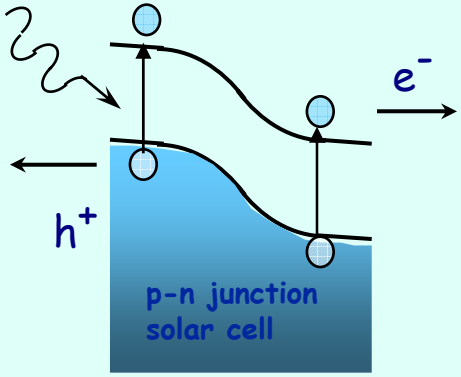
Generation of hydrogen from the Solar Photolysis of Water

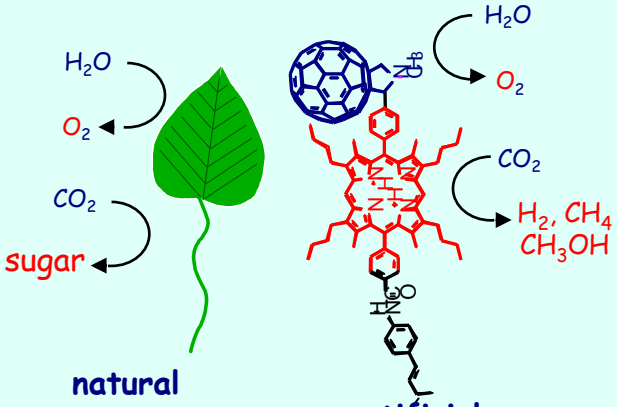
Hydrogen Conference, UC Santa-Barbara August 20-25, 2006

Michael Graetzel, LPI, EPFL LAUSANNE

Michael.graetzel@epfl.ch

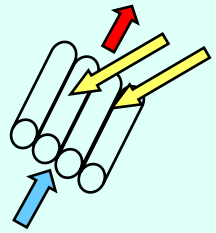
Solar Energy Utilization



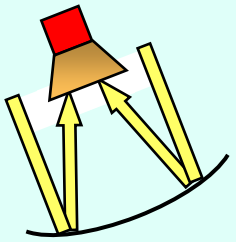


natural photosynthesis

artificial photosynthesis

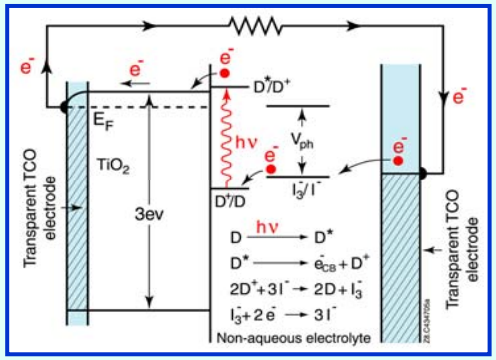


50 - 200 °C
space, water heating



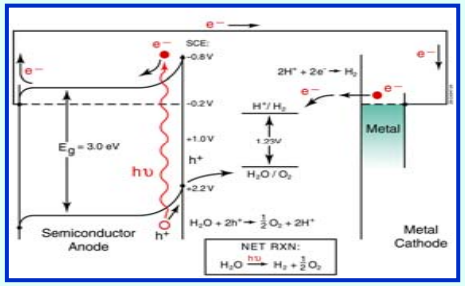
500 - 3000 °C
heat engines
electricity generation
process heat

Solar Thermal



dye sensitized cell and photoelectrochemical solar cells

Solar Electric



photoelectrolysis/H_2O splitting

Solar Fuels

~ 14 TW additional C-free energy by 2050

THE SOLAR CHALLENGE

- ***With a projected global population of 12 billion by 2050 coupled with moderate economic growth, the total global energy consumption is estimated to be ~28 TW. Current global use is ~11 TW.***

- ***To cap CO_2 at 550 ppm (twice the pre-industrial level), most of this additional energy needs to come from carbon-free sources.***

- ***Solar energy is the largest non-carbon-based energy source (100,000 TW).***

- ***However, it has to be converted at reasonably low cost.***

"A Vision for Photovoltaic Energy Production" Report by the European Photovoltaic Technology Research Advisory Council ((PV-TRAC)" EUR 21242 (2005)

Photoelectrochemical tandem cell for hydrogen generation from water by visible light

In collaboration with the groups of Prof. Jan Augustynki (Uni Geneva).Prof. Gion Calzaferri, (Uni Berne)

Dr. Albert Goosens (Delf University of Technology)

and Solaronix SA, Aubonne, CH).

LPI/EPFL coworkers involved: Dr. M. Nazeeruddin, Alexis Duret (Ph.D. thesis completed),Ilkay Cesar (Ph.D student), Dr. Andreas Kay (part time), Dr. Monica Barroso (started January 1, 2006)

Financial support by the Swiss Federal Office of Energy (OFEN)

as well as the Hydrogen Solar Production Company Ltd (London) is gratefully acknowledged.

OUTLINE

1. Introduction
2. photoelectrochemical tandem cells
   - work on oxygen evolving Fe_2O_3 photoanode
   - work on bottom electrode
3. Future work and conclusions

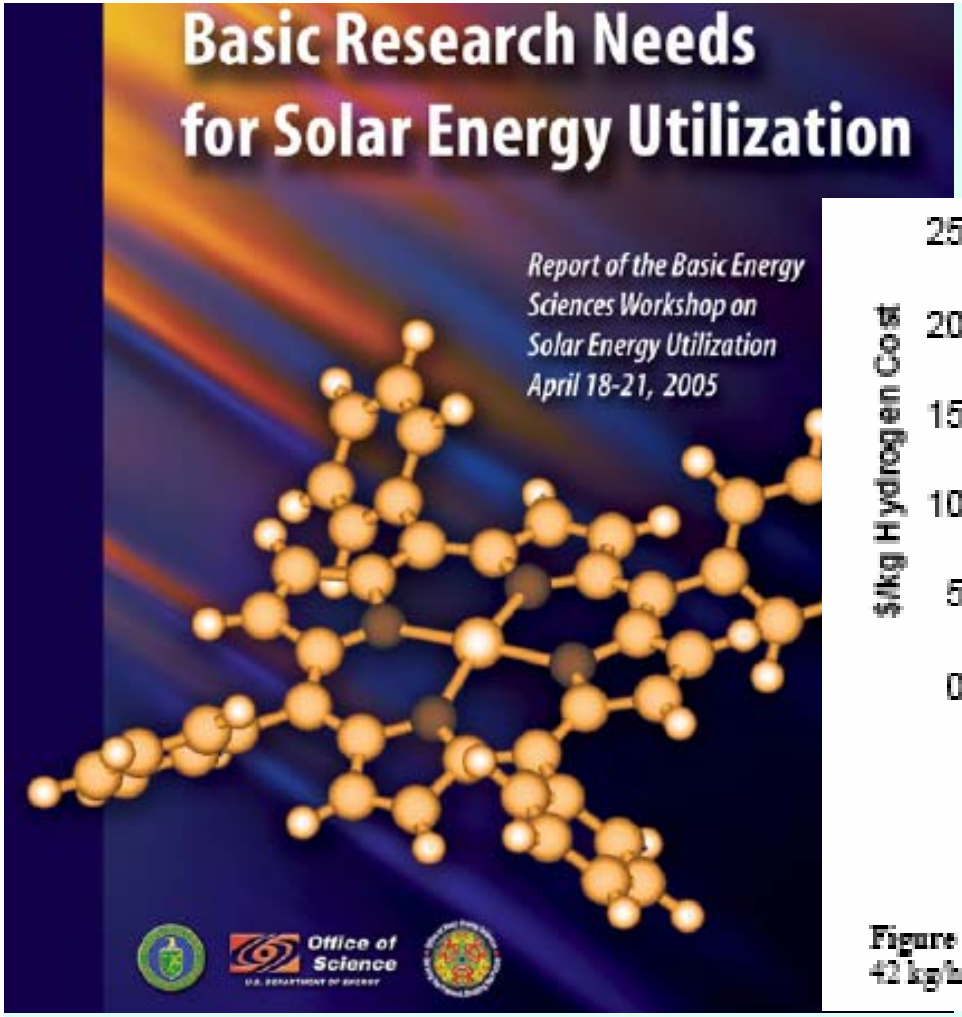
Hydrogen generation by solar photolysis of water

The three options:

1. **The brute force approach:**
   connect at least 4 silicon PV cells in series and couple to water electrolyzer

2. **The integrated tandem cell approach**

3. **The direct water decomposition by photoelectrochemical cells.** **Remains the "Holy Grail" of research in photoelectrochemistry**



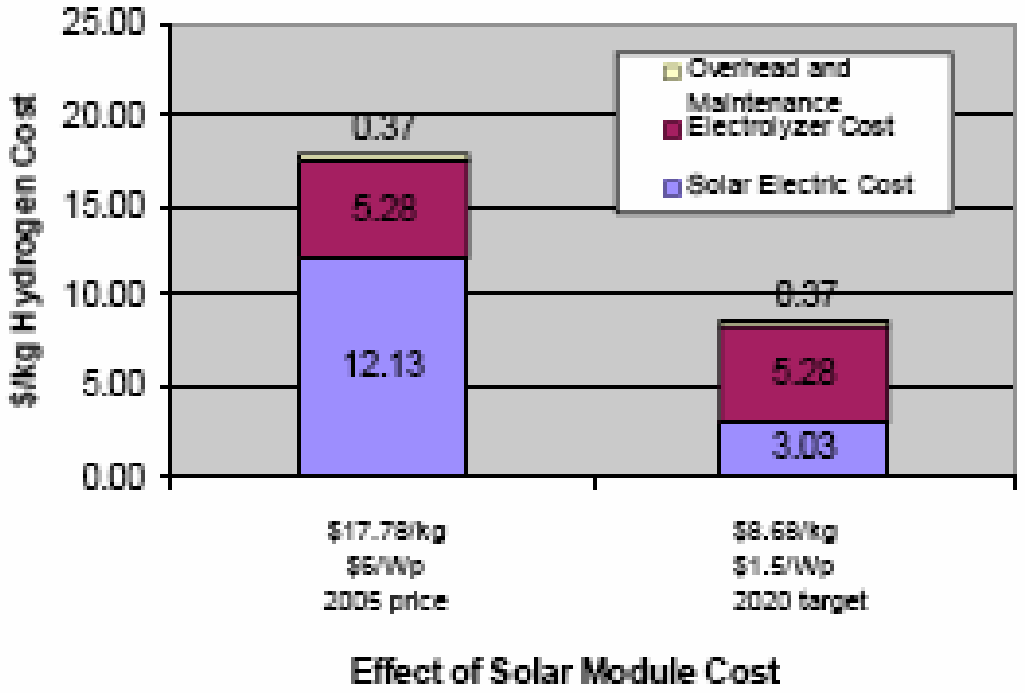


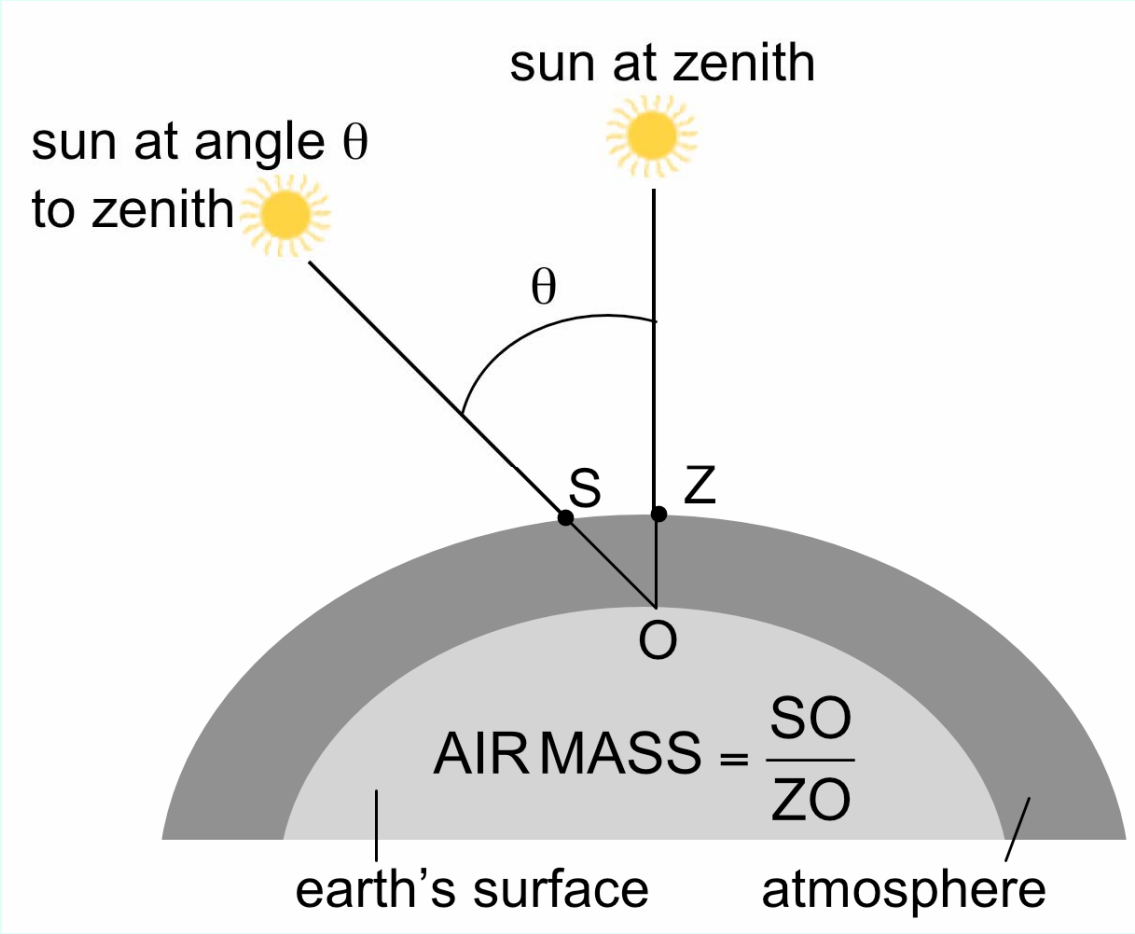
Figure 72 Hydrogen selling price for carbon-free solar electricity (assumes 42 kg/hour production rate)

With a 2020 solar efficiency of 20% and an electrolyzer system efficiency of 65%, the overall solar conversion efficiency will be about 13%. It is not unreasonable to foresee that by 2020, systems for photocatalytic hydrogen evolution, where hydrogen is evolved directly from a photocatalytic surface, would probably be more effective than electrolyzers in generating hydrogen fuel.

Quotation from the DOE report page 209

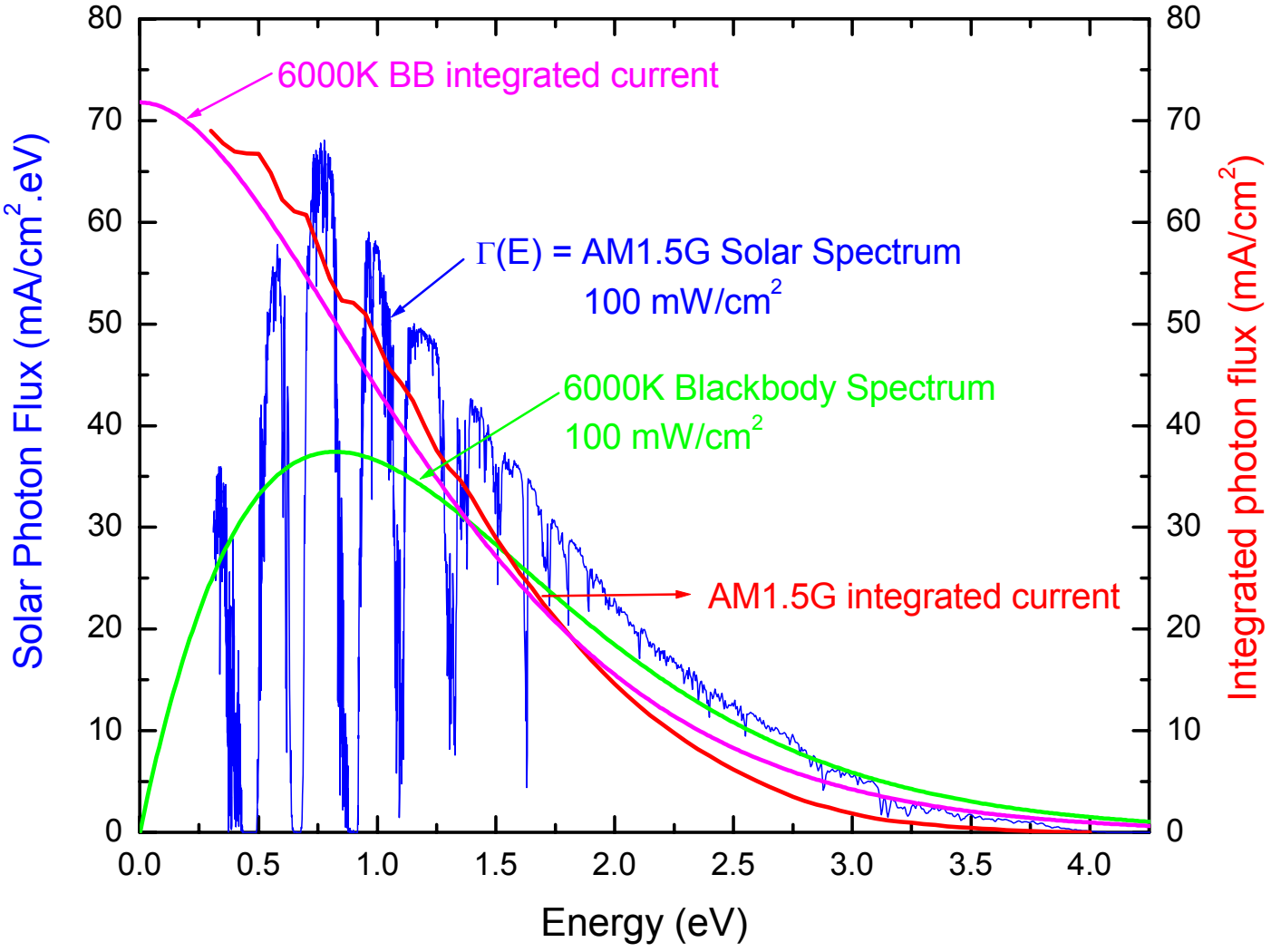
Characterisation Standard Air Mass1.5

- **intensity of 1000 W/m^2**
- **spectral power distribution corresponding to AM1.5 ≡ 1Sun**
- **temperature 298 K**

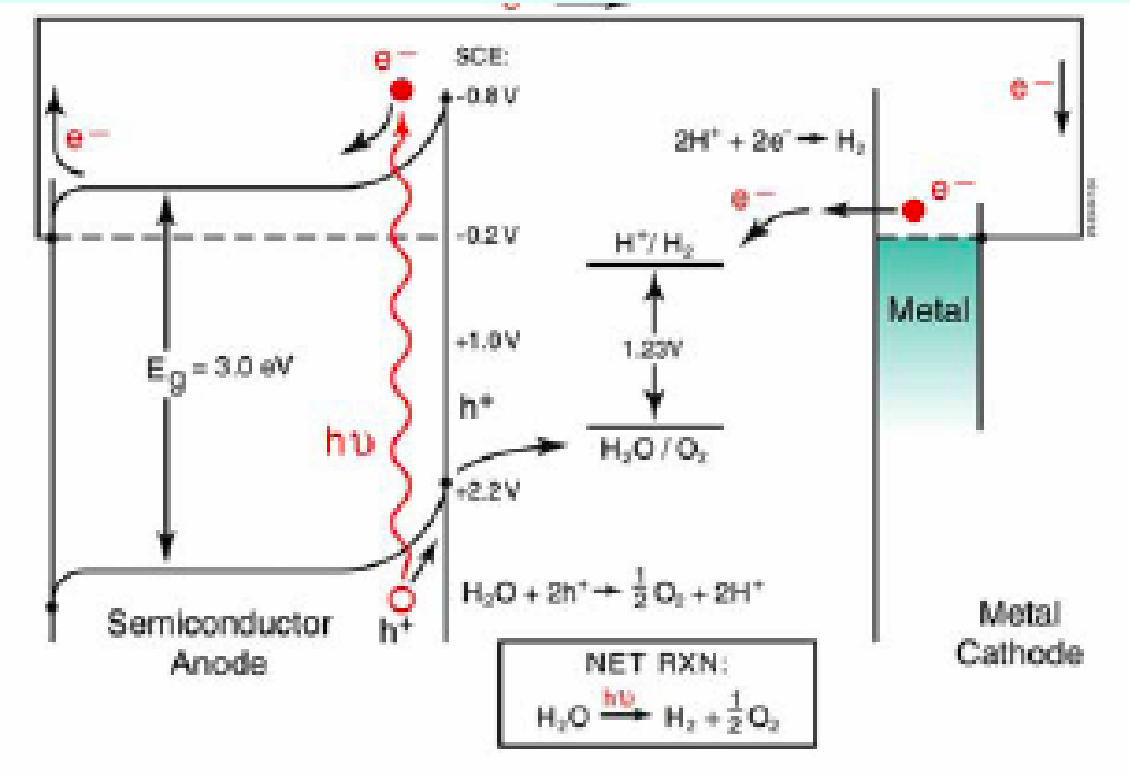


THE SOLAR RESOURCE

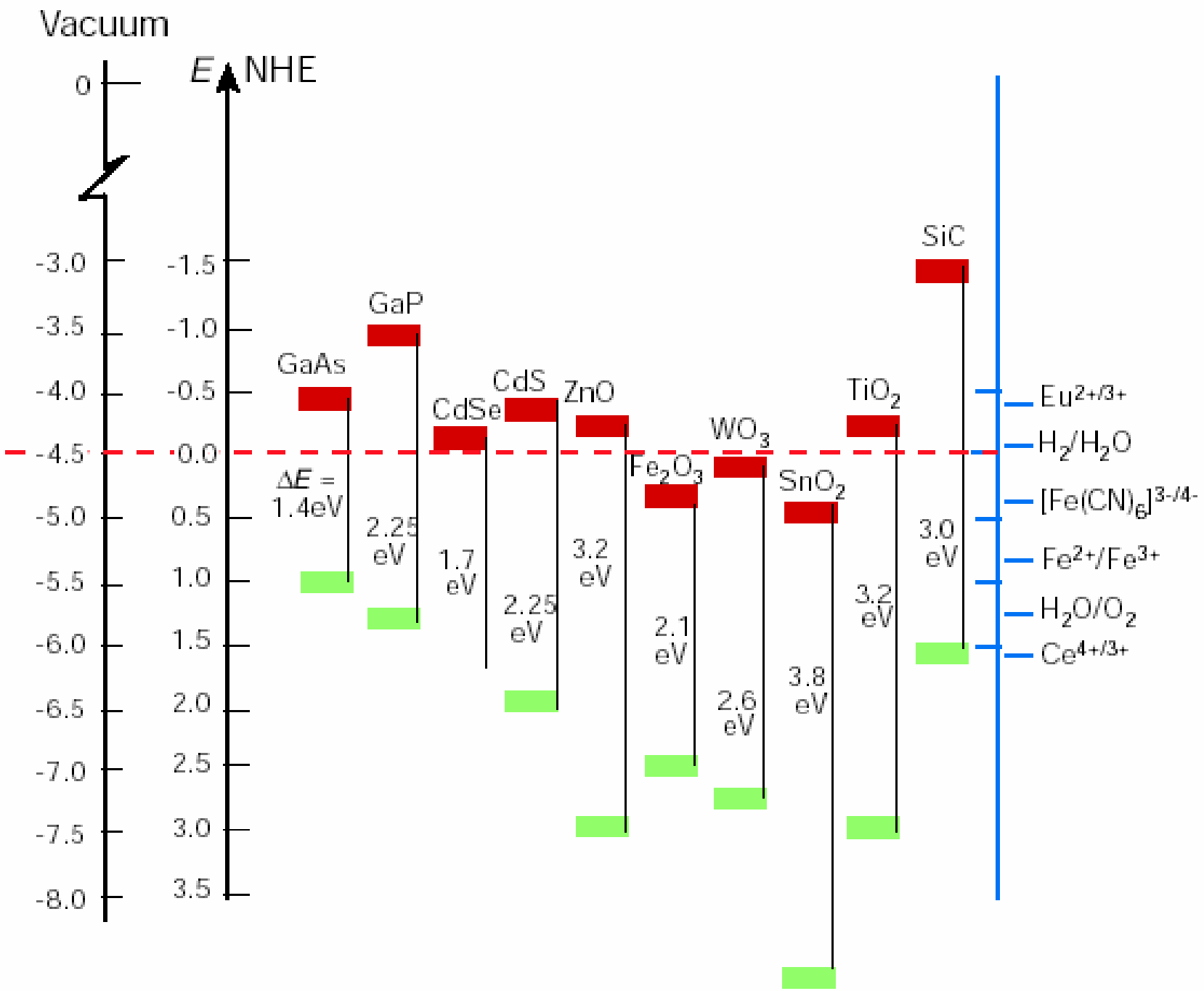
Solar Spectrum and Available Photocurrent



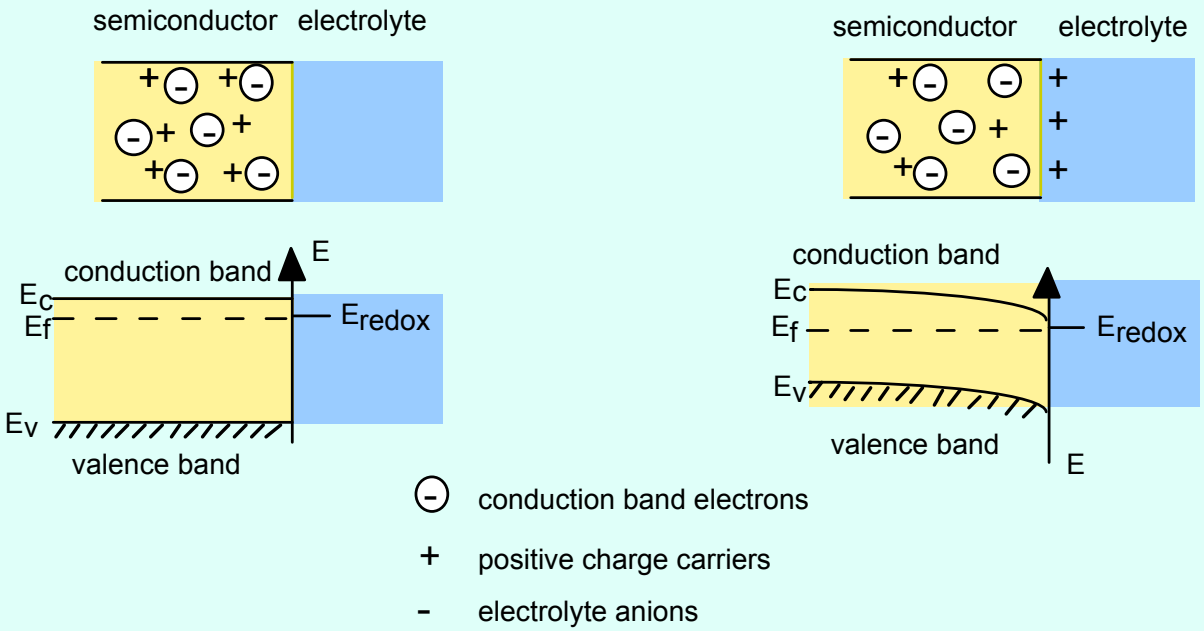
Water Photoelectrolysis Cell



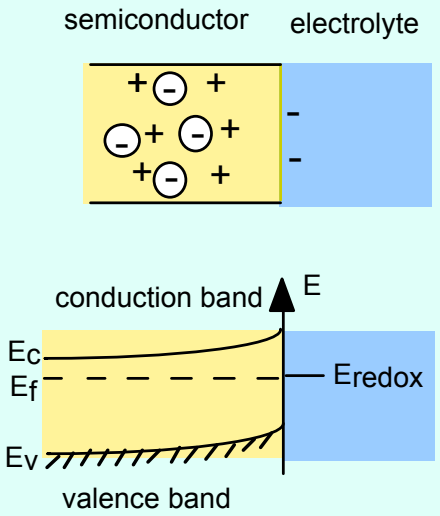
Main advantage: energy capture conversion and storage are combined in a single system


Vacuum
E NHE
0
-3.0
-3.5
-4.0
-4.5
-5.0
-5.5
-6.0
-6.5
-7.0
-7.5
-8.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
GaAs
GaP
CdSe
CdS
ZnO
Fe2O3
WO3
SnO2
TiO2
SiC
ΔE = 1.4eV
2.25 eV
1.7 eV
2.25 eV
3.2 eV
2.1 eV
2.6 eV
3.8 eV
3.2 eV
3.0 eV
Eu2+/3+
H2/H2O
[Fe(CN)6]3-/4-
Fe2+/Fe3+
H2O/O2
Ce4+/3+

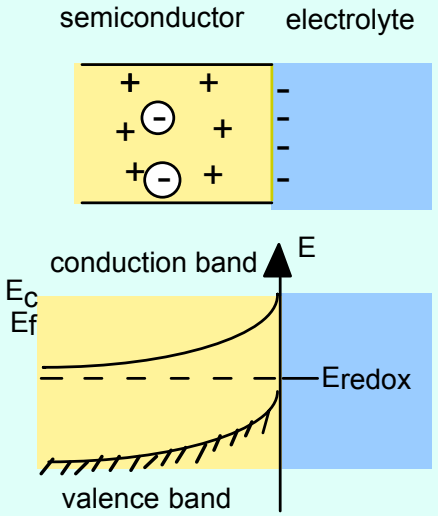
The semiconductor /electrolyte interface



C. depletion layer

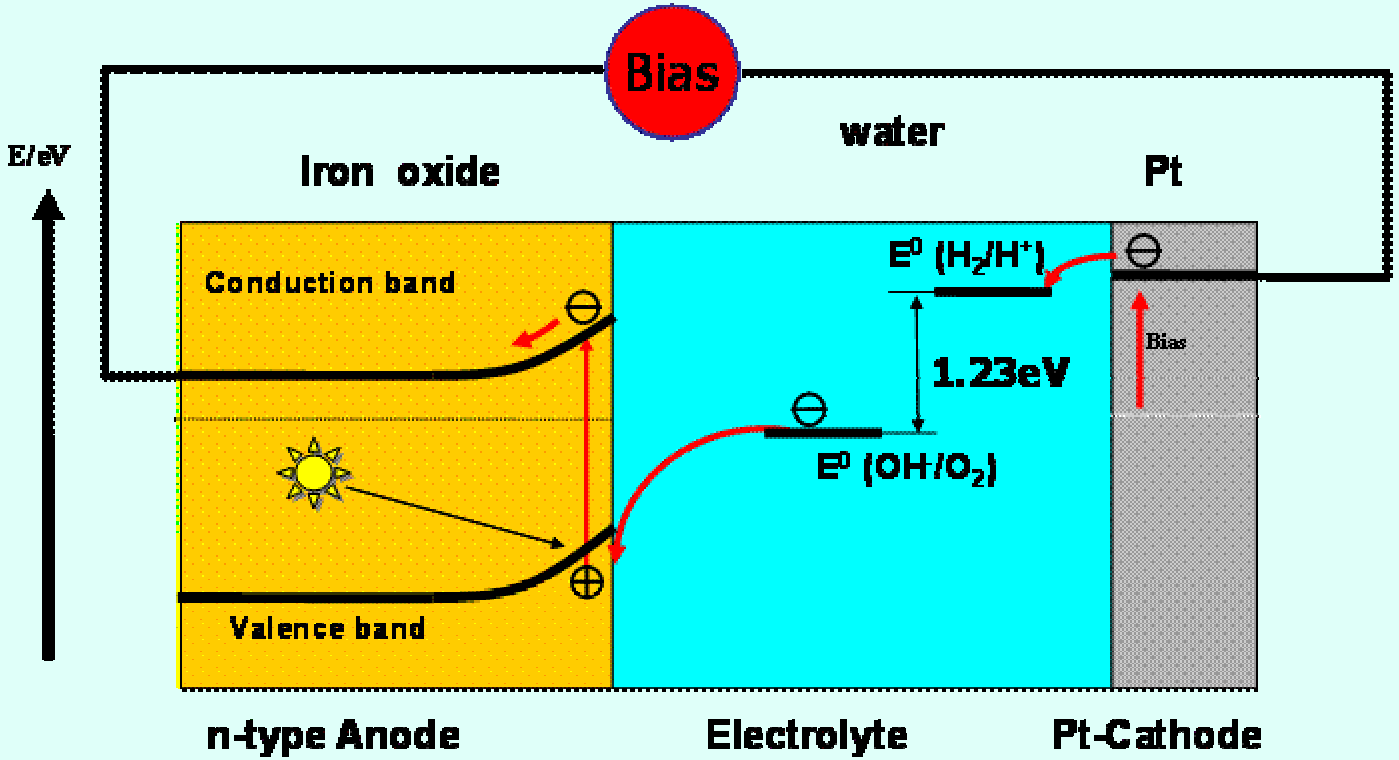


D. inversion layer



Generation of hydrogen by photoelectrolysis of water

n-type semiconductor electrode



$$4\,OH^- \rightarrow O_2 + 2H_2O + 4e^- \qquad 4\,e^- + 4\,H_2O \rightarrow 2H_2 + OH^-$$

$$2H_2O + 4\,h\nu \rightarrow O_2 + 2H_2$$

A. Fujshima and K. Honda Nature 1972, 238, 37-38, Water photolysis on TiO2 electrodes

Conversion efficiency

Input: solar light of air mass 1.5 global (1000 W/m2)

Output: hydrogen, standard heat of combustion
ΔH = - 280 kJ/mol (=1.45 eV/electron)

Solar to chemical conversion efficiency: output/input

$$\eta = I_{ph}\,[mA/cm^2] \times (1.45 - V_{bias})$$

or

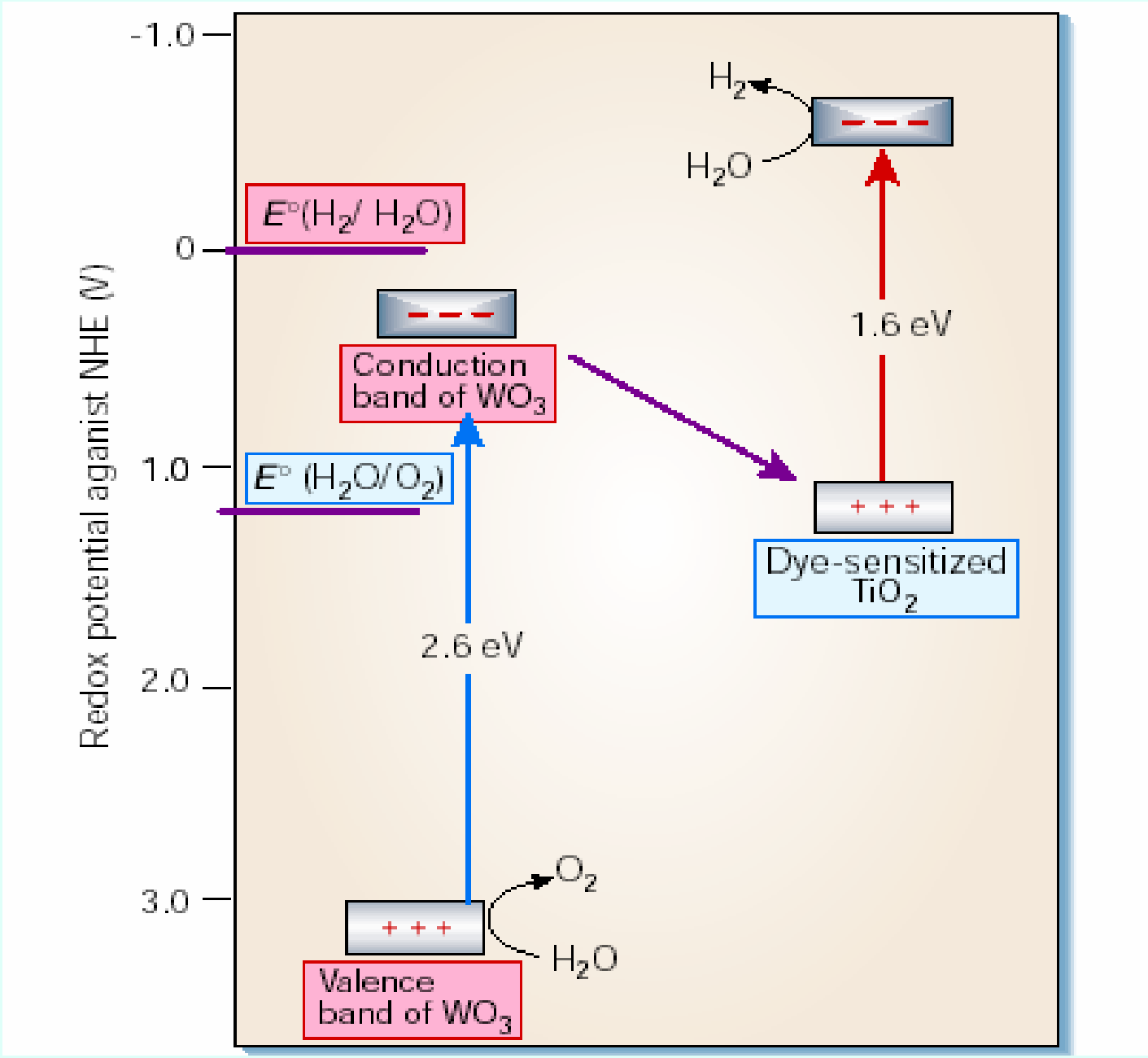
$$\eta = I_{ph}\,[mA/cm^2] \times (1.23 - V_{bias})$$

in terms of free energy of combustion

OUTLINE

1. Introduction
2. photoelectrochemical tandem cells
   - work on oxygen evolving Fe_2O_3 photoanode
   - work on bottom electrode
3. Future work and conclusions

The Z Scheme of biphotonic Water Photolysis



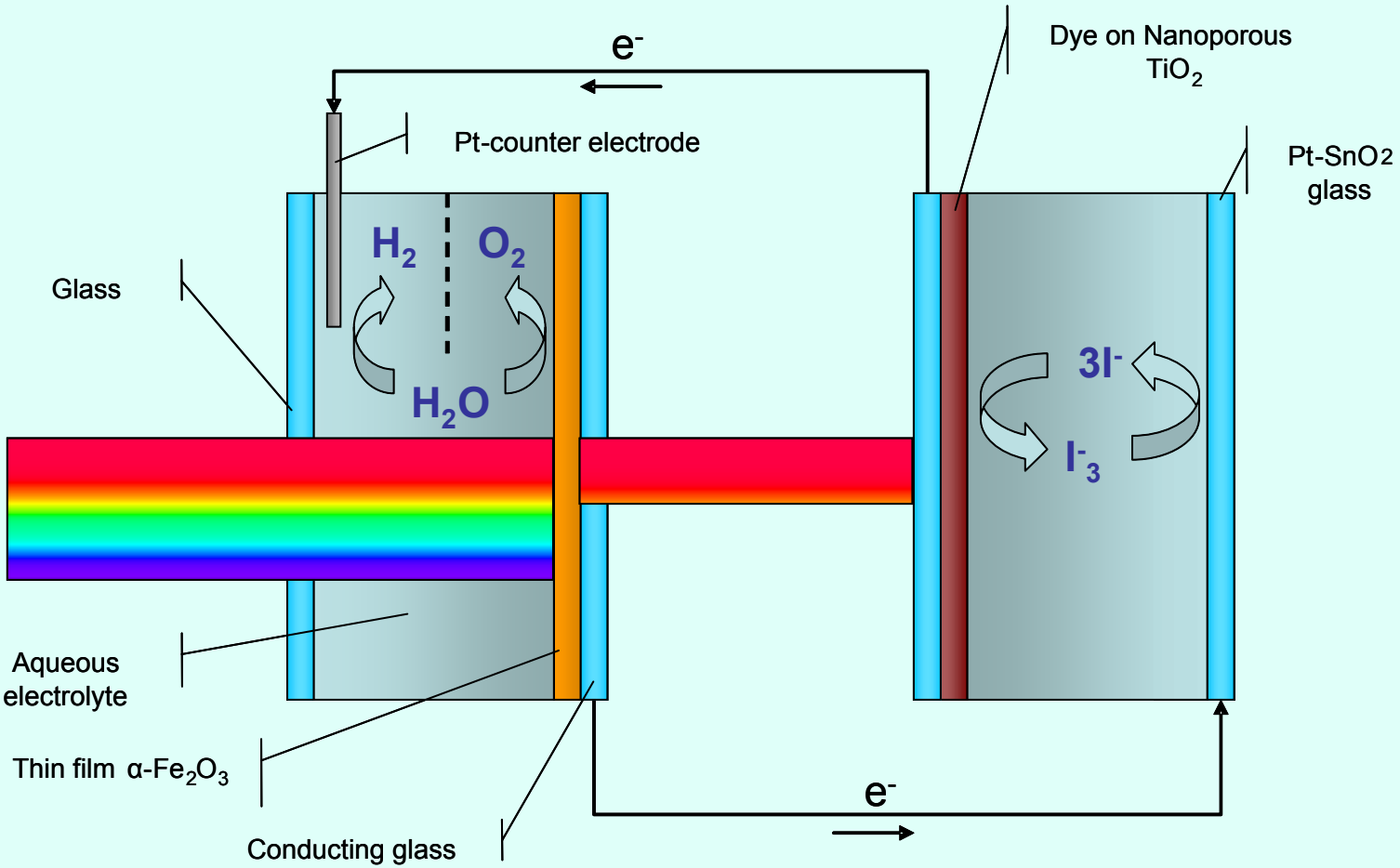


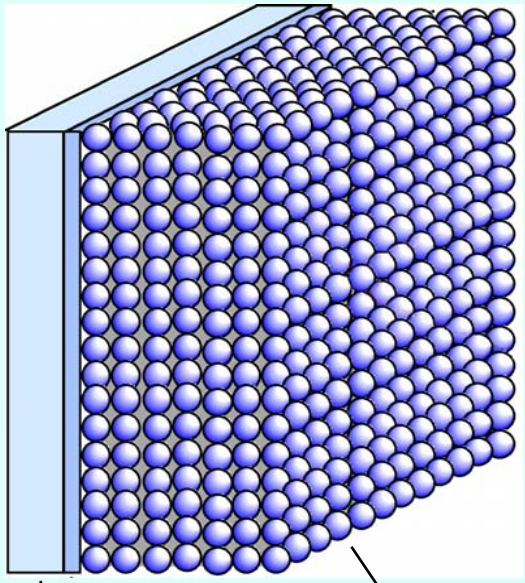
Figure 3: Schematics of tandem cell: Current flow, light absorption and device composition. Red part of spectrum drives solar cell.

The oxide semiconductor top electrode

Effects photocatalytic water oxidation

Absorbs ultraviolet and blue solar light

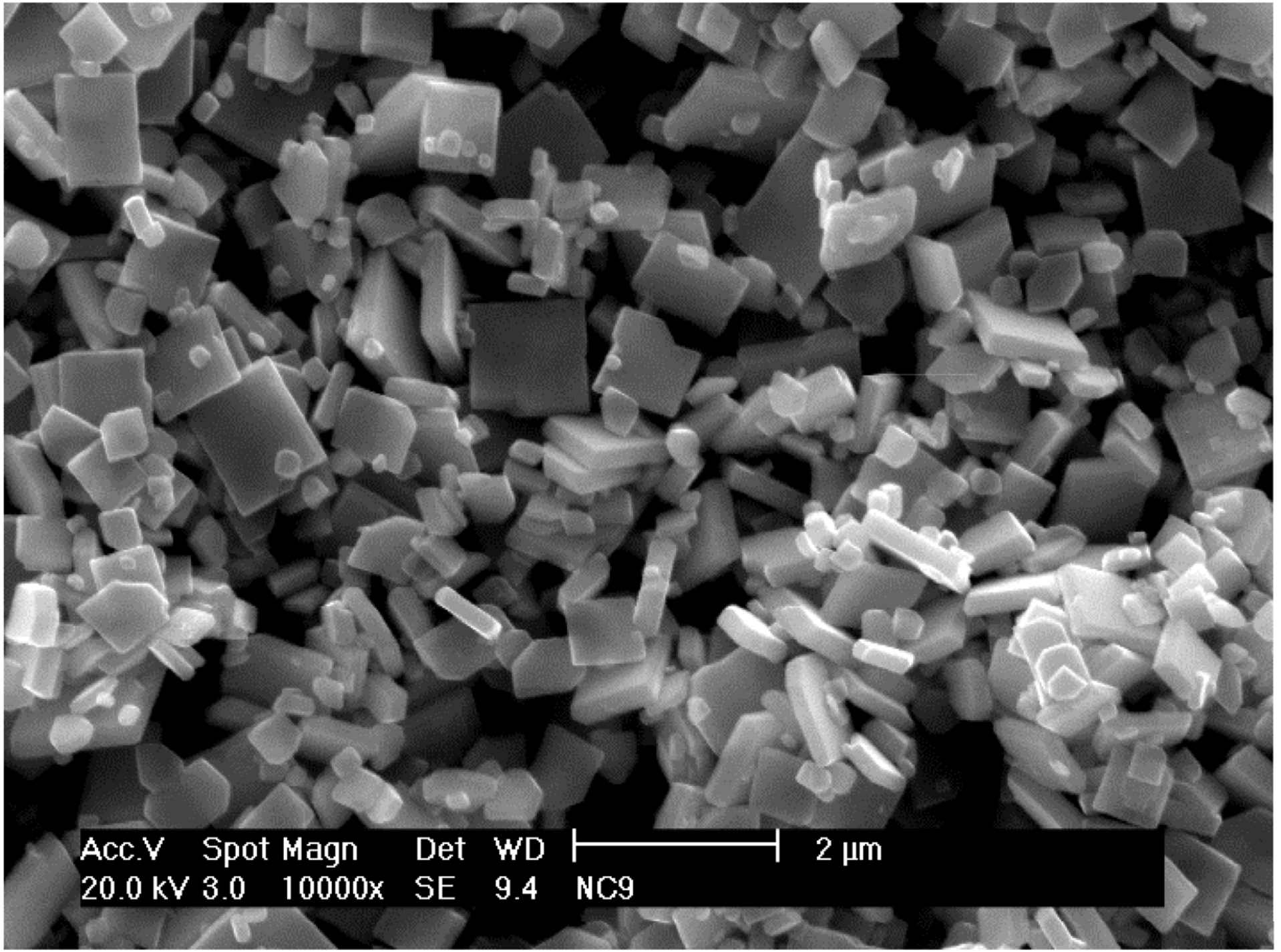
Nanocrystalline oxide photoanode



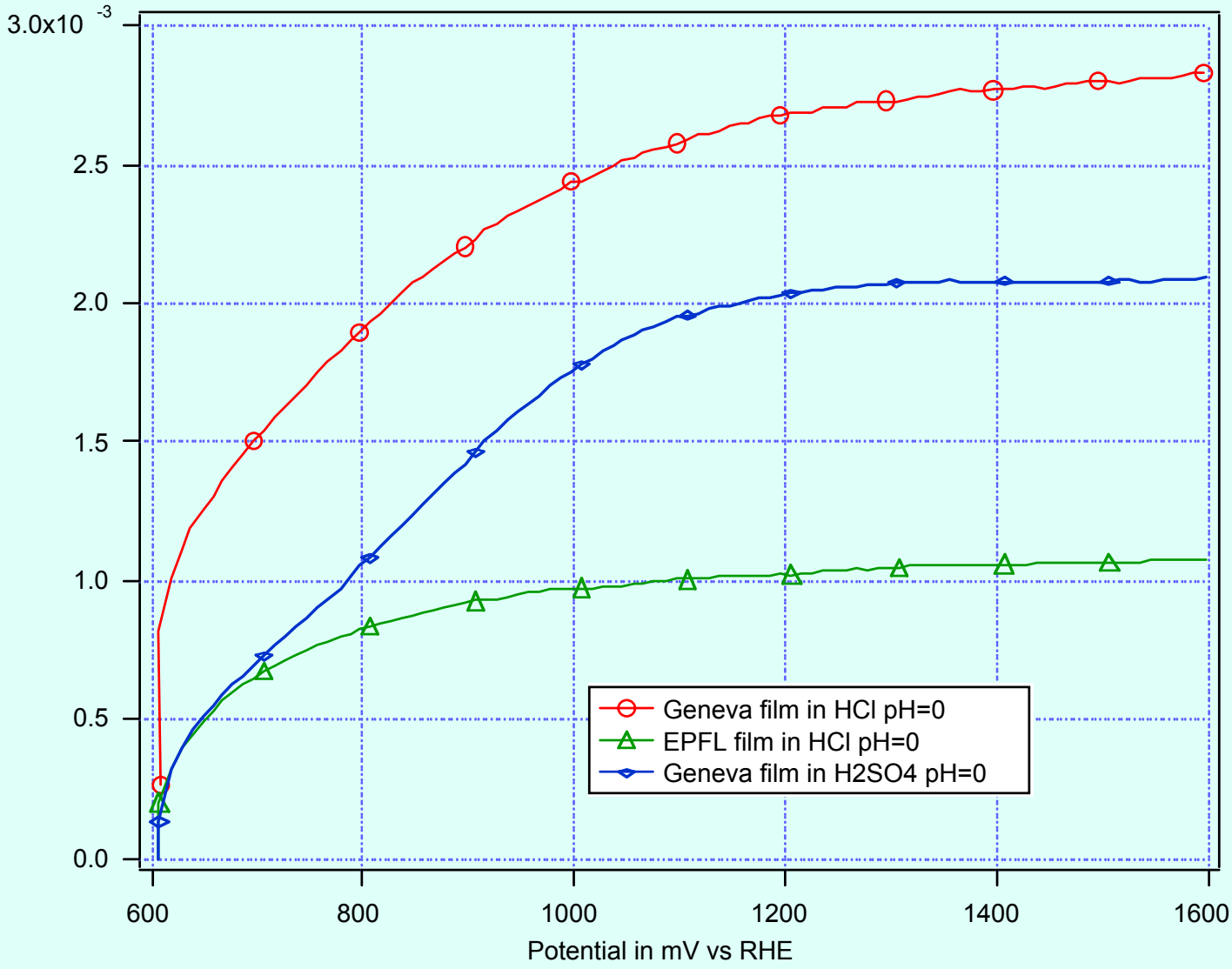
Advantage of nanocrystalline Oxides electrodes:

1) translucent electrode - avoids light scattering losses

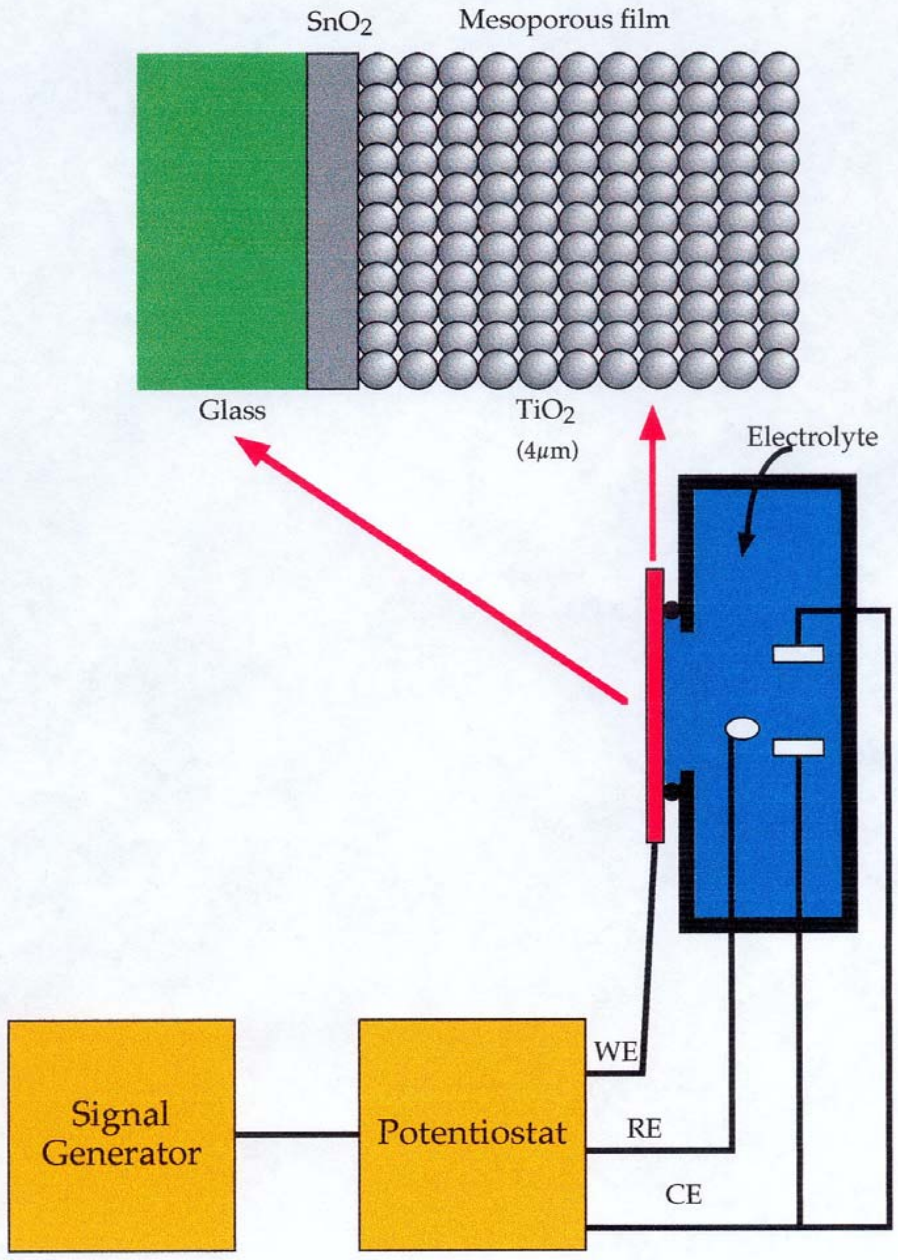
2) Small size is within minority carrier diffusion length, the valence band holes reach the surface before they recombine.

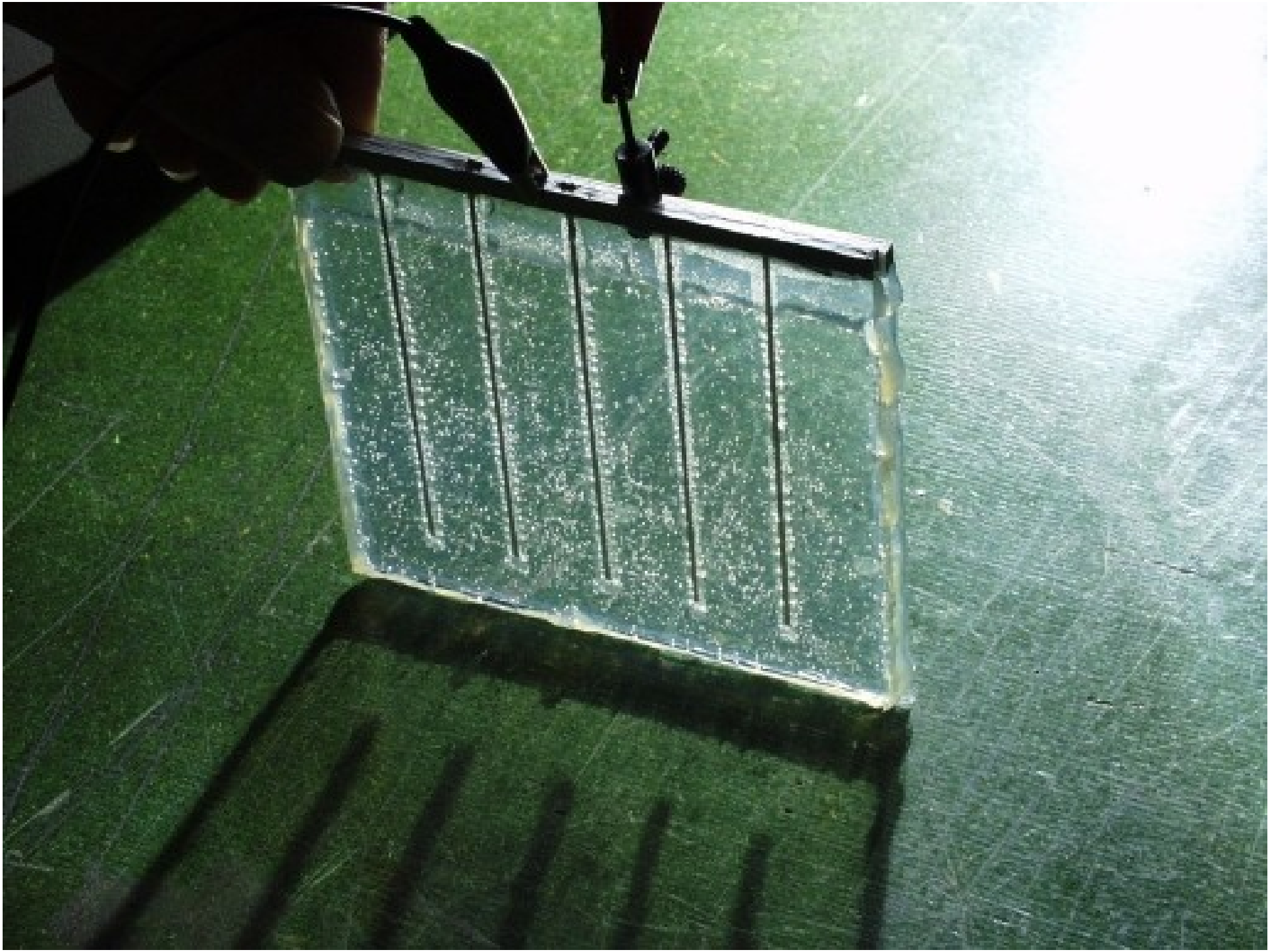

Acc.V Spot Magn Det WD 2 µm
20.0 kV 3.0 10000x SE 9.4 NC9

I-V curves for WO_3 films measured in HCl (at pH = 0) and in H_2SO_4 (at pH = 0) under AM 1.5 Sun light



Transparent Mesoporous Oxide Electrodes





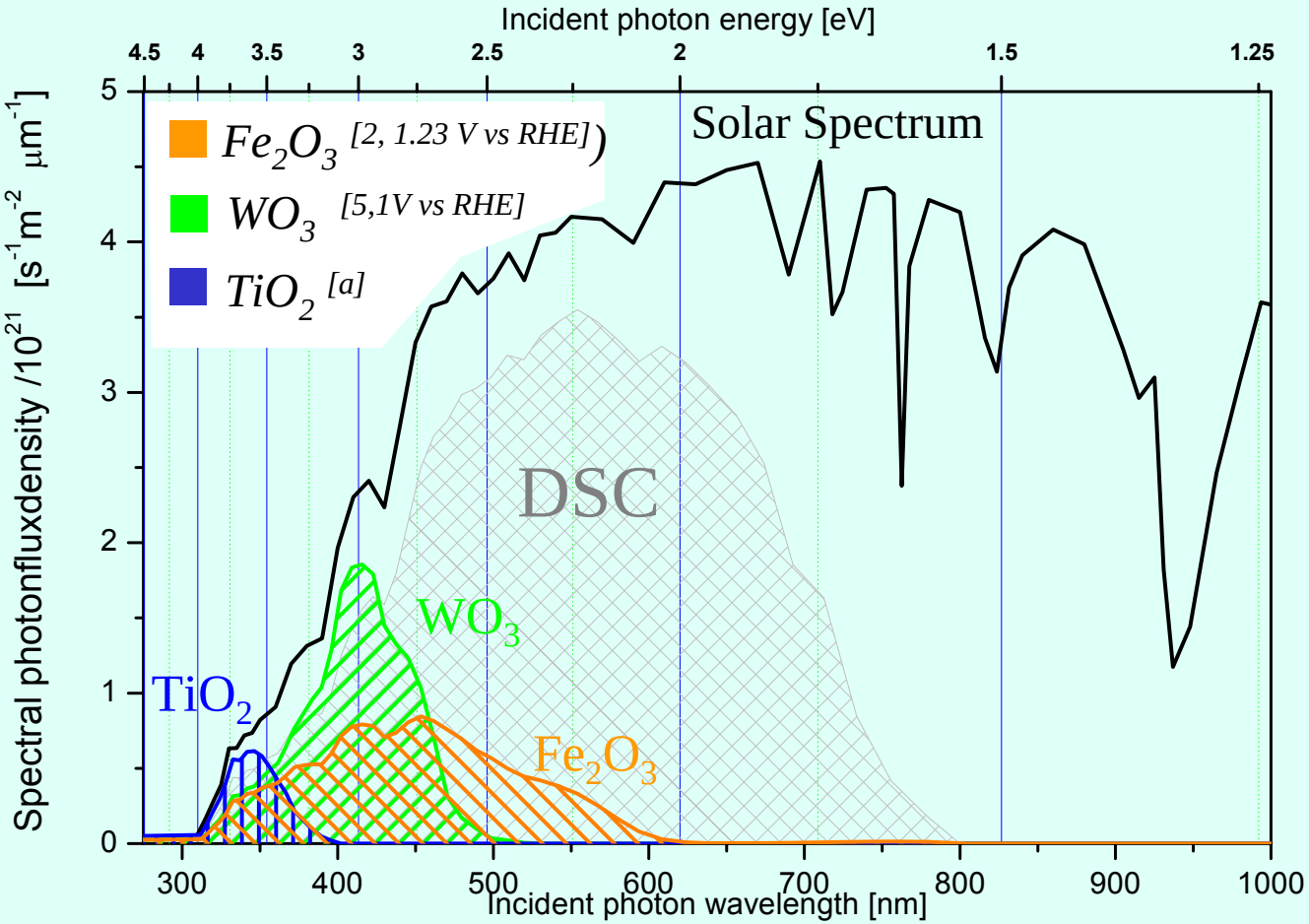


Figure 2; ■ *Solar photon flux density (AM 1.5 Global normalised to 1000 W/m²) harvested photons by* ■ *dye-sensitized solar cell and spectral faradaic watersplitting activity of Fe_2O_3 prepared in our laboratory, compared to (to our knowledge) best performing anode materials: WO_3 and TiO_2.*

Conversion efficiency

Input: solar light of air mass 1.5 global (1000 W/m2)

Output: hydrogen, standard heat of combustion
ΔH = - 280 kJ/mol (=1.45 eV/electron)

Solar to chemical conversion efficiency: output/input

$$\eta = I_{ph}\,[mA/cm^2] \times (1.45 - V_{bias})$$

or

$$\eta = I_{ph}\,[mA/cm^2] \times (1.23 - V_{bias})$$

in terms of free energy of combustion

Research work on the photo-anode

The top electrode consists of an oxide semiconductor (Fe_2O_3) absorbing the green, blue and UV photons from the solar light but transmitting the yellow, red and IR light. Photo-excitation produces conduction band electrons and valence band holes

$$Fe_2O_3 + h\nu \Rightarrow Fe_2O_3\,(e^- - h^+)$$

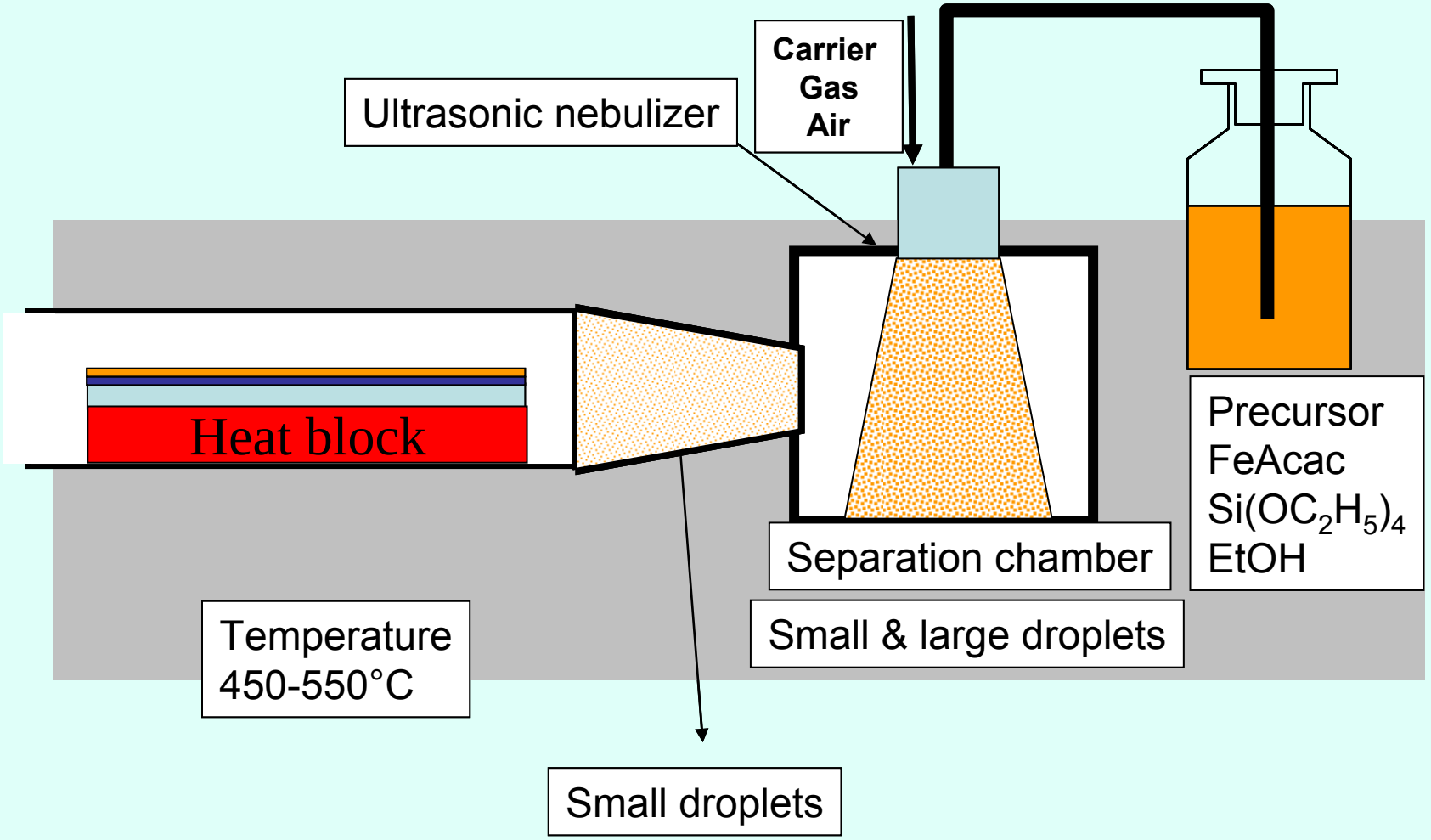
The valence band holes oxidize water to oxygen:

$$4\ h^+ + 2\ H_2O \Rightarrow O_2 + 4\ H^+$$

The chemical potential of the conduction band electrons is raised by the bottom cell providing an electrical bias to afford hydrogen generation from water

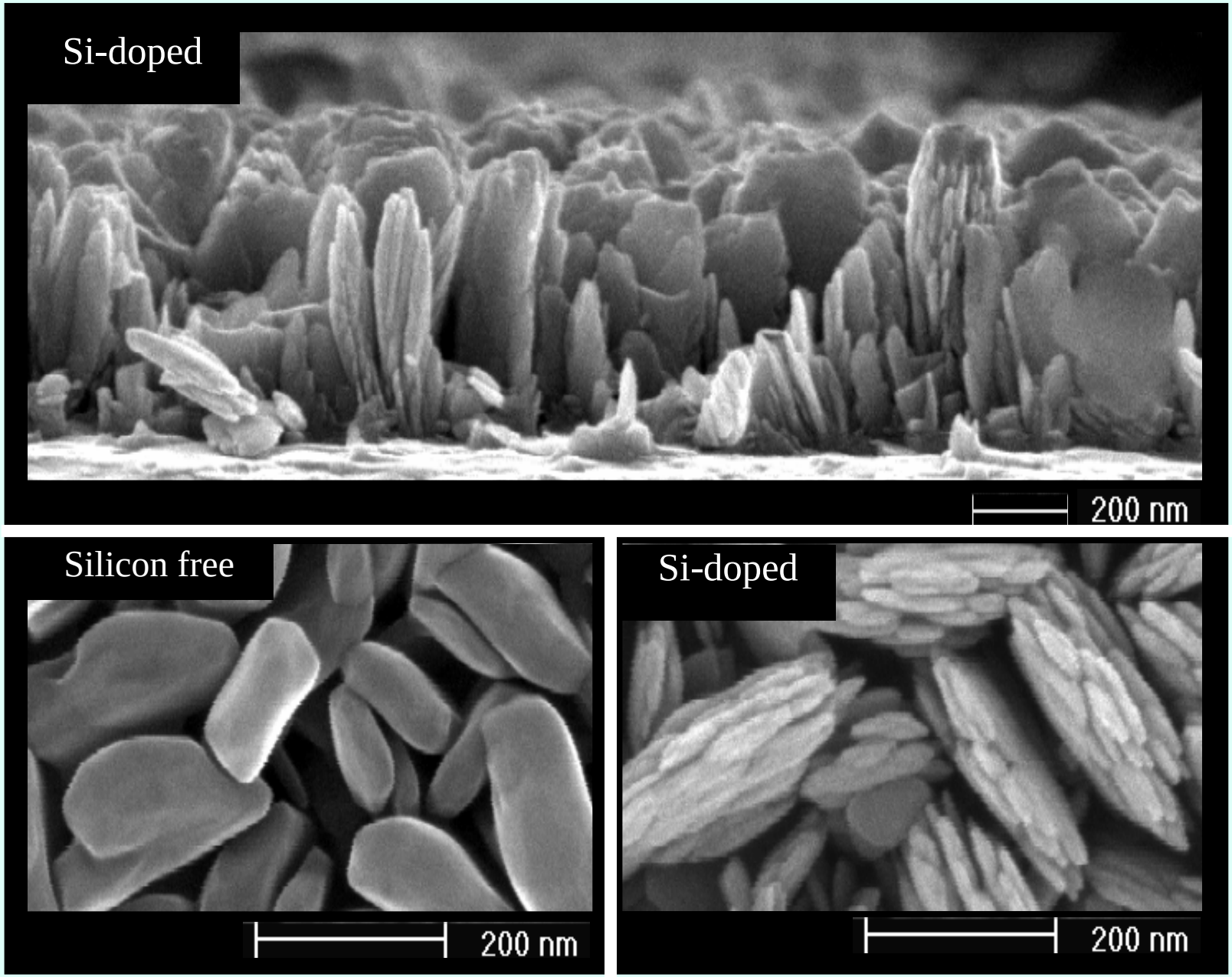
$$4\ H^+ + 4\ e^- \Rightarrow H_2$$

Ultrasonic Spray Pyrolysis



Ultrasonic spray pyrolysis

Duret, Alexis; Graetzel, Michael. **Visible Light-Induced Water Oxidation on Mesoscopic α-Fe2O3 Films Made by Ultrasonic Spray Pyrolysis.** Journal of Physical Chemistry B (2005), 109(36), 17184-17191



Ultrasonic spray pyrolysis

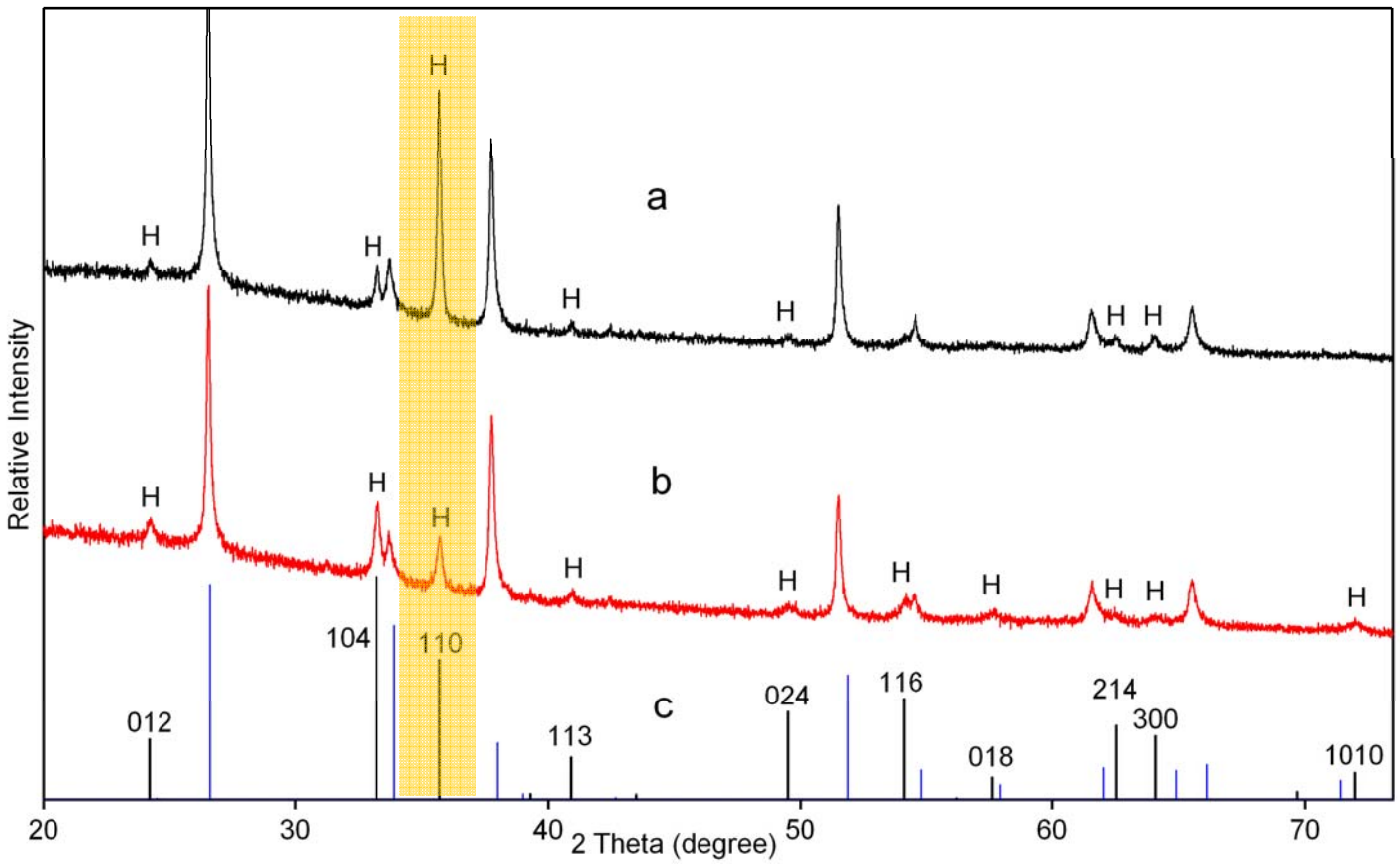
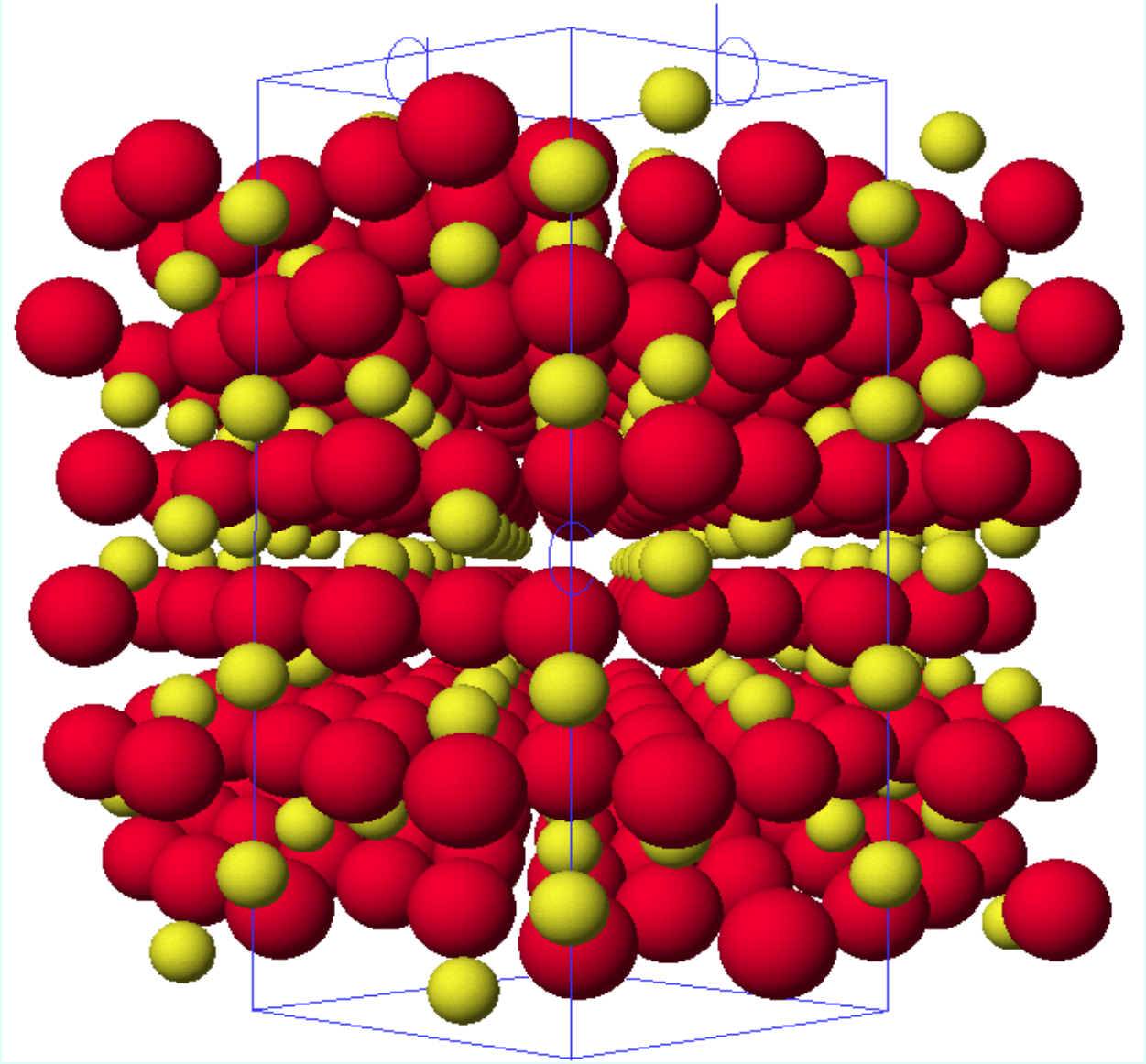


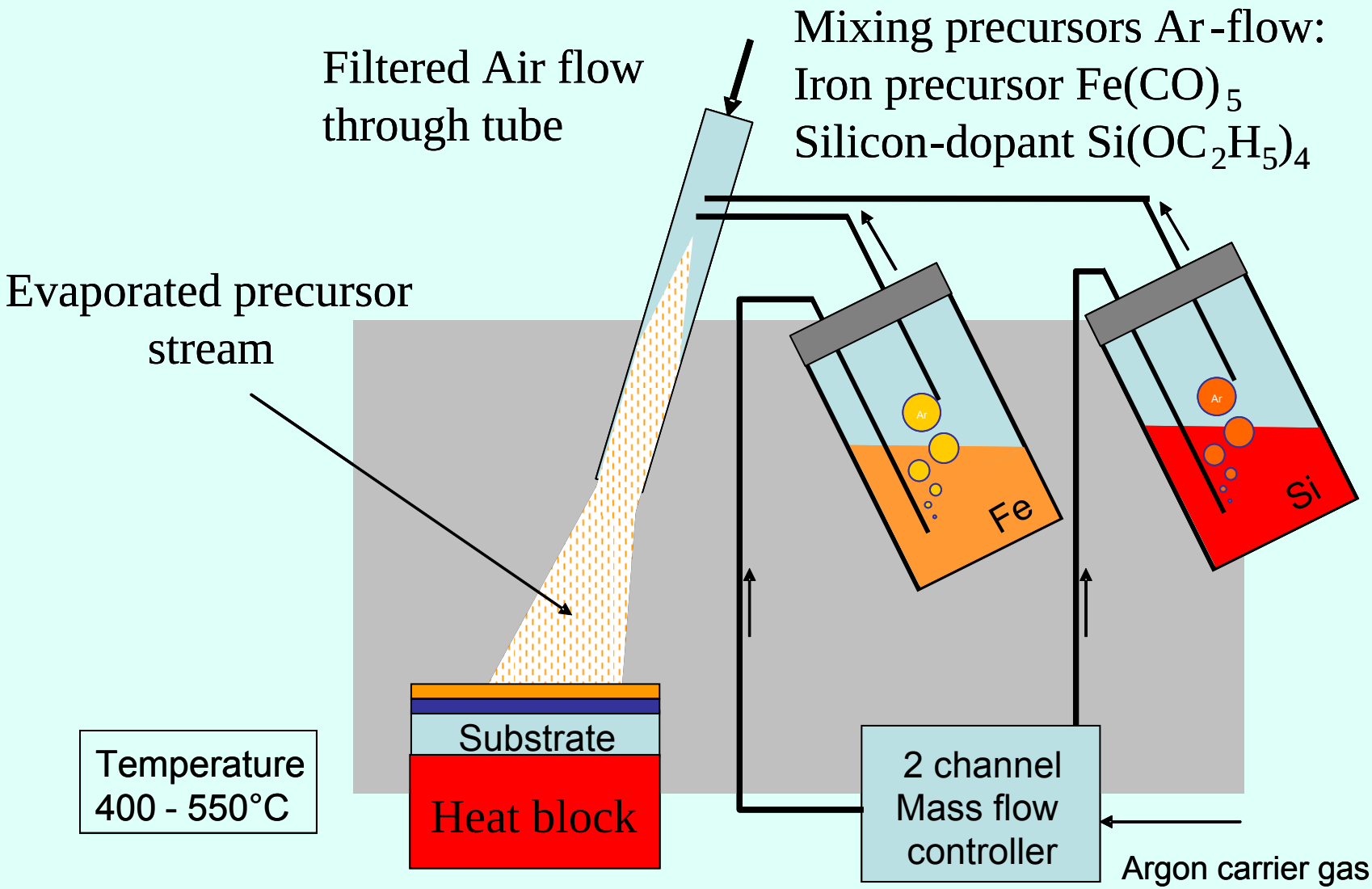
Figure 7: X-ray diffraction pattern of a) Si doped Fe_2O_3 film on SnO_2 (hematite peaks marked with H), b) undoped Fe_2O_3 film on SnO_2, c) standard powder pattern of α-Fe_2O_3 (hematite, black lines with plane indices in hexagonal coordinates) and SnO_2 (cassiterite, blue lines). Films prepared by APCVD[2].

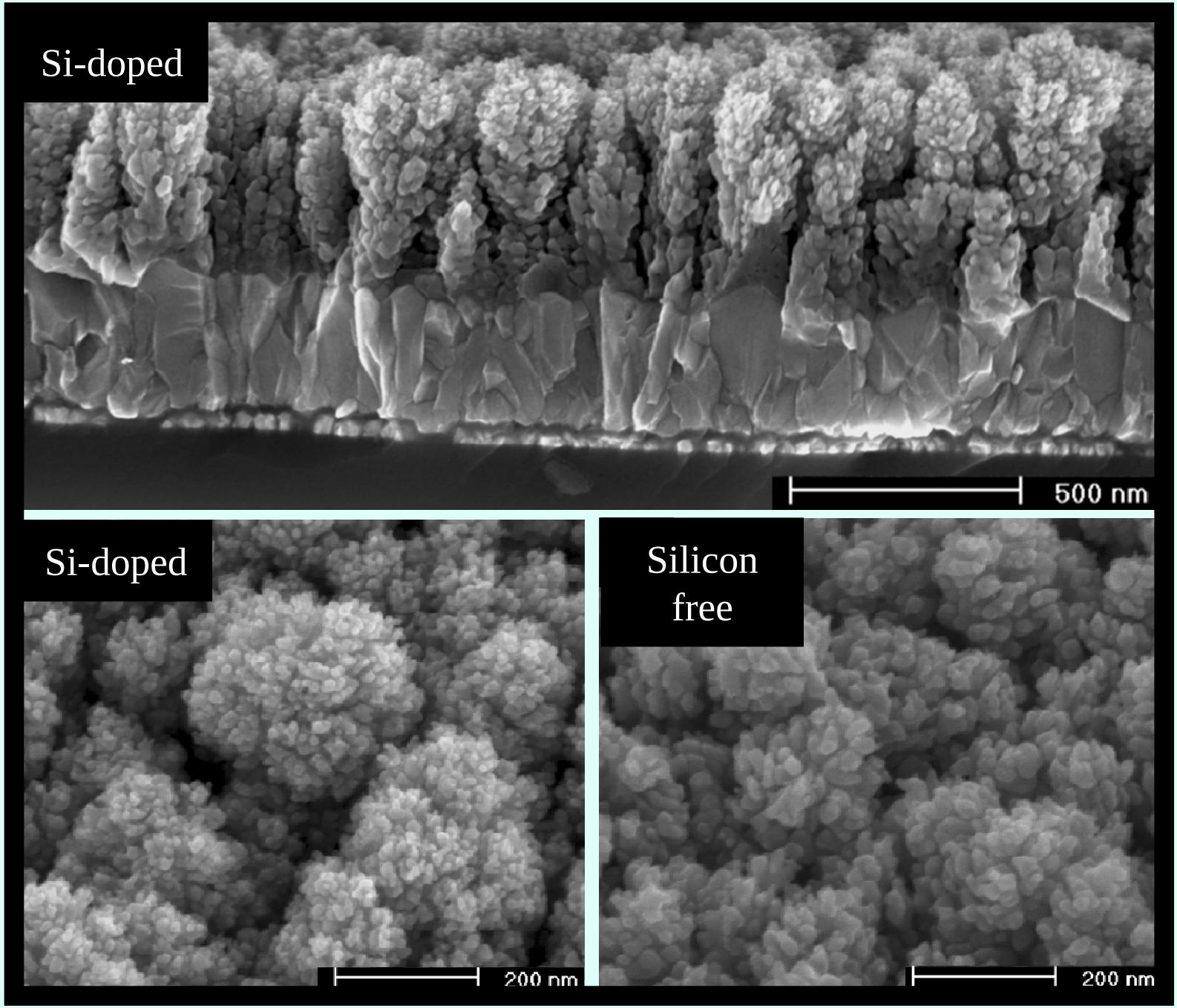


Model of the hematite crystal lattice viewed in [110] direction, which is preferentially oriented vertically on the SnO_2 substrate, illustrating alternating iron bilayers and oxygen layers parallel to the (001) basal plane (oxygen: red, iron: yellow, hexagonal unit cell: blue).

Atmospheric pressure chemical vapour deposition (APCVD)

Atmospheric pressure chemical vapor deposition





APCVD

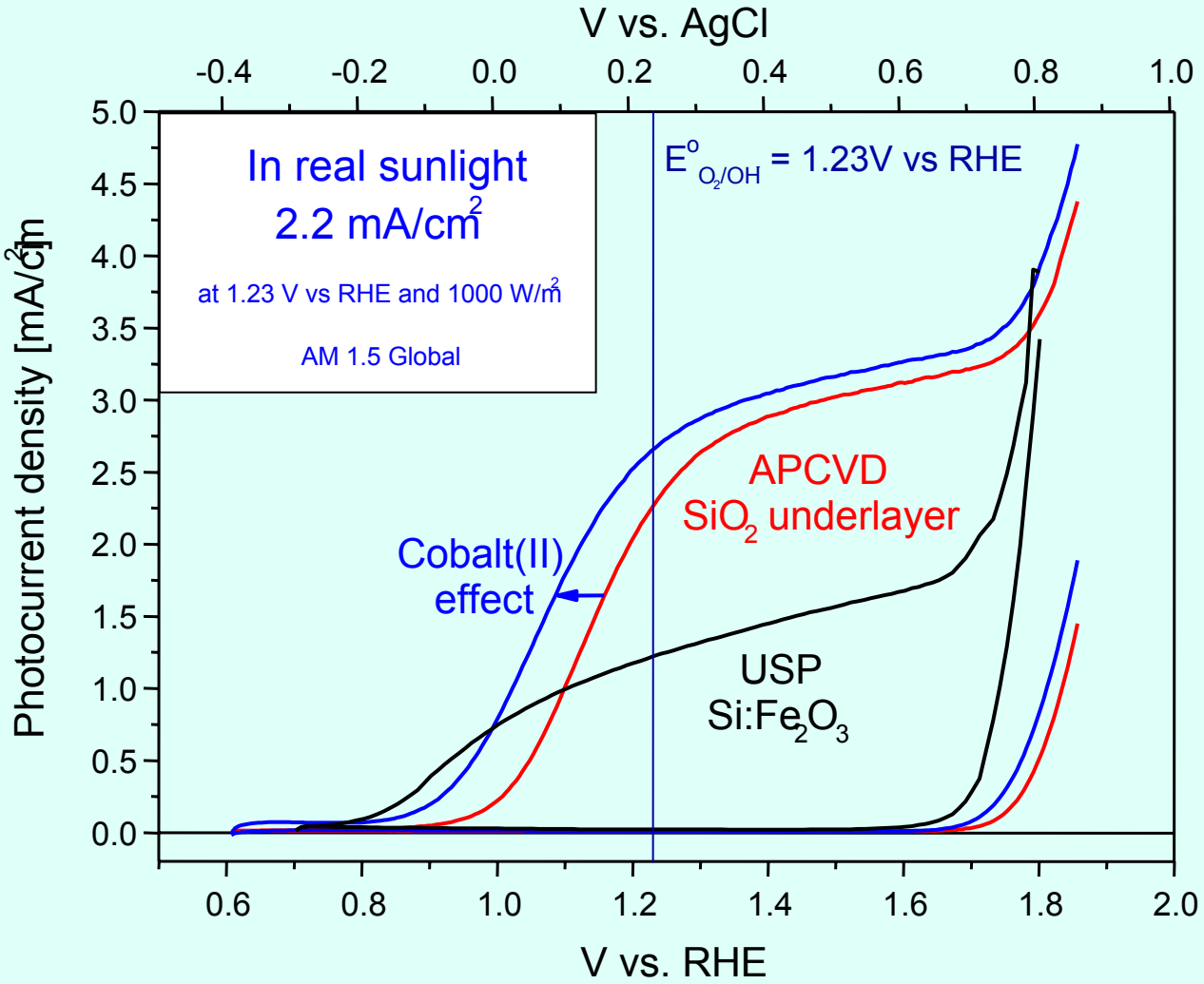
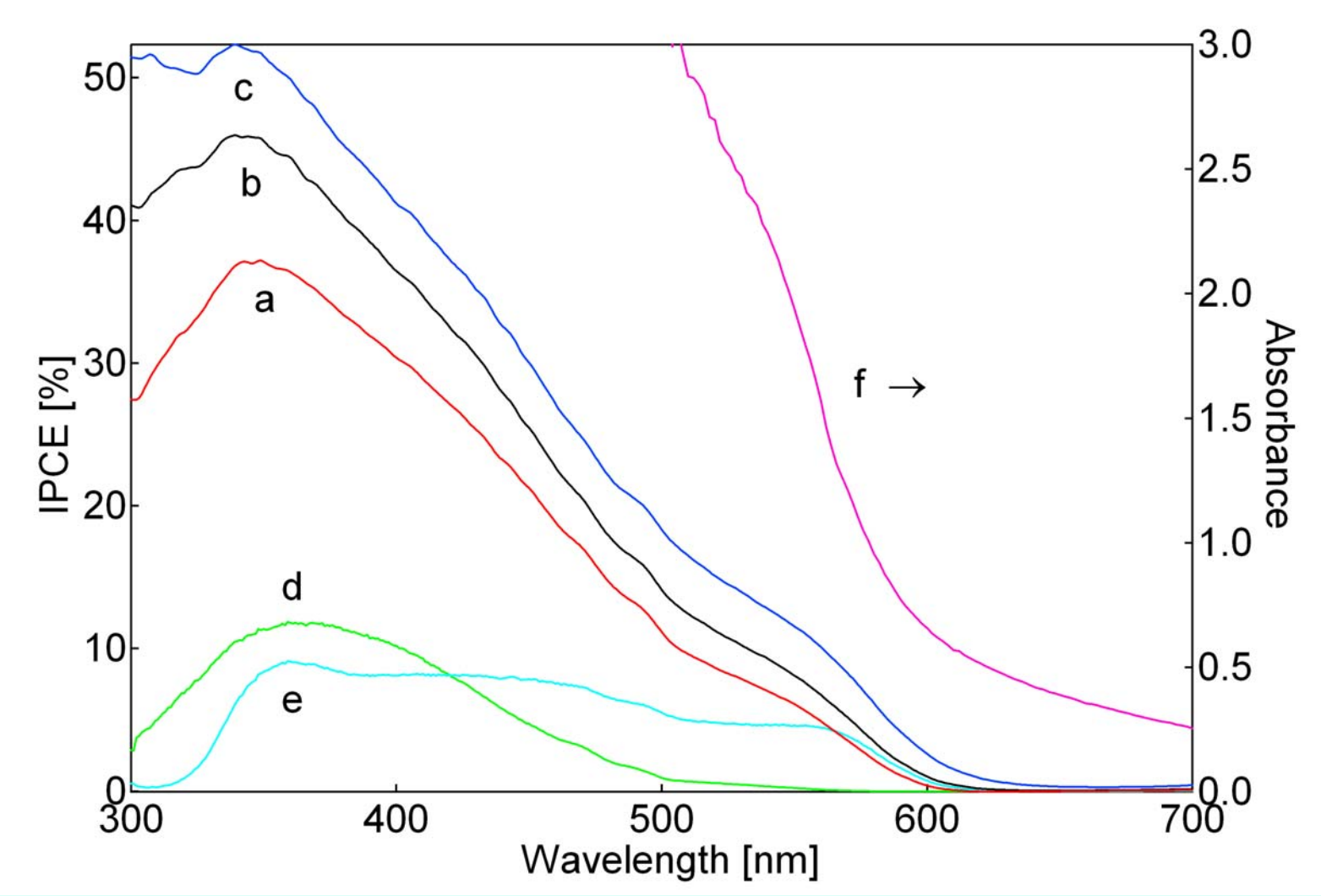
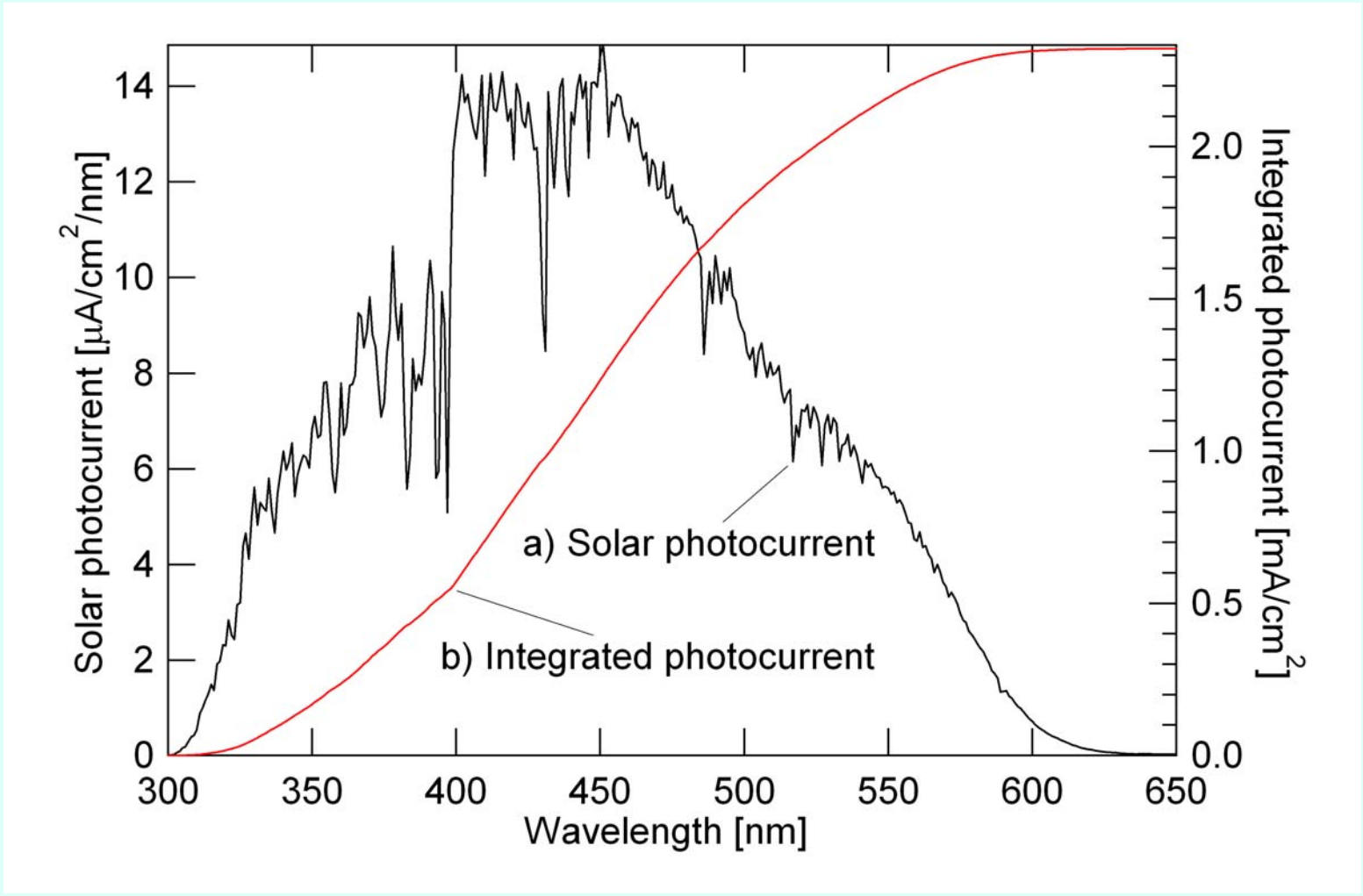


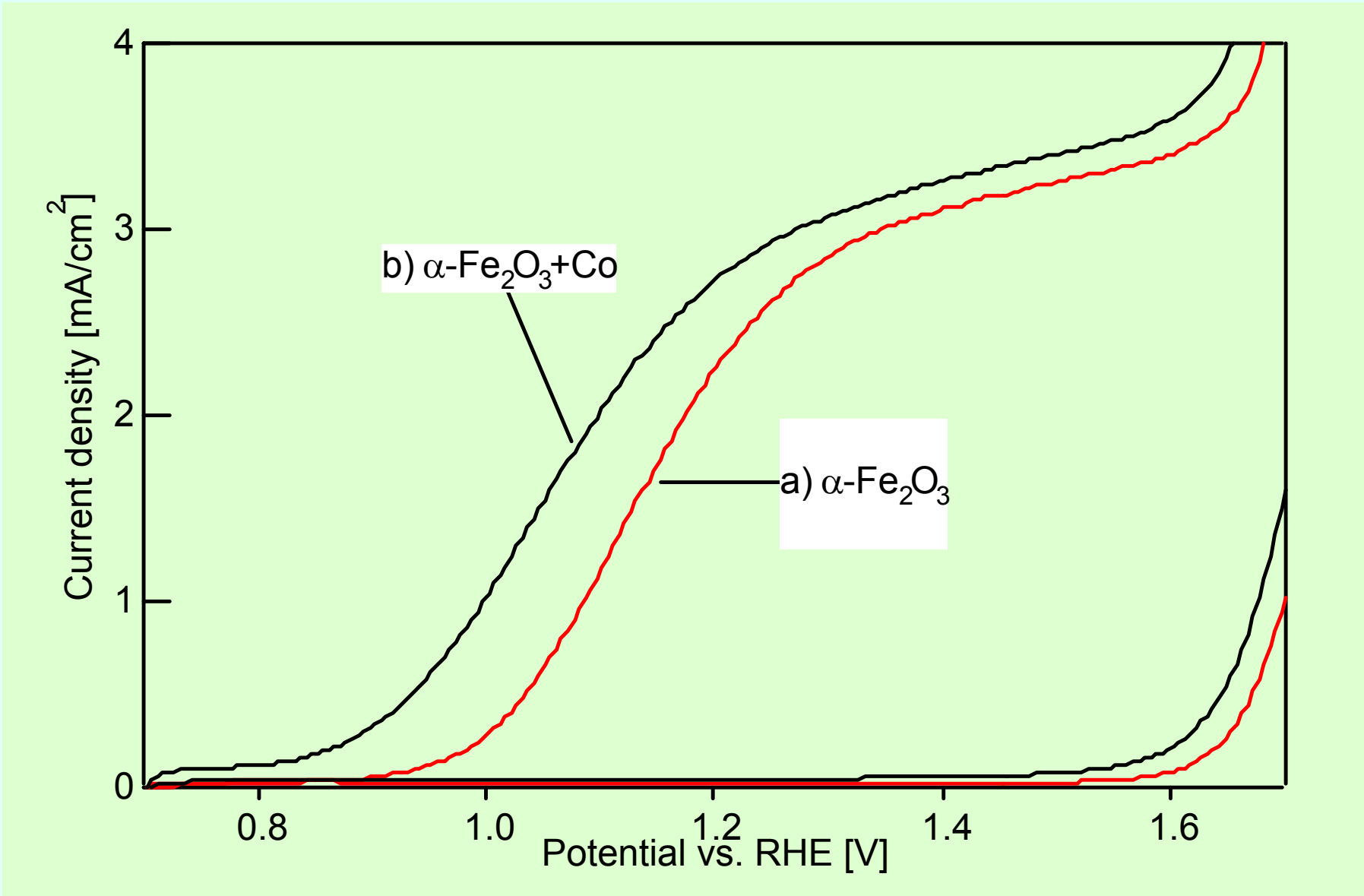
Figure 6: Current-voltage characteristics of Silicon doped Fe_2O_3 in darkness and under simulated sunlight at pH=13.6 (1M NaOH). a) ■ USP[3] b) ■ unmodified APCVD Fe_2O_3[2], c) ■ the same electrode as b after cobalt treatment[2]. The spectral mismatch factor for the USP and APCVD measurement is 1.1 and 1.2 respectively.

Light harvesting + Incident photon to current conversion efficiency

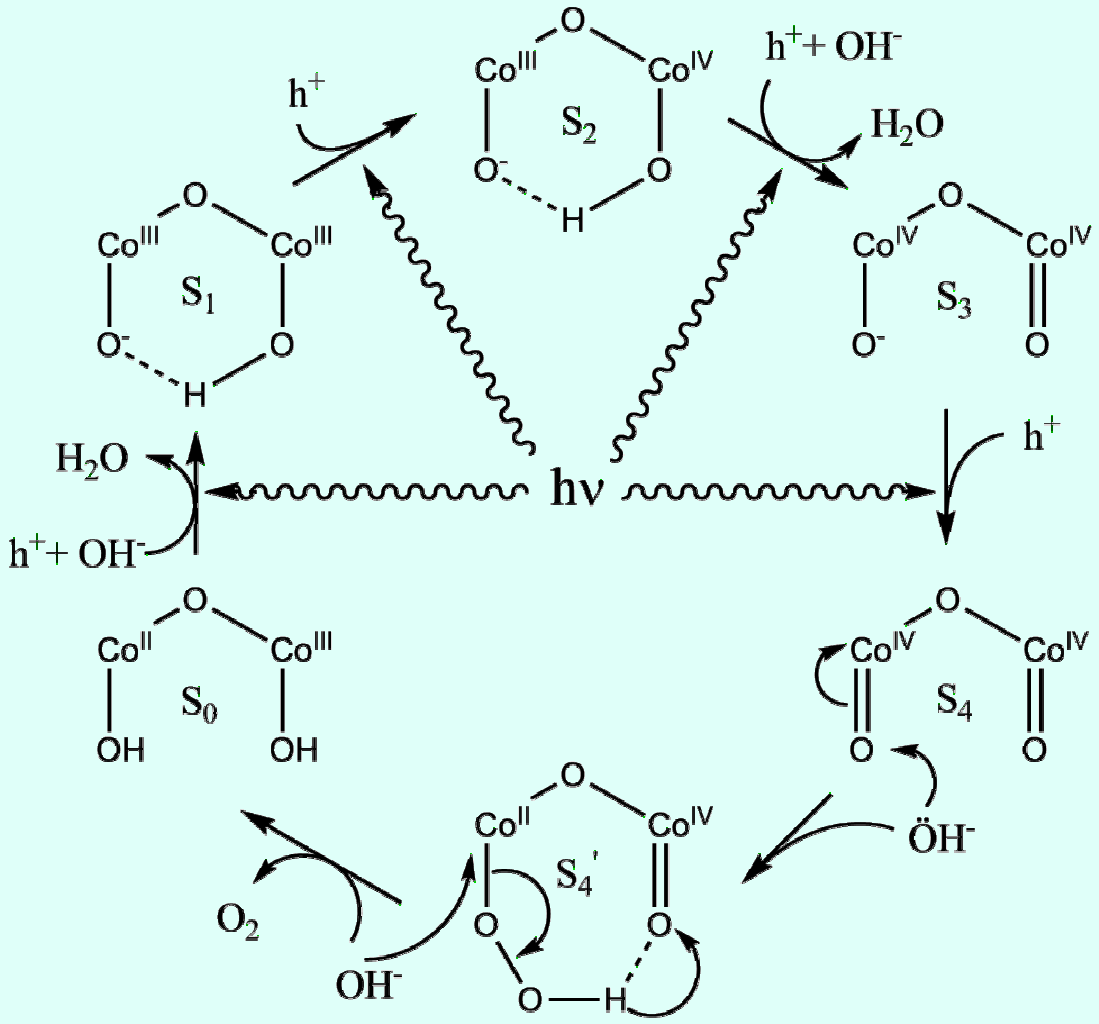




Solar photocurrent spectrum of the cobalt treated Fe_2O_3 electrode at 1.23 V_{RHE} obtained by multiplication of its *IPCE*-spectrum (Fig. 6b) with the photon flux spectrum of global sunlight (1000 W/m^2 AM 1.5 G). b) Total photocurrent under global sunlight between and a 300 nm given wavelength (integral of curve a).


Current density [mA/cm^2]
4
3
2
1
0
0.8
1.0
1.2
1.4
1.6
Potential vs. RHE [V]
b) α-Fe$_2$O$_3$+Co
a) α-Fe$_2$O$_3$

Mechanism for water oxidation catalysis



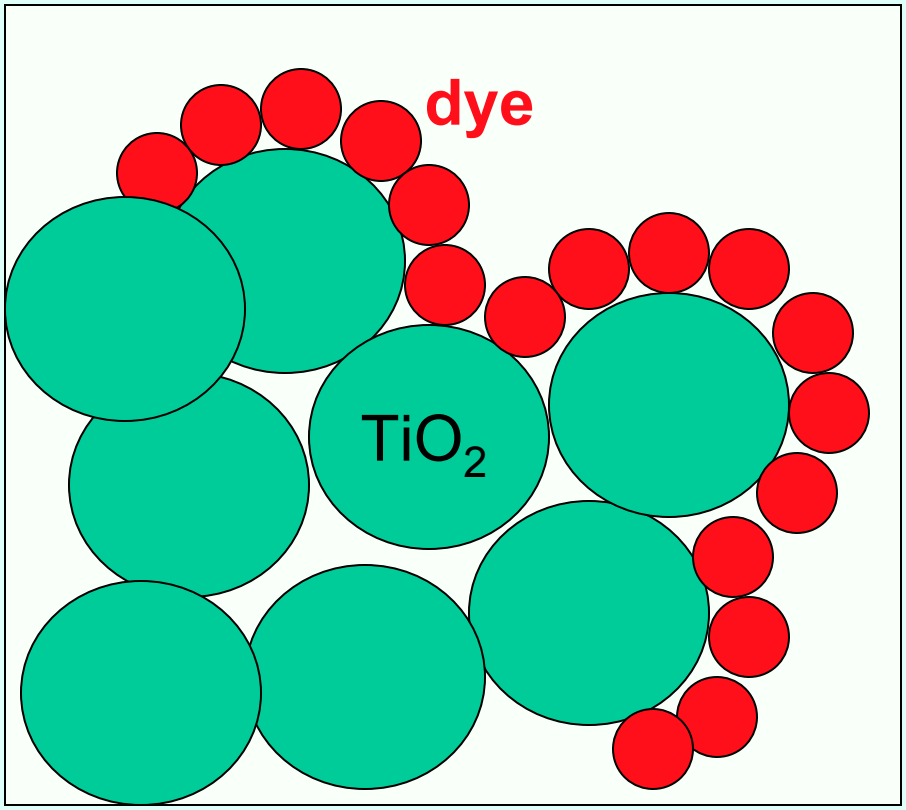
Research work on the bottom cell

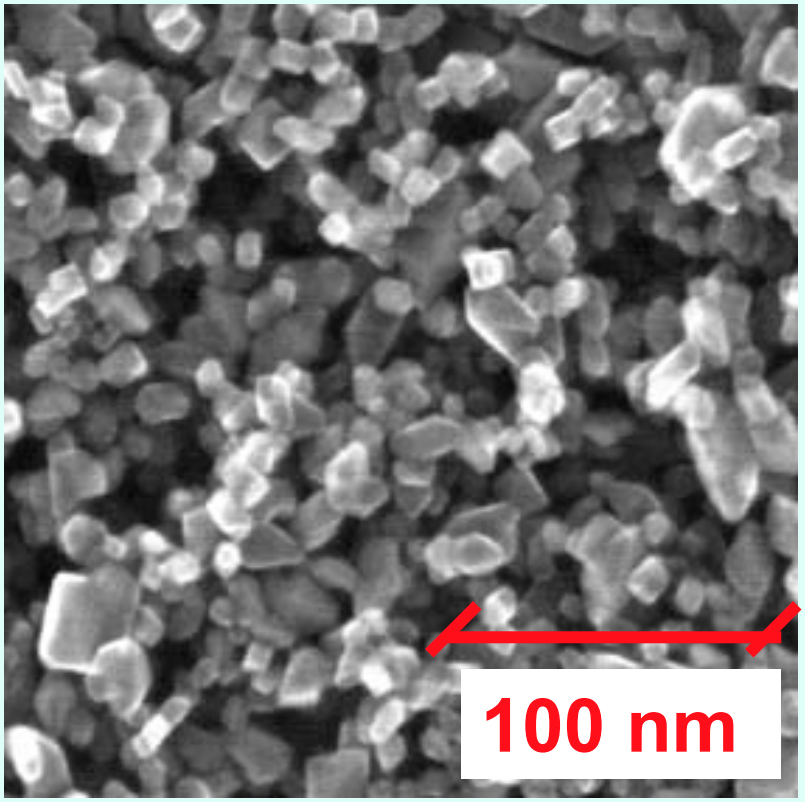
The bottom cell provides the bias potential required to raise the chemical potential of the conduction band electrons to a level where hydrogen generation from water can occur

$$4\,H^{+} + 4\,e^{-} \Rightarrow H_2$$

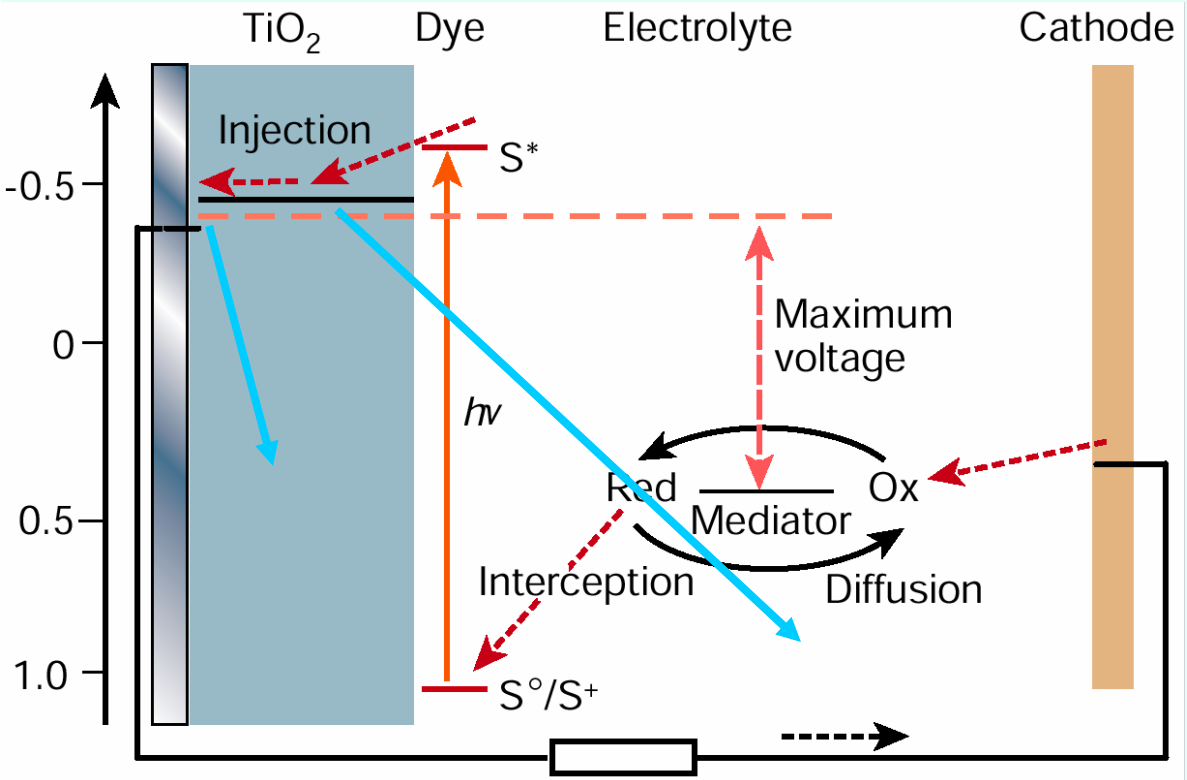
The bottom cell must sustain the photocurrent generated by the top cell using the yellow red and near IR part of the sunlight that is transmitted through the top cell.

Dye sensitized solar cell

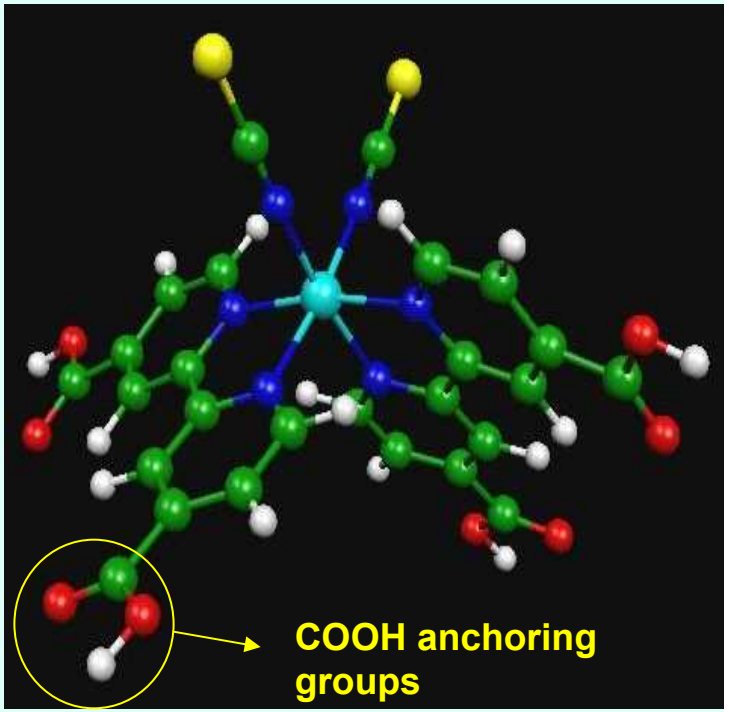




Dye-sensitized photovoltaic cells:

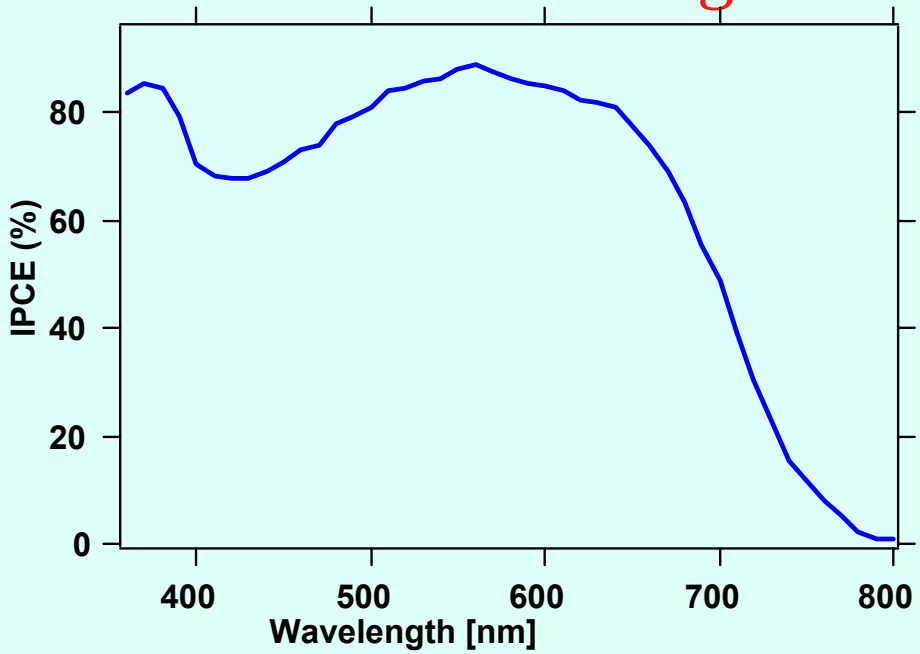


$$\eta = i_{ph}\, V_{oc}\, ff / I_s$$

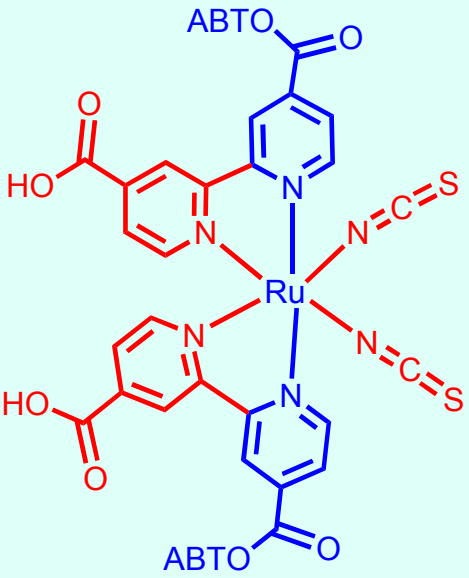


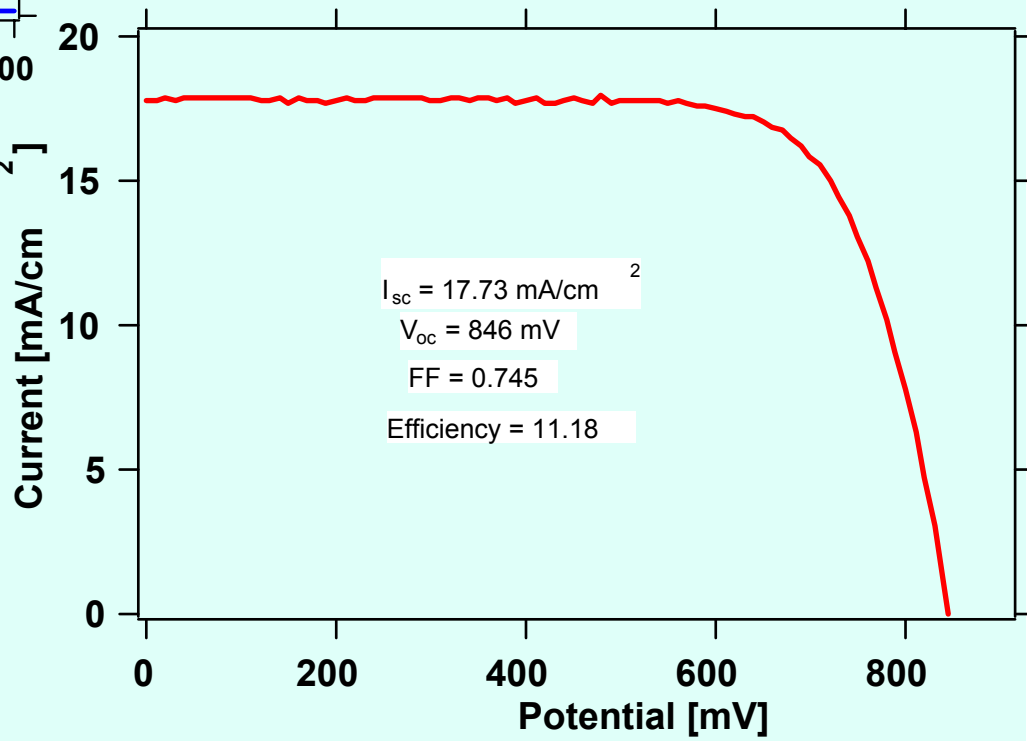
M. Graetzel, *Nature*, 2001, 414, 338.

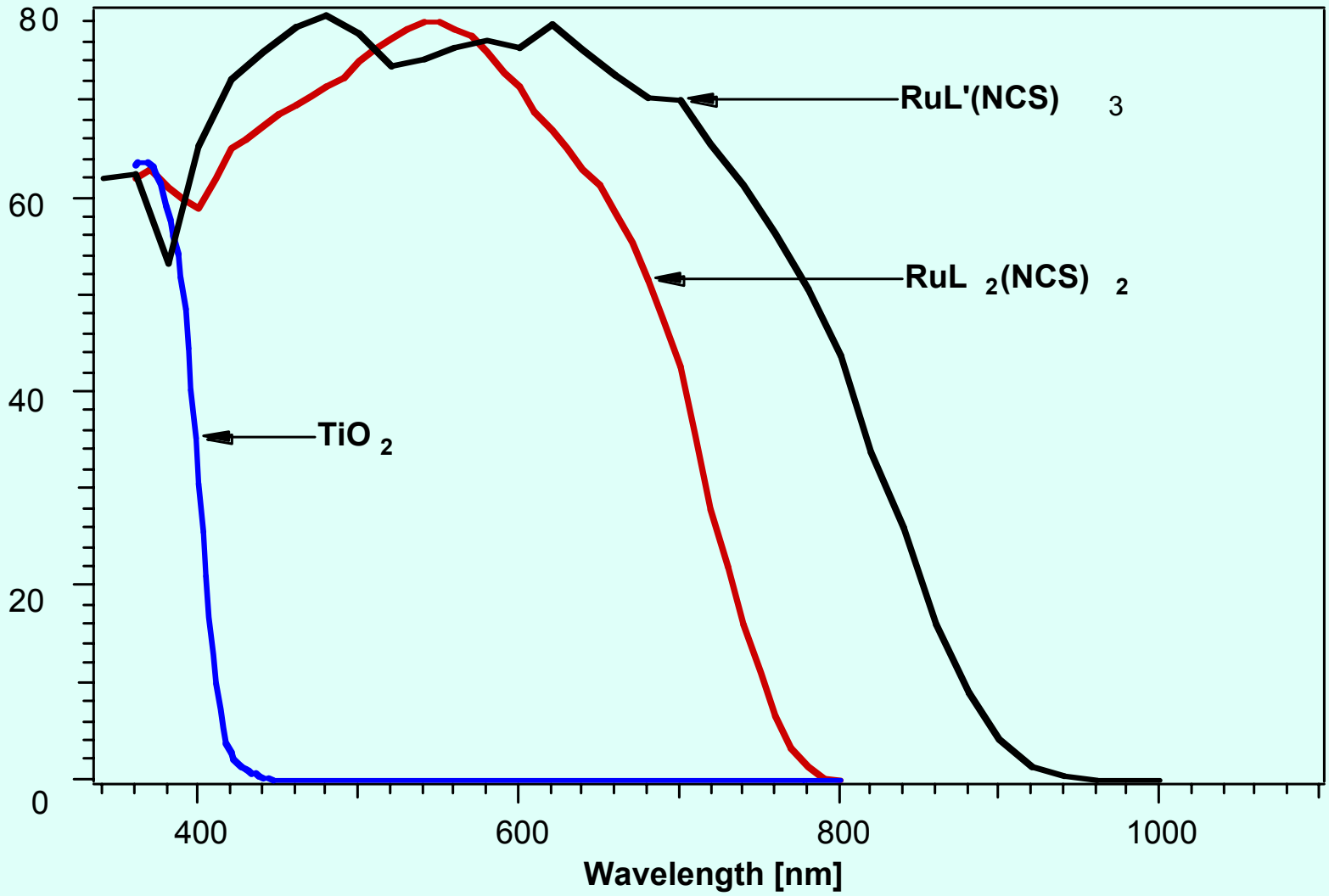
Photocurrent-voltage characteristics of N719-1H dye



Film mésoscopique de TiO2 sensibilisé par le colorant N-719



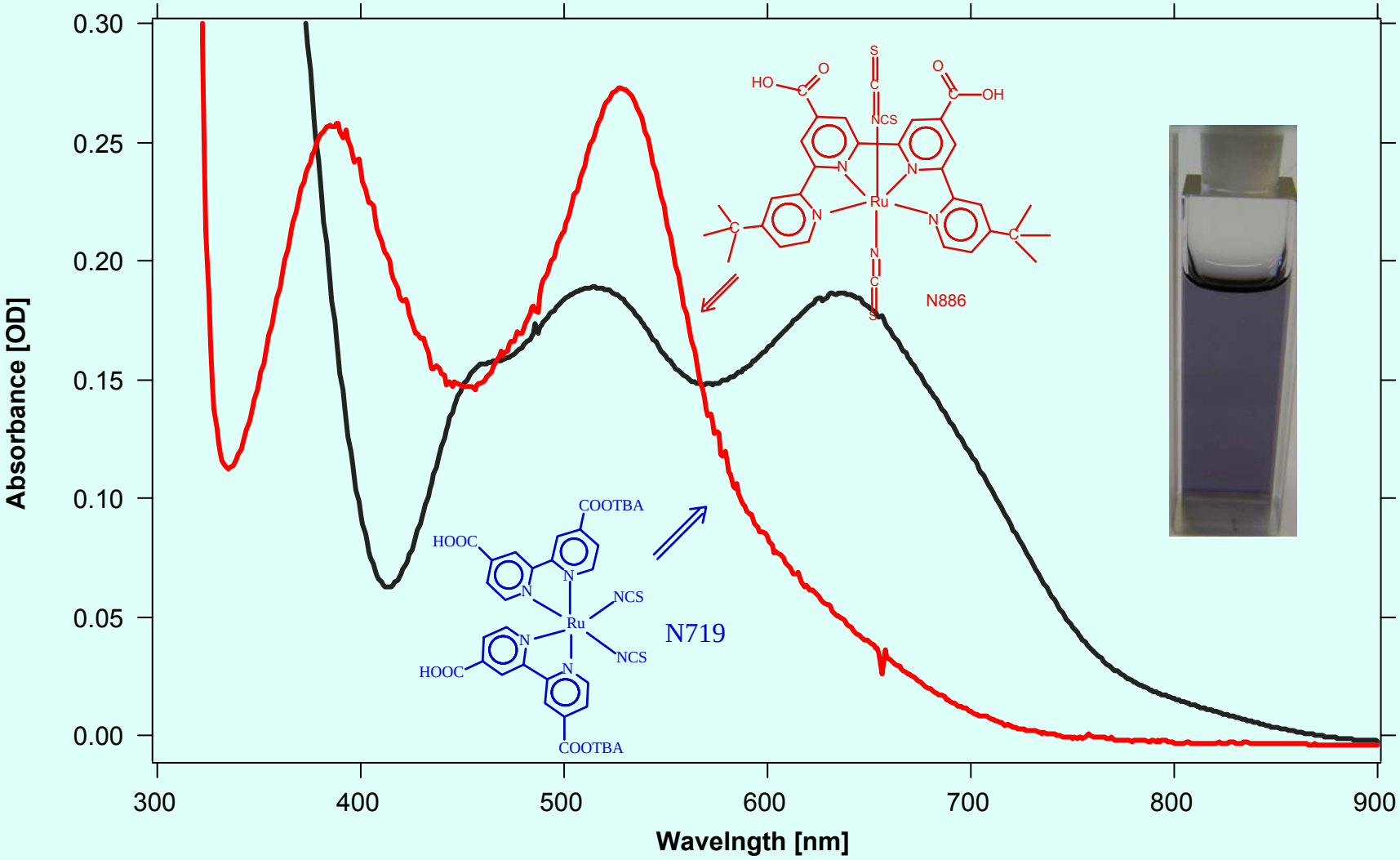




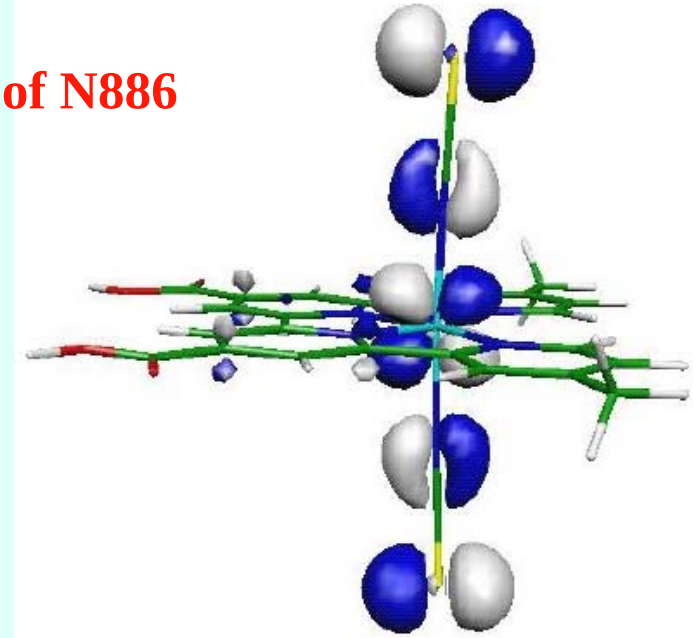
L = 4,4'-COOH-2,2'-bipyridine

L' = 4,4',4''-COOH-2,2':6',2''-terpyridine

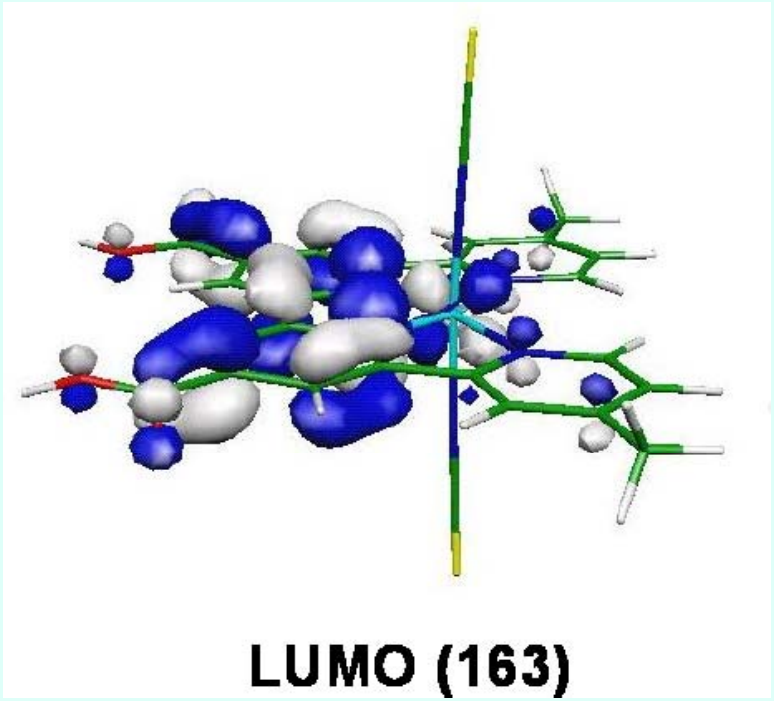
N719 and trans-[Ru(L)(NCS)$_2$]: enhanced near IR response of trans isomer



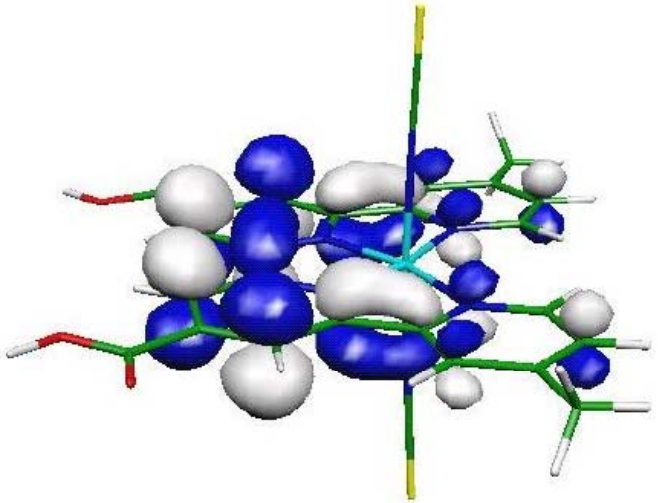
Isodensity plots of main frontier orbitals of N886



HOMO (162)

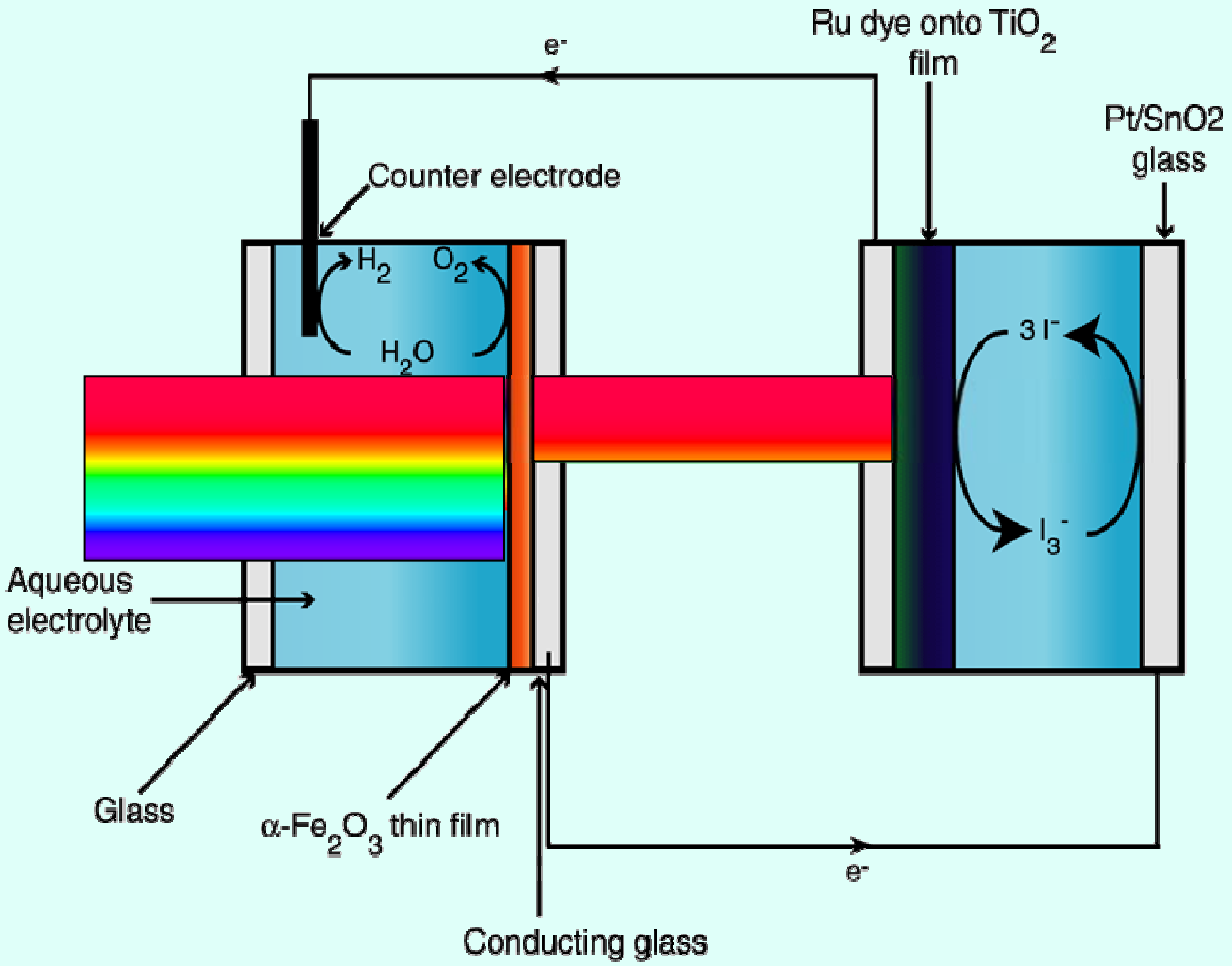


LUMO (163)

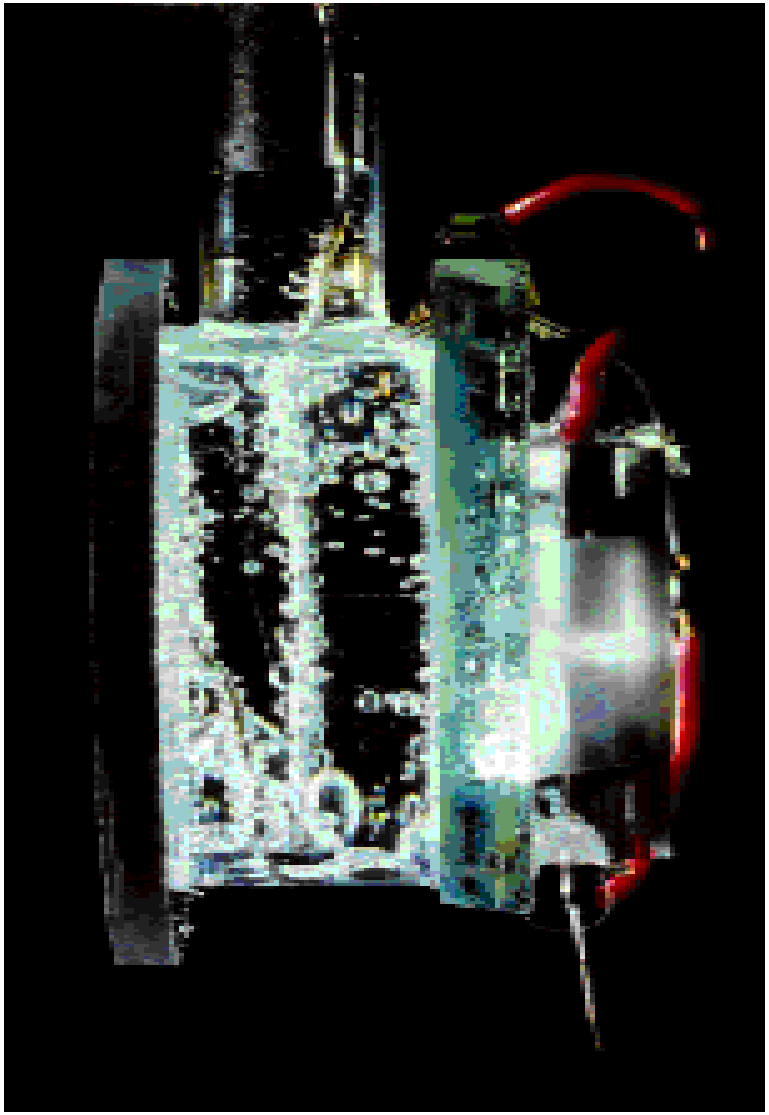


LUMO+1 (164)

Tandem cell scheme



Decomposition of Water using a Tandem Cell Consisting of a Mesoporous WO_3 Film and a Mesoporous Dye Sensitized TiO_2 Electrodes



Future work

Solid state tandem cells

Replace CIGS (Si) bottom cell by CuInS2 nanocomposite (Delft) or DSC using sensitizer with extended near IR absorption.

Photoelectrochemical cell

1. Continue work on mesoscopic Fe2O3 films, investigate dopants other than silicon, optimize juntion between conducting glass subtrate and Fe2O3
2. Examine new mixed oxide photoanode materials, e.g. BiVO4, TaON
3. Develop DSC with enhanced response in the red and near IR

Solar energy supply to the earth: ca 3 million exajoules per year

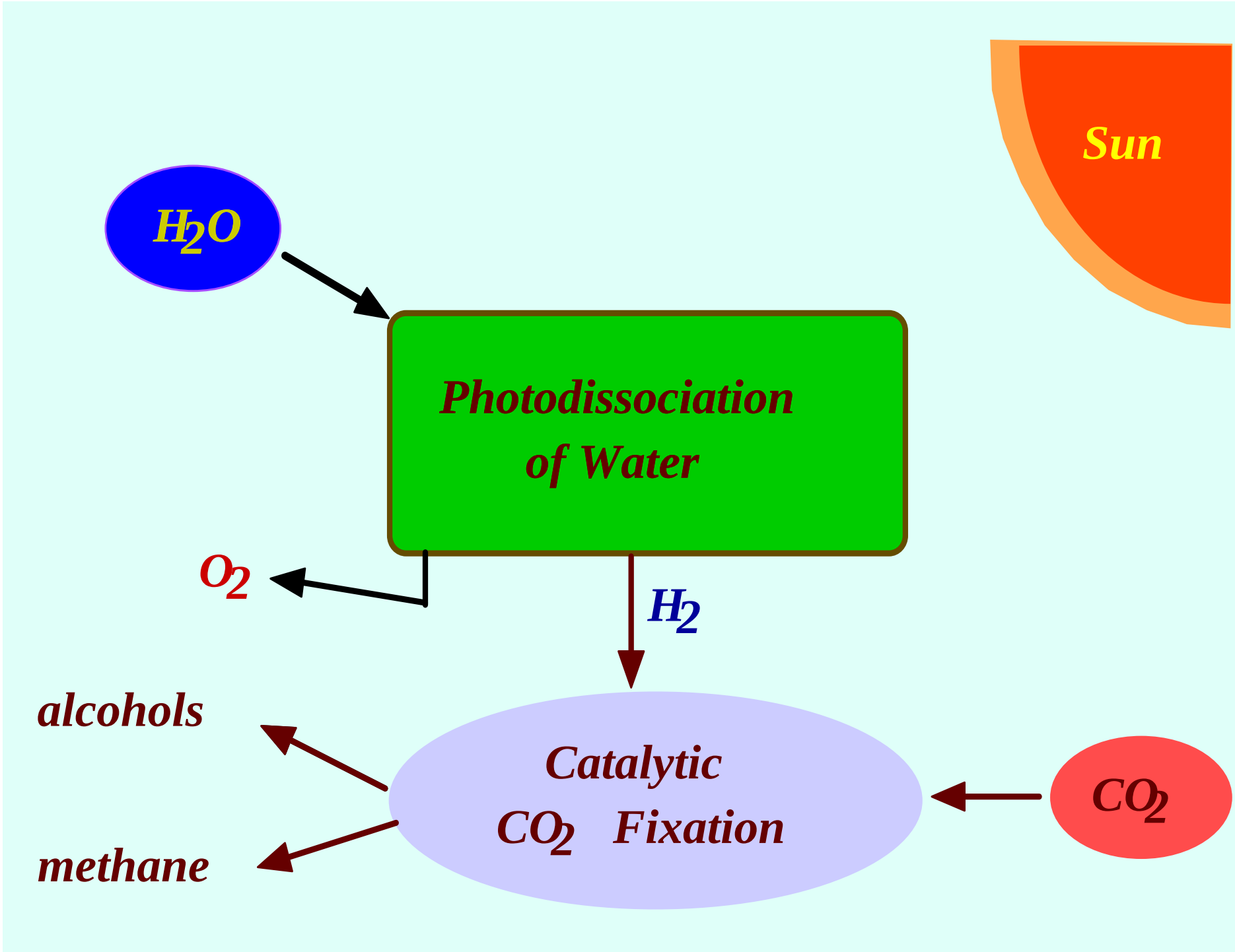
- Current energy demand of the world is 400 exajoules per year This could be fully met by covering ca 0.5% of the earth's surface with PV panels having 10% efficiency.

1 exajoule = 10^{18} Joules

Economics:

A tandem cell of on one square meter surface area that delivers 10 mA/cm2 photocurrent in full sun would need about 1 month in desert climate to produce 1 kg of hydrogen.

If such a cell could be produced at about 100 $/m2 in large scale, the yearly return on investment from selling the hydrogen would be 12 %


Sun
H_2O
Photodissociation of Water
O_2
H_2
alcohols
methane
Catalytic CO_2 Fixation
CO_2

Synthetic Liquid Hydrocarbons

Is this the Future?