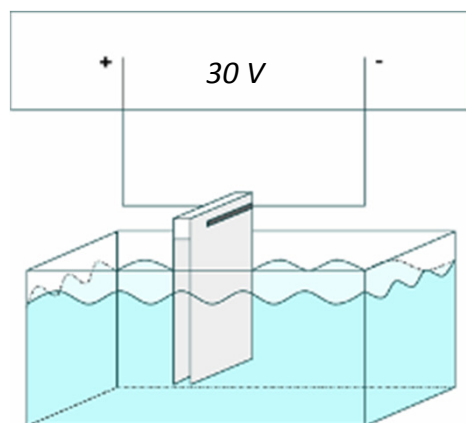


Photoanode on FTO

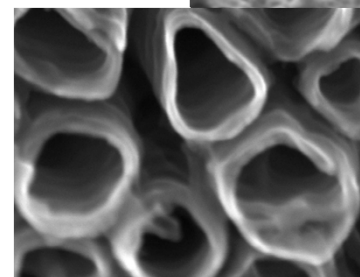
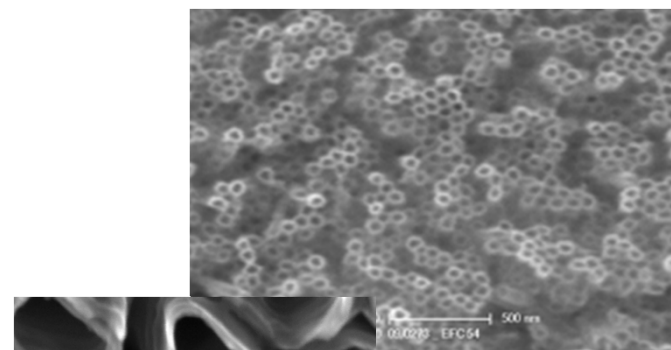


eni

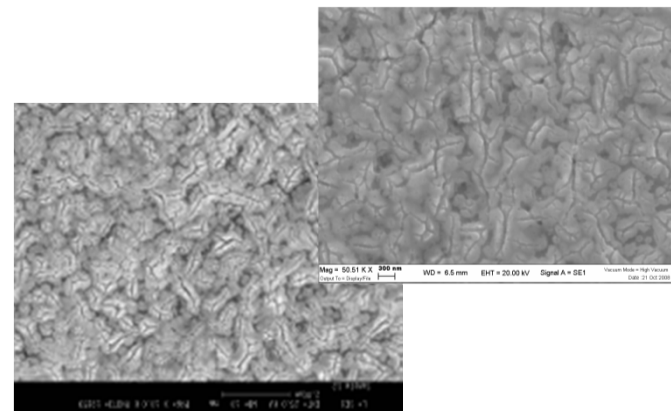
Electro-anodized nanostructures



*Ti: EG + NH₄F, RT
+ calc. 500 ° C*



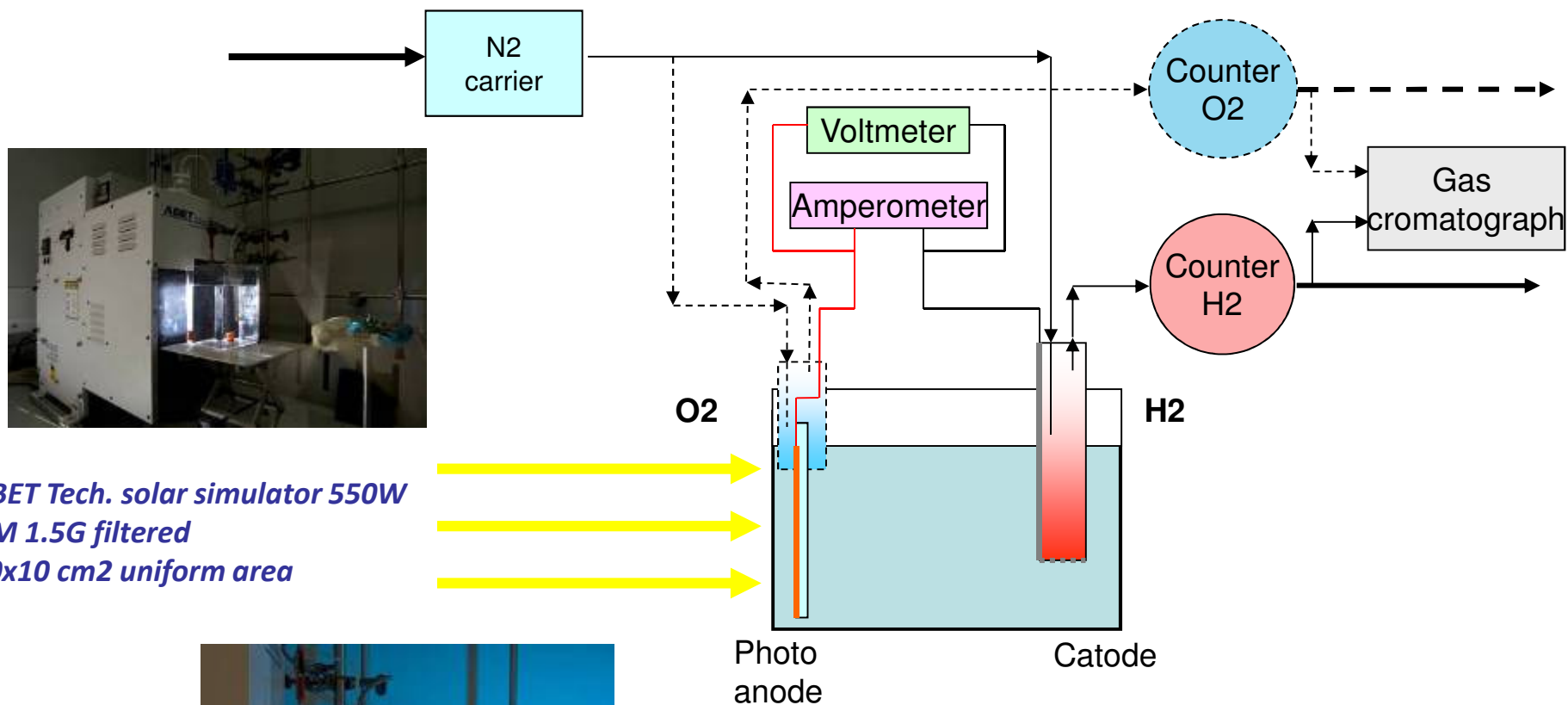
*W: H₂O + NMF + NH₄F, 40
° C
+ calc. 500 ° C*



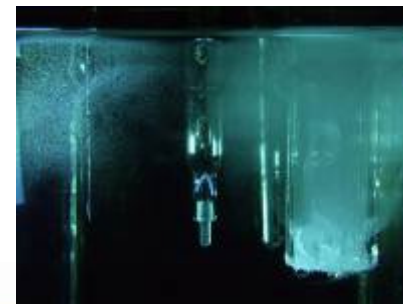
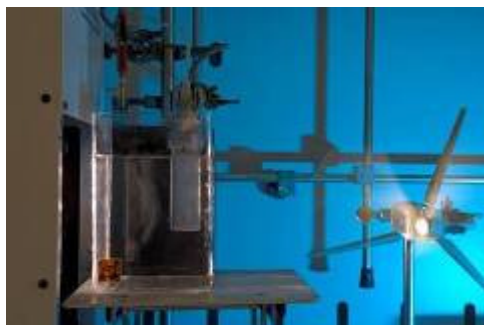
eni

S. Caramori, V. Cristino, C.A. Bignozzi, L.Meda, *Topics in Current Chem.* Vol. 303 (2011) 215

Current-voltage measurements and gas collection under solar simulated illumination

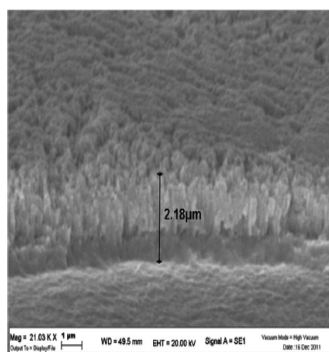
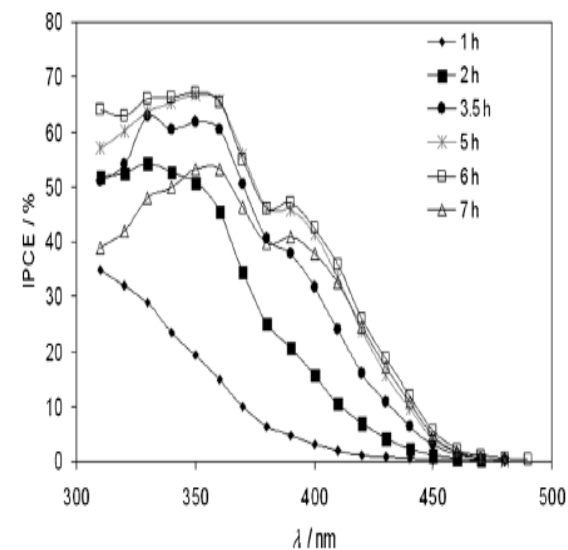
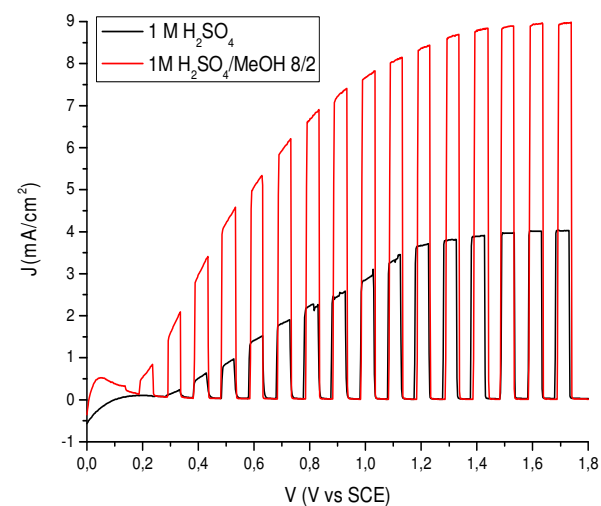
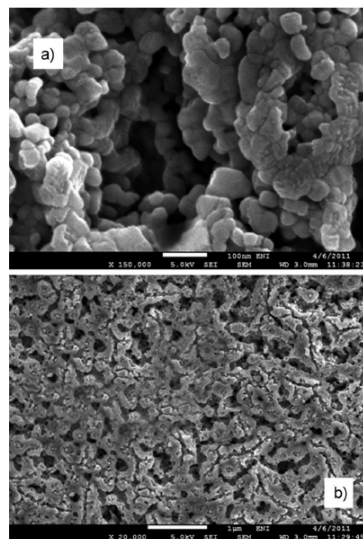


ABET Tech. solar simulator 550W
AM 1.5G filtered
10x10 cm² uniform area



eni

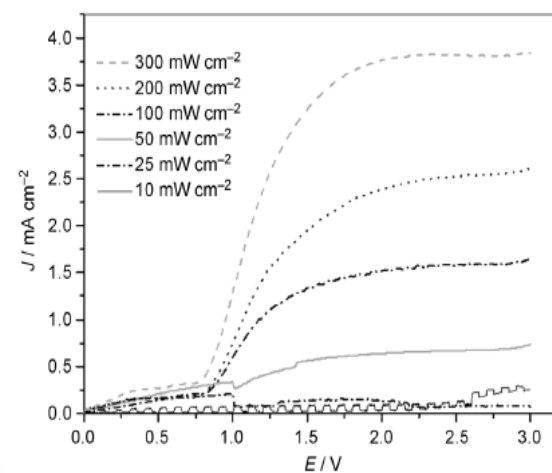
Anodized WO₃



S. Caramori, V. Cristino, C.A. Bignozzi, L. Meda,
Topics in Current Chem. Vol. 303 (2011), 215

V. Cristino, S. Caramori, CA. Bignozzi, L. Meda
Langmuir 27(11) 2011, 7276

A. Tacca, L. Meda, G. Marra, A. Savoini, S. Caramori,
V. Cristino, C. Bignozzi, S. Gimenez, J. Bisquert
Chem PhysChem, 13(12) 2012, 3025

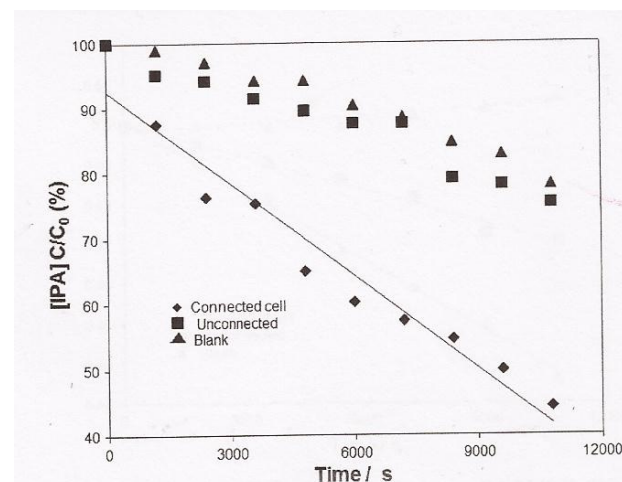
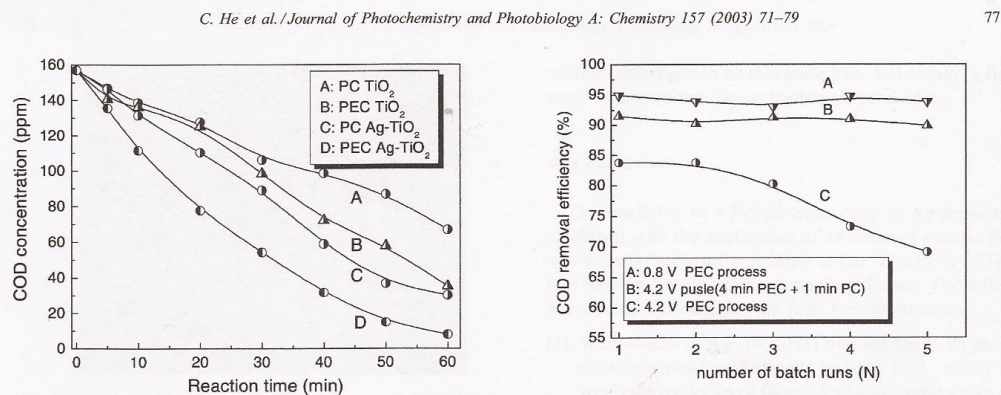


eni

Wastewater treatment & H₂ photoproduction

“...if the hydrogen production is combined with wastewater treatment, the system becomes economically viable...”

[M. R. Hoffmann et al., Solar-Powered Electrochemical Oxidation of Organic Compounds Coupled with the Cathodic Production of Molecular Hydrogen, *J. Phys. Chem. A* 7616, 2008, 112, 7616]



He C. et al. *J. of Photochemistry and Photobiology A: Chemistry* 157 (2003) 71-79

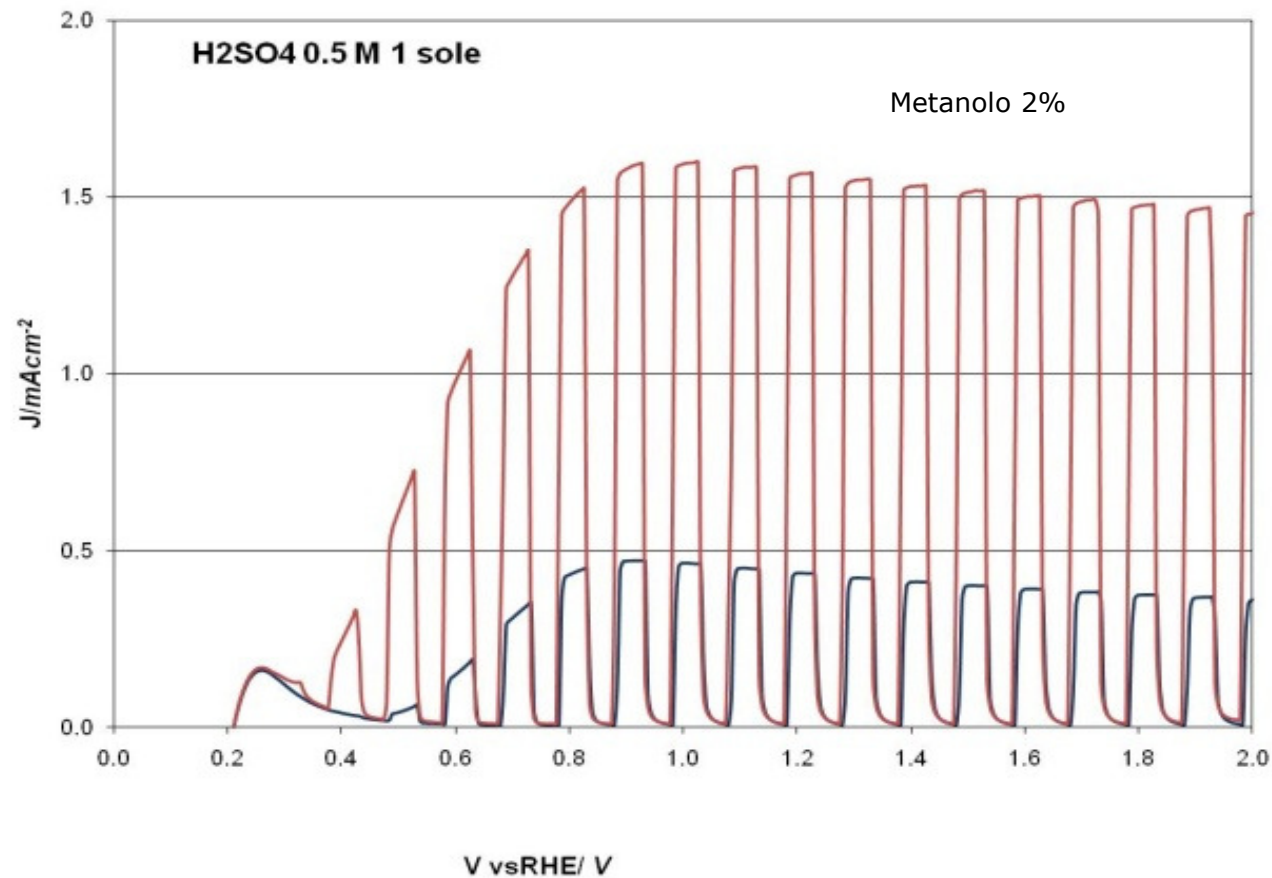
Enright P. et al. *J. Appl. Electrochem*, DOI: 10.1007/s10800-010-0244-1, 2010



eni

Waste treatment

The presence of methanol in the electrolyte strongly increases the photocurrent; in this way the methanol oxidation is added to water splitting.



eni

Efficiencies : Energy OUT / Energy IN

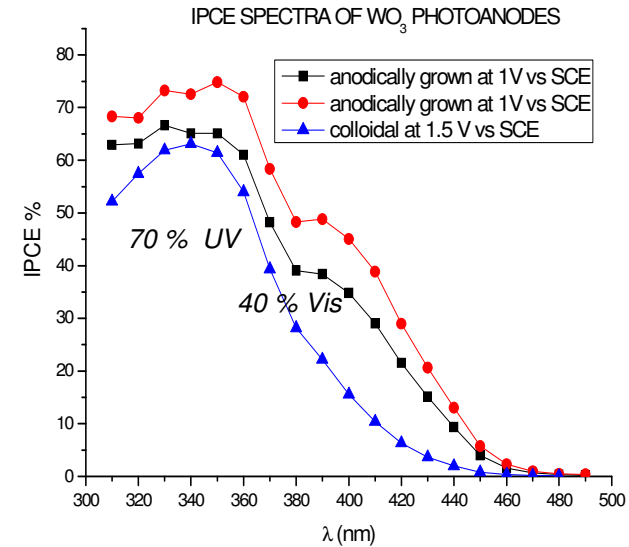
Quantum Efficiency = electrons / photons

$$IPCE = \frac{h \cdot c \cdot J}{P \cdot \lambda}$$

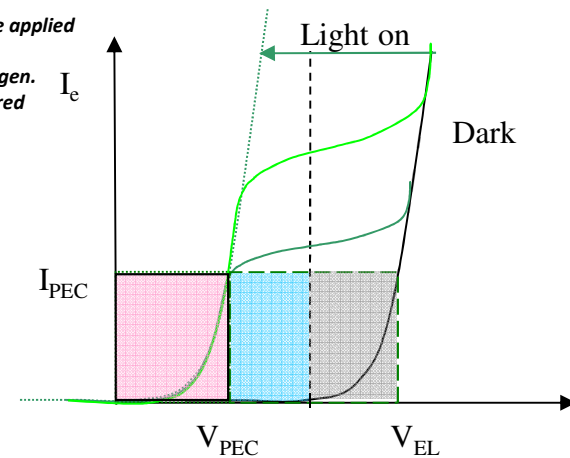
Global Efficiency STH

$$STH = \frac{J \cdot \Delta V^0}{P}$$

$$STH = \frac{J \cdot (\Delta V^0 - V_{bias})}{P}$$



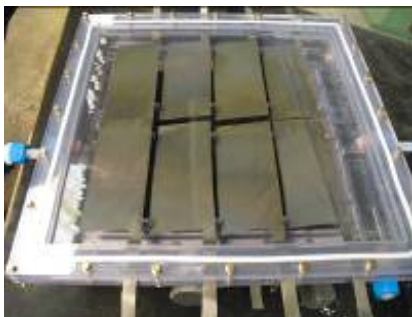
The **pink** area represents the power spent due to the applied bias.
 The **blue** area represents the power stored as hydrogen.
 The sum **pink + blue** areas represents the global stored power.
 The **grey** area is the power spent for electrolysis.



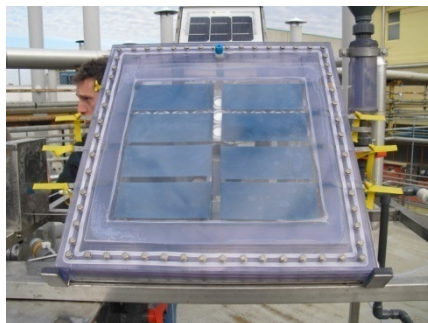
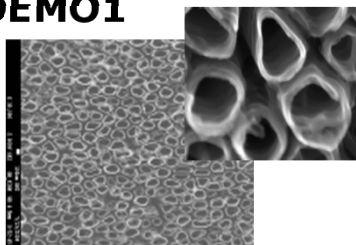
eni

Z. Chen et al., J. Mater. Res. 25 (2010) 3

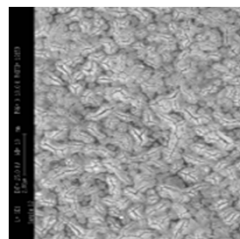
Outdoor demonstrators



DEMO1



DEMO2



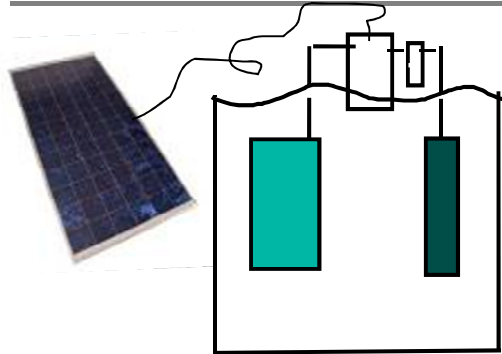
PEC cell	PHOTO-CURRENT density [mA/cm ²]	H ₂ production [NL/h/m ²]	PEC cell COST [€/m ²]	SOLAR H ₂ COST* [€/kg]
DEMO1 - TiO ₂	0.25	1.1	164	43
DEMO2 - WO ₃	1.00	4.2	302	20



eni

EU target (2020) PEC H₂ = 5 €/kg, STH = 10%

Comparison between PV+EL and PEC



PV + EL

Si-PV absorbs 60% of solar spectrum

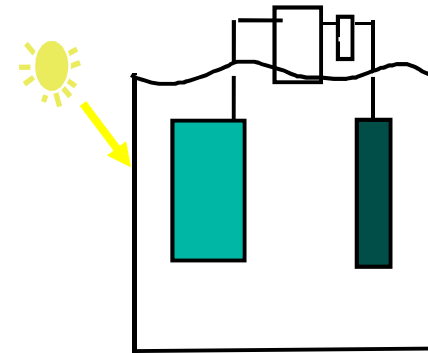
STH: $15\% \times 70\% = 10\%$

High Energy dissipation

Voltage required : $> 2 \text{ V}$

Solar H₂ Cost : 30 €/kg

Lifetime 5 years



PEC

WO₃ absorbs 9% of solar spectrum

Efficiency STH: 1%

Lower Energy dissipation

Voltage required : $< 1 \text{ V}$

Solar H₂ Cost : 60 €/kg

Lifetime 10 years (?)

Improvements are in PV efficiency...

**... there are continuous improvements
and 10% is not impossible...**



eni

Cost considerations

For **PV+EL** costs are reported as 20:80

EL is the main cost because it uses noble metals electrodes and has short lifetime.

PEC exploits solar energy to drive chemical reactions
the requirement for water splitting voltage is reduced
and so the cost is.

Solar H₂ PEC cost depends on materials, efficiency and duration:



USA-DOE Final Report (2009)

"Techno economic Analysis of PEC H₂ Production"

by B.D. James, G.N. Baum, J. Perez, K.N. Baum.



eni

Thanks to collaborators !



*“ ...I believe that water will one day be employed as fuel,
that hydrogen and oxygen that constitute it will furnish
an inexhaustible source of heat and light,
of an intensity of which coal is not capable...
...Water will be the coal of the future ! ”*

From: *L'Île mystérieuse* by *Jules Verne (1874)*

*L. Abbondanza
G. Bianchi
R. Paglino
R. Preda
A. Romano
F. Rubertelli
F. Simone
A. Tacca
G. Tozzola*



eni