NanoPEC
(FP7, Project 227179)

Prof. Michaël Grätzel
EPFL

Basic project information

Michaël Grätzel, EPFL-LPI
Thin films, electrochemical and physical characterization

Teddy Püttgen, EPFL-CEN:
Project Management

Roel van de Krol, TU Delft:
Thin films, electrochemical and physical characterization

Jan Augustynski, U. Warsaw:
WO_3, surface chemistry, electrochemistry

Avner Rothschild, Technion:
Pulsed laser deposition, nanofiber synthesis, physical characterization

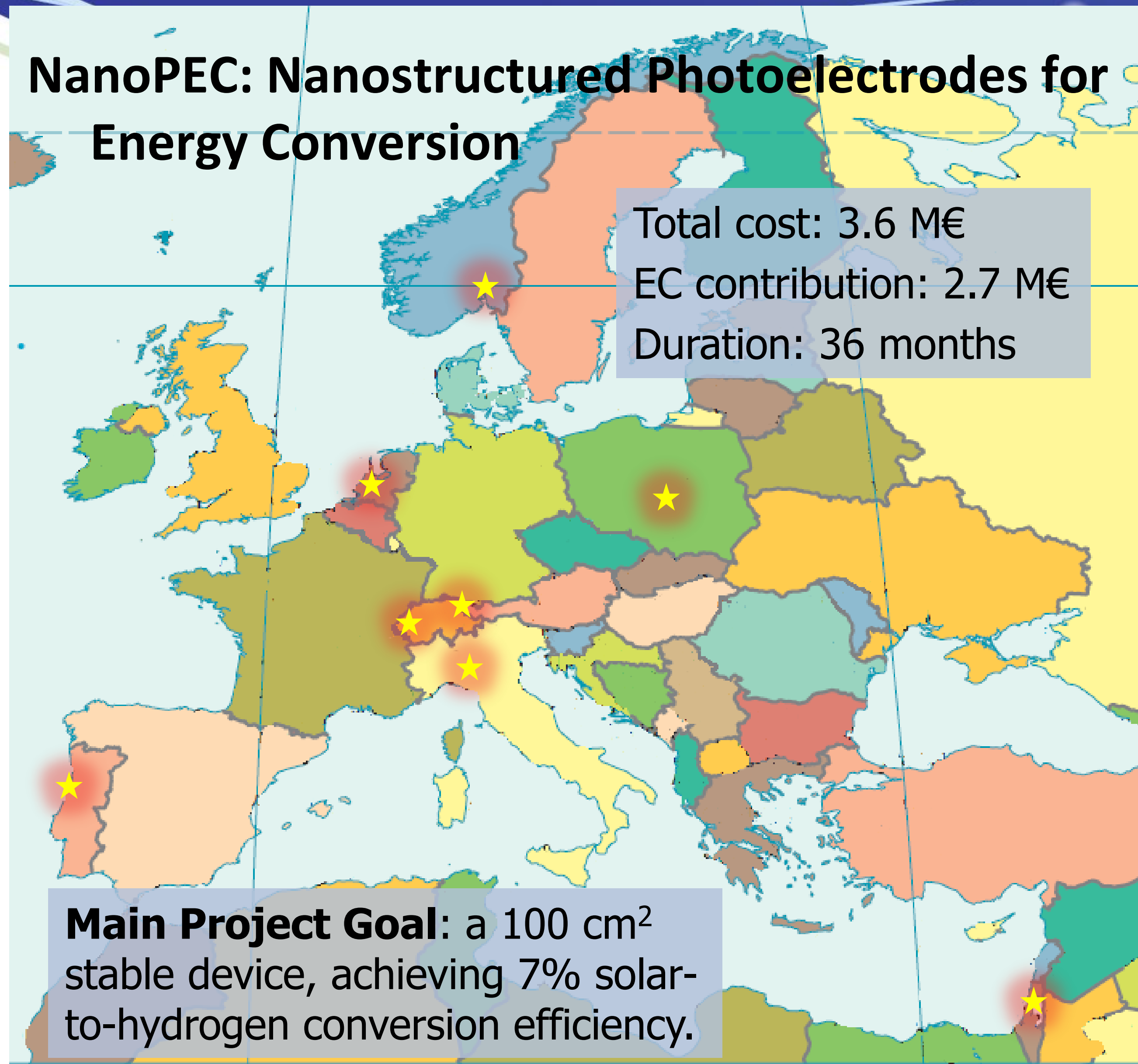
Artur Braun & Anke Weidenkaff, EMPA:
Synchrotron characterization techniques, spray flame synthesis, oxynitrides

Andrej Kutzenov, U. Oslo:
ZnO, nanowires

Adelio Mendes, U. Porto:
Device engineering and modeling, long-term testing

Laura Meda, Eni S.p.A.:
Theory, semiconductor synthesis, large-scale testing

NanoPEC: Nanostructured Photoelectrodes for Energy Conversion



Total cost: 3.6 M€
EC contribution: 2.7 M€
Duration: 36 months

Main Project Goal: a 100 cm^2 stable device, achieving 7% solar-to-hydrogen conversion efficiency.

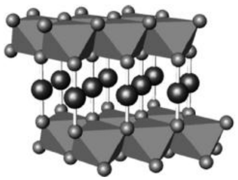
Approach in performing the activities

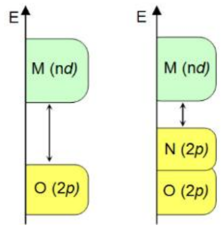
Developing new/promising nanostructures

- Guest-host mesostructures
- Nanostructured semiconductor synthesis
- Plasmon enhanced photoelectrolysis
- Band engineering in nanowire heterostructures
- Overlayer protection

Identifying and developing new/promising materials

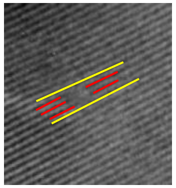
- P-type oxides
- Ternary and higher n-type oxides
- Oxynitrides

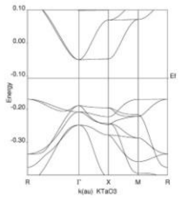




Dissecting material-structure-performance relationships

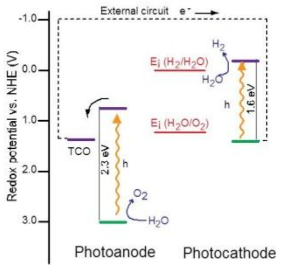
- Model thin films
- Defect and interface analysis
- Ab-initio calculations



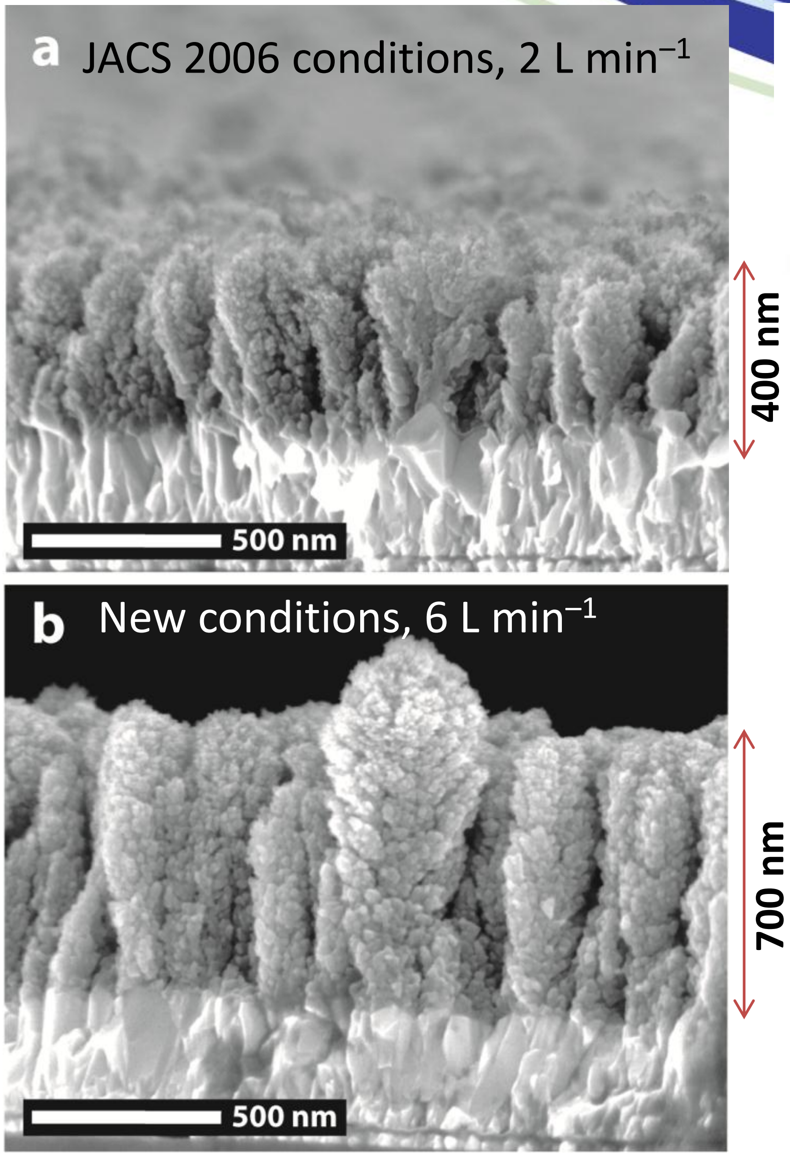


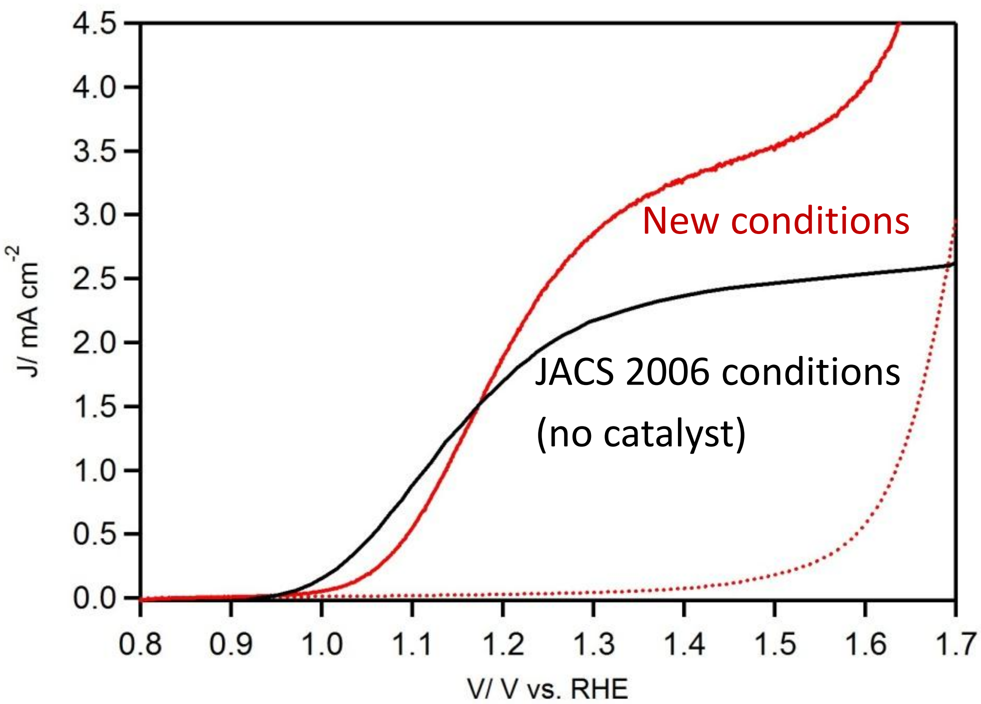
Putting the pieces together

- Promising dual electrode device architecture
- And become the standard for testing methods
- Standardized testing bench
- Solution side engineering
- Device-level modeling



WP1. Advanced nanostructures

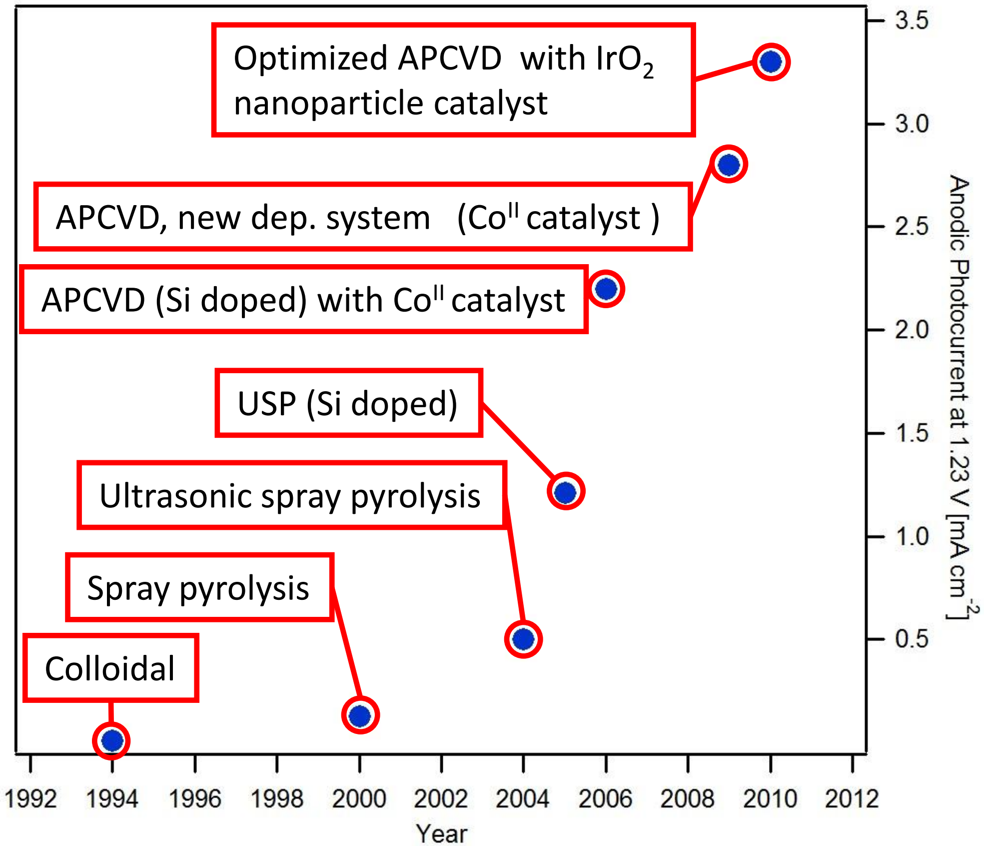


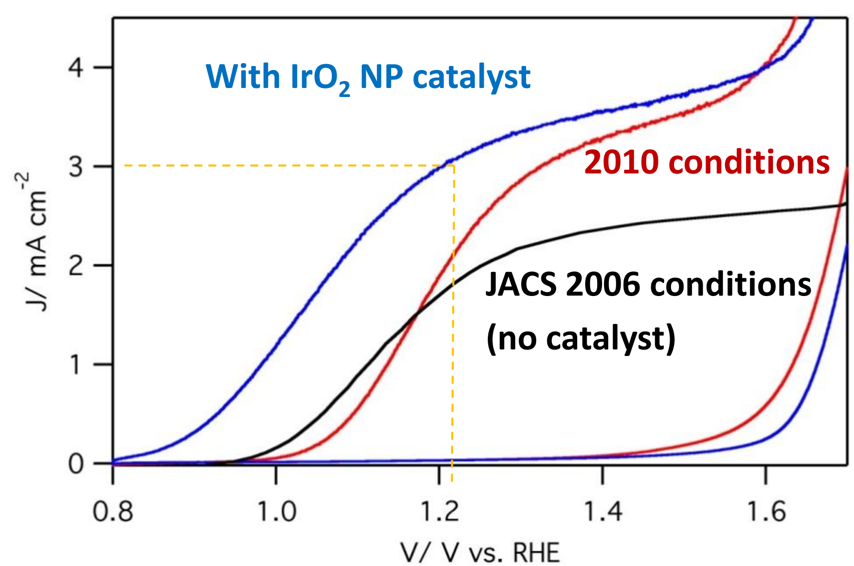


- Optimized film thickness is greater at 6 L min^{-1}
- Photocurrent is increased by 40%
- General reproducibility increases

Angew. Chem. Int. Ed. ***2010***, 49, 6405.

WP 1. The-state-of-the-art performance for hematite photoanodes



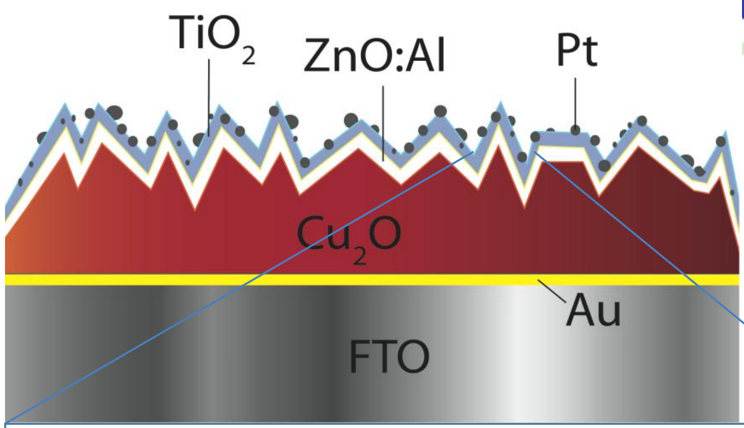


Current at 1.23V corresponds to **4% solar-to-hydrogen** efficiency in combination with an ideal tandem device. Project goal is **10% solar-to-hydrogen efficiency**.

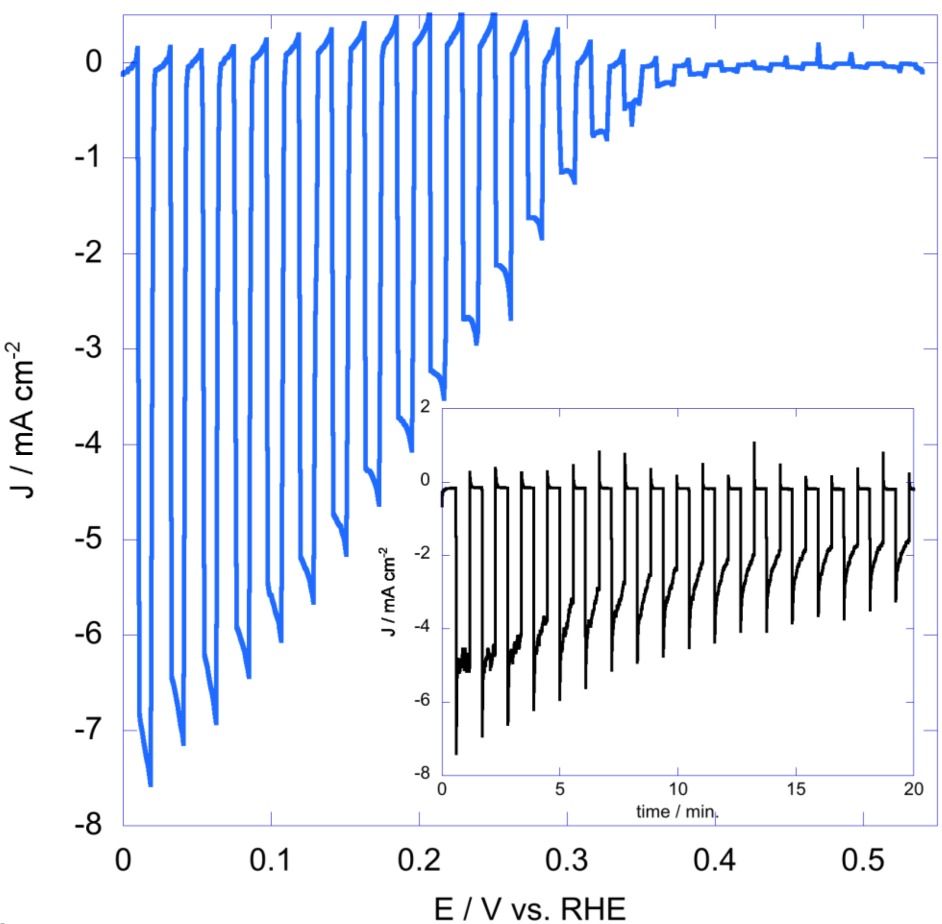
- Advancing towards the project goal of **7 mA cm^{-2} under AM 1.5 illumination** (a 1 cm^2 electrode).

S. D. Tilley, M. Cornuz, K. Sivula, M. Grätzel, *Angew. Chem. Int. Ed.* **2010**, *49*, 6405-6408.

WP2. New/promising materials and nanostructures



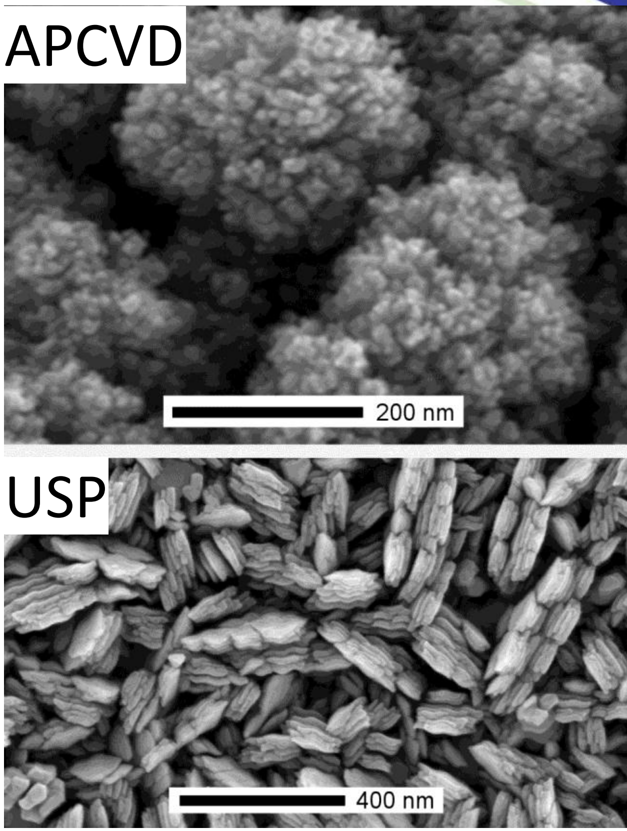
- ZnO:Al provides conductive and pinhole-free surface
- TiO_2 provides stability in aqueous conditions
- Pt acts as a good catalyst for water reduction

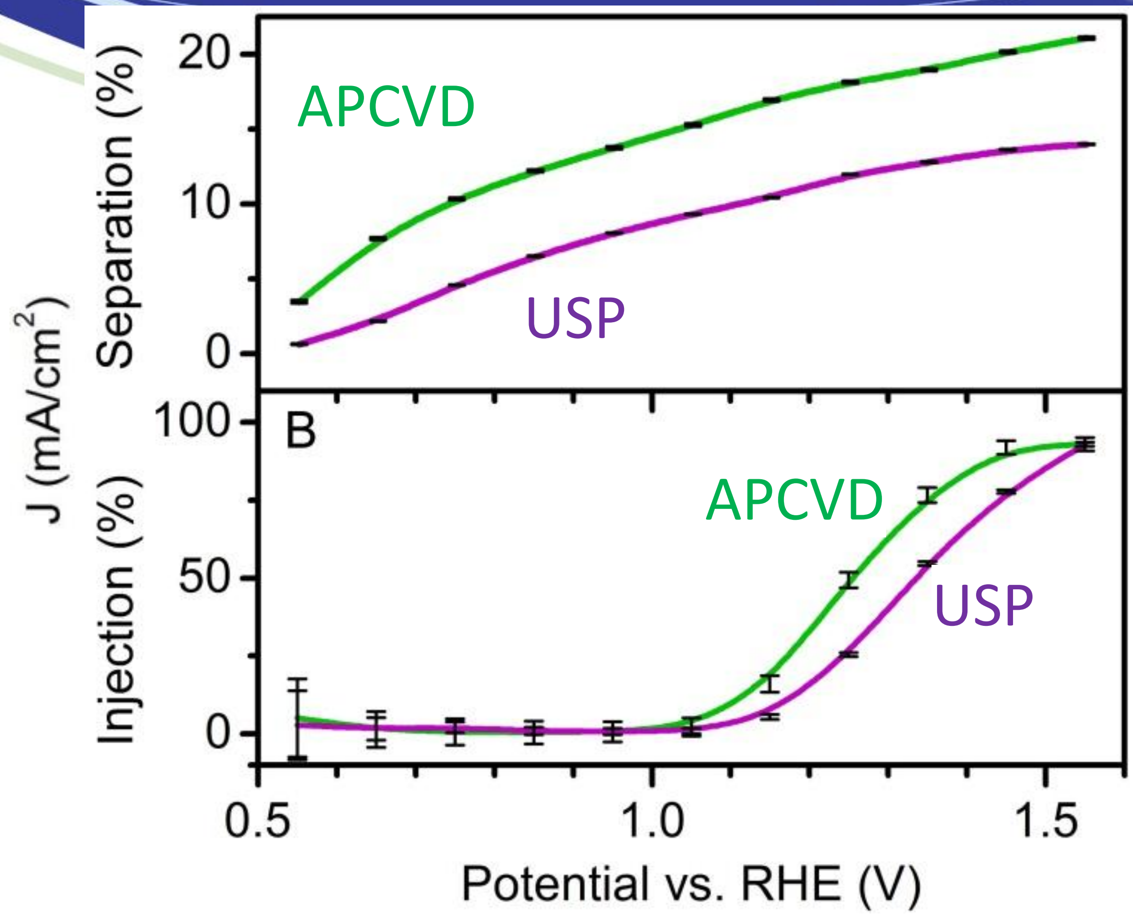


- Photocurrent goal met!
- Advancing towards the project goal of **5000 hour stability** (less than 10% loss of initial activity).

Adriana Paracchino *et al. Nature Materials* **2011,** *10*, 456–461.

WP3. Fundamental investigations: a new diagnostic tool for PEC electrodes



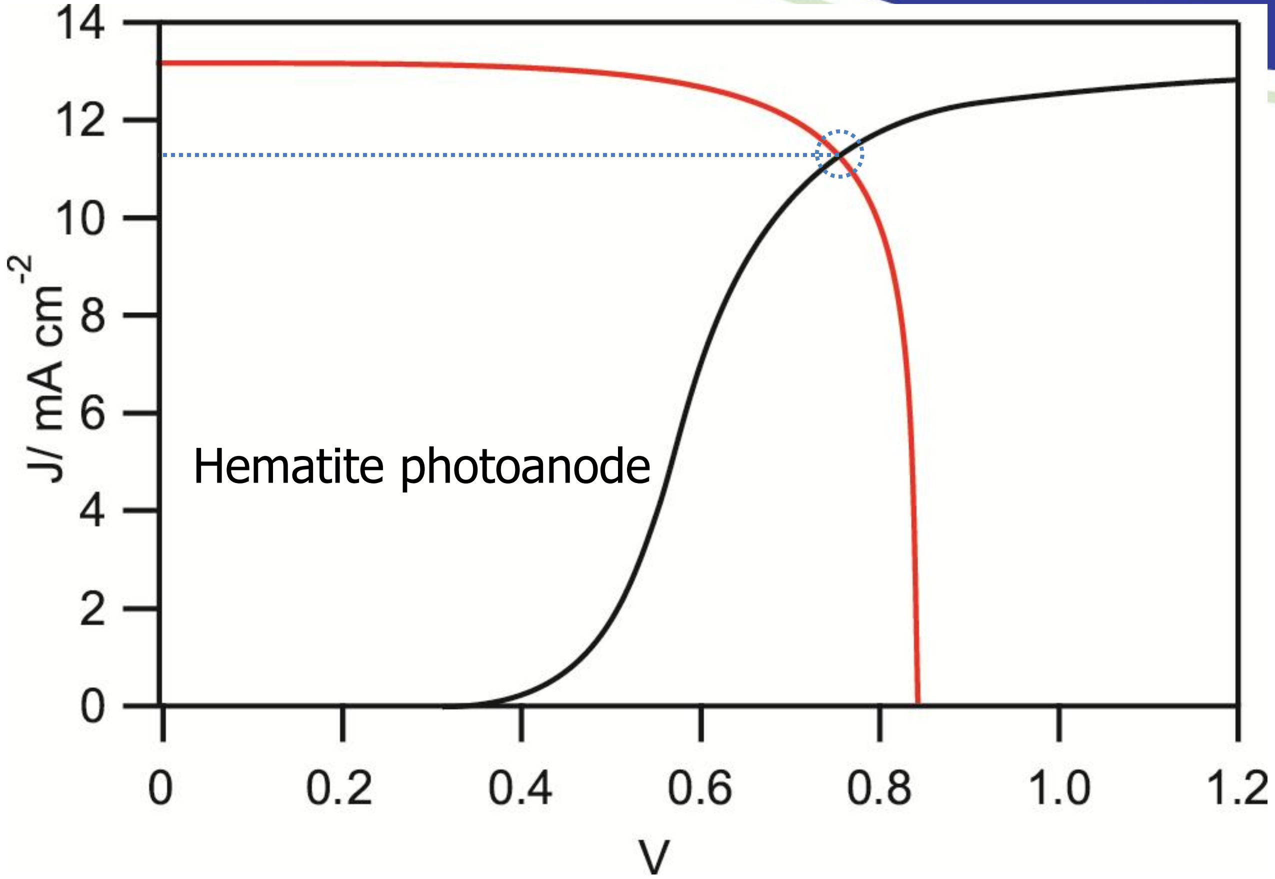


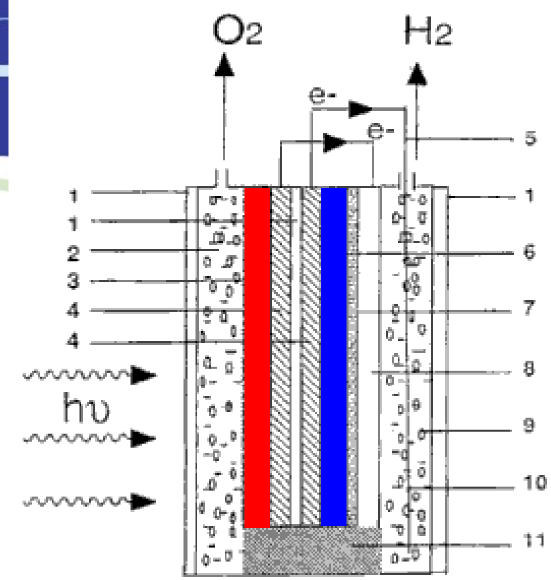
$$J^{H_2O}{}_{photocurrent} = J_{\text{absorbed}} \times P_{\text{charge separation}} \times P_{\text{charge injection}}$$

$$J^{H_2O_2}{}_{photocurrent} = J_{\text{absorbed}} \times P_{\text{charge separation}}$$

Energy Environ. Sci., **2011**, *4, 958-964*

The Tandem Cell to meet the Technical Goal





US-patent 6936143, filed Apr 7, 2000

If: $\eta_{\Delta G}$ = 10%

PEC cell cost \$80/m^2

10 year lifetime

Then:

H_2 = \$6.90/kg H_2

at scale of 1000 kgH_2/day.

Solar to chemical conversion efficiency (η) = output/input:

$\eta_{\Delta H} = \eta_F \times I_{ph} \times (1.45 - V_{bias})/(100\ mW/cm^2)$ = 16 % (4.8 %)

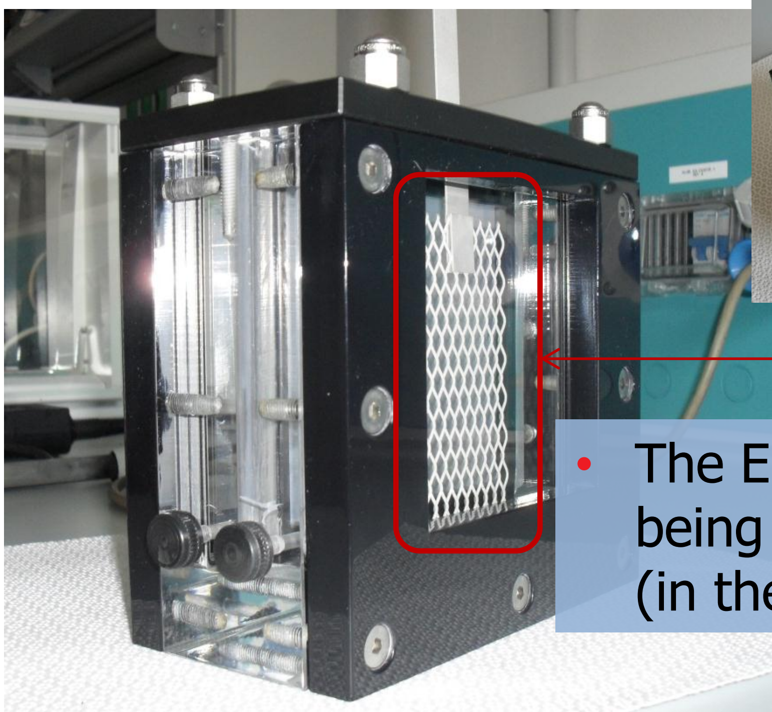
$\eta_{\Delta G} = \eta_F \times I_{ph} \times (1.23 - V_{bias})/(100\ mW/cm^2)$ = 13.5 % (4.1 %)

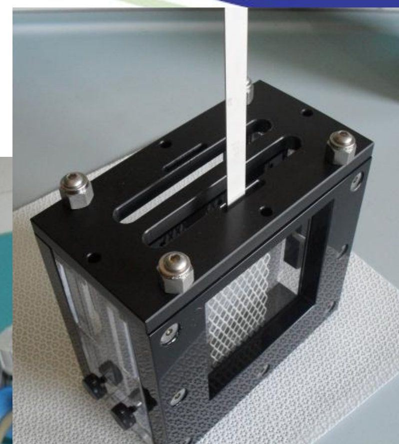
(shown possible based on photocurrent)

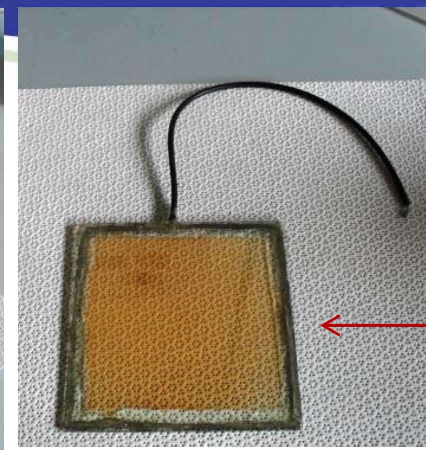
B. D. James, G. N. Baum, J. Perez, K. N. Baum, Technoeconomic Analysis of Photoelectrochemical (PEC) Hydrogen Production **2009.**

The *PortoCell* for large photoelectrodes

10 x 10 cm^2 Active Area



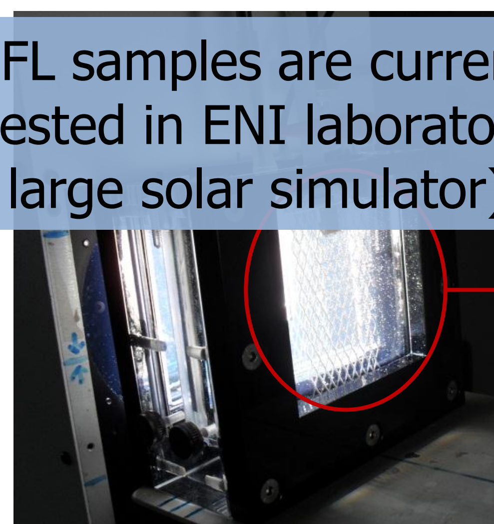


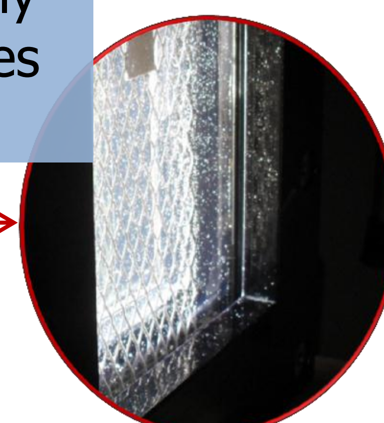


10x10 hematite photoanode

- Platinized Titanium Mesh Cathode

- The EPFL samples are currently being tested in ENI laboratories (in the large solar simulator).





- Able to perform:
  - Temperature studies;
  - Studies with electrodes separator (Teflon diaphragm);

MAIP – Hydrogen Production & Distribution

- The midterm target is to supply 10-20% of the anticipated hydrogen energy demand with CO_2 lean or CO_2 free hydrogen by 2015. ***A second objective is to start preparatory work to enable the introduction of a widely spread hydrogen infrastructure beyond 2020-2030.***

- Accordingly, the main emphasis of this application area will be on research and development of mature production and storage technologies and on ***breakthrough orientated research of longer term, fully sustainable hydrogen production*** and supply pathways.

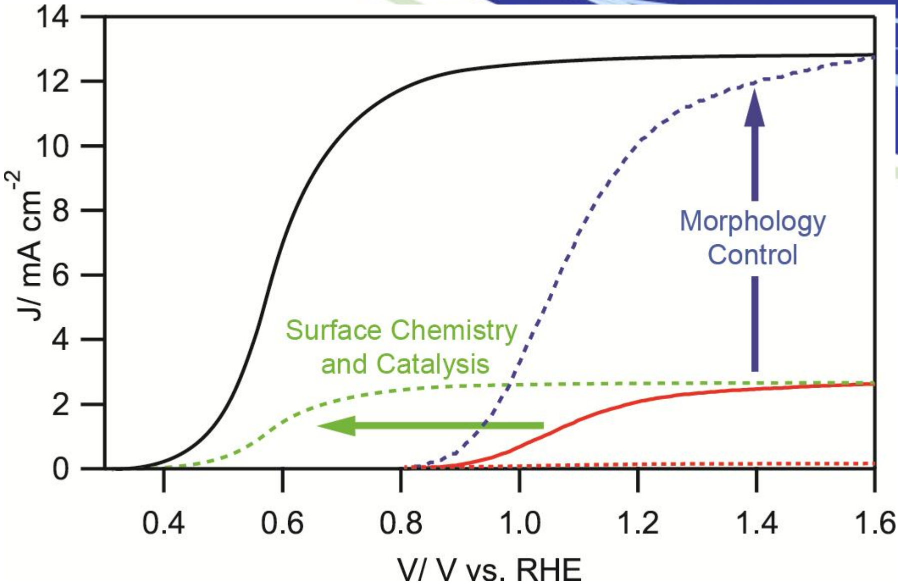
- Technical Target for 2015: ***Cost of H_2 delivered at refuelling station < €5/kg (€ 0.15/kWh)***

- ***Photoelectrochemical Water Splitting is our answer to these goals.***

How we get there

WPs	Achievements	Delivery date (month)	Achieved with
1,2	Photoelectrodes with a 3 mA/cm^2 photocurrent at 1.23 V vs. RHE and AM1.5 based on nanostructuring approaches of known semiconductors.	15	Fe_2O_3 ✓
1,2	Small scale photoanode with photocurrent of 3.3 mA/cm^2 at 1.23 V vs. RHE under AM 1.5.	18	Fe_2O_3 ✓
1,2	Photoelectrode demonstrating a 5 mA/cm^2 photocurrent at 1.23 V vs. RHE at AM1.5.	24	Cu_2O ✓
1,2	Small photoelectrode with a 6 mA/cm^2 photocurrent at 1.23 V vs. RHE at AM1.5 using novel semiconductors or nanostructuring.	30	Cu_2O ✓
1,2,4	Three prototypes each of 10% efficiency (6.6 mA/cm^2) small cells (1 cm^2) using new materials and 7% efficiency (4.6 mA/cm^2) based on a larger cell (100 cm^2), all under AM1.5 simulated sunlight.	36	**in progress**

Challenges to overcome in future projects



Photocurrent onset will be improved by enhancing surface kinetics with catalysts and suppressing surface defects by overlayers

Photocurrent will be increased by fabricating ultrathin electrodes on a highly-rough conductive substrate

Stability of the electrodes will be extended by refinement of protective overlayers

Scalability of high-performance electrodes will be managed by applying newly-developed liquid phase processes

Dissemination of Our Work

http://nanopec.epfl.ch

(March and April, 2011)

http://www.emrs-strasbourg.com/index.php?option=com_abstract&task=view&id=135&year=2011&Itemid=&id_season=4 (May, 2011)

Creation of PECHouse

A Photoelectrochemical Center of Excellence in Switzerland

- PECHouse is a project funded by the Swiss Federal Office of Energy (SFOE) from August 2007 until December 2011 (4.5 years). The budget is 5.4M Swiss Francs (CHF) over the course of 4.5 years. The SFOE portion of this amount is 1.5M CHF, ~330'000 CHF per year. The Toyota Motor Corporation (TMC) has contributed a total of 300'000 CHF over the course of this project, **and we expect continued support from TMC.**

- Funding for PECHouse has been renewed for 2012-2015 (so-called **PECHouse2**) with a budget of **1.5M CHF** over 3 years, of which the SFOE portion is 900'000 CHF. The project will focus more on scale-up as well as simulation in order to identify the bottlenecks in our system.

- In addition, we have **created a new HyTech project** with a budget of **8.8M CHF** over 3 years that will explore hydrogen production at different scales: **PEC water splitting** for small-to-medium scale, concentrated solar to drive a ZnO cycle for large scale water splitting, as well as the investigation of different hydrogen storage strategies such as metal hydrides and formic acid.

The future of the project

- One of the goals of PECHouse1 was to find financial support from the European Union. This is where **NanoPEC** was born.

Goals of PECHouse1:

Strategic	Scientific and technical (Fe_2O_3)	Team network and technology transfer
• Find the most practical technology • Prepare strategic partnerships • Monitor progress of all technologies for potential of success	• 4.5 % STH by 12/2009 • 7 % STH by 12/2011 • 1000 hours with 5% degradation • Production costs by 2015: 5€/kg H_2	• Coordination of national research interests • Participation in ongoing EU research activities • Locate strategic partners and future finances

On the web @ pechouse.epfl.ch

- The knowledge and experience gained that was enabled by PECHouse1 and **NanoPEC** will now be carried forward in Swiss projects Hytech and PECHouse2.