Fotosintesi artificiale:

Materiali e tecniche per la produzione di idrogeno dall'energia solare

Padova, 6 aprile 2016

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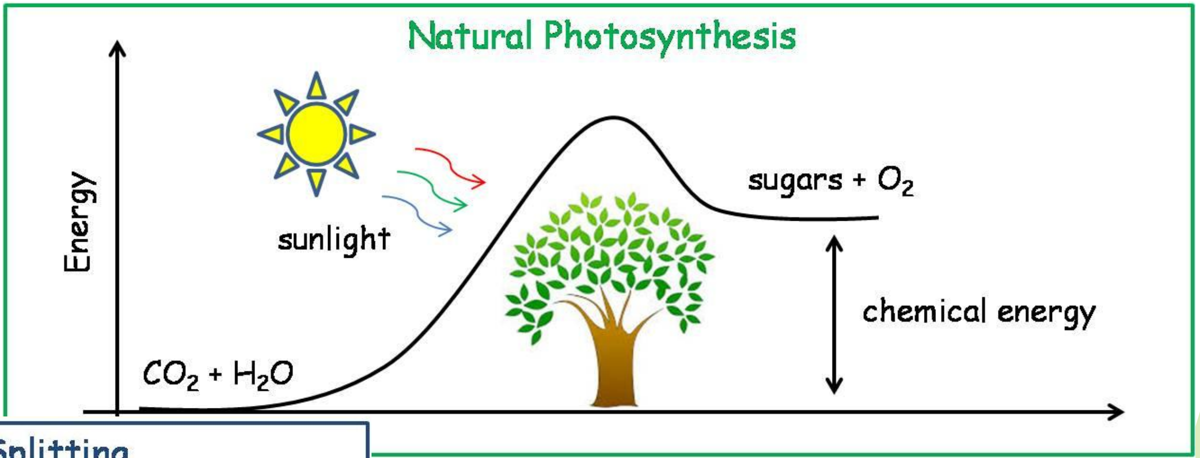
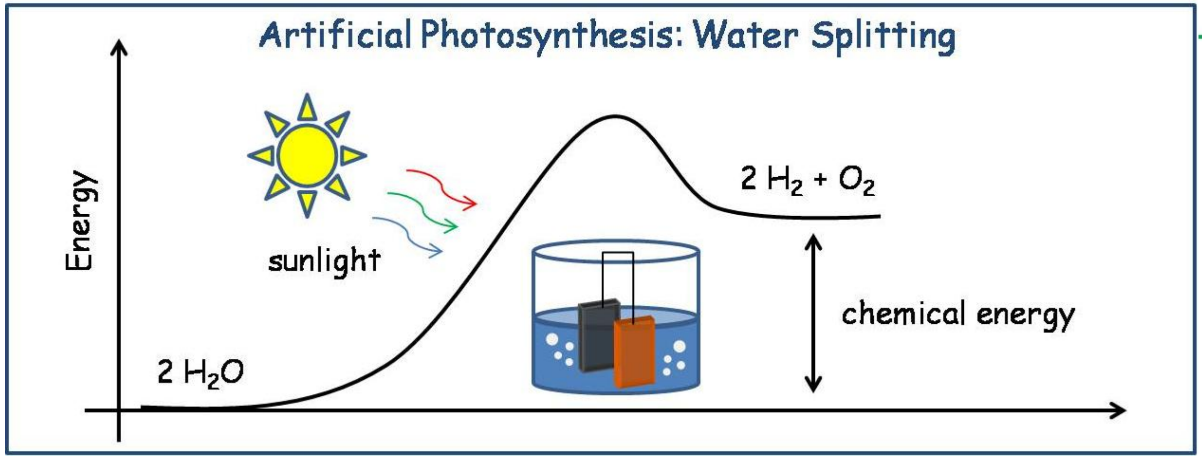
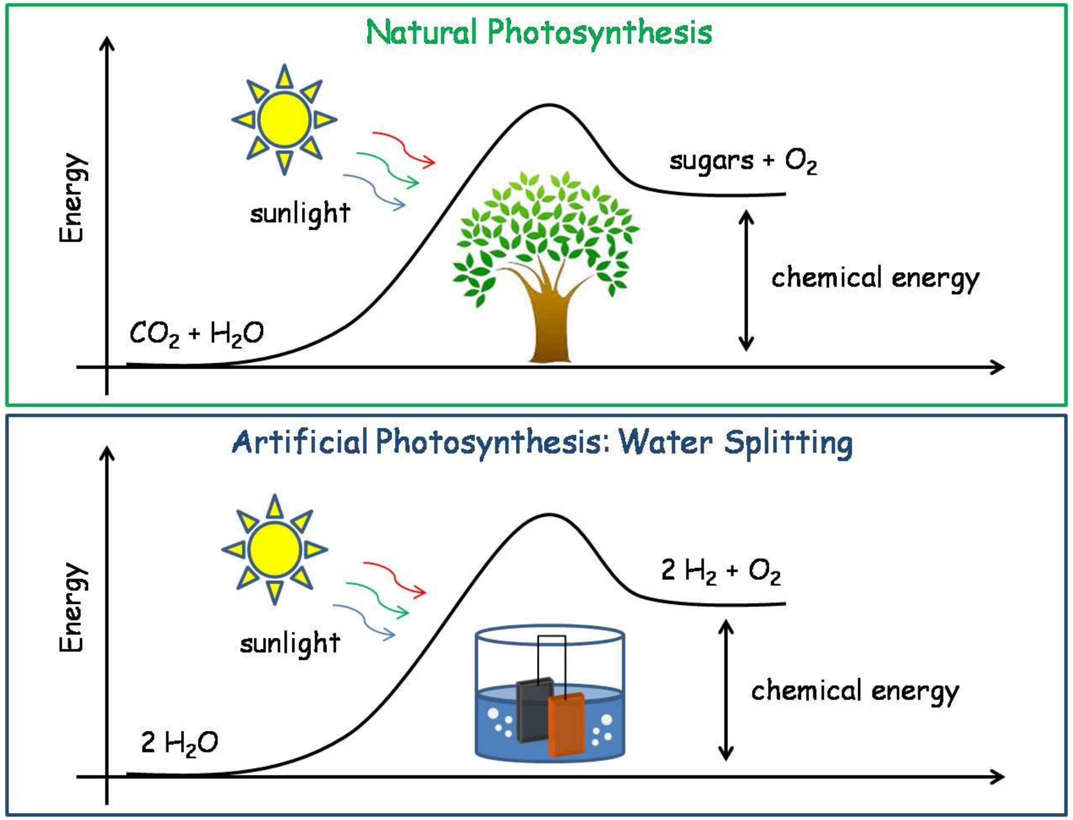




Artificial photosynthesis: solar fuels



Store solar energy in form of chemical bonds

to reduce energy transport inefficiencies

to match energy production and demand

Hydrogen
Methane
Methanol
Formic acid
Carbon monoxide

Three reasons to choose hydrogen

1. Carbon-free cycle

2. Highest energy content per unit mass

3. High efficiency of fuel cells

   tank-to-wheel efficiency

   45% fuel cell vehicle

   22% diesel vehicle

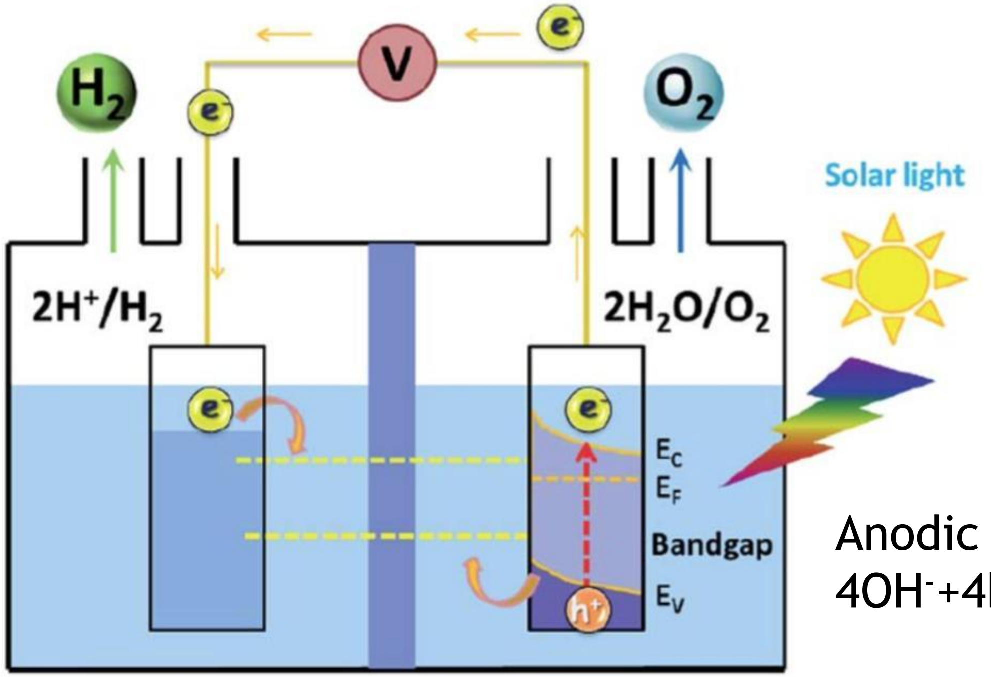
"Solar Hydrogen Generation" edited by K. Rajeshwar et al. (Springer, New York, 2008).

Fuel	HHV (MJ/kg)	LHV
Hydrogen	141.9	119.9
Methane	55.5	50.0
Gasoline	47.5	44.5
Diesel	44.8	42.5
Methanol	20.0	18.1

Photo–electrochemical water splitting

Materials for Photo–Electrochemical Cells (PEC)
- Solar light absorbers
- Photocatalysts

Cathodic half reaction
$4H_2O+4e^-\rightarrow \mathbf{2H_2}+4OH^-$



Anodic half reaction
$4OH^-+4h^+\rightarrow \mathbf{O_2}+2H_2O$

$$2H_2O \rightleftarrows 2H_2+O_2$$

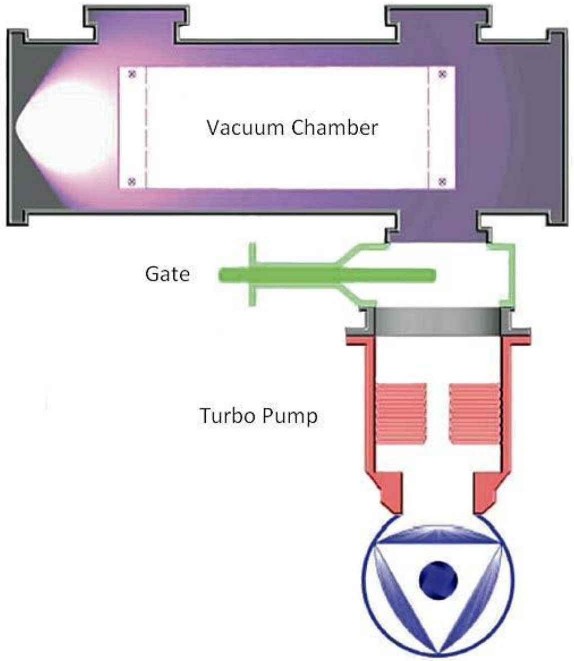
IdEA Laboratory @ UniTN

- Physical Vapor Deposition techniques:
  Pulsed Laser Deposition (PLD),
  RF-sputtering, Electron Beam Deposition
- Solar energy absorbers for photoelectrodes in photoelectrochemical cells
- Innovative materials for electrocatalysis and photocatalysis of water splitting
- Nanostructured materials for water and air purification (dye degradation, CO oxidation)

Presentation outline

1. Photoelectrochemical water splitting
   - Semiconductors in water splitting
   - Catalysts: improving reaction kinetics
   - Photo-Electrochemical Cells (PEC)
   - Top PEC efficiencies

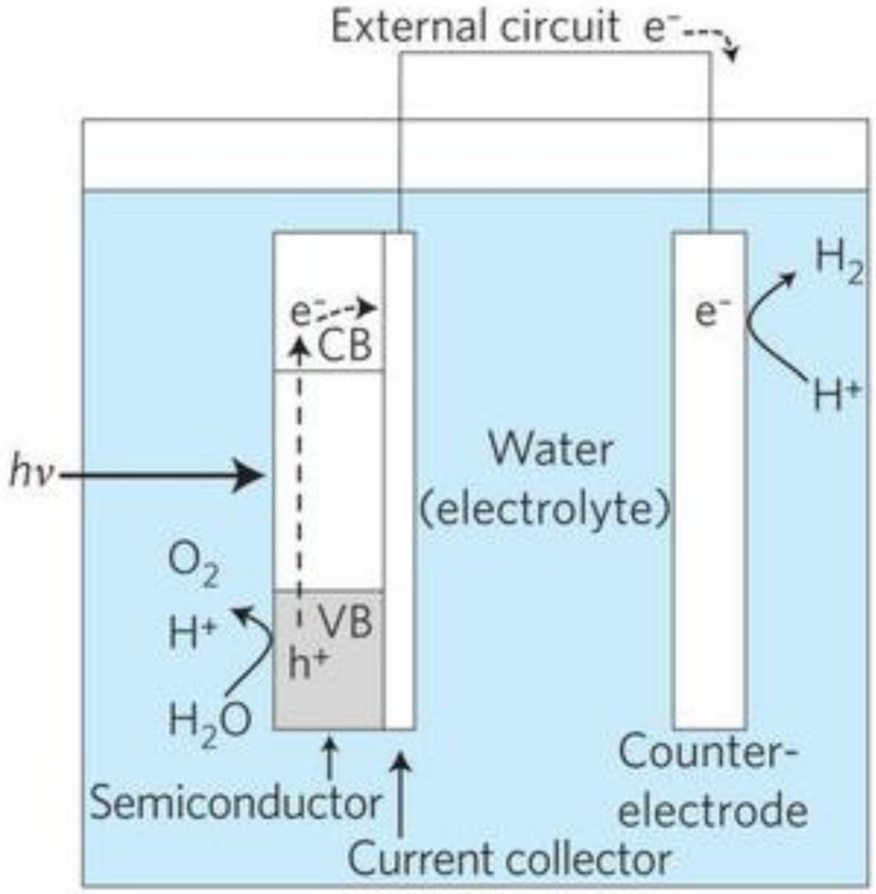
2. Deposition techniques
   - Physical Vapor Deposition
   - RF-magnetron sputtering
   - Pulsed Laser Deposition



3. IdEA laboratory results
   - Photoactive materials
   - Nanostructured catalysts

Semiconductors in solar water splitting

- Sunlight absorption
- Charge separation
- Carrier migration
- Chemical reaction



The energy band gap E_G of the absorber has to be coupled with the water oxidation and reduction potentials

$$E^0_{H_2} = 0 \text{ V}$$

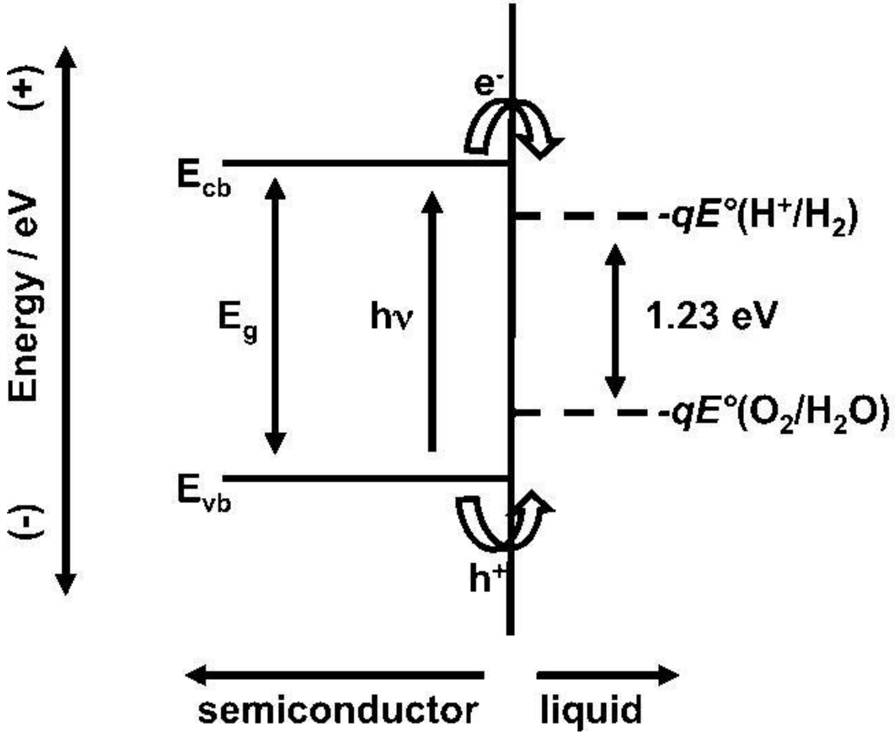
$$E^0_{O_2} = 1.23 \text{ V}$$

Semiconductors in solar water splitting

- Solar light irradiates the cell
- Photons with $h\nu > E_G$ are absorbed
- e^-/h^+ pair is formed
- If $E_{CB} > -qE^0_{H2}$ the e^- can reduce
- If $E_{VB} < -qE^0_{O2}$ the hole can oxidize water

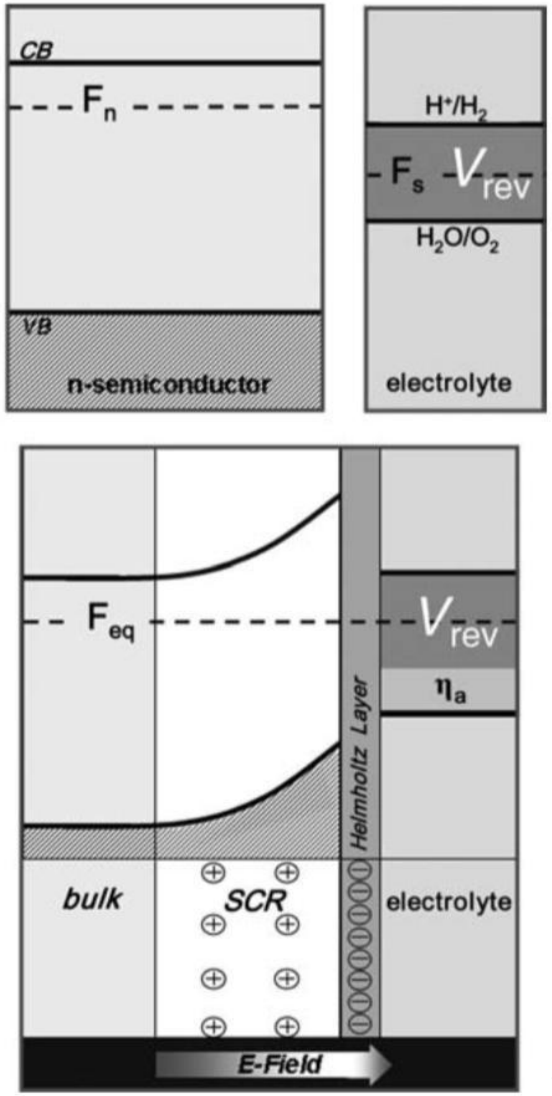
1.23 eV is stored in chemical bonds

hv-1.23 eV is wasted



M.G. Walter et al. Chem Rev. **110** (2010) 6446

Charge separation: lighted junction

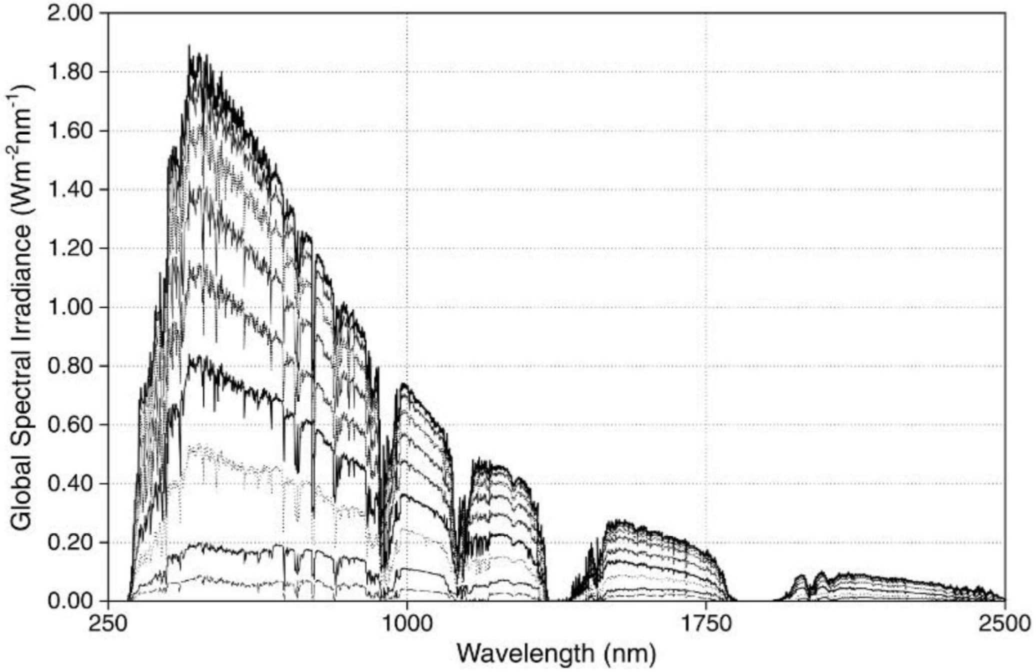


Example: n-type anode / electrolyte junction

- Equilibration of the Fermi level (sc. and electrolyte)
- Band bending
- Formation of Space Charge Region:
  electric field induces charge separation
- Driving force vs. disorder
  (charge separation vs. charge recombination)

L. Vayssieres, *"On Solar Hydrogen & Nanotechnology"*
(John Wiley & Sons, 2009)

Solar spectrum harvesting



Global total hemispherical distribution of solar irradiance from 0° (top curve) to 80° (bottom) respect to the zenith.

"Solar Hydrogen Generation" edited by K. Rajeshwar et al. (Springer, New York, 2008).

- A semiconductor with bandgap E_G can only absorb photons with $h\nu > E_G$
- E_G >1.8 eV for real water splitting (λ<700 nm)

Material requirements

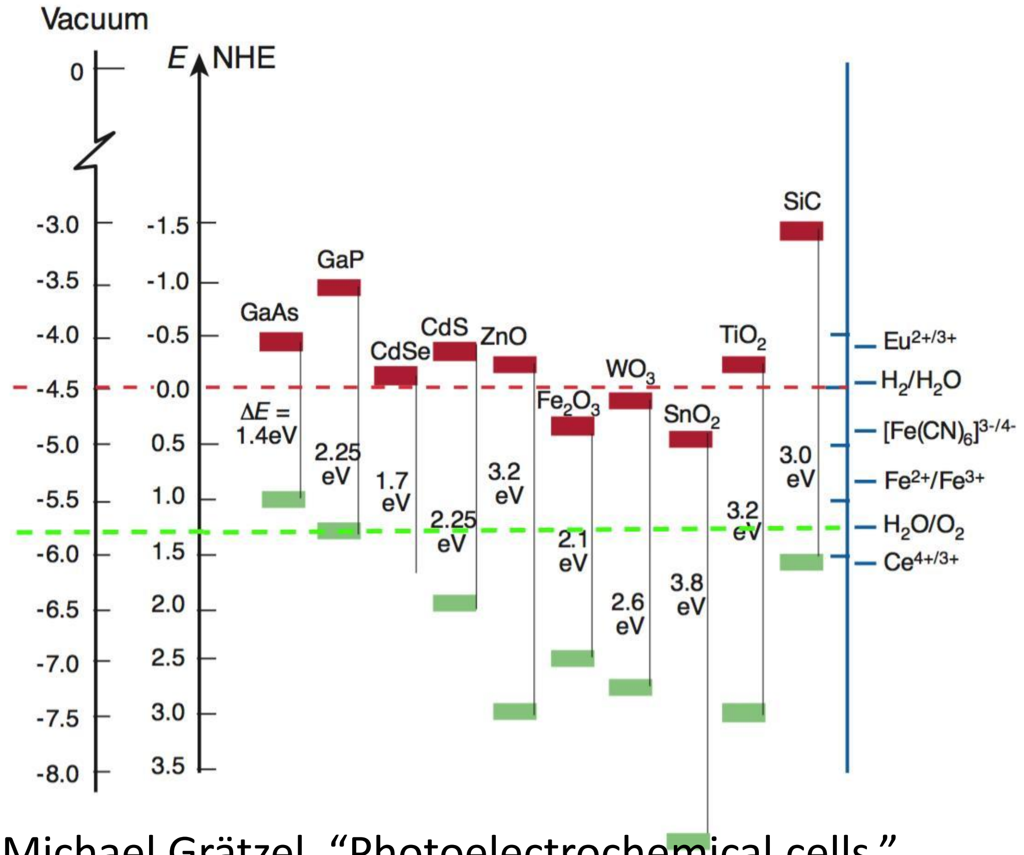
Quantum efficiency (ability to generate and separate e^-/h^+ pairs)

absorption in the SCR, recombination…

Favorable band gap and position

Stability issues

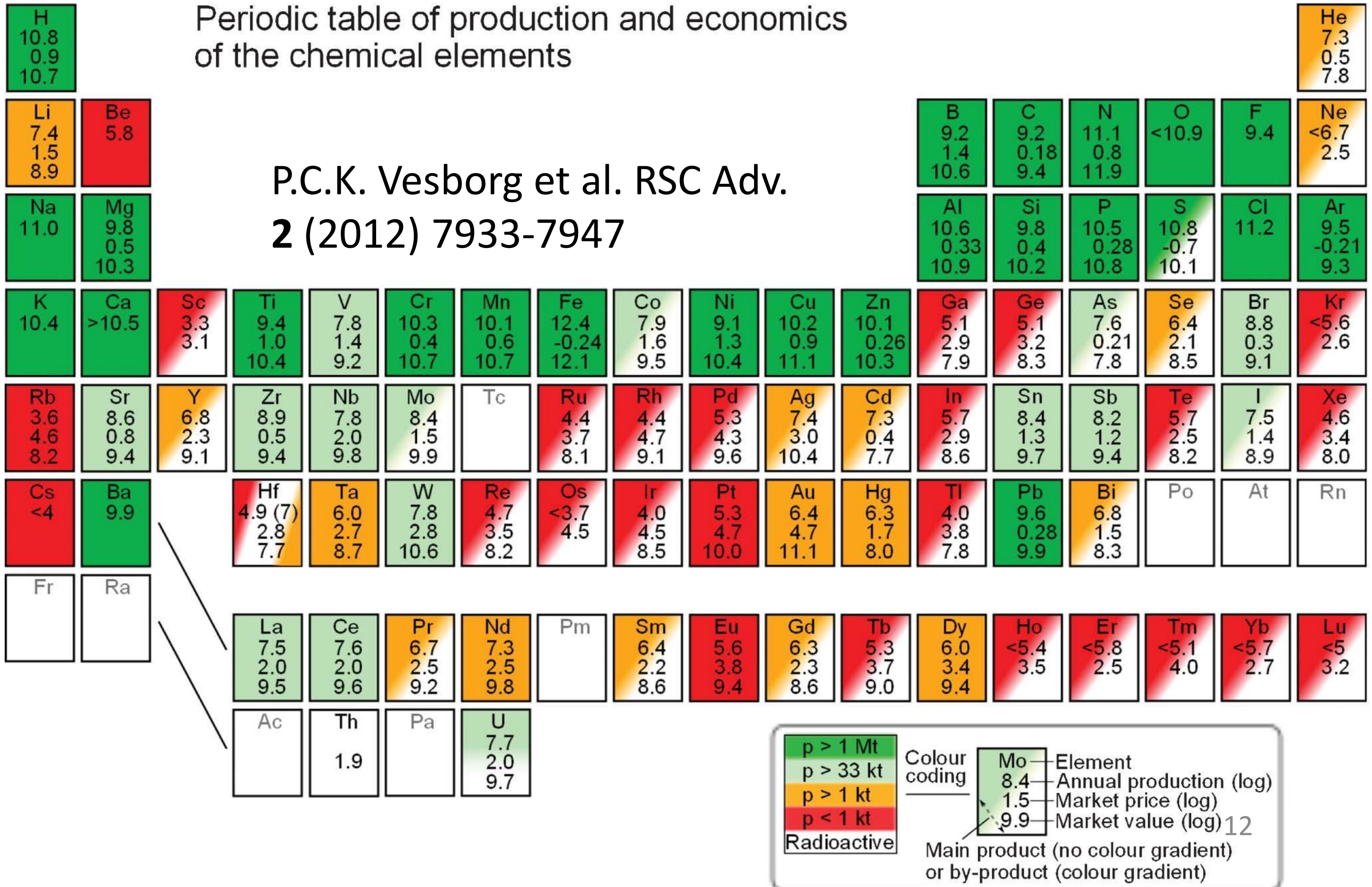
- Chemical stability in water
- Stability to electrochemical corrosion
- Photostability (photodegradation)



Michael Grätzel. "Photoelectrochemical cells." Nature 414.6861(2001), pp.338–344

Material requirements

Material scalability (cheap, earth abundant materials)



P.C.K. Vesborg et al. RSC Adv. **2** (2012) 7933-7947

Environmentally friendly materials

Catalysts: improving reaction kinetics

Water splitting: a 4 e^- redox process

HER	$4H_2O + 4e^- \rightarrow \mathbf{2H_2} + 4OH^-$	WRC
OER	$4OH^- + 4h^+ \rightarrow \mathbf{O_2} + 2H_2O$	WOC
	$2H_2O \rightarrow \mathbf{2H_2} + \mathbf{O_2}$	

1. Water Reduction Catalysts

   Precious metal based catalysts: Pt, RuO_2

   Mixed-metal catalysts: Ni-Co, Ni-Mo, Ni-Mo-Fe …

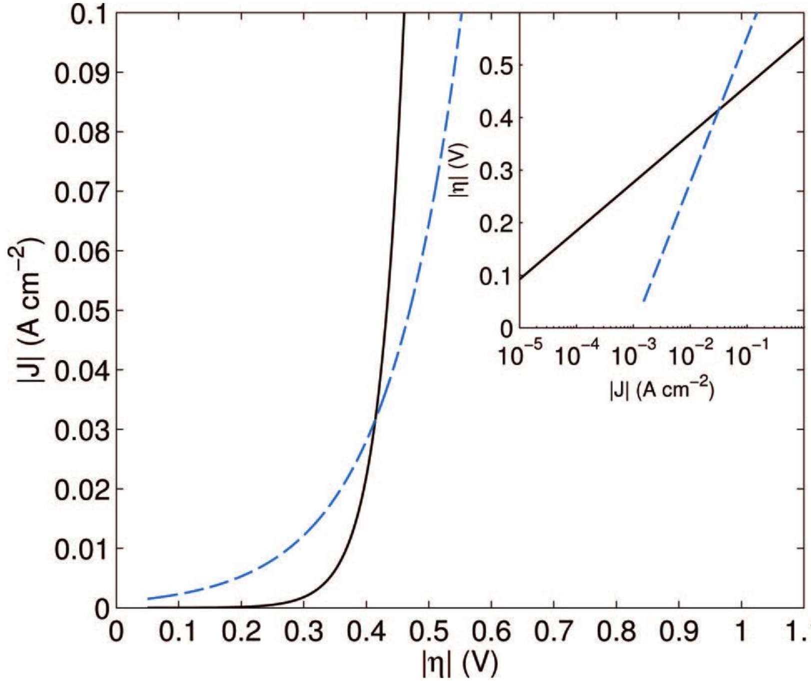
   Metal-nonmetal: Sr_xNbO_{3-x}, NiS_x, WC_x …

2. Water Oxidation Catalysts

   Precious metal based catalysts: RuO_2, IrO_2

   Cheap metal oxides: Co_3O_4, $NiCo_2O_4$, Fe_2O_3, CoP

Catalysts at electrode-electrolyte interface have to optimize reaction kinetics by offering a large quantity of active sites



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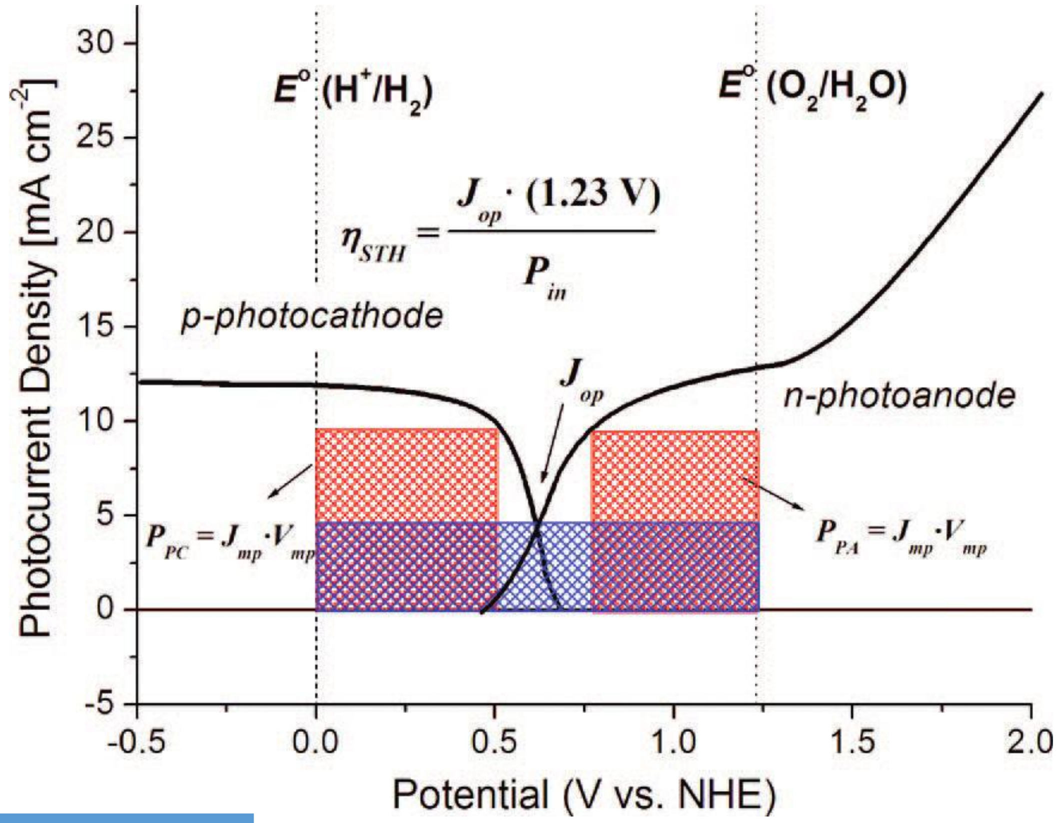
Defining the PEC efficiency

Efficiency for water splitting PEC that requires an external bias

$$\eta = \frac{J(1.23\ \mathrm{V} - V_{\mathrm{app}})}{P_{\mathrm{in}}}$$

Solar to hydrogen efficiency

$$\eta_{\mathrm{STH}} = \frac{J_{\mathrm{mp}} V_{\mathrm{mp}}}{P_{\mathrm{in}}}$$



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Top η_{STH} in literature:

Absorbers	Catalysts	Configuration	η_{STH}
AlGaAs/Si	Pt/RuO_2	2 PVs	18%
$CH_3NH_3PbI_3$	$Ni\text{-}Fe(OH)_x$	tandem PV	12,3%

Top PEC efficiencies

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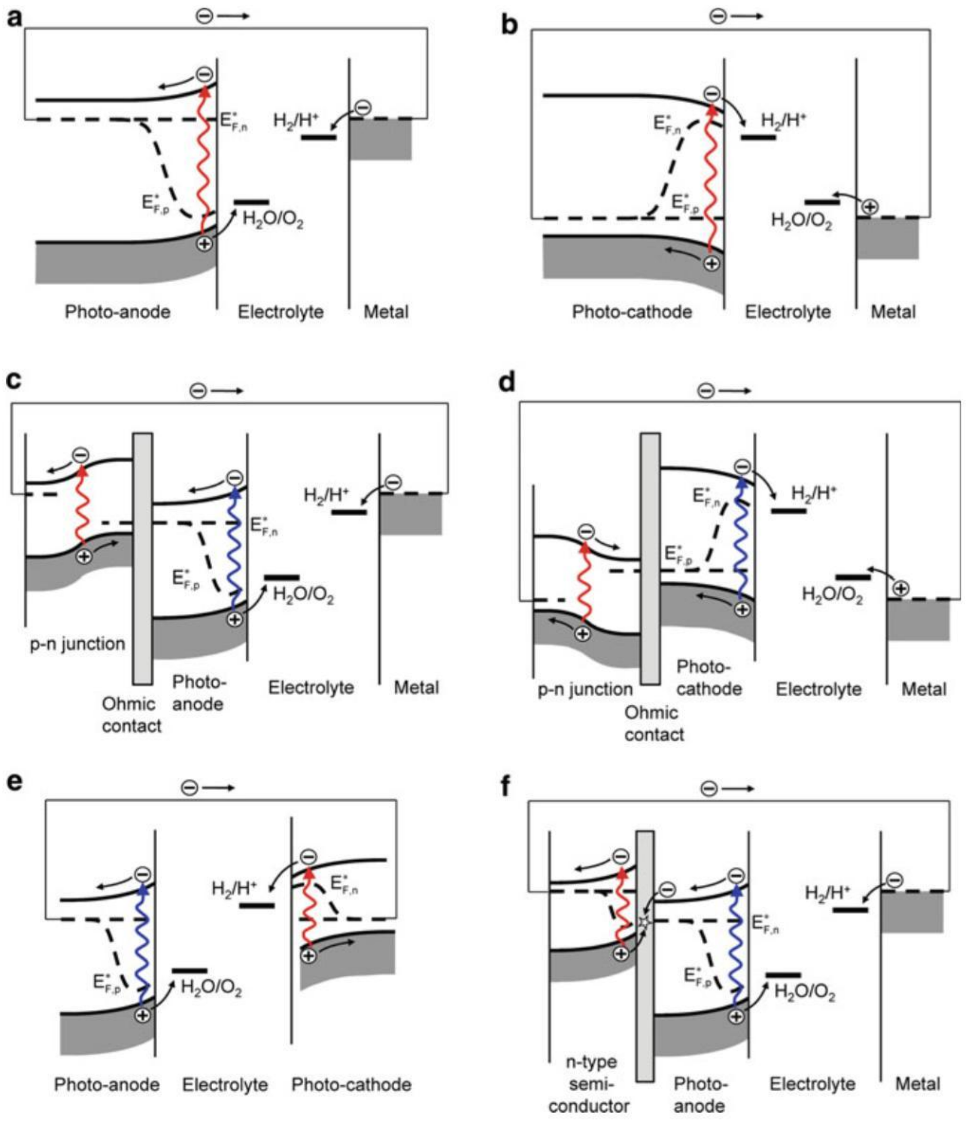
Solar irradiation: $1\ kW/m^2$
Cell efficiency: 18% → $180\ W/m^2$ output power
Effective current: $J_{eff} = 180\ W / 1.23\ V = 146\ A/m^2$
H_2 production rate: $\frac{J_{eff} \cdot MM}{2\ \mathrm{el.}/H_2 \cdot e} = 5.5\ g/hm^2$
Energy content: $5.5\ g/h \cdot LHV = 0.65\ MJ/hm^2$*

1 liter gasoline: 33 MJ**

* Some energy required to store H_2 at high pressure
** Internal combustion engine efficiency

10 m^2 device, 5÷7 h H_2 peak production
=1 liter gasoline

PEC configurations



Different PEC configurations under light illumination

Single semiconductor devices with a metal counter electrode for (a) photoanode and (b) for photocathode semiconductor materials

Single semiconductor PEC devices integrated with a photovoltaic module (p-n junction) at (c) anodic part or at (d) cathodic part.

(e) PEC tandem: photoanode + photocathode sc.
(f) PEC heterojunction: two ore more n-type semiconductors are coupled in order to increase the absorbed spectral range

M.G. Walter et al. Chem Rev. **110** (2010) 6446

Improving material performance

1. Semiconductor doping

Introduce small amount of impurities (usually some ‰) to tailor band gap and band positions

Improving material performance

2. Nanostructuring

The deposition technique and parameters are relevant to design the film morphology

- Shorten diffusion path in the sc.

  (reduce charge recombination)
- Active surface area

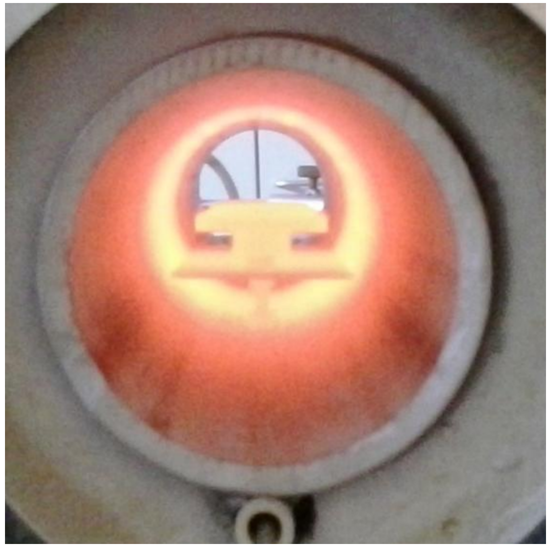
  (number of catalyst active sites)

Improving material performance

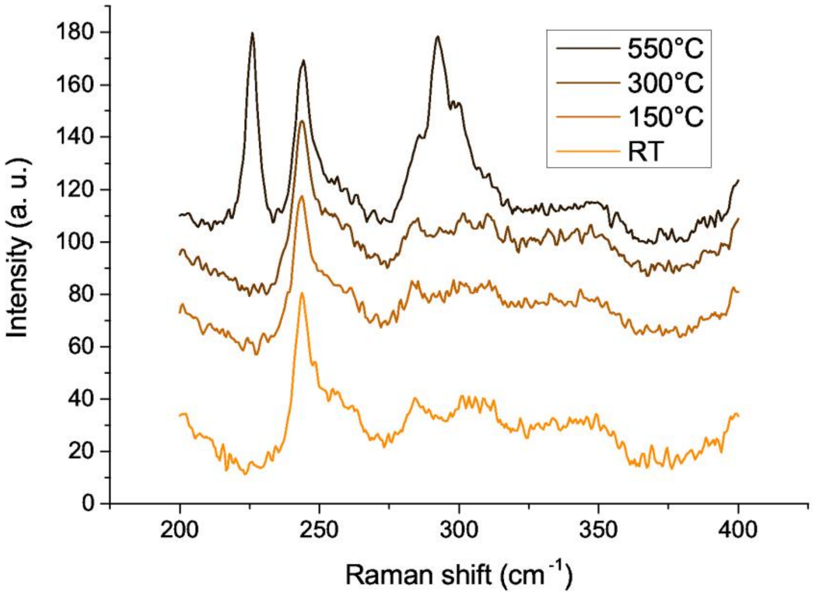
3. Crystalline phase

Post-deposition thermal treatments

to induce re-crystallization



Sample annealing in air at high temperature

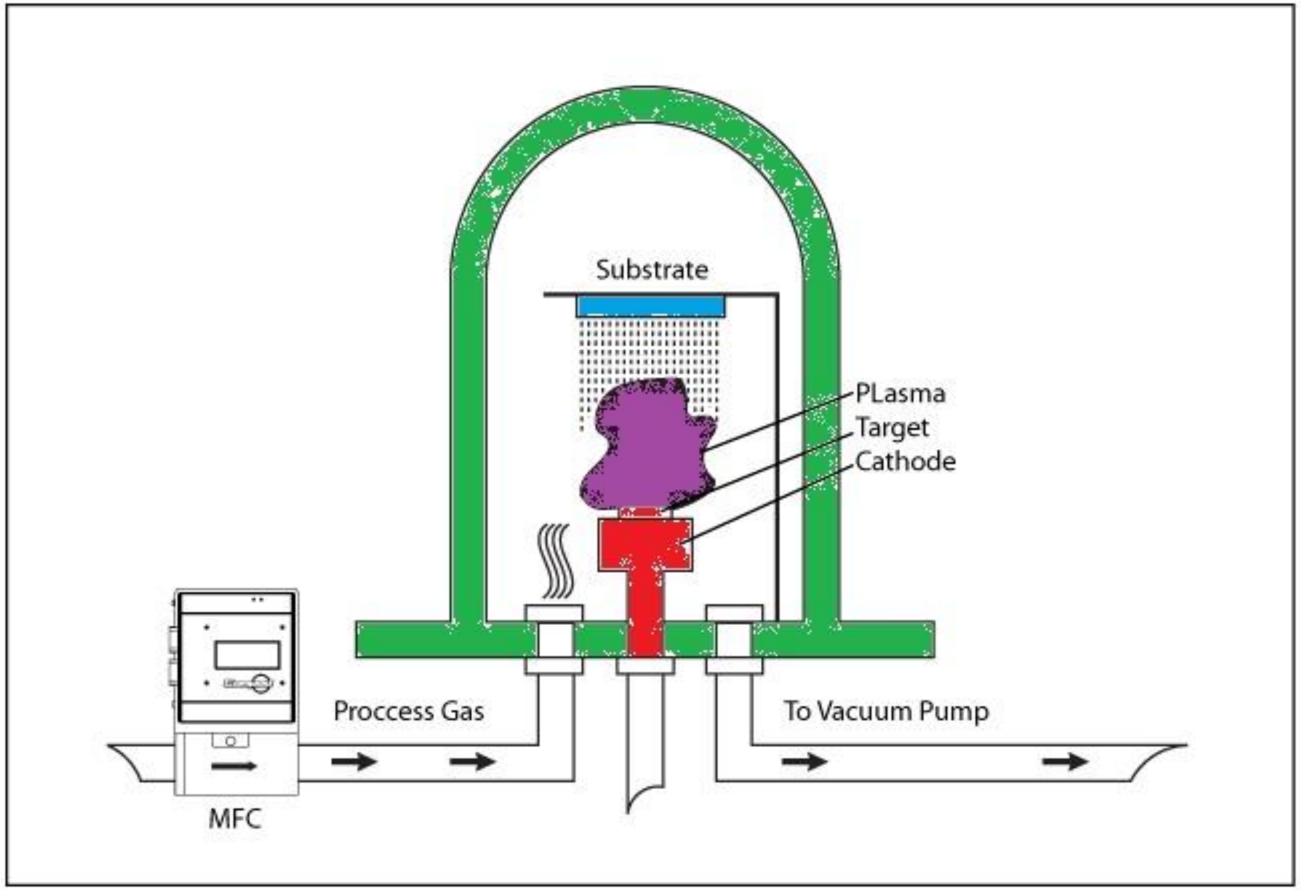


Raman spectroscopy of a−Fe2O3 deposited by PLD

Change in crystalline degree and structure
At material−dependent threshold temperatures

Physical Vapor Deposition techniques

- Vacuum chamber (10^{-8} ÷10^{-1} Pa)
- Vaporization of a precursor material (target)
- Eventual chemical reactions during flight
- Deposition on a substrate of thin films (thickness nm÷µm)

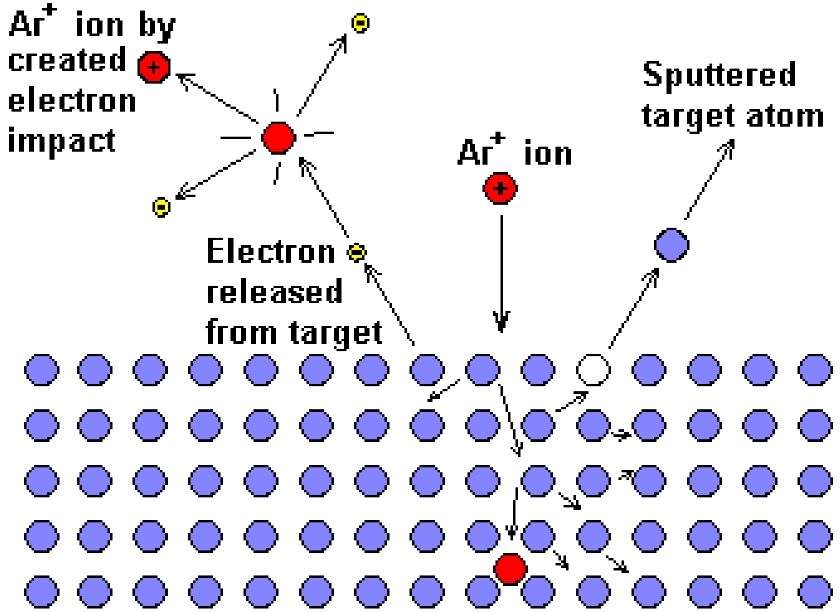


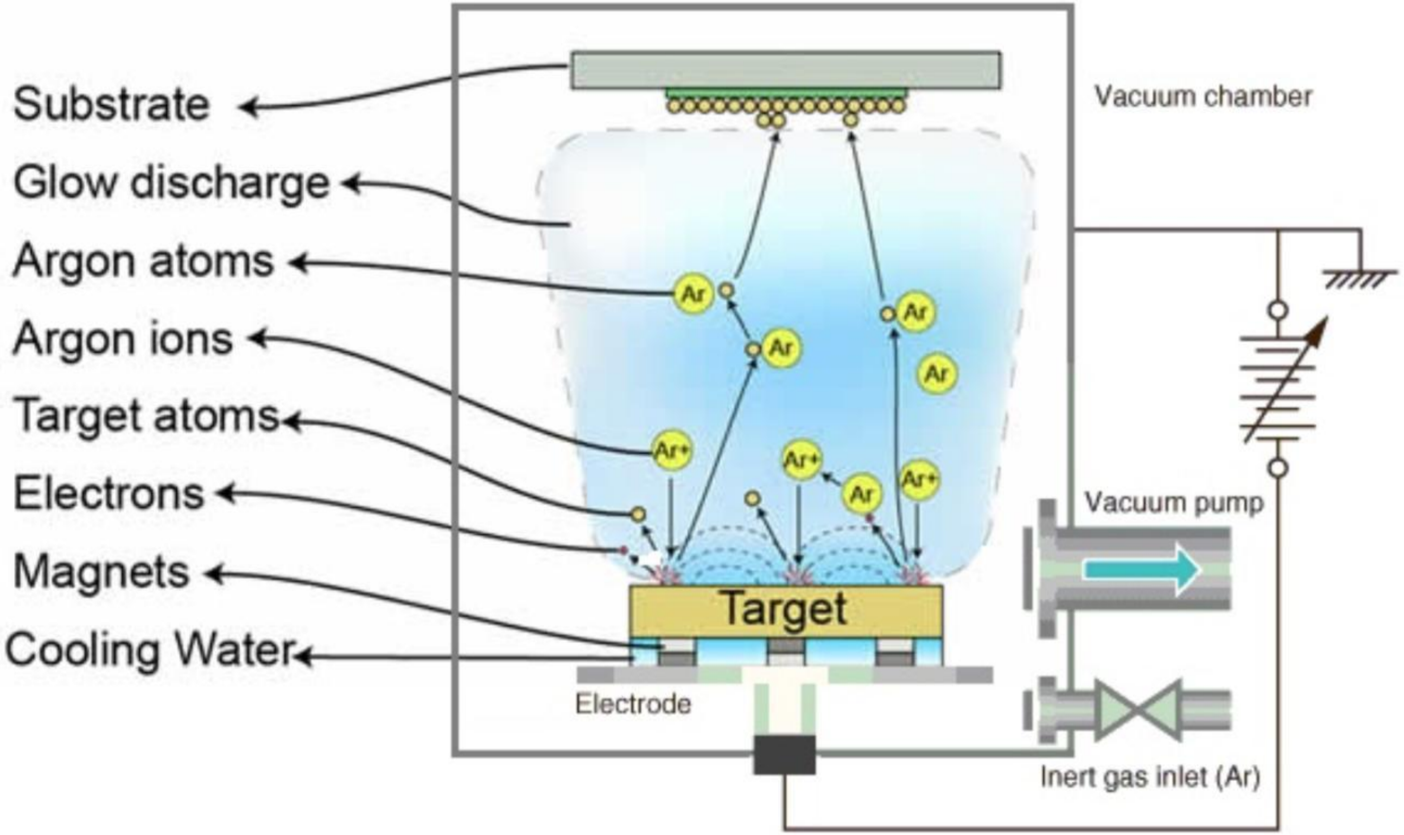
Different deposition techniques depending on the heating system

1. Electron beam
2. High energy ions
3. Pulsed laser

RF-magnetron sputtering

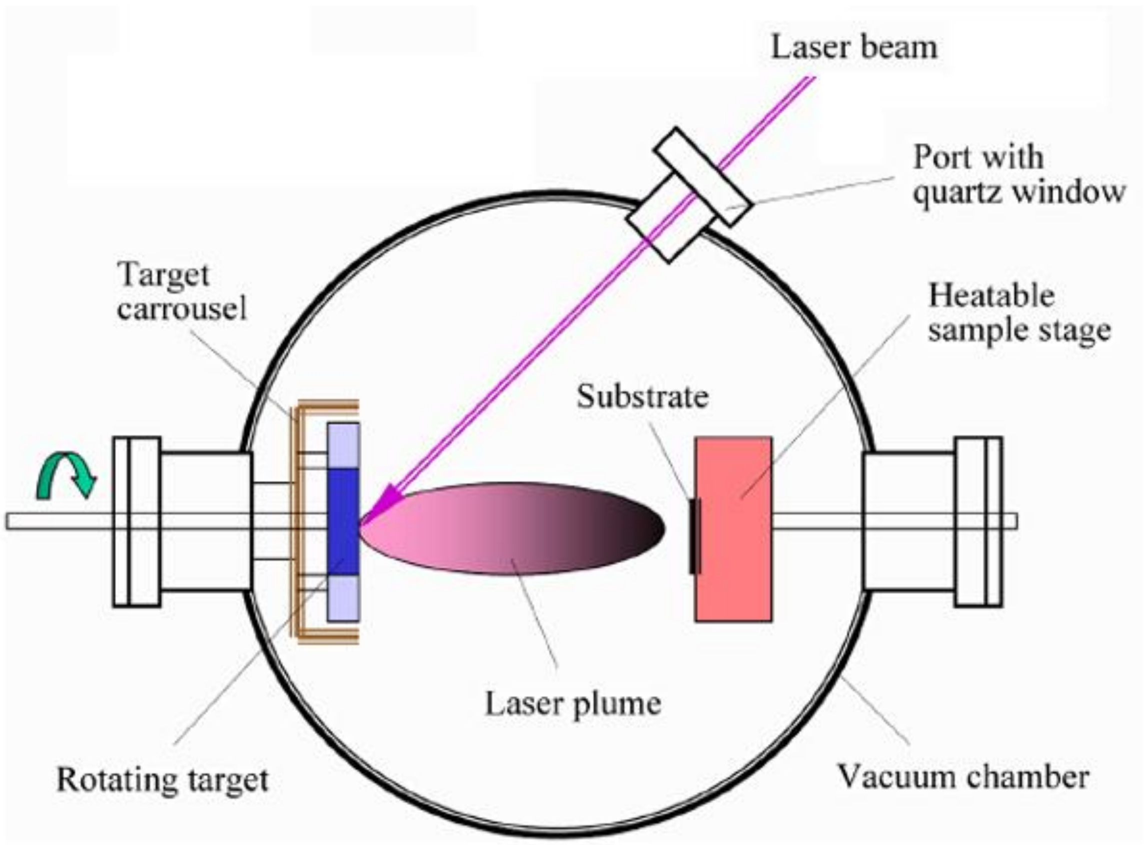
- Heating source: inert gas plasma (Ar)
- Radiofrequence (MHz) oscillating electric field
- Target: solid (usually semiconductors)
- Reactive atmosphere: O_2, N_2 added
- Magnetic plasma confinement
- Substrate heating system

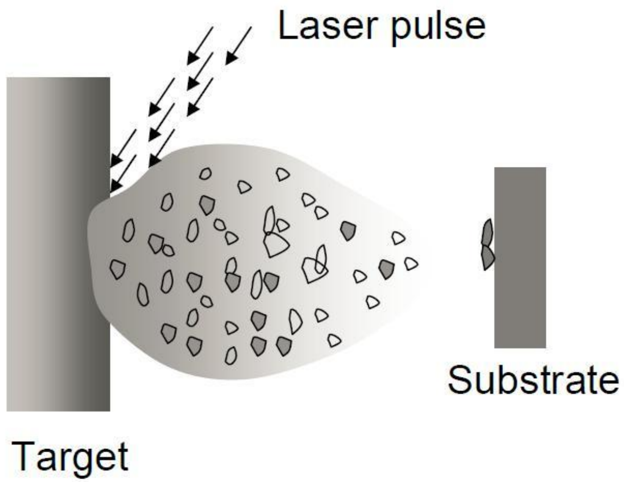




Pulsed Laser Deposition

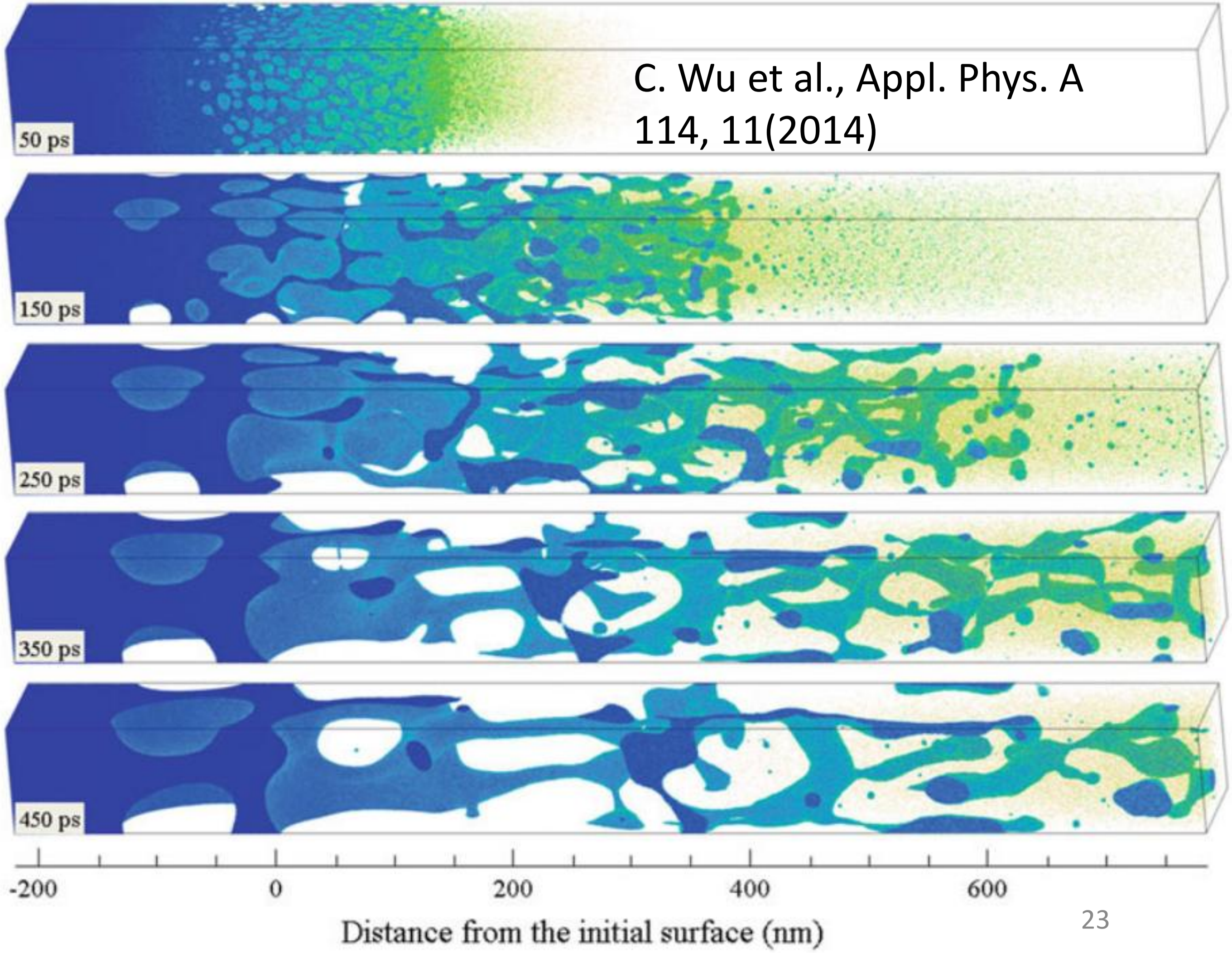
- Heating source: pulsed laser (ns÷fs)
- Surface ablation: vapor and nanoparticles
- Target: insulator, semiconductor, metal (as bul material or powder)
- Background gas: inert or reactive
- Substrates heating system





Pulsed Laser Deposition

- The effect of photon momentum is negligible
- Photons are absorbed at the target surface
- Rapid surface heating (10^{12} K/s)
- Explosive l-v phase transition



C. Wu et al., Appl. Phys. A 114, 11(2014)

RF-magnetron sputtering

Single molecule – small clusters ejection
Continuous film growth
Easy to deposit crystalline materials

Employed for transparent conducting oxides and solar absorbers (semiconductors)

Pulsed Laser Deposition

Vapor-nanoparticle ejection
Highly nanostructured layers
Generally amorphous materials

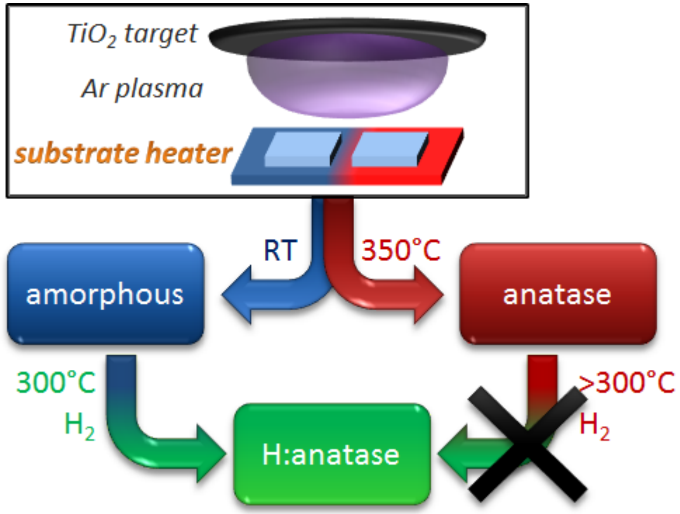
Efficient to deposit thin films
Used for nanostructured catalyst coatings

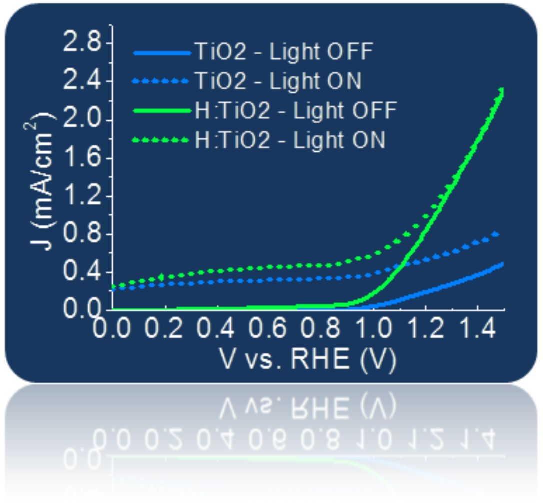
H-TiO_2 as solar absorber

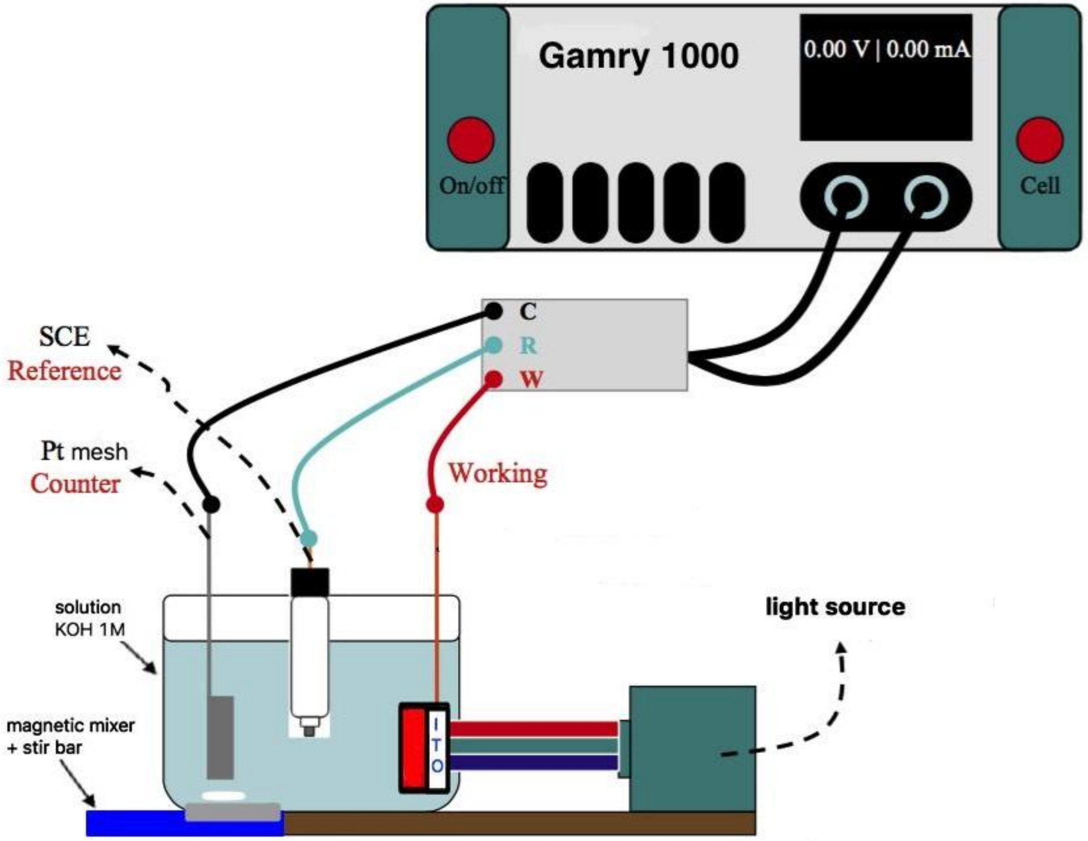
Typical photoelectrochemical characterization

Photoanode material under artificial illumination

- 1 M KOH electrolyte solution
- Pt counter electrode
- Three electrode configuration setup
- Calibrated solar simulator







H doping and crystallization: annealing at 300°C, 1bar H_2, 10 min

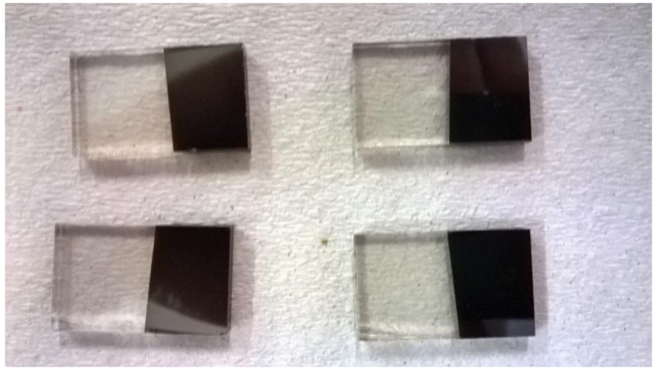
E. Binetti et al., Applied Catalysis A: General 500 (2015) 69–73

Nanostructured WS_2 water reduction catalyst

PLD of tungsten sulfide catalyst for water reduction

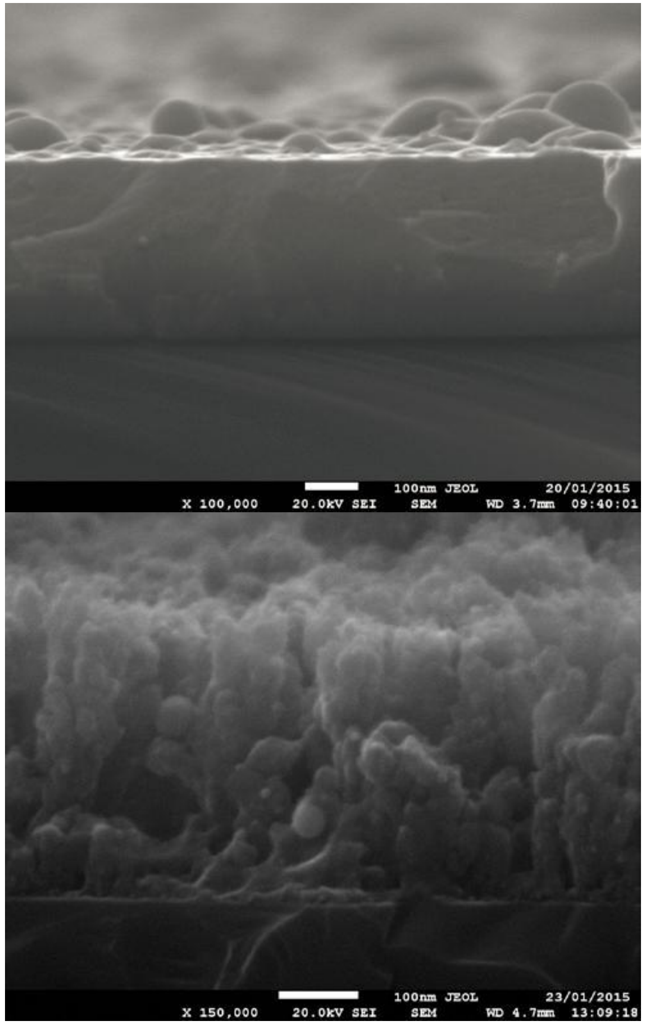
Target: WS_2 pressed powder target
Background gas: Ar (to induce recondensation)

Deposited film: partially amorphous WS_2



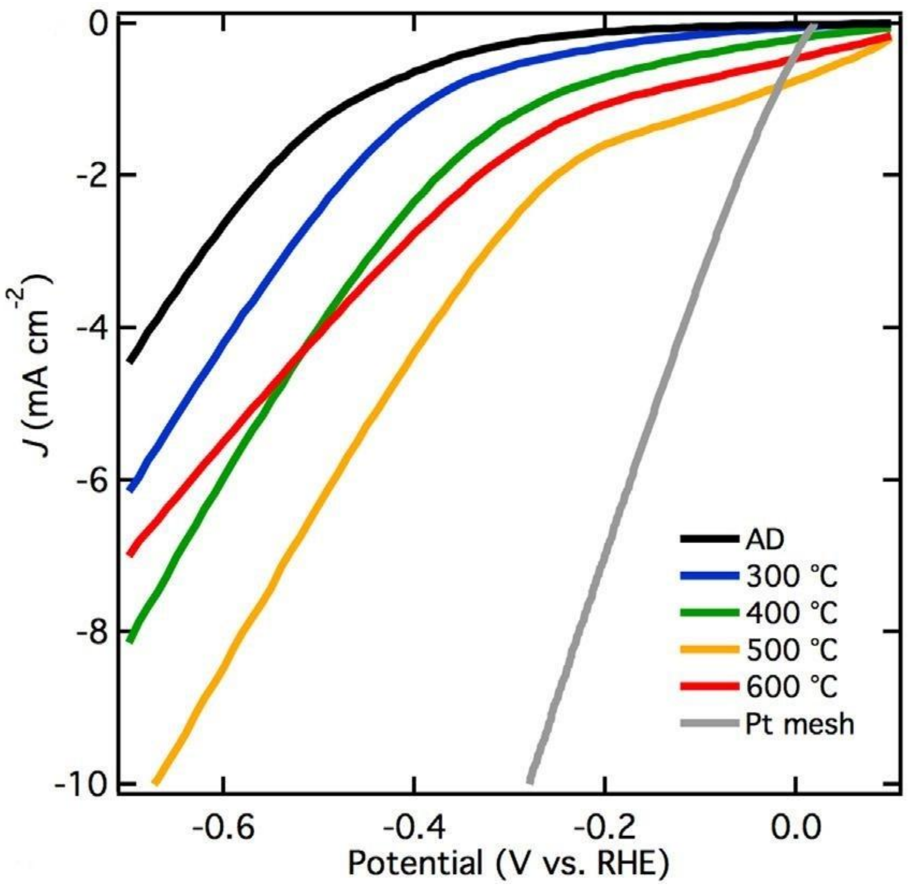
Thermal treatments to increase WS_2 cristallinity
Annealing in vacuum at 300, 400, 500, 600°C

SEM images
for samples deposited at
$P_{\mathrm{Ar}} = 4.5 \times 10^{-2}$ mbar (top)
and 4.5×10^{-1}mbar (bottom)



M. Schenato et al.
Applied Catalysis A: General
510 (2016) 156–160

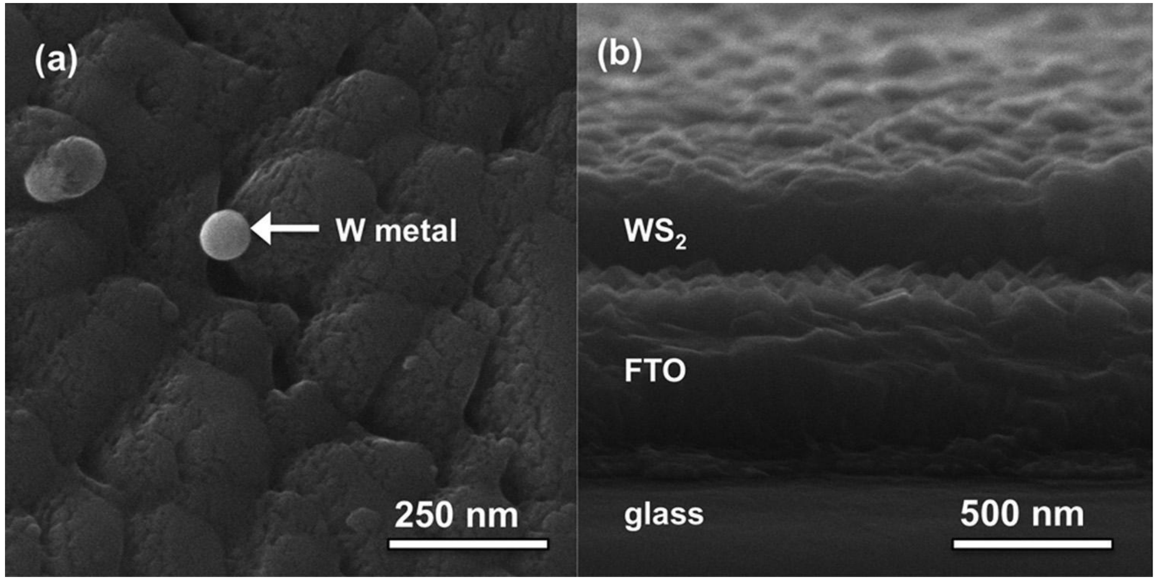
Nanostructured WS_2 water reduction catalyst



Thermal treatments to increase WS_2 cristallinity

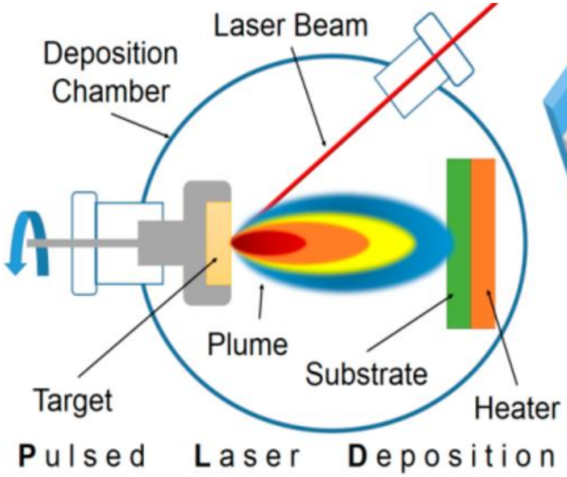
Increasing catalytic activity with increasing annealing temperature

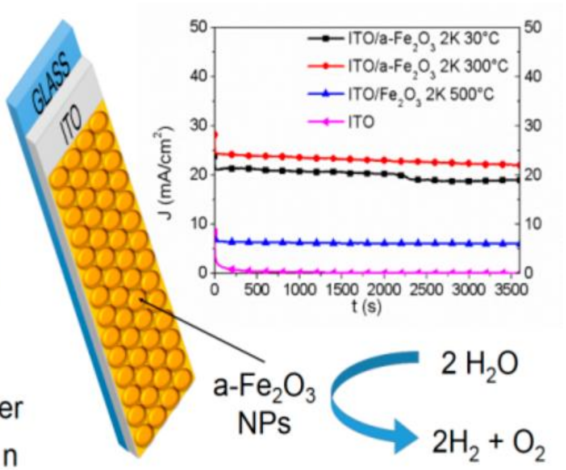
- Crystalline WS_2 shows higher efficiency as a WRC
- Lower activity of 600°C sample due to conductive layer degradation



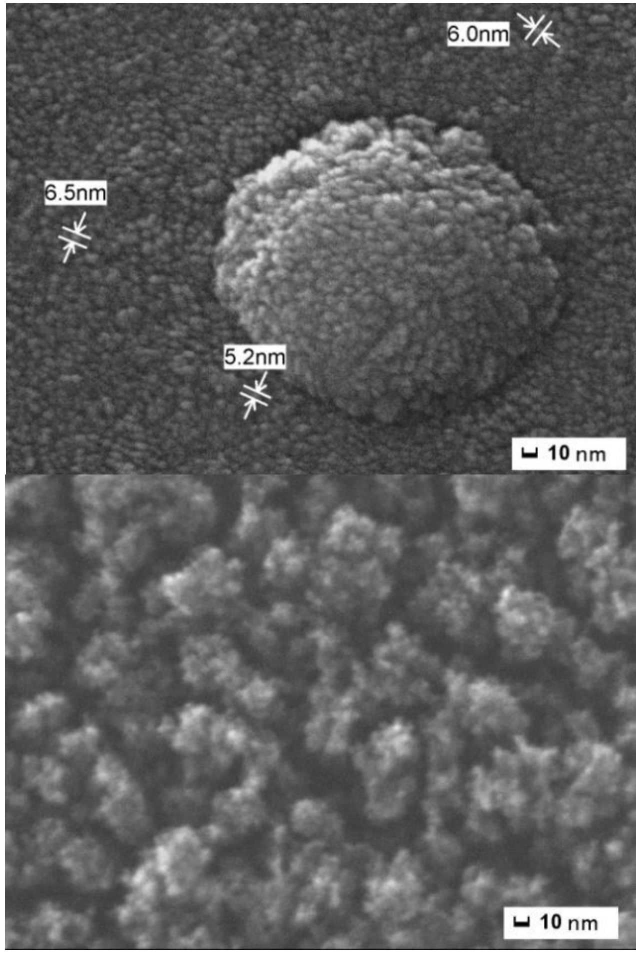
M. Schenato et al., Applied Catalysis A: General 510 (2016) 156–160

Nanostructured Fe_2O_3 WOC





M. Orlandi et al.
Appl. Mater. Interfaces
6 (2014) 6186−6190



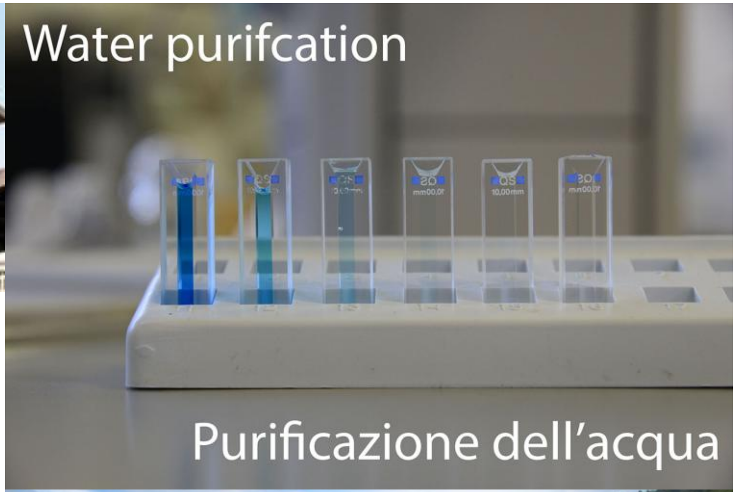
Synthesis of nanostructured iron oxide catalyst for water oxidation

Target: pure Fe
Background gas: O_2

Deposited film: partially crystalline Fe_2O_3

SEM images
for samples deposited at
$P_{O_2} = 4.5 \times 10^{-2}$ mbar (top)
and 4.5×10^{-1}mbar (bottom)

Opportunità al laboratorio IdEA



- Opportunità per tesi magistrali in collaborazione
- Dottorato in Fisica @ UniTN

  prossimo bando: luglio–agosto

http://idea.physics.unitn.it/

Ringraziamenti

<u>Gruppo IdEA</u>

- Prof. Antonio Miotello

  assegnisti, postdoc

- Dr. Michele Orlandi, Dr. Enrico Binetti, Dr. Raju Edla

  dottorandi

- Dr. Zakaria El Koura, Federico Gorrini

  staff tecnico

- Nicola Bazzanella, Marco Bettonte, Massimo Cazzanelli, Claudio Cestari, Luigino Vivaldi

  neo−laureati

- Giacomo Arban, Matteo Schenato, Denis Ganin, Teodoro Klaser

Università di Trento

Provincia Autonoma di Trento

Consiglio Nazionale delle Ricerche

Università degli Studi di Ferrara

University of Mumbai

Colorado School of Mines

Letture ed approfondimenti

- M.G. Walter et al. *“Solar Water Splitting Cells”* Chem Rev. **110** (2010) 6446-6473.
- *“Solar Hydrogen Generation”* edited by K. Rajeshwar et al. (Springer, New York, 2008).
- L. Vayssieres, “*On Solar Hydrogen & Nanotechnology”* (John Wiley & Sons, 2009).
- P.C.K. Vesborg et al. *“Addressing the terawatt challenge: scalability in the supply of chemical elements for renewable energy”* RSC Adv. **2** (2012) 7933-7947
- Plataforma Solar de Almeria psa.es/en/ Impianto solare purificazione dell’acqua
- http://idea.physics.unitn.it/

LEDS
L'ENERGIA DEGLI STUDENTI

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DI TRENTO

IdEA
Idrogeno
Energia Ambiente

Grazie per l’attenzione!

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