Torino – NIS Colloquium – 23 Giugno 2008

Water Photosplitting by using Oxide Thin Films

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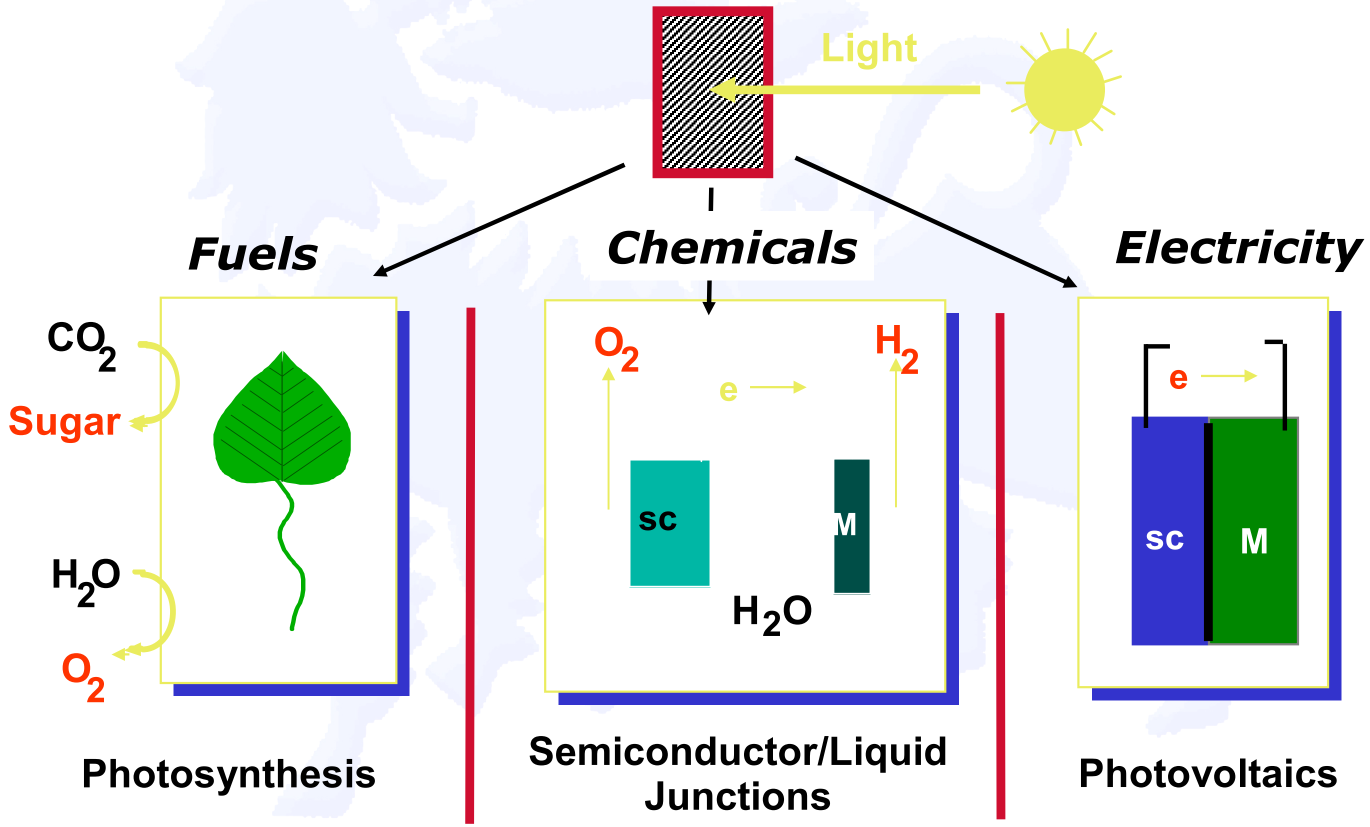
Solar Energy Conversion Strategies

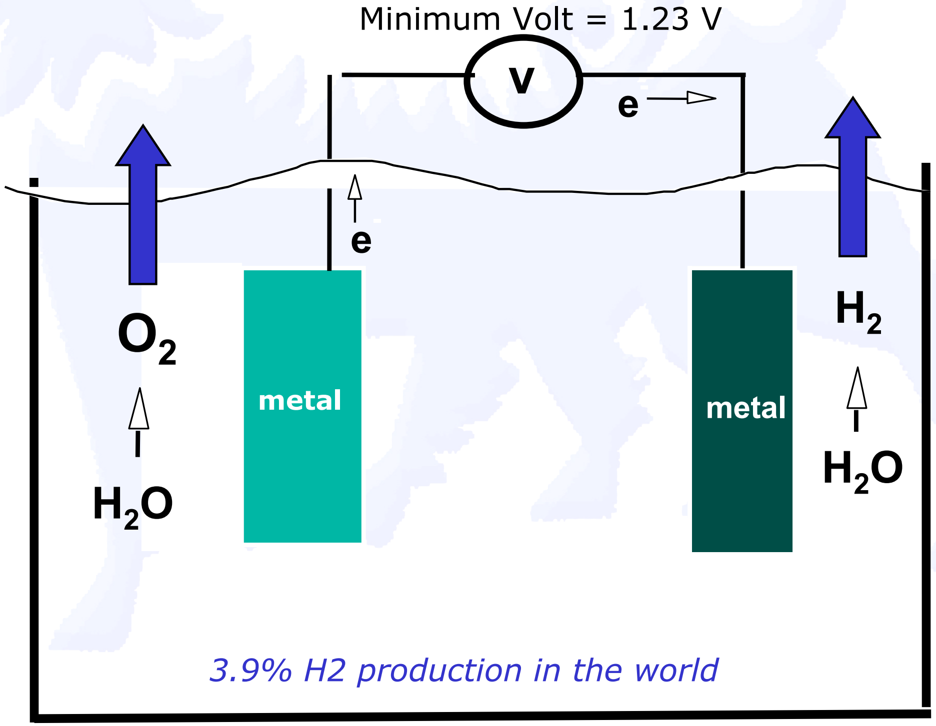


The Electrolyzer

Electricity is converted to chemical energy

η = 80% (from cm3/h to 100 m3/h)

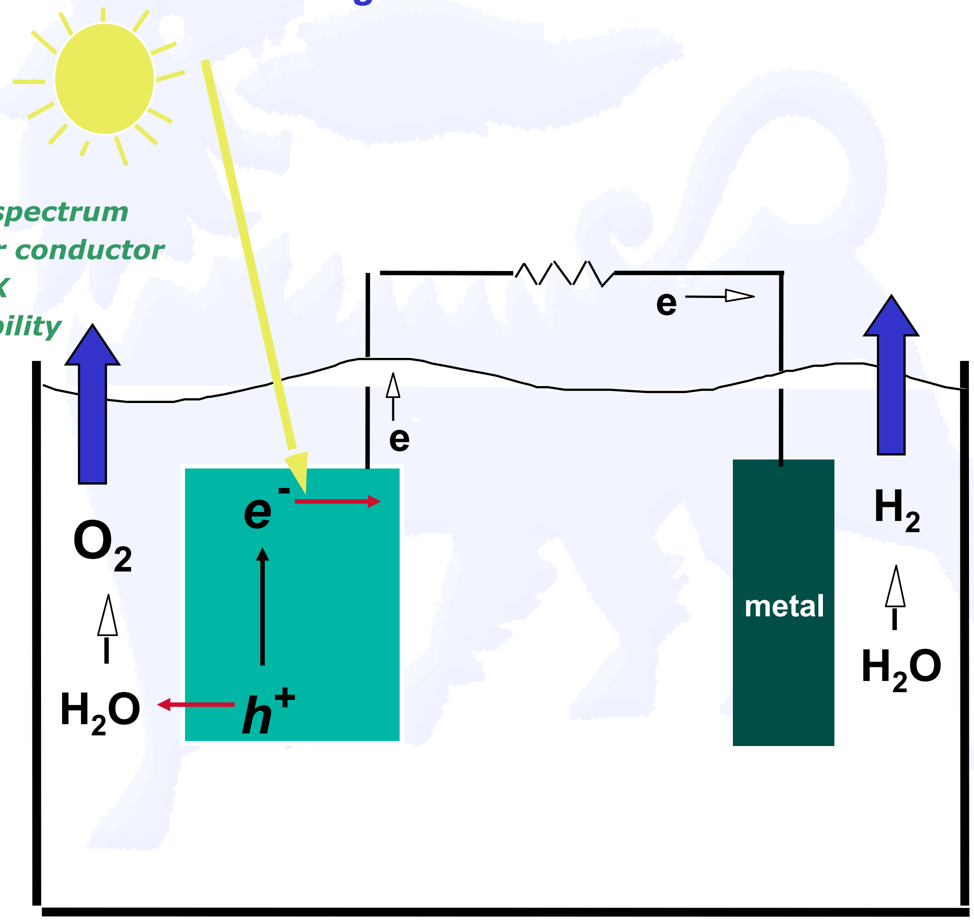
with solar cell → η(sc) 10-15% x η(el) 80% = η(tot) 8-12%



The Photoelectrochemical Cell

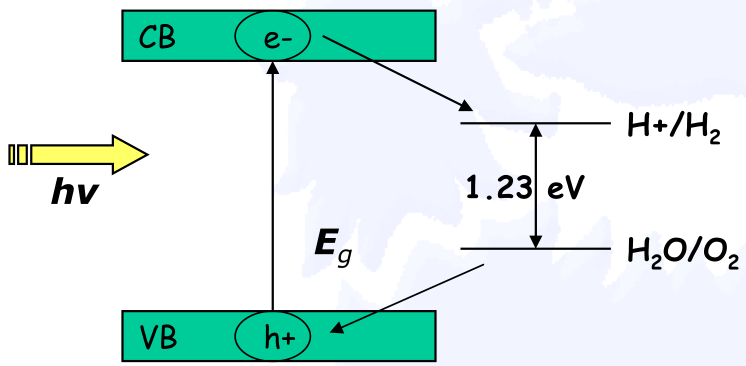
Light is converted to carriers → chemical energy

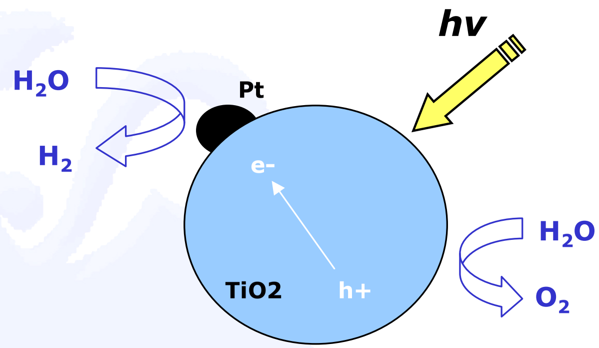
- *Absorb solar spectrum*
- *Charge carrier conductor*
- *Water RED-OX*
- *Long Life Stability*



Catalytic process from particles

Suspended particles can spontaneously split water when irradiated





A **semiconductor** produces e-/h+
when irradiated with hv > Eg,
charge transfer → water splitting

To spontaneously photosplit water, CB and VB levels must bracket the H_2O redox levels → high recombination rate

A wireless system does not allow neither an electrical characterization nor a polarization of the material

hv + *semic.* → e- + h+

2 H2O - 4 e- → O2 + 4 H+
4 H+ + 4 e- → 2 H2

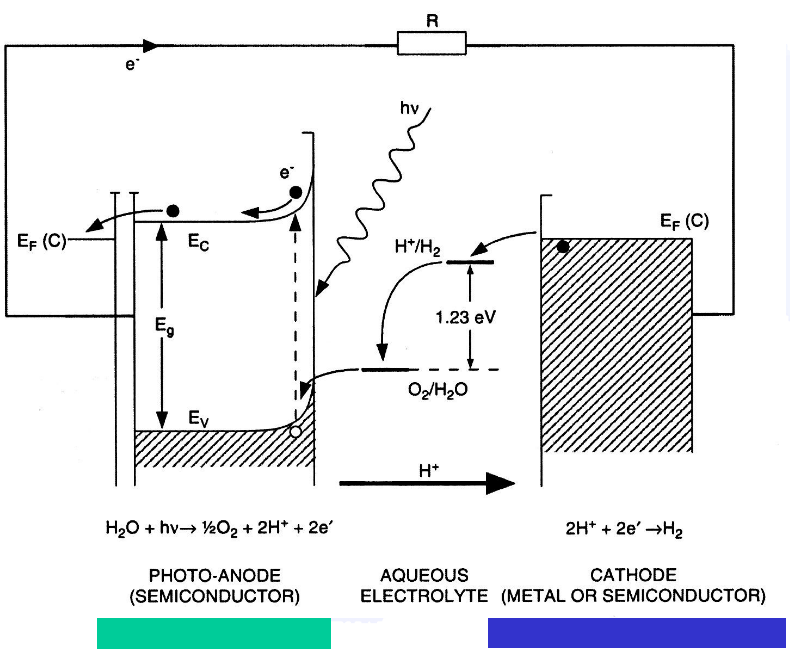
2 H2O + *hv* + *semic.* → O2 + 2 H2

Fujishima, K. Honda, Nature 238 (1972) 37; S. Sato at al. Chem. Phys. Lett. 72(1980) 83; J. Catal. 69 (1981) 128; Y. Inoue, J. Phys. Chem. 95 (1991) 4059; K. Sayama, H. Arakawa, Res. Chem. Intermed. 26 (2000) 145…….

Photo-electrochemical process for Water Splitting

Energy diagram of a PEC cell

J. Nowotny et al./International Journal of Hydrogen Energy 32 (2007) 2609–2629



The *photo-anode* is a semiconductor layer

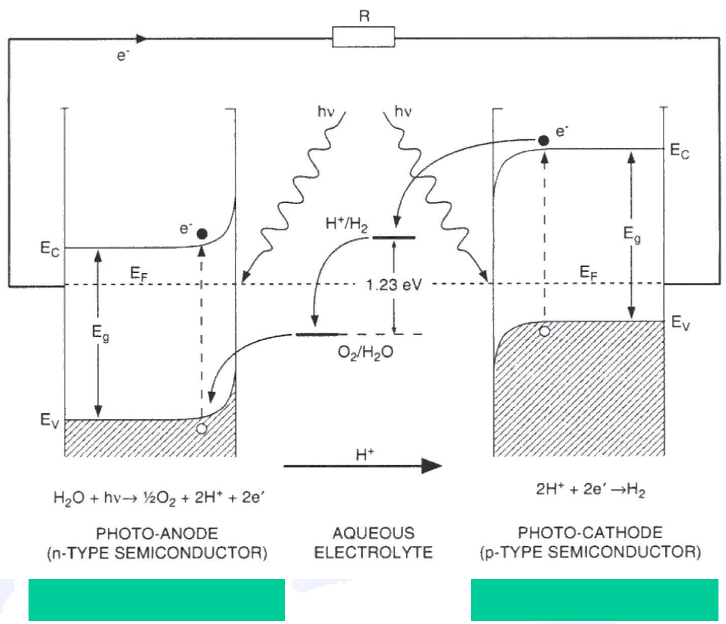
The *cathode* is a metal

Bard, Nano Letters 6 (2006) 24
M. Gratzel et al., JACS 128 (2006) 15714
C. Grimes et al. Nano Letters 7 (2007) 2356

Dual semiconductor cell: the "*twin-photosystem*"

Two-semiconductor photoelectrode cell could have advantages:

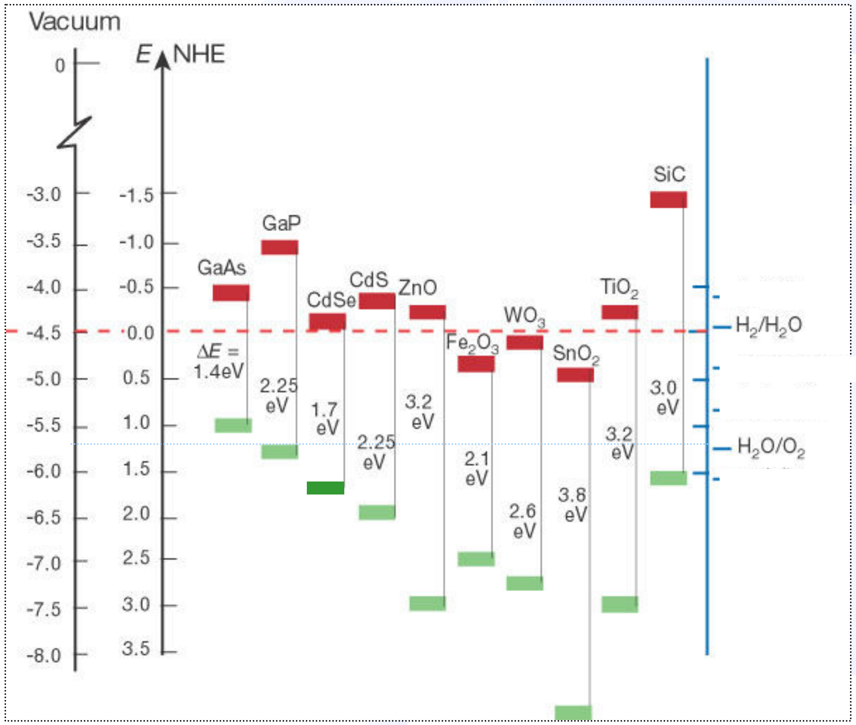
- *It can absorb in different solar spectrum portions*
- *It sums two potentials to reach the splitting threshold voltage*



H. Yoneyama, Electrochem. Acta, 20 (1975) 341;
Heller, Science 223 (1984) 1141; L. Fornarini, A. Nozik, JPC 88(1984) 3238;
S. Licht JPC 105 (2001) 6281; M. Gratzel, Chem Lett. 34 (2005) 8;

Ideal Bandgap

pH=1



From: M. Gratzel, Nature 414 (2001) 338

Thermodynamic request
1.23 eV
+ Kinetic losses
E_g = 2 eV

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

High Eg *→ poor harvesting (UV) but high stability*

Low Eg *→ good harvesting but poor stability*

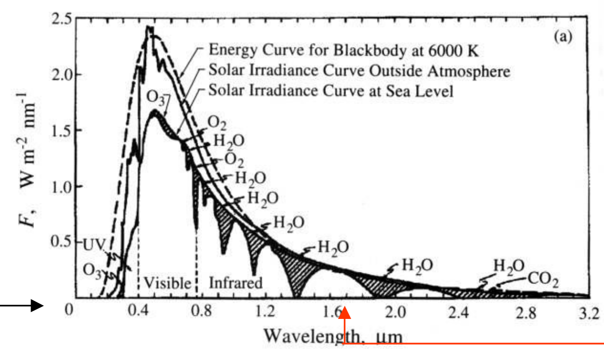
⬇

Not a single material !

Harvesting

How to improve it?

λ(nm) = 1239.8/ E(eV) →



$In_{(1-x)}$ Ga_x N
(E_g = 0.7 eV)
covers the full solar spectrum

Examples:

- ***by multi-junction layers with graded Eg***
- ***by dye-sensitized semiconductors***
- ***by mixed-oxides structures***
- ***by doped oxides***

J. Turner, O. Khasalev, (1998) NREL
p-GaInP + n-p GaAs tandem cell

Z. Wang, JACS 126 (2004) 16720
Pt-porphyrines on CNT
M.K. Nazeeruddin, M. Gratzel (2001)
TiO2/Ru-PC

Z. Zou and H. Arakawa, Nature 414 (2001) 625
Ni-In TaO4

Y Sakatani et al. J. Mat. Sci. 19 (2004) 2100
N:Co-TiO2

A.B. Ellis et al. JPC 80 (1976) 1325
Nb:KTaO3

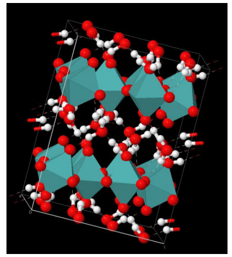
D.M. Schleich, MRS Bulletin 12 (1977) 321 SrTiO3 / BaTiO3

J. Koenitzer, J. Solid State Chem. 35 (1980) 128 Bi2WO6

Photoanode studies in NOVARA

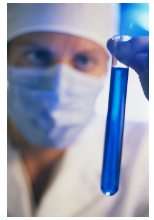
Theoretical Studies

- Ab-initio band-structure calculations for model systems to study electronic properties



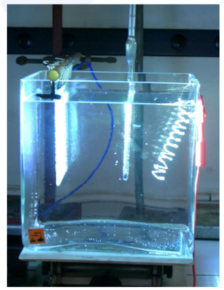
Preparation

- Nanocrystalline **oxides** via sol-gel techniques
- doctor-blade/spin coating deposition on FTO-glass
- Thermal treatments (500°C - 600°C) in air



Characterization & Testing

- Powder and film characterizations
- Current vs. Voltage characteristics
- Water-splitting test → H_2 collection

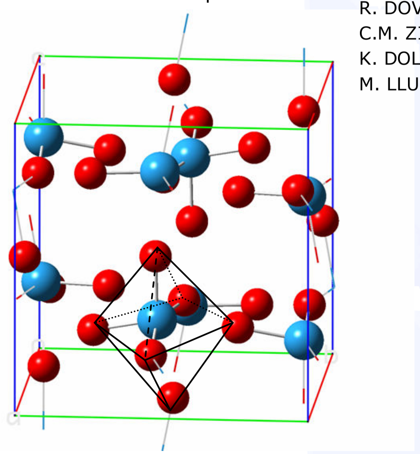


Modeling of monoclinic WO_3

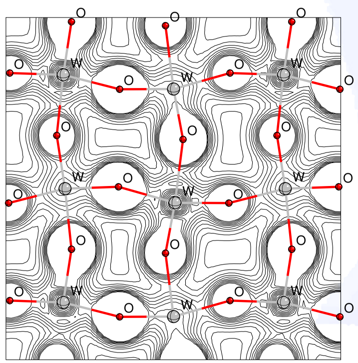
(CRYSTAL 06 DFT= B3LYP, basis set 1) pseudopotentials 70 el-)

R. DOVESI, V.R. SAUNDERS, C. ROETTI, R. ORLANDO, C.M. ZICOVICH-WILSON, F. PASCALE, B. CIVALLERI, K. DOLL, N.M. HARRISON, I. J. BUSH, Ph. D'ARCO, M. LLUNELL

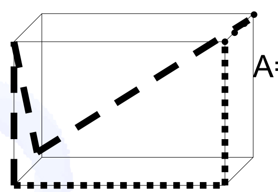
P 2_1/n

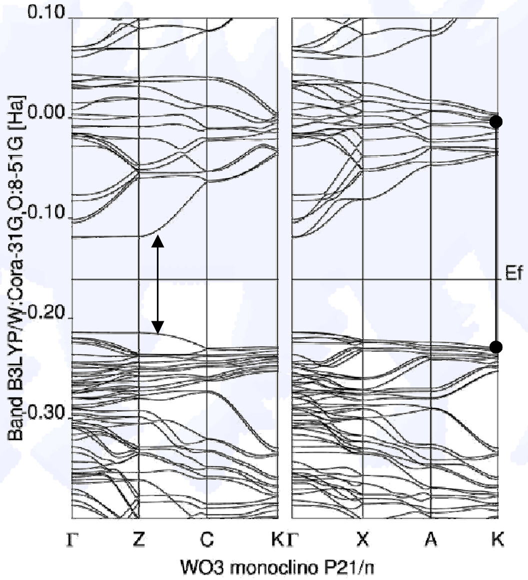


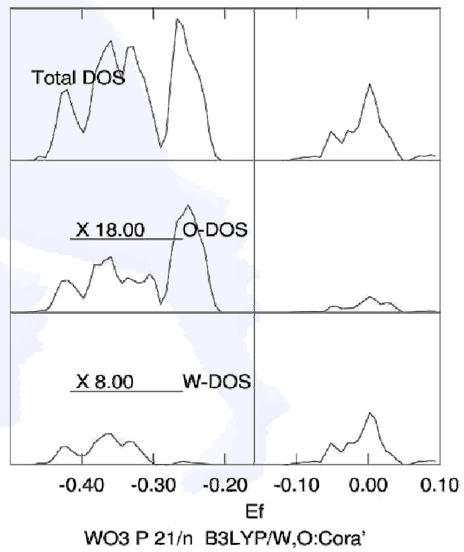
Charge cross-section



BZ







Egap = 2.64 eV

Ef = - 4.4 eV

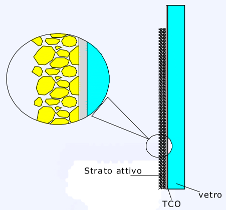
[L. Abbondanza]

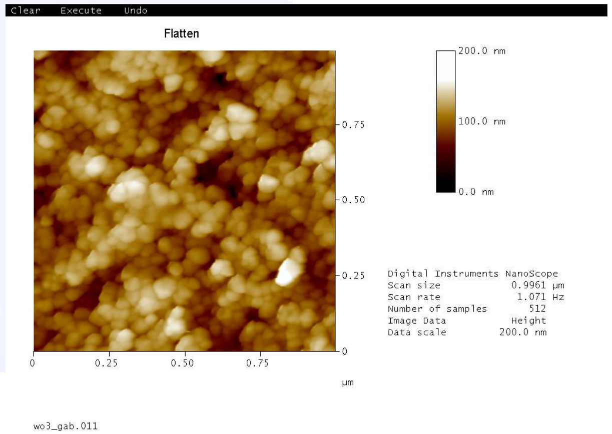
Eni S.p.A. Direzione Strategie e Sviluppo – Istituto ENI Donegani

Sol-Gel Preparation

10 x 10 cm2

- $WO_2(OH)_2$ in ethanol (SOL) + organic disperdent (GEL)
- GEL deposition on conductive support (FTO);
- Thermal treatments in the range 500°C-600°C



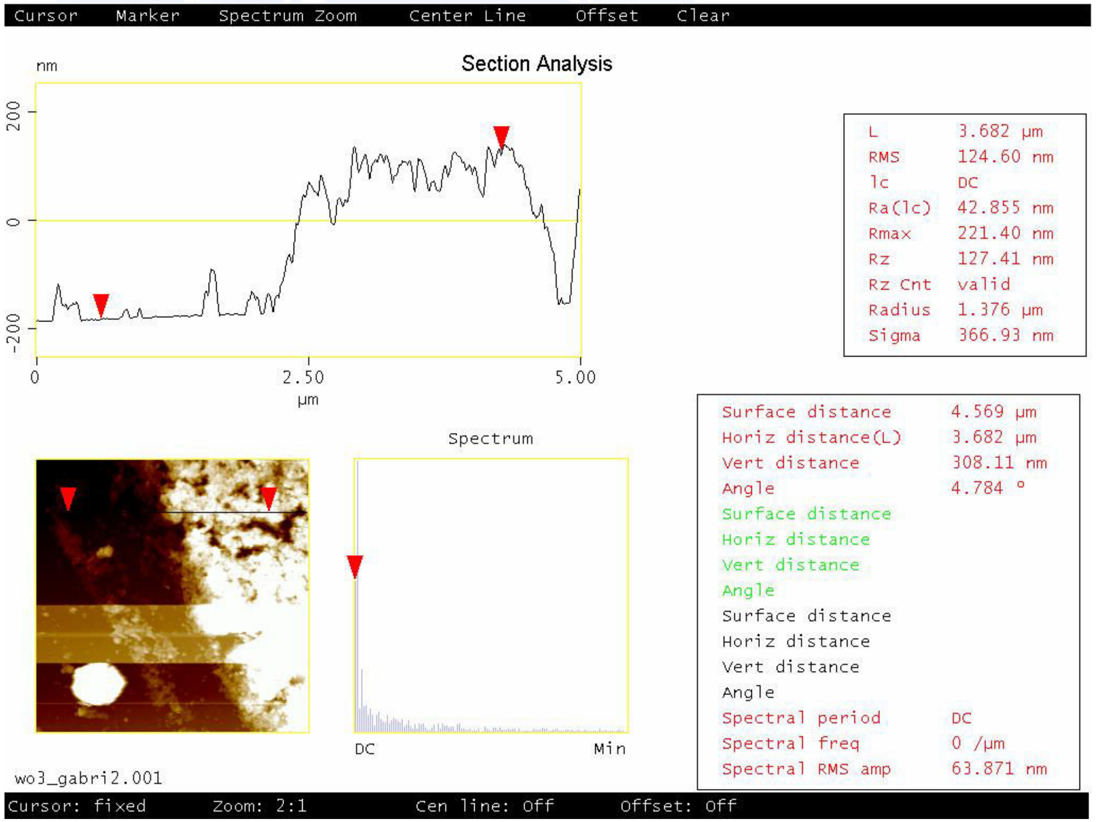


Other collaborations:
-> TiO_2 WO_3 nanotubes (Univ. FE, *Bignozzi, Caramori*)
-> Fe2O3 sprayed gas phase (ENI-NO, *Buzzoni)*
-> Mixed Oxides $Sm_2Zr_2O_7$/$Nd_2Zr_2O_7$ (VE-Tecnologie, *Marella)*

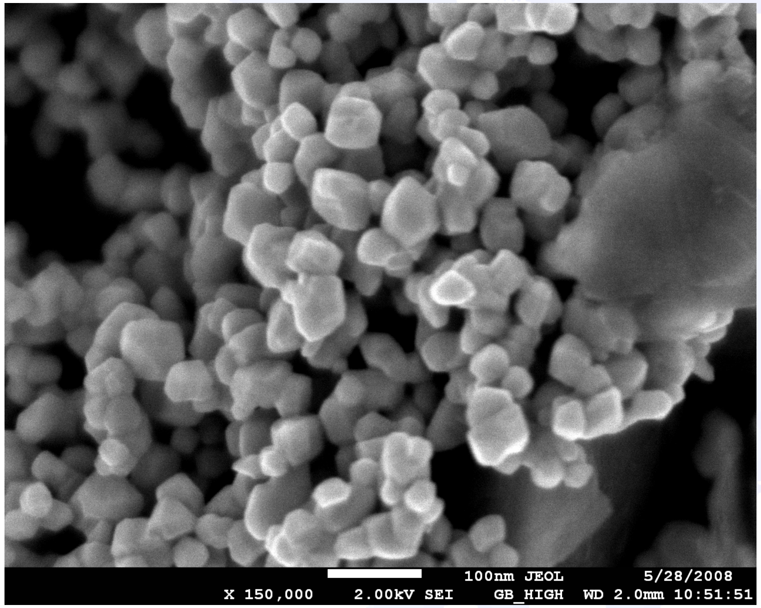
[C. Santato, J. Augustynski, et al. J.A.C.S. 123 (2001) 10639]

[G. Tozzola, G. Bianchi]

WO3 layer thickness by SPM

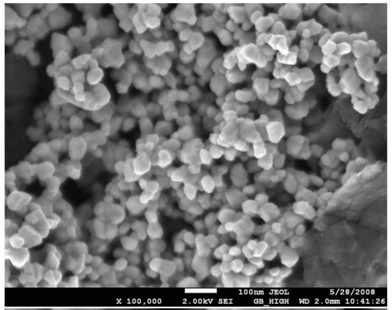


SEM Micrographies



WO3

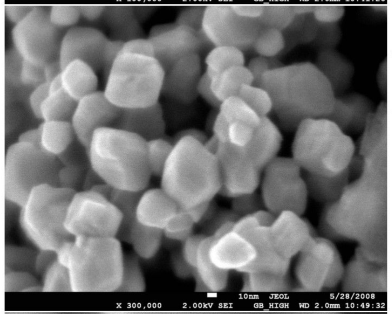
GB Mode



WO3-06
Instrument:7500F

Accel.Volt(kV):2.00
Photo Mag. x100,000
Image:SEI
<SEI(Upper)>

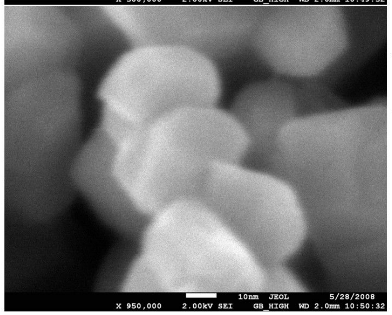
Date:2008/05/28
GB GUN : 4.00
GB BIAS : 2.00



WO3-08
Instrument:7500F

Accel.Volt(kV):2.00
Photo Mag. x300,000
Image:SEI
<SEI(Upper)>

Date:2008/05/28
GB GUN : 4.00
GB BIAS : 2.00

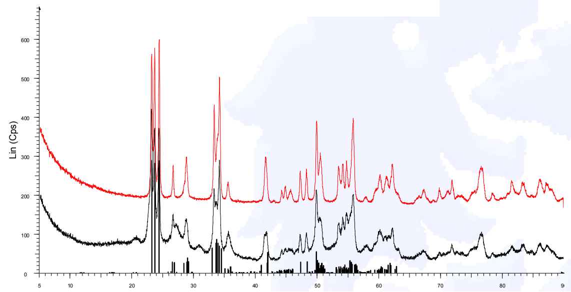


WO3-09
Instrument:7500F

Accel.Volt(kV):2.00
Photo Mag. x950,000
Image:SEI
<SEI(Upper)>

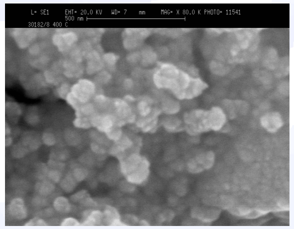
Date:2008/05/28
GB GUN : 4.00
GB BIAS : 2.00

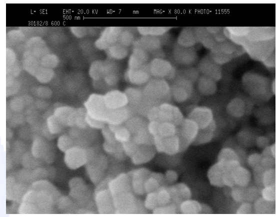
WO_3 Structure and Morphology



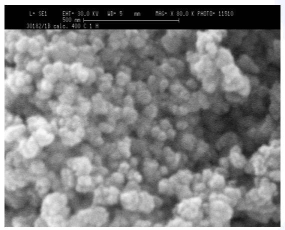
XRD
Crystal phase: monoclinic
Crystalline average domain: 45 nm

SEM after 500°C
Particle size 30-50 nm

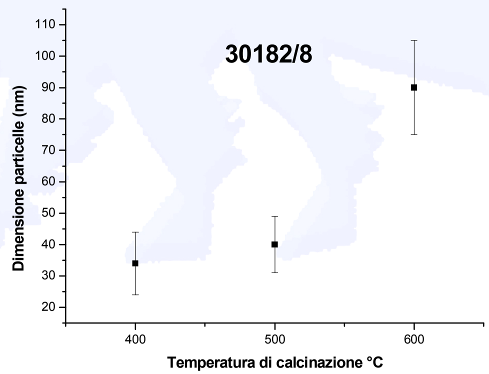




SEM after 600°C
Particle size 70-100 nm

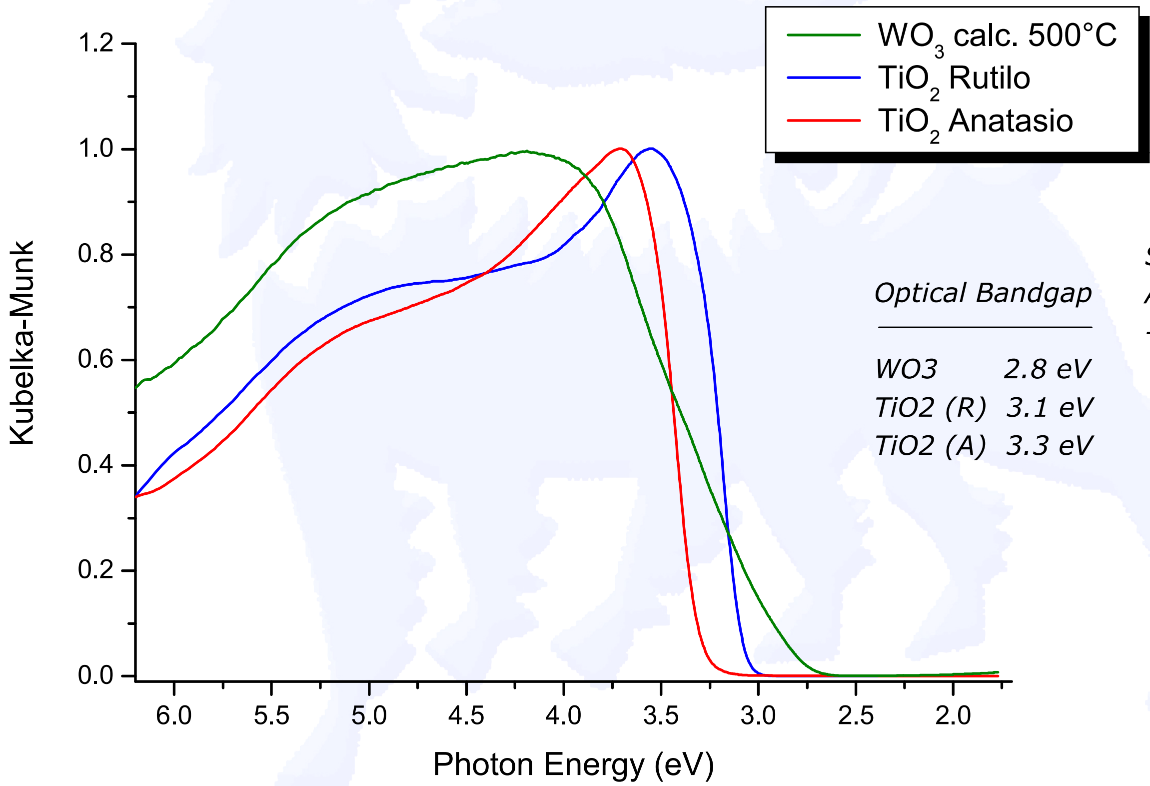


SEM after 400°C
Particle size 25-40 nm



[G. Marra]

WO_3 and TiO_2 Spectra by Diffuse Reflectance UV-VIS

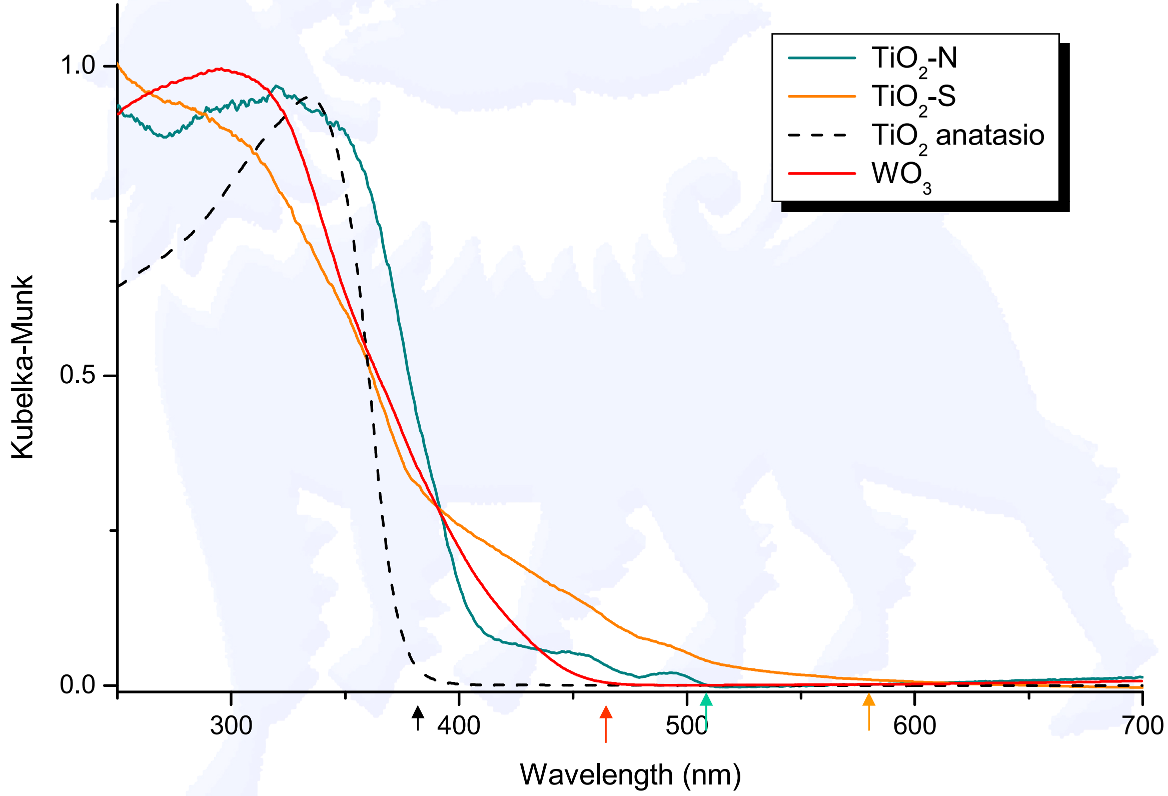


Optical Bandgap		Solar Spectrum Absorption
WO3	2.8 eV	12%
TiO2 (R)	3.1 eV	
TiO2 (A)	3.3 eV	4%

[M. Salvalaggio]

WO3 and doped-TiO2 Spectra

by Diffuse Reflectance UV-VIS

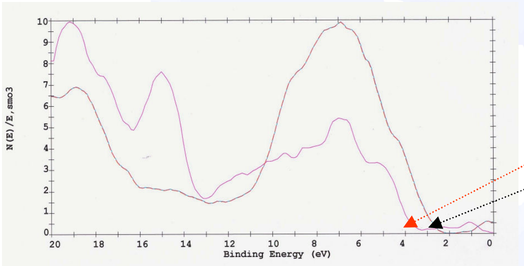


[M. Salvalaggio]

WO_3 surface components (XPS)

Valence Band: as prepared/calcined

O2s C2s O2p-W5d-O2p

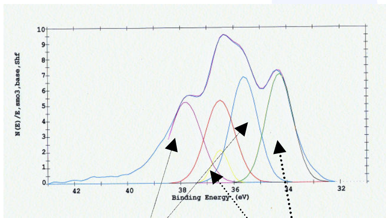


DE = 4.0 eV

DE = 2.3 eV

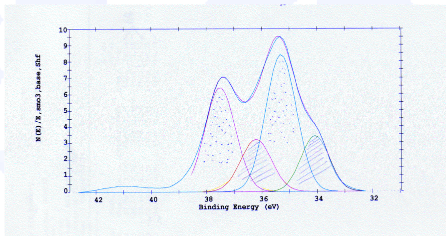
Core levels: W 4f 7/2 e 5/2

As prepared W2:W1 50:50

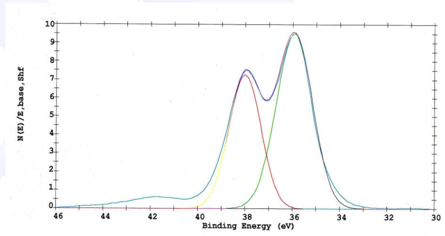


W2 **W1**

400°C 1h W2:W1 70:30



550°C 3h W2 100%



W2 = W(VI) oxide

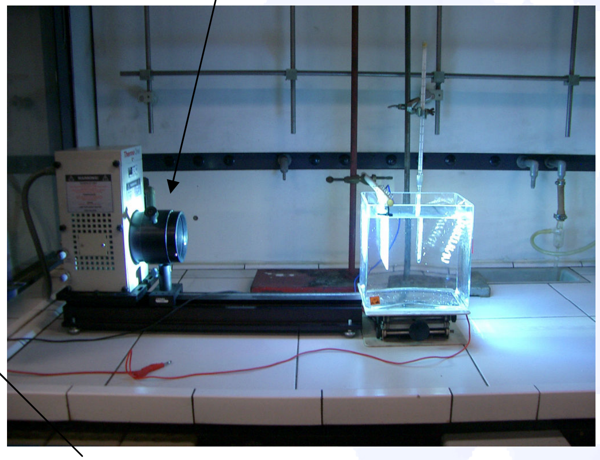
W1 = WO2(OH)2 tungstic acid

[L. Meda, M. Aratti]

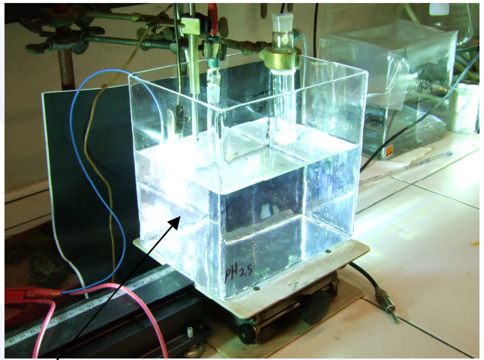
Eni S.p.A. Direzione Strategie e Sviluppo – Istituto ENI Donegani

Experimental cell for testing

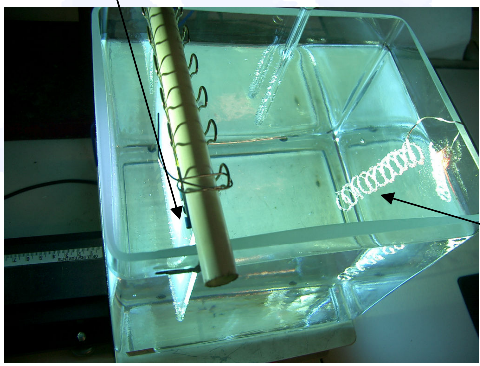
Hg lamp 300W

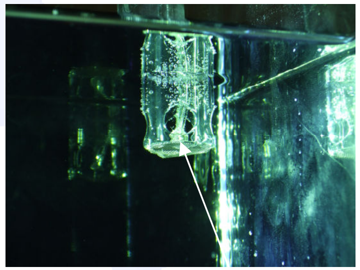


External bias



10x10 cm2
WO3 photoanode





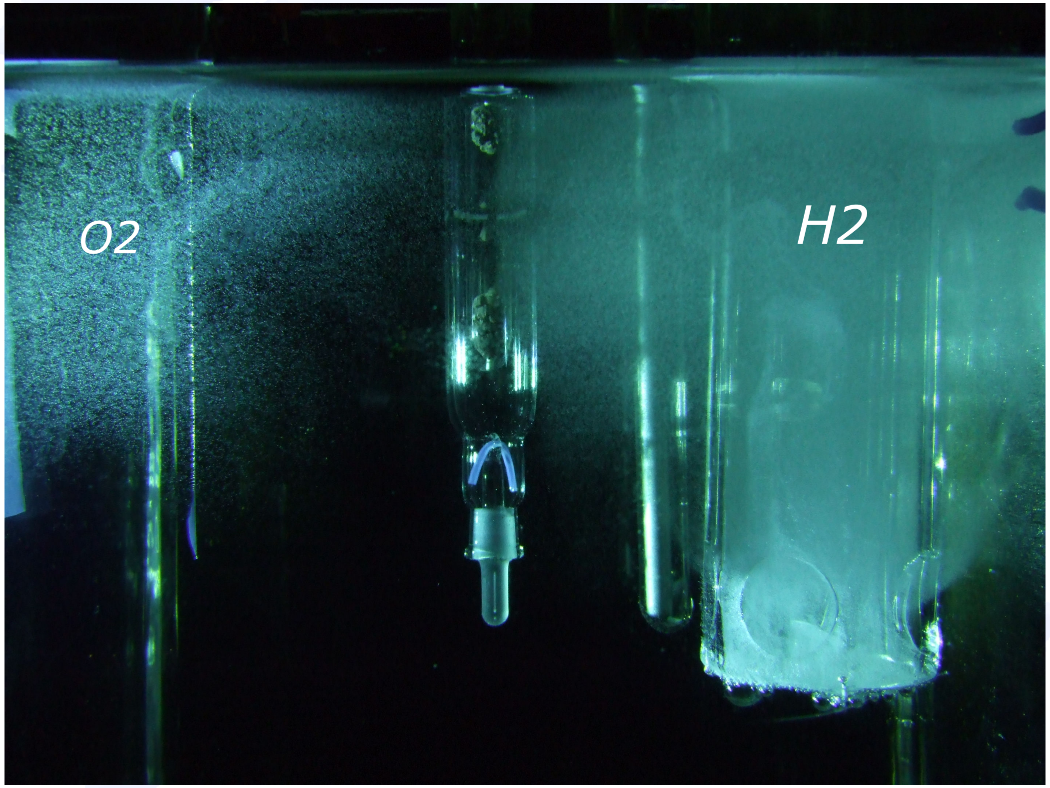
Pt grid

Pt wire

[C. Zannoni, M. Gavinelli, R. Paglino]

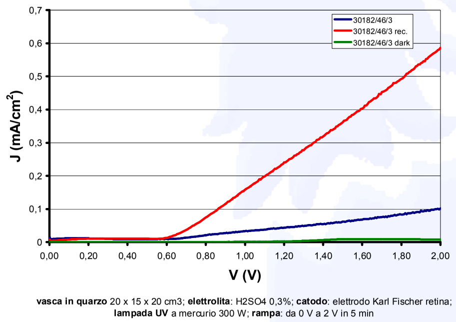
Gas evolution

anode *reference* *cathode*



J/V Characteristics of WO_3 photoanodes

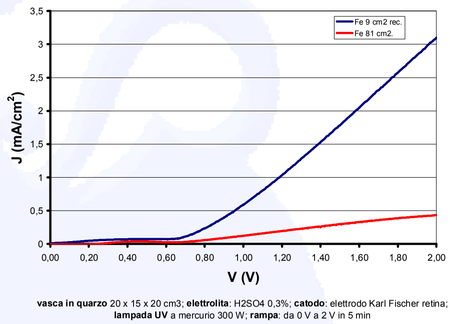
Thin layer (300 nm) – multiple calcination



500°C 3h + 3h

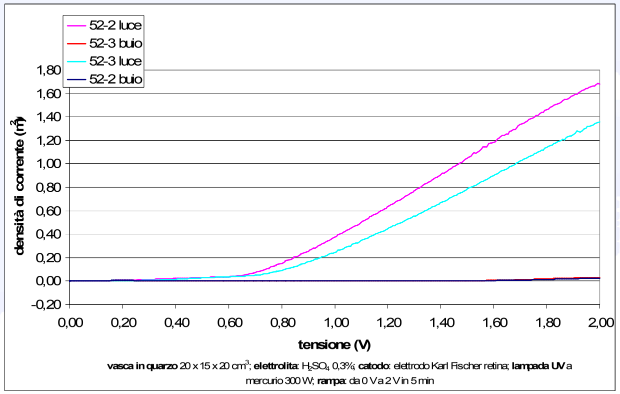
500°C 3h

Thick layer (2 μm) – different areas



3x3 cm2

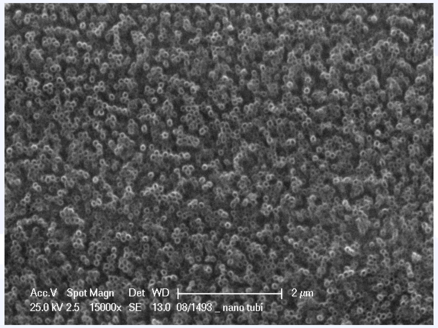
9x9 cm2



[C. Zannoni, R. Paglino]

TiO2-C nanotubes by anodic oxidation

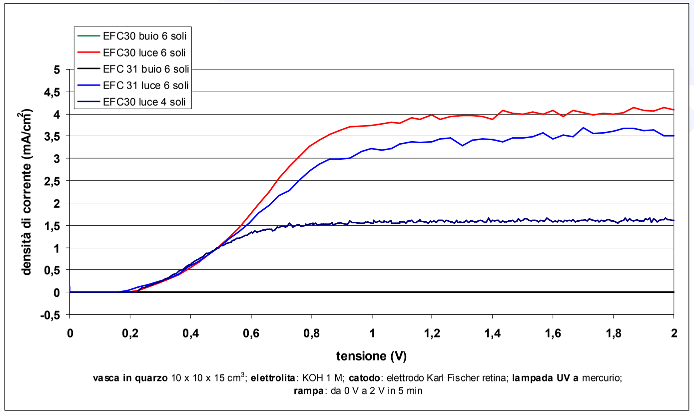
Ti sheet in electrochemical bath (H_2O, NH_4F, ethylenic glycol)
30 V   1h

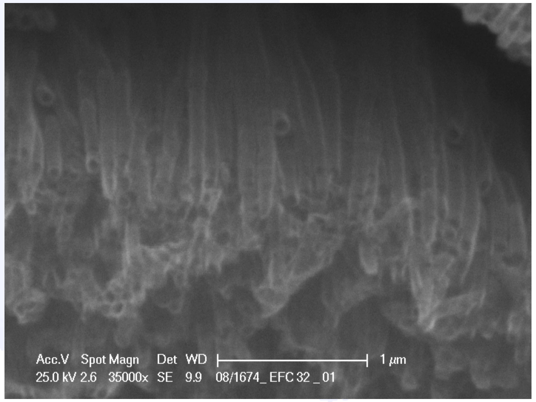


Diameter = 75 nm ± 5 nm

Border = 20 nm ± 3 nm

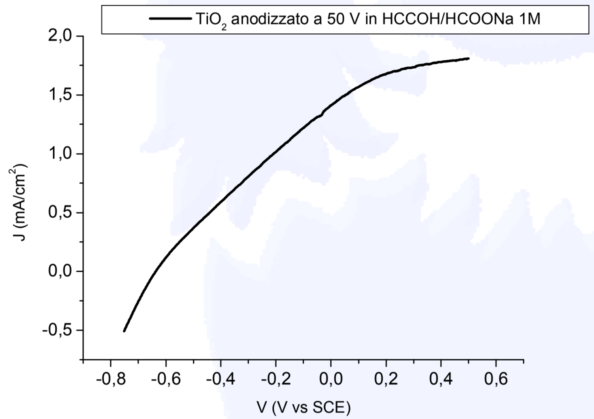
Length > 1 micron



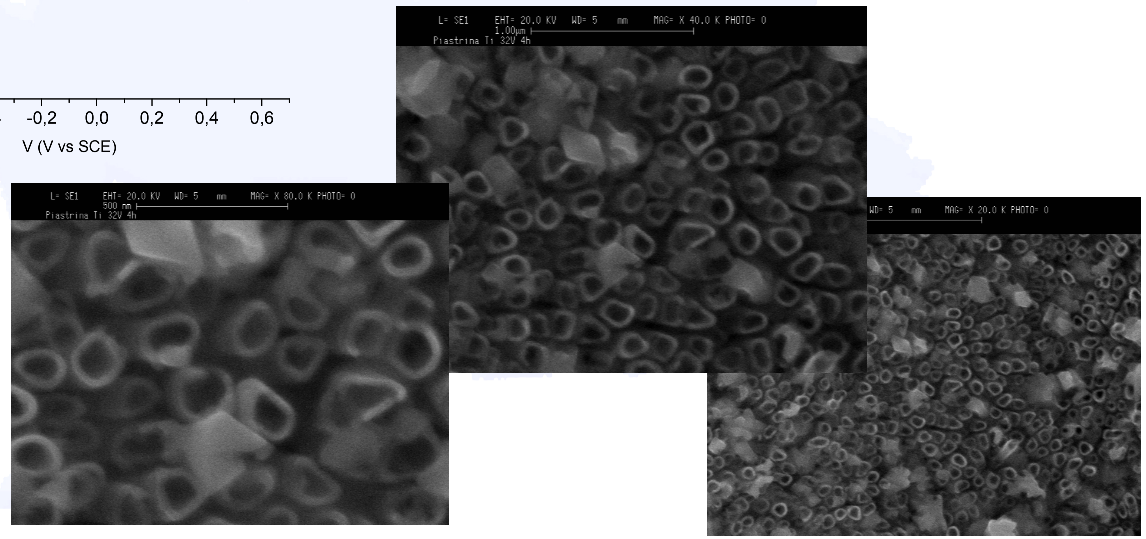


[M. Marella]

TiO_2 nanotubes by anodic oxidation
of Ti sheet



Diameter = 150 nm ± 10 nm
Border = 40 nm ± 5 nm

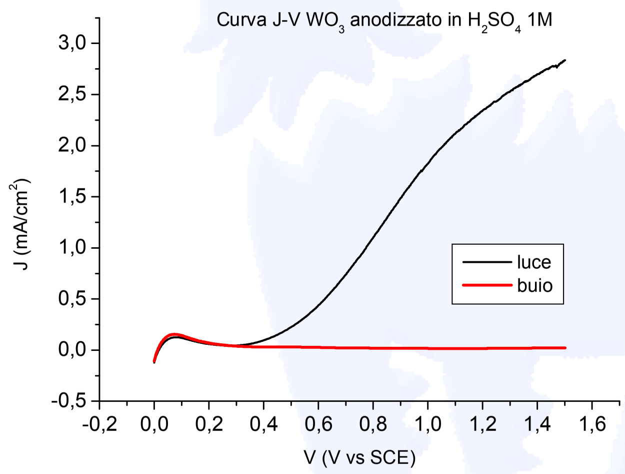


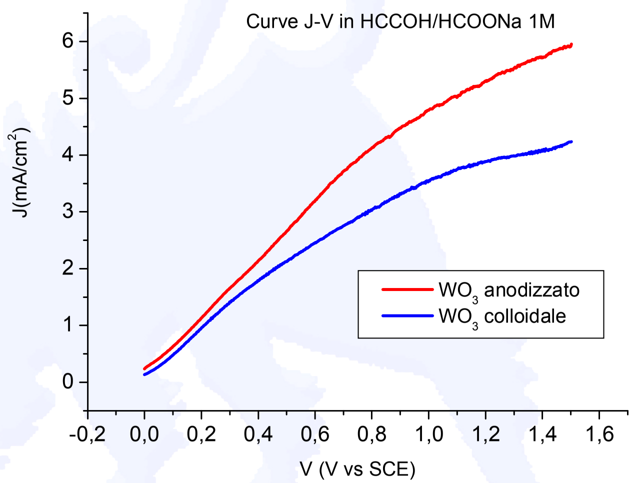
[S. Caramori, C. Bignozzi, unpublished]

WO3 by anodic oxidation

of W sheet

alogen lamp – 0.2 W/cm2

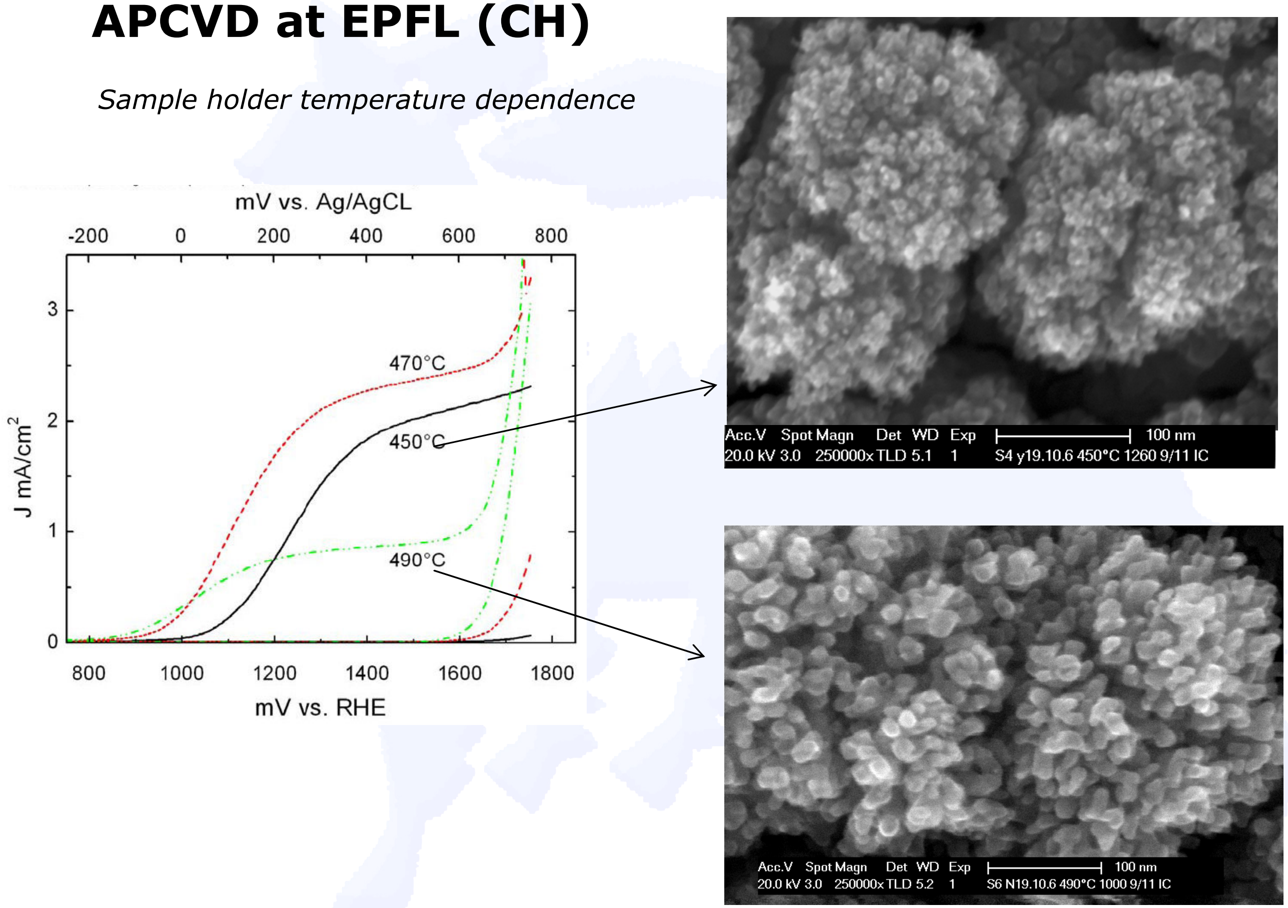




[S. Caramori, C. Bignozzi, unpublished]

Good Results with Fe_2O_3 APCVD at EPFL (CH)

Sample holder temperature dependence



*A. Kay; I. Cesar; M. Grätzel, JACS **2006**, 128, 15714*

Literature Top Results

1.

Tandem monolithic cell
Thin films p-GaInP +
n-pGaAs solar cell
by vapor-phase epi
Halogen lamp 150 W
EFF.= 12.4 %
Lifetime: few days

J. Turner, O. Khasalev, SCIENCE 280 (1998) 42, NREL

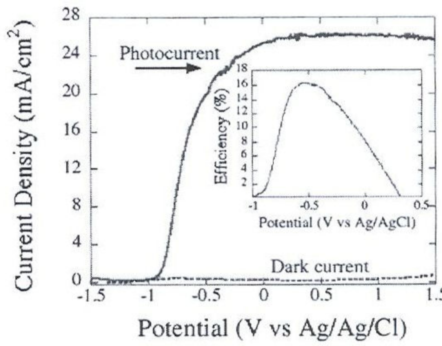


Figure 6. Photocurrent density and corresponding photoconvers efficiency generated from ≈45 μm long nanotube arrays, 550 annealed, under 95 mW/cm² 320–400 nm UV illumination. 1 maximum value of 16.25% is achieved at −0.52 V vs Ag/AgCl.

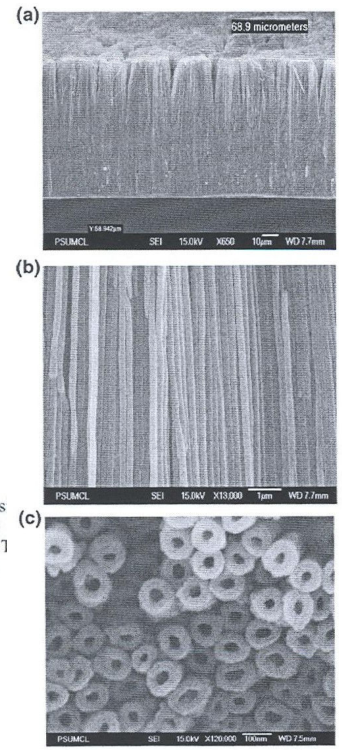


Figure 4. FESEM images of TiO_2 nanotubes grown in FA-based electrolyte at 35 V for 48 h showing (a) a cross section at lower magnification, (b) a cross section at higher magnification, and (c) a top surface image.

2.

TiO2 nanotube array
by anodic growth
UV-lamp
EFF.= 16.25 %
Long stability

M. Paulose, C.A. Grimes et al.
J. Phys. Chem. B Lett. 110 (2006) 16179
Penn. State Univ.

Conclusions

The Strategic Research agenda of EU H2 Technology Platform states that H2 is expected to serve 50% of transport fuels by 2050…

For that some objectives have to be addressed since now:

- *total efficiency > 10%*
- *operation time 5000 h*
- *stability within 10%*

… The ability to fabricate, characterize and understand complex nanostructures is key to success with semiconductor-based water splitting

and impressive progress has been made recently in exploring materials for solar hydrogen…

From: G.W. Crabtree, M.S. Dresselhouse, MRS Bulletin 33 (2008) 423

Aknowledgements

Thanks to all collaborators !