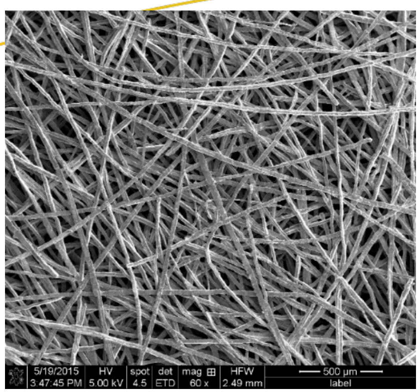
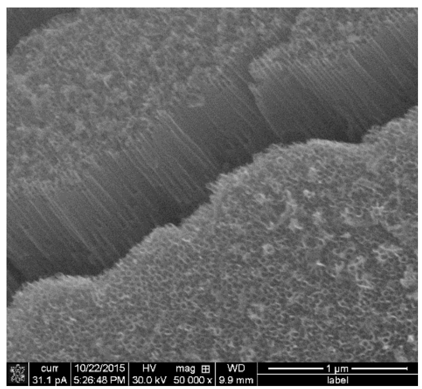
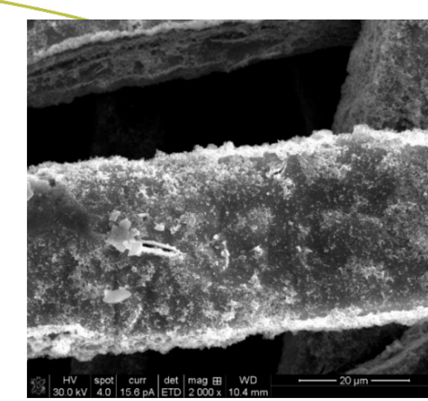
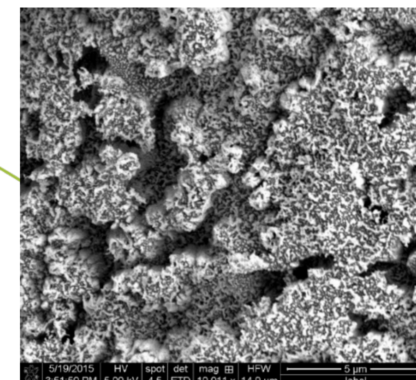
DIFFER

Towards visible light activated porous photoanodes in conjunction with polymeric electrolyte photoelectrochemical cells with gaseous reactants









T. Stoll, G. Zafeiropoulos, H. Genuit, M.N. Tsampas

Lab of catalytic and electrochemical processes for energy applications,

Dutch Institute For Fundamental Energy Research

m.tsampas@differ.nl

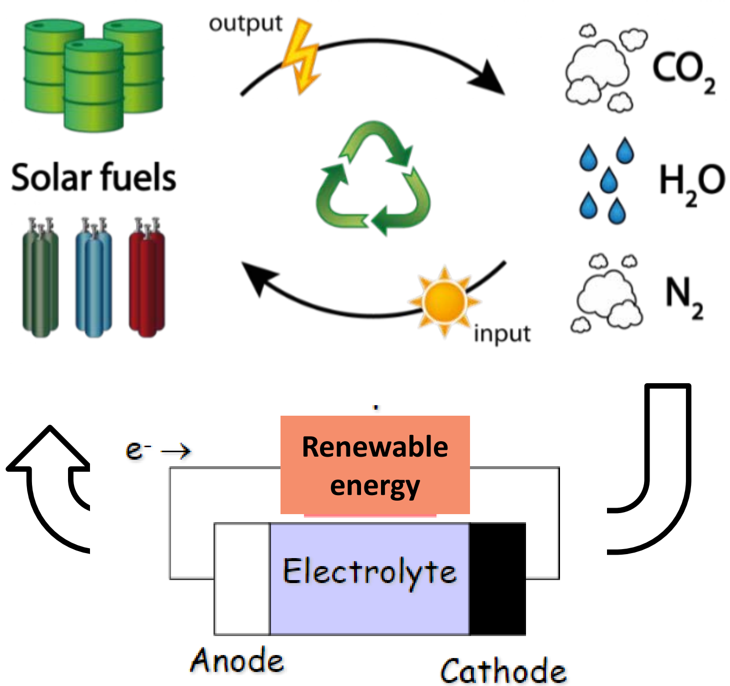
EERA European Energy Research Alliance

AMPEA Advanced Materials and Processes for Energy Applications

EERA AMPEA workshop, SINTEF, Oslo (Norway), February 7-8th, 2017

DIFFER is part of NWO

Activities in my group



Activities of my group: Electrochemical devices with solid electrolytes for energy storage.

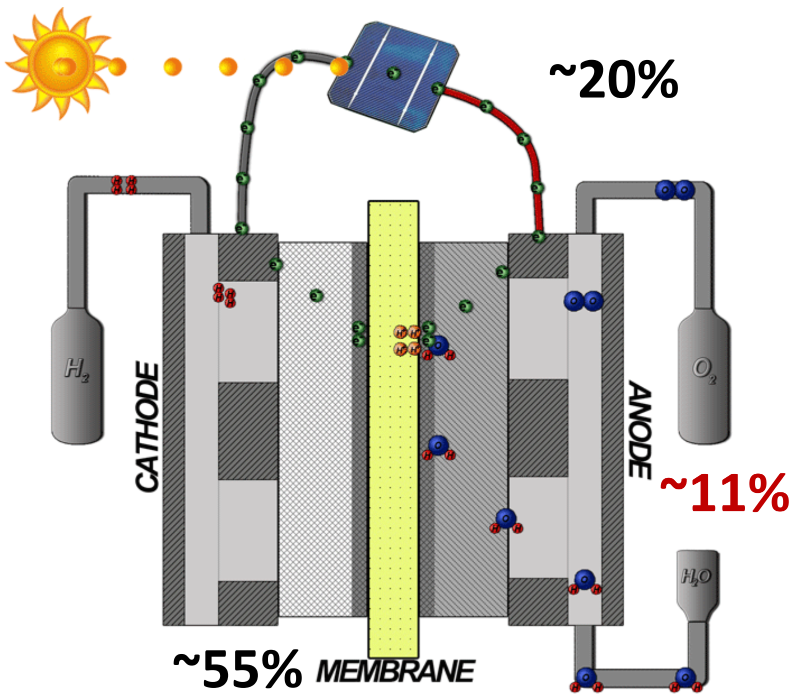
- Light assisted processes
- Electrochemical activation of catalysis
- Plasma assisted electrocatalysis

Novel design of photoelectrochemical (PEC) cells for energy applications based on polymeric electrolyte membrane (PEM)

Inspiration of conventional PEM electrolyzers → design → Conventional PEC cells → Novel PEM-PEC cells with new **modes of operation**

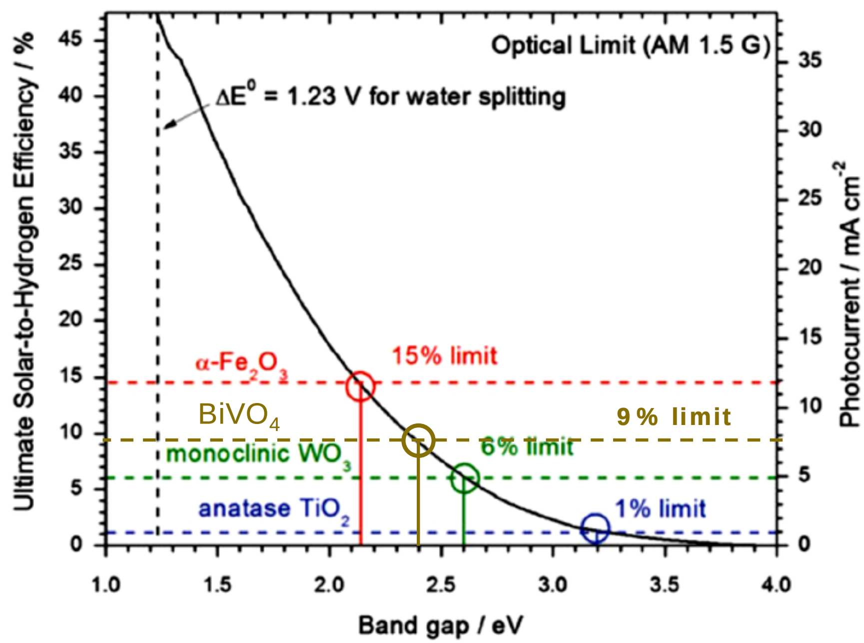
Tools → Possible application in PEM FCs or ECs

Motivation for photoelectrochemical (PEC) cell research



PEM electrolyser coupled with PV for indirect SF production: Expensive noble metal (i.e. Pt, Ir-Ru) electrode materials → Not sustainable solution at the moment.

Theoretical efficiency of PEC cells based on the photoelectrode bandgap under illumination on earth surface



PEC for direct SF production:

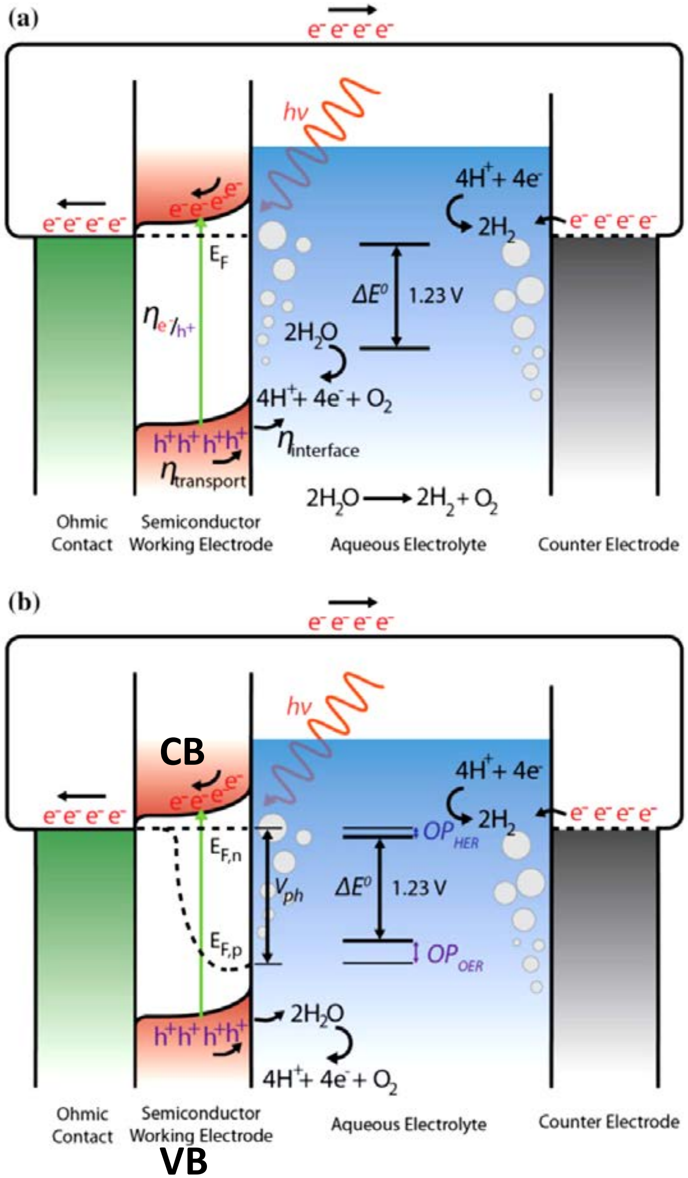
- Cheap abundant electrode materials
- Ongoing research for materials
- Scaling up → design modification
- Novel operation modes

Van de Krol R, Grätzel M, editors. Photoelectrochemical hydrogen production. New York: Springer; 2012

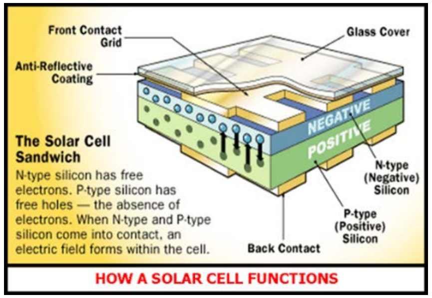
Concept of PEC cells for water splitting

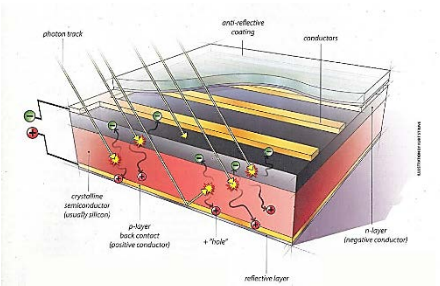
When a **semiconductor** catalyst absorbs photons whose energy is more than the semiconductor's band gap, the electron in valence band (VB) can transit to the conduction band (CB).

- *Photogenerated electrons and holes are formed in the CB and VB*
- *Holes drive the oxygen evolution reaction*
- *Electrons (via external circuit) drive the hydrogen evolution reaction*

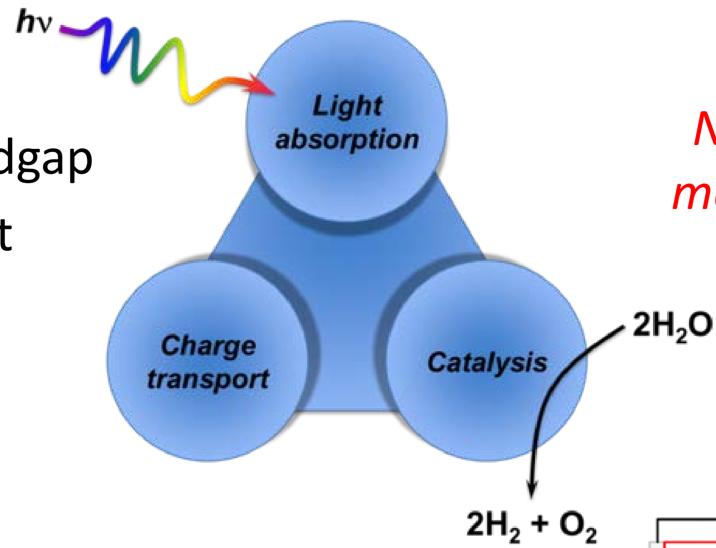


PEC design inspiration for PVs.





Ideal photoelectrode material for PEC



The ideal photoelectrode:

- Light adsorption - Small bandgap
- Correct band edge alignment
- Charge separation-transport
- Catalysis → HER, OER
- Stability and low cost

No semiconducting material meets these criteria

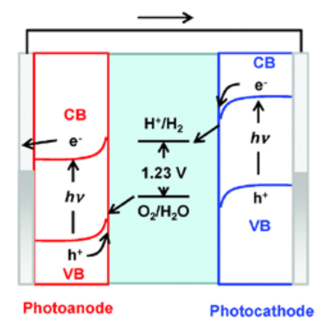
Trade-off solution

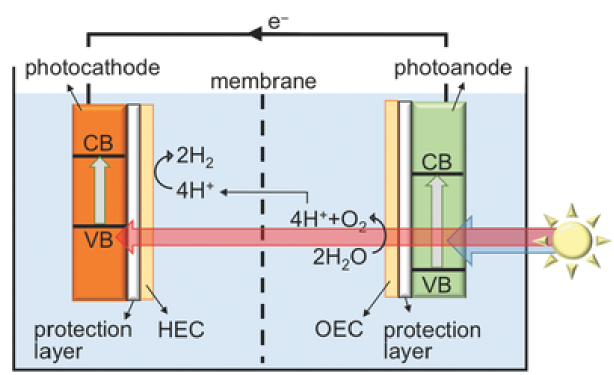
➢ development of composite photoelectrodes → different materials fulfill different functionalities

➢ Nanostructuring

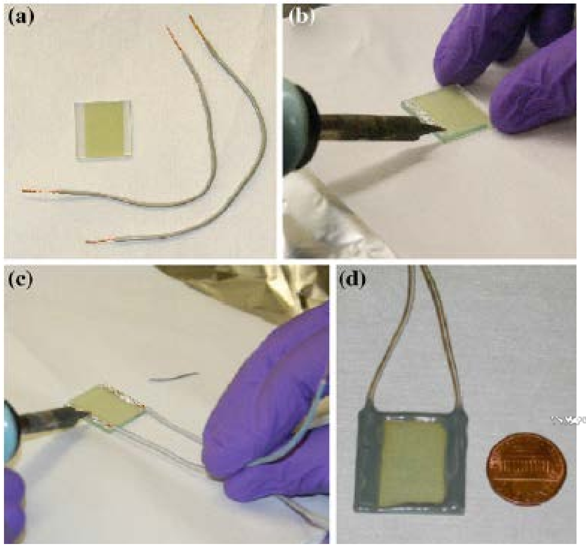
➢ Co-catalysts

➢ Z-scheme: Photoanode + photocathode



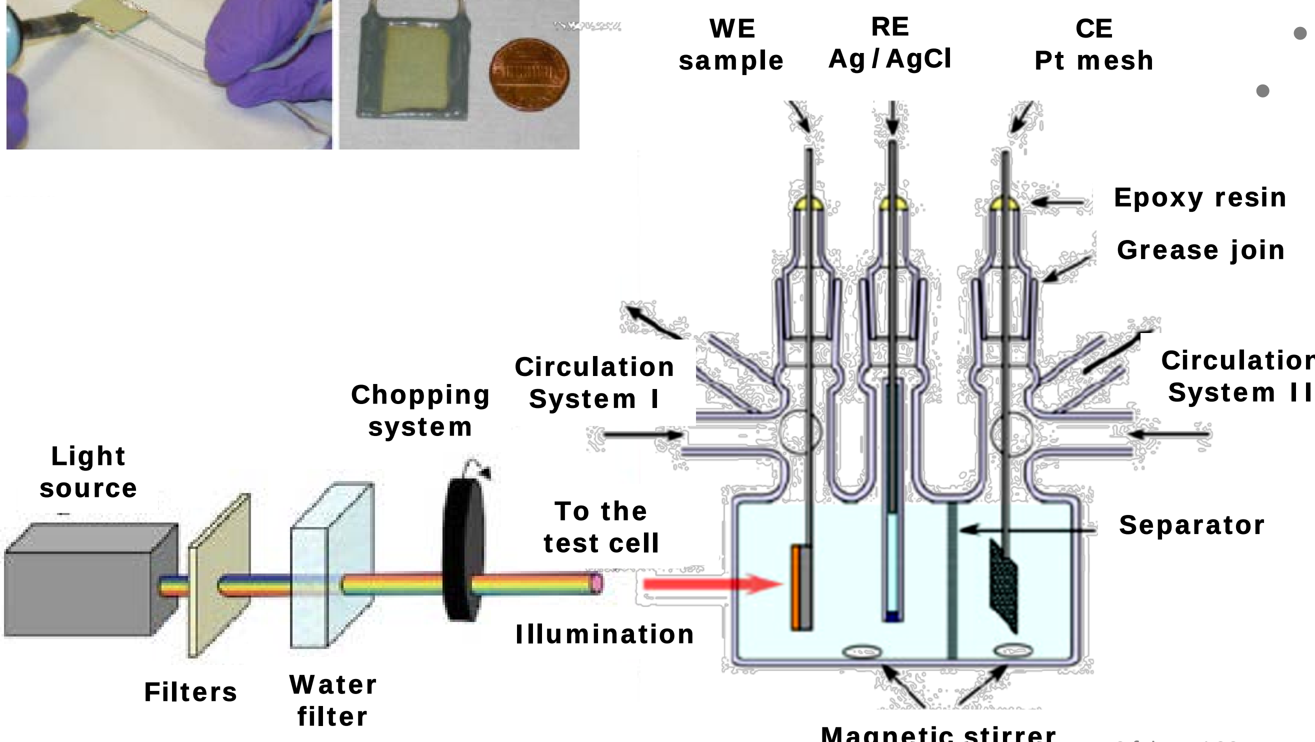


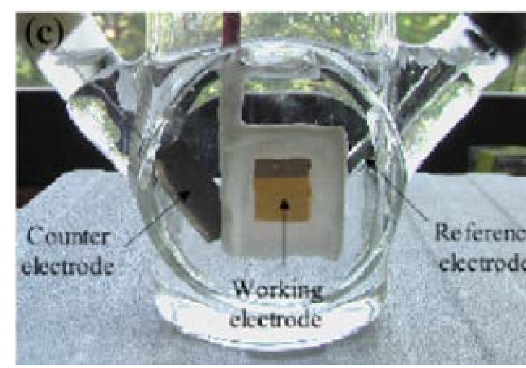
Conventional PEC design: aqueous electrolytes



Photoelectrode for conventional PEC cells (liquid electrolytes): Semiconducting layer deposited on a transparent glass substrate (with an electronically conducting layer).

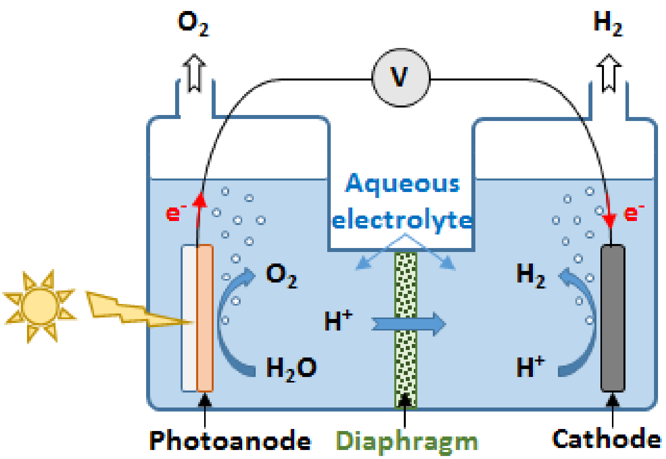
- *Challenges in scaling up*
- *Limited modes of operation*



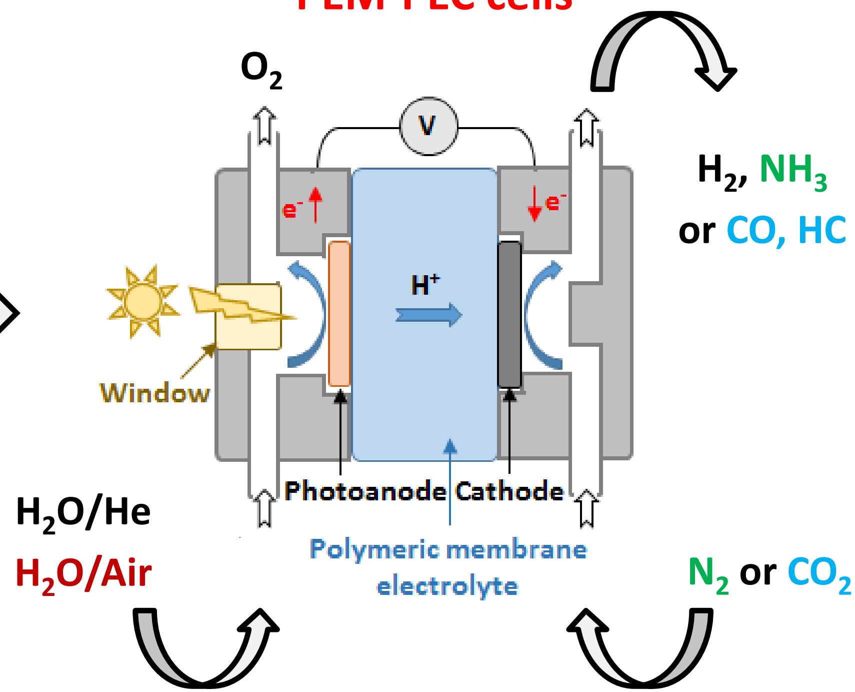


Solid state PEC or PEM-PEC

Conventional PEC cells



PEM-PEC cells



PEM-PEC cells advantages:

- New modes of operation
- Capturing H_2O from ambient air*
- CO_2 or N_2 fixation
- Operation in microgravity environment
- No need for replenishing the electrolyte
- Operation at elevated T, P
- Mechanistic studies: FTIR and Raman

*J. Ronge et al, RSC Adv 4 (2014) 29286

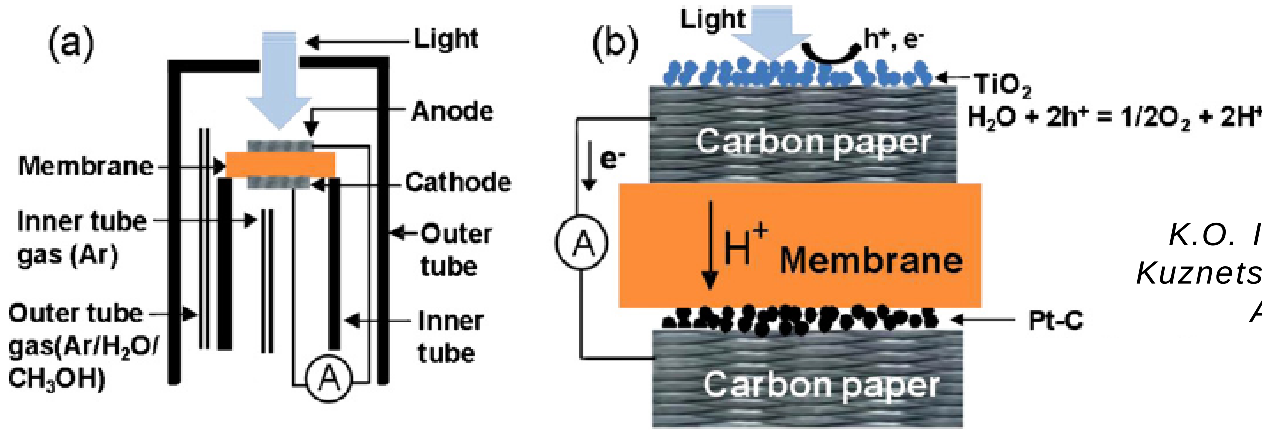
PEM-PEC modes of operations:

- ***Anode:*** *H_2O carried by He or air*
- ***Cathode:*** *N_2 or CO_2 reduction*

PEM-PEC challenges:

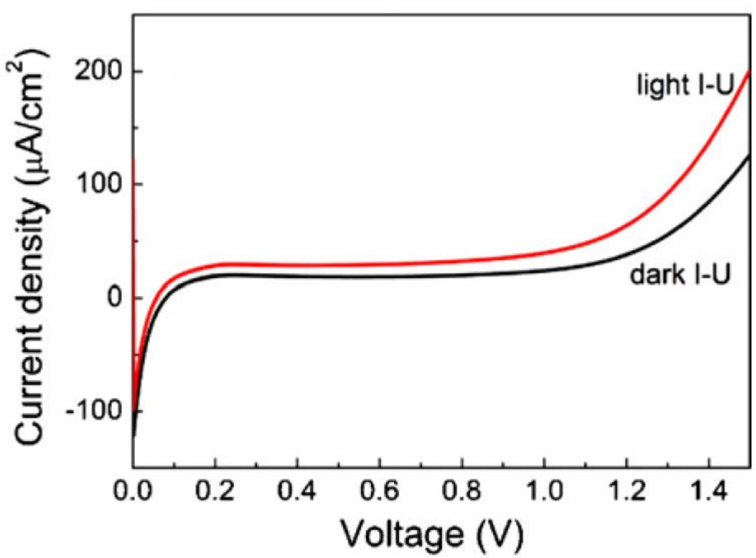
- Porous photoelectrodes → new fabrication route
- Electrode electrolyte compatibility

Solid state PEC with powder TiO_2 photoelectrode and gas phase operation

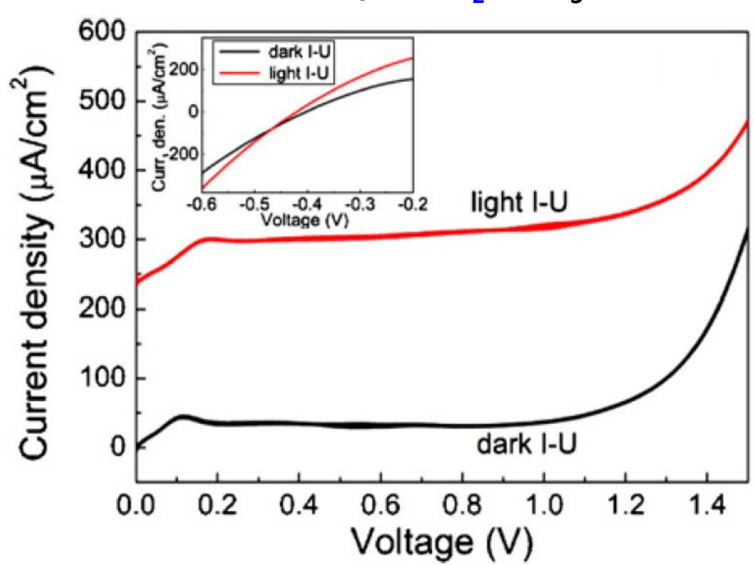


K.O. Iwu, A. Galeckas, A. Yu. Kuznetsov, T. Norby, Electrochim. Acta, 97 (2013) 32.

Cathode feed: H_2O

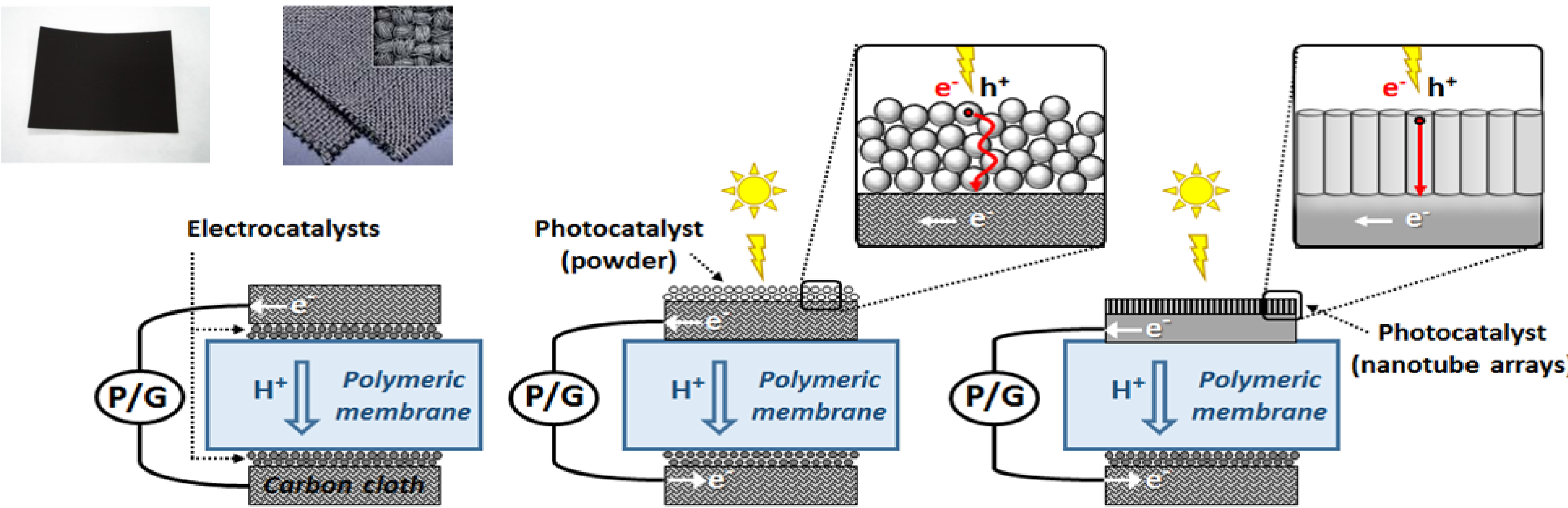


Cathode feed: H_2O, CH_3OH



PEM-PEC electrode design

PEM technology is based on **porous electrodes** that allows access to gas in the electrode electrolyte interface → gas diffusion electrodes.

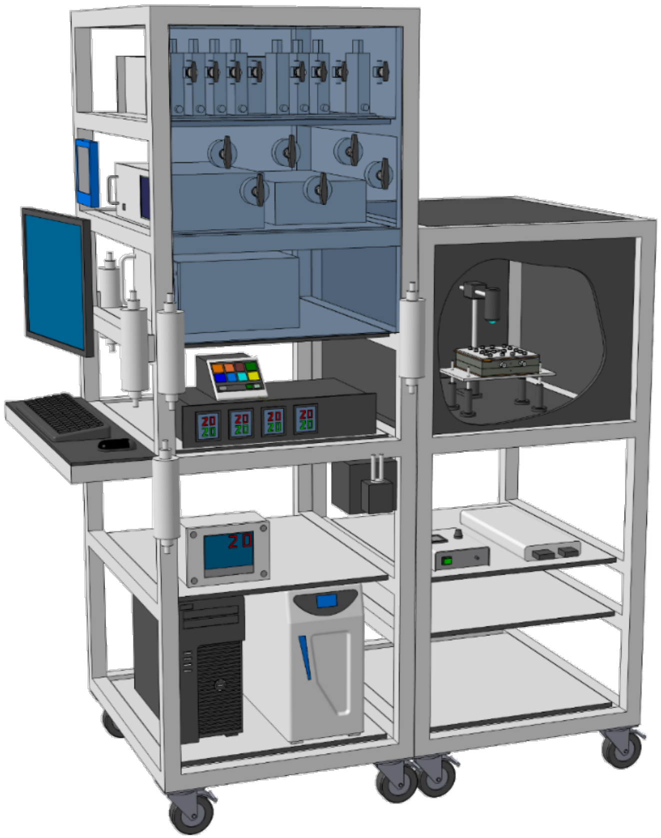


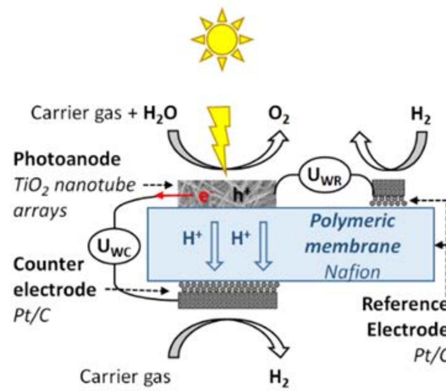
Membrane electrode assembly for PEM electrolysis

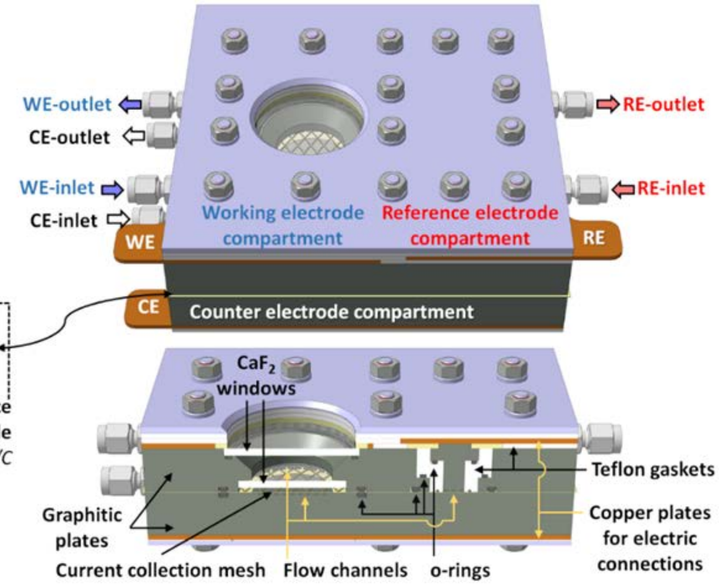
Photoelectrodes based on semiconductors in the form of powders

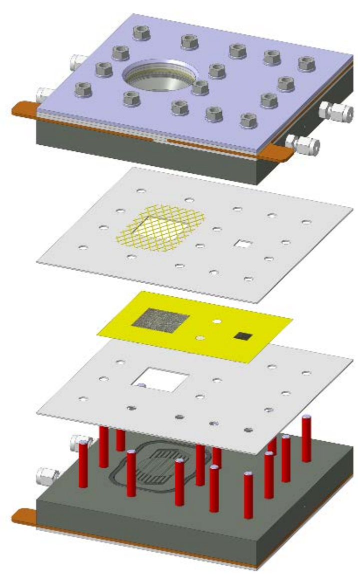
Our approach for high surface area photoelectrodes

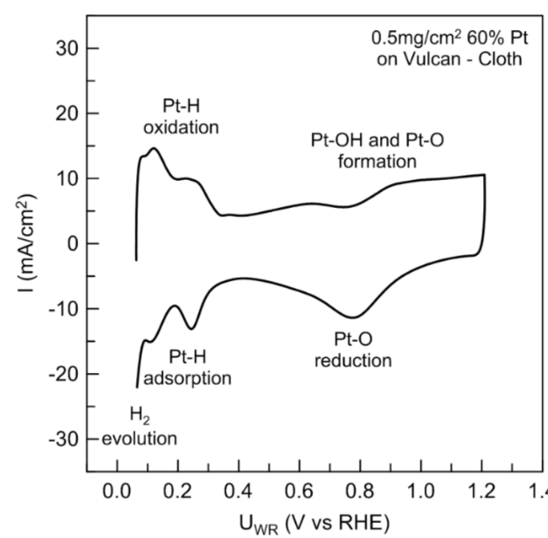
PEM-PEC cell design











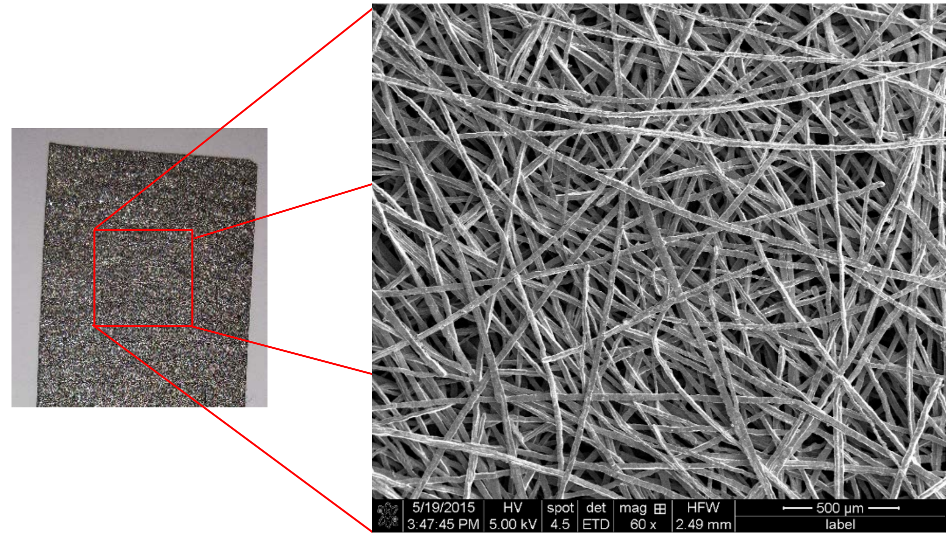
- Operation with liquid and gaseous reactants
- Reference electrode
- Applicable also for alkaline and bipolar membranes

Fabrication: Photoelectrodes for PEM-PEC

Starting material Ti felt (3D web of microfibers):

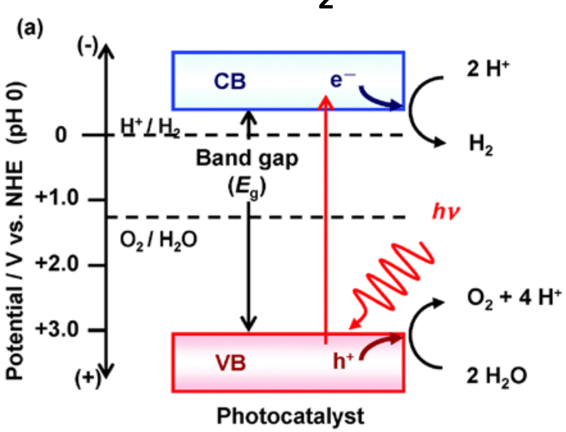
(i) TiO_2 nanotube arrays → **$LaTiO_2N$**

(ii) Deposition of **WO_3 / $BiVO_4$** junction



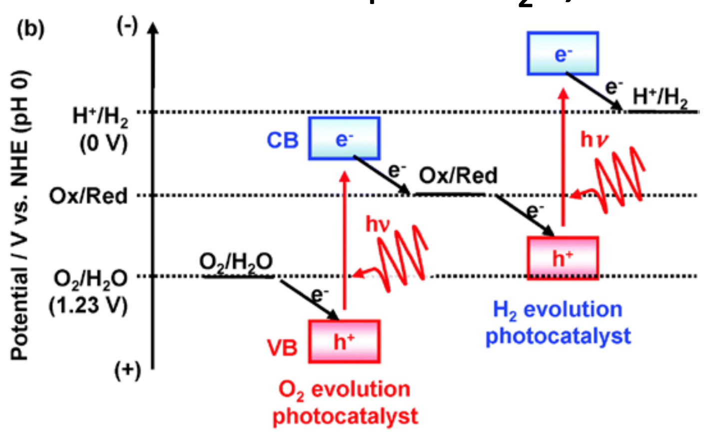
Photoanode

$LaTiO_2N$

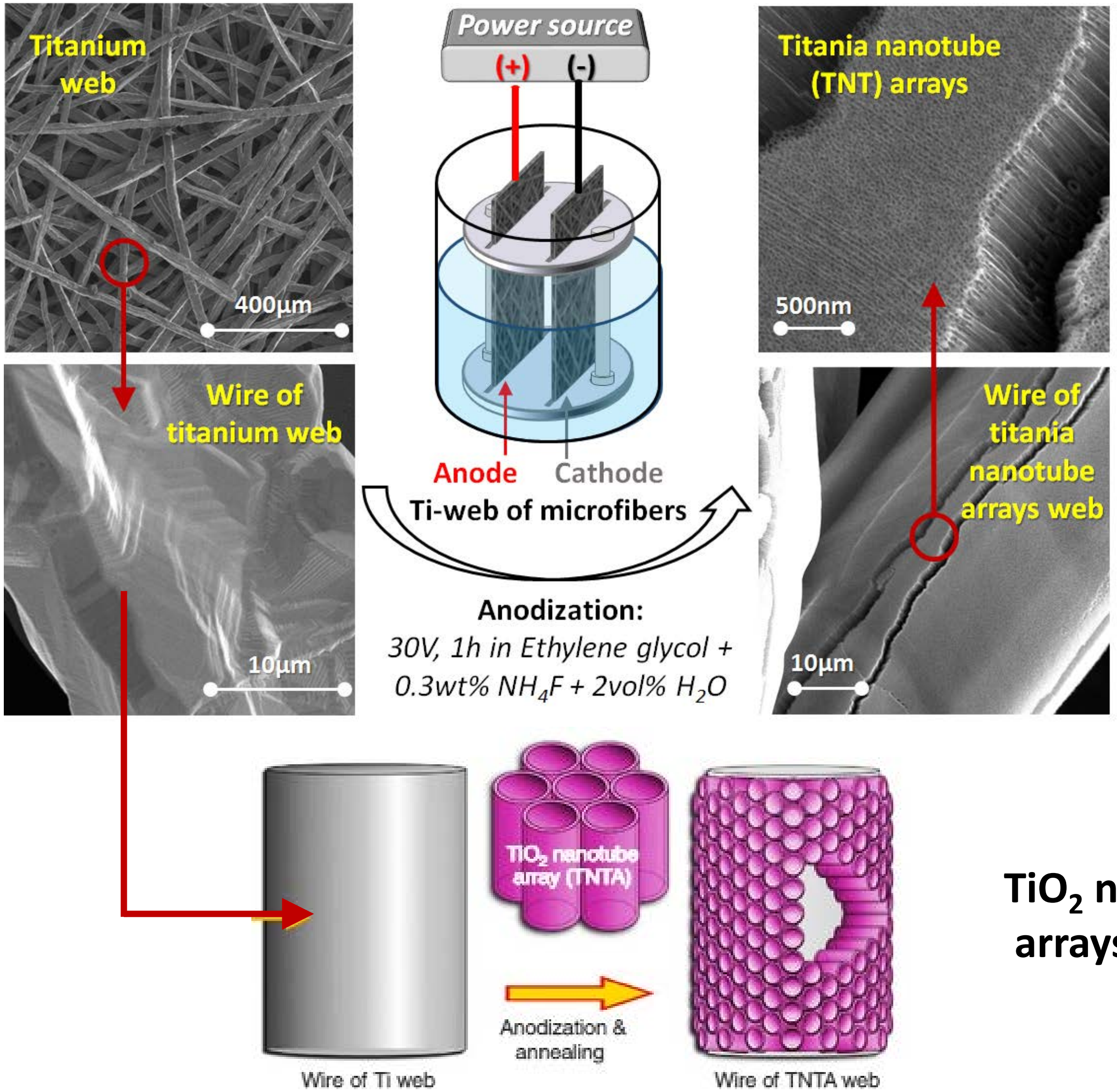


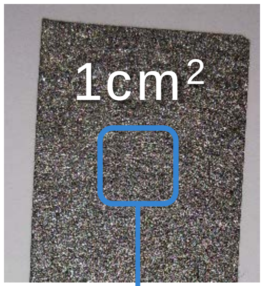
Tandem cell

$BiVO_4$ **Cu_2O, CZTS**



TiO_2 nanotube arrays photoelectrodes





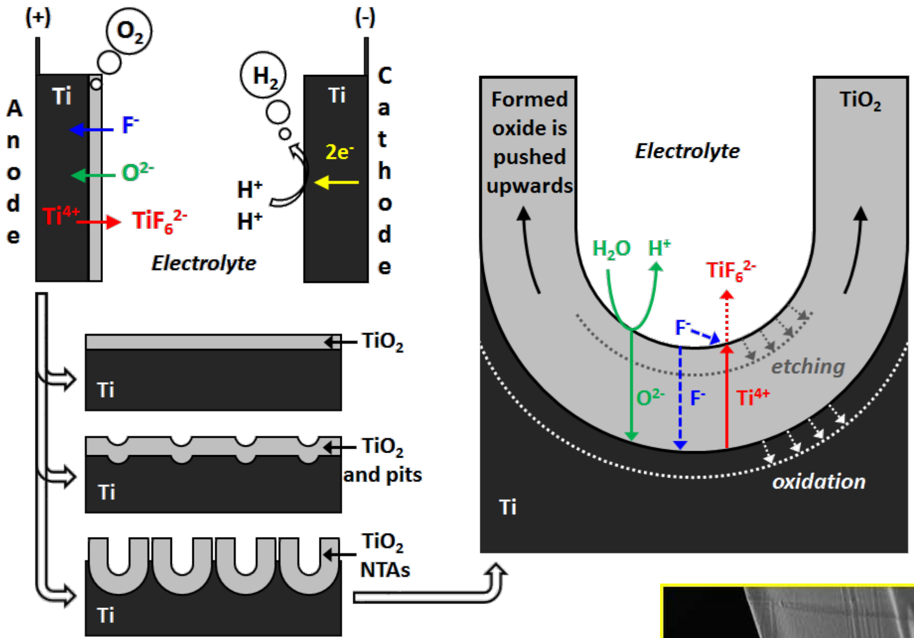
1h anodization

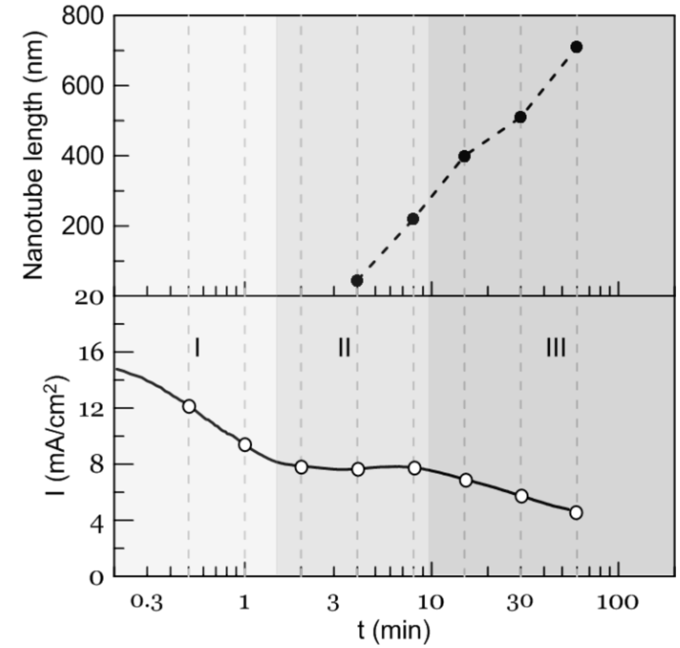
BET measurement
1300cm^2
2.7m^2/gr

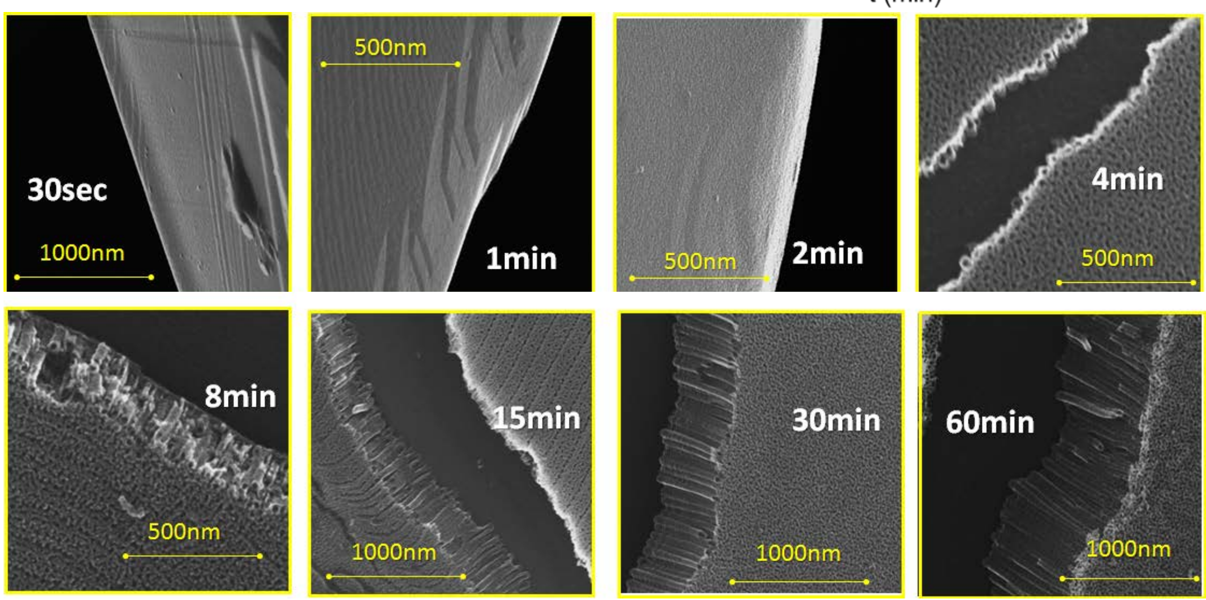
TiO_2 nanotube arrays (TNTA)

T. Stoll et al, Int. J. Hydrogen Energy, 41, 40 (2016) 17807-17817.

Fabrication: Steps of titania nanotube arrays formation







Oxidation

$2H_2O \rightarrow O_2 + 4e^- + 4H^+$

(field assisted)

$Ti + O_2 \rightarrow TiO_2$

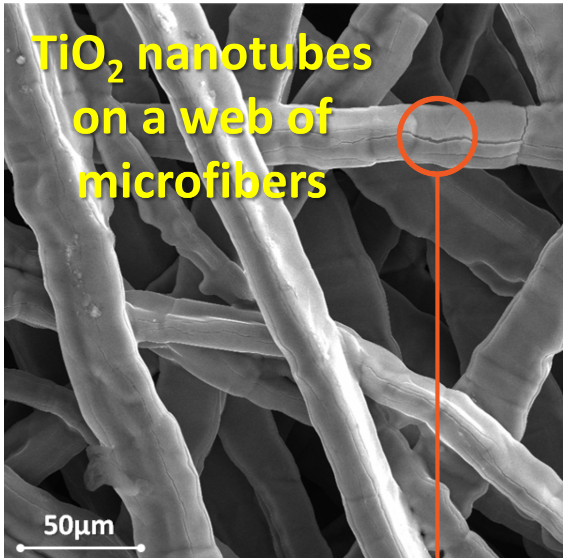
(field assisted)

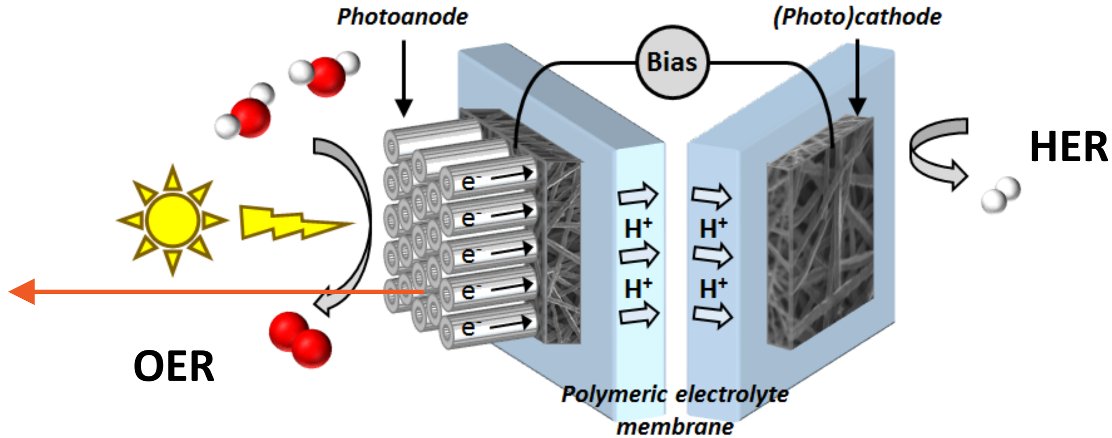
Dissolution (due to the presence of fluoride ion)

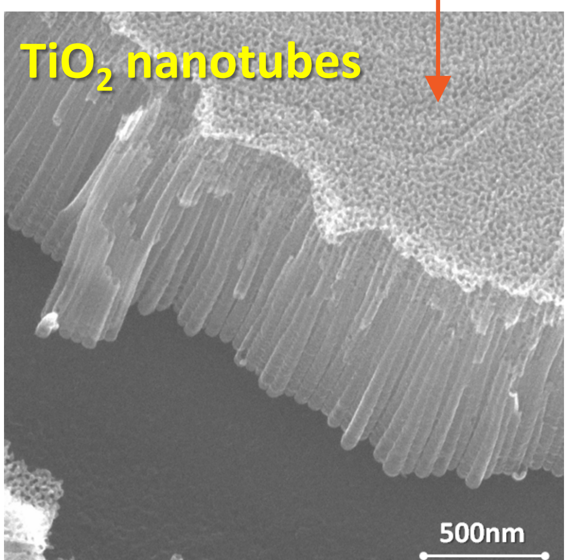
$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O$

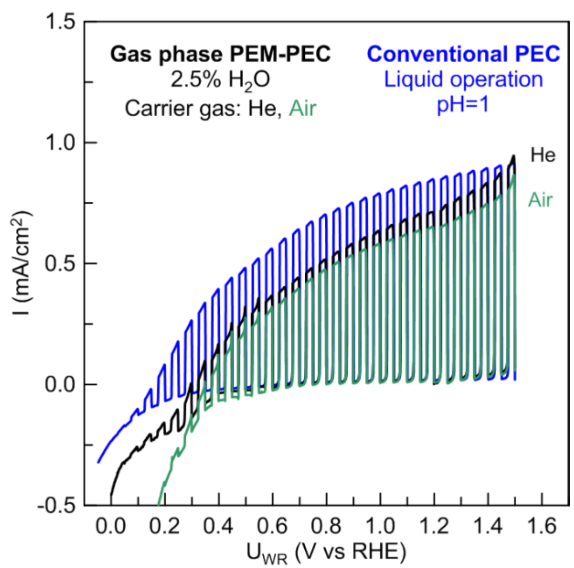
(field and chemical dissolution)

TiO_2 nanotube arrays photoelectrodes









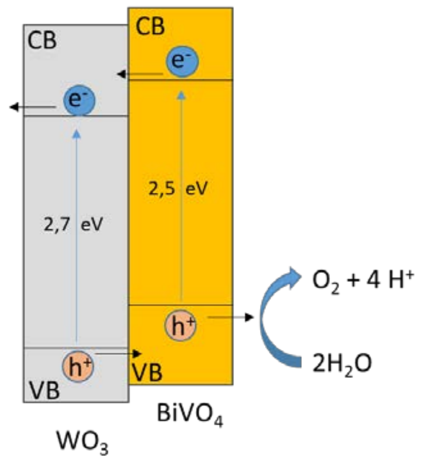
PEM-PEC evaluation

- He carrier + 2.5% H_2O → close to liquid phase operation in conventional PEC.
- Air carrier + 2.5% H_2O → ~90% vs He carrier. "Water neutral" process.
- 2-10 times higher than the TiO_2 state-of-the-art

T. Stoll et al, Int. J. Hydrogen Energy, 41, 40 (2016) 17807-17817.

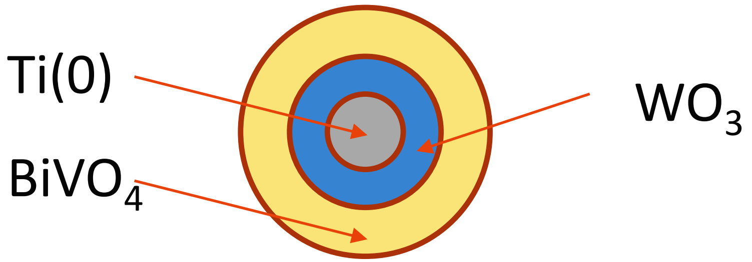
Light harvesting → $BiVO_4$ / WO_3 / TiO_2 photoelectrodes

- $BiVO_4$ is among the most promising materials for **visible light** induce photoelectrochemical water splitting thanks to appropriate band gap and band positions.
- Its relative **stability** in acidic and alkaline medium allows its use in a wide range of conditions.
- It exhibits synergic properties when interfaced with WO_3.

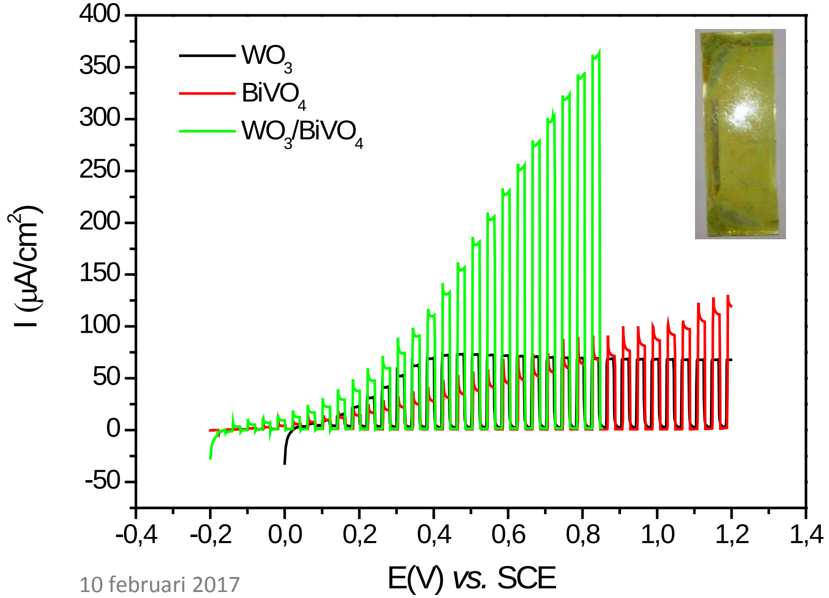


S. Kimura J. Mater. Chem. A, 2014, 2, 3948-3953

The objectives is to fully cover the Ti felt with a first layer of WO_3 and then to form the junction with $BiVO_4$.

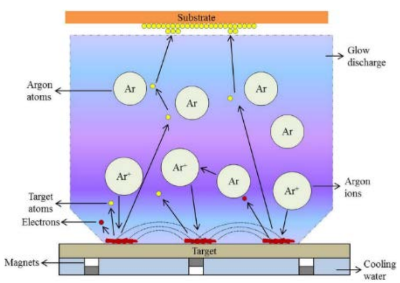


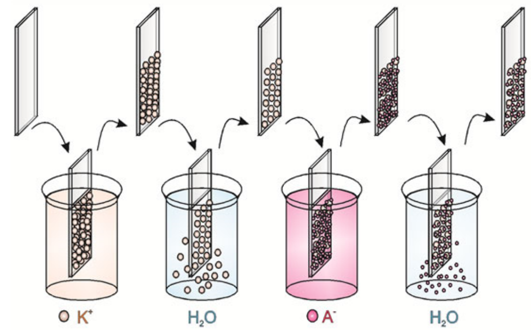
F. Abdi Fet al, Nat Commun 2013;4:2195. 1-7.



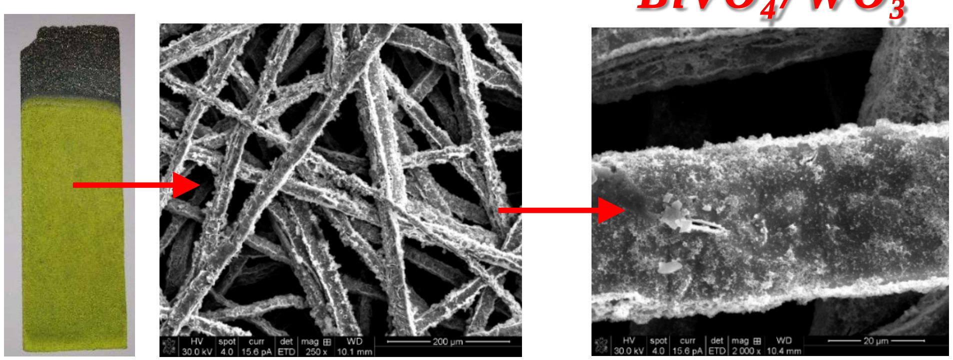
Light harvesting → $BiVO_4$ / WO_3 / TiO_2 photoelectrodes

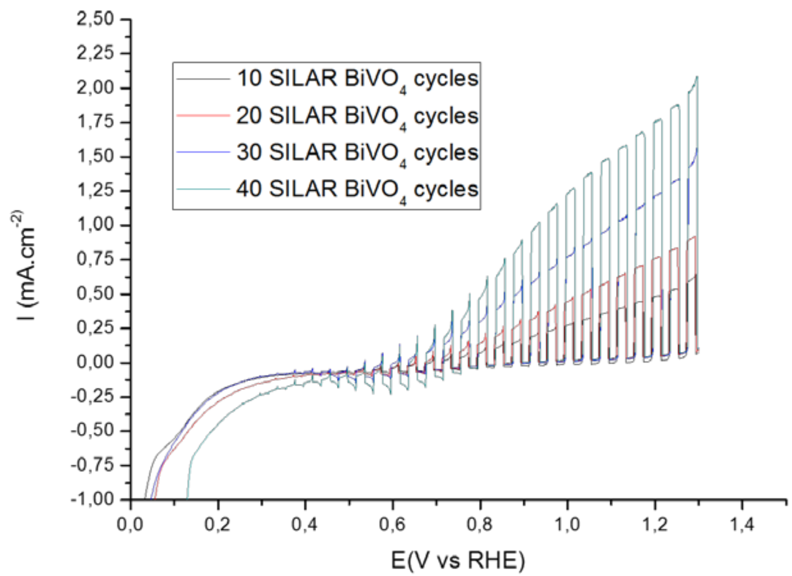
W-sputtering → **Anodization of W** → **$BiVO_4$ deposition via SILAR**





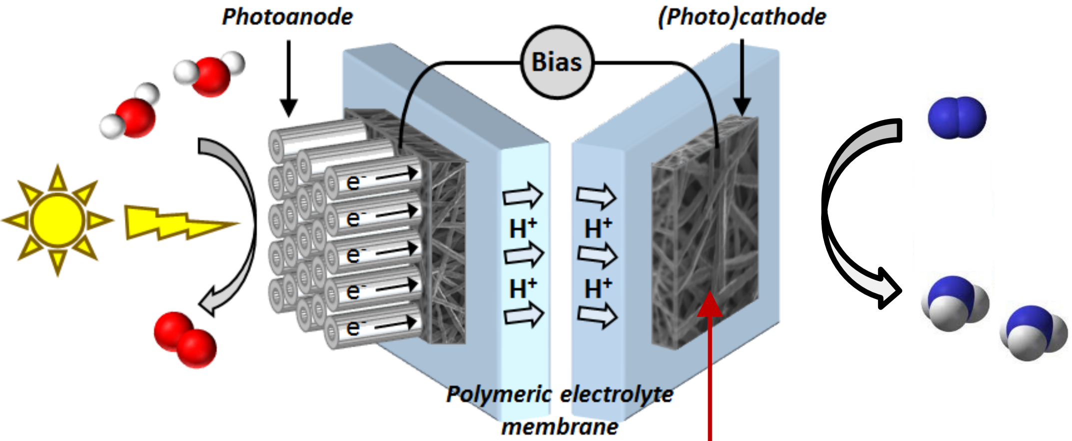
$BiVO_4$/WO_3





T. Stoll et al, Electrochem Commun in preparation

Ammonia synthesis with plasma activation

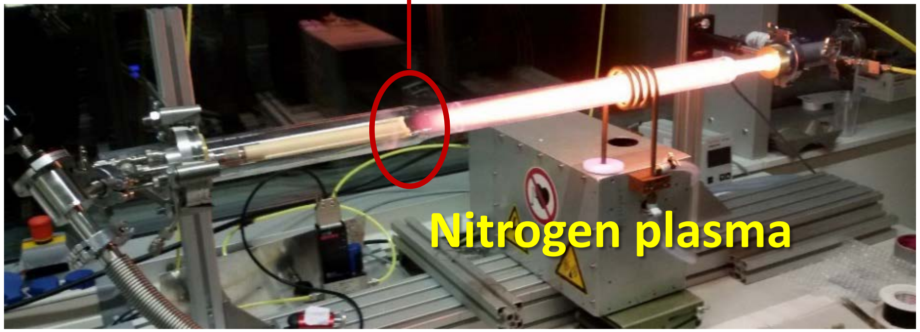


Nitrogen fixation at the cathode:

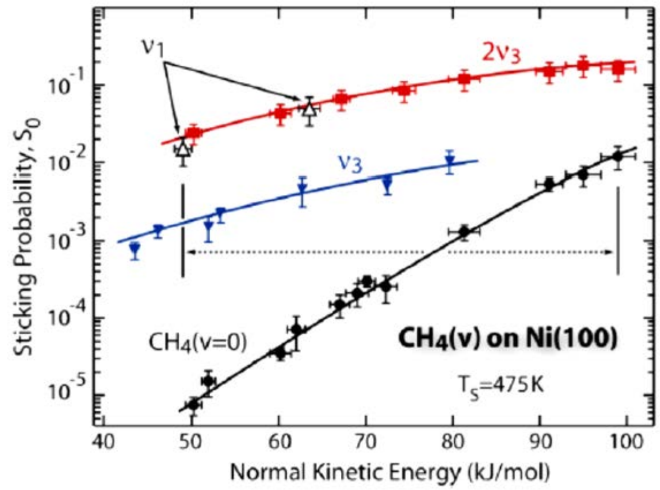
$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$ (NRR)

$6H^+ + 6e^- \rightarrow 3H_2$ (HER)

Kinetics of HER >> NRR



Probostat like reactor

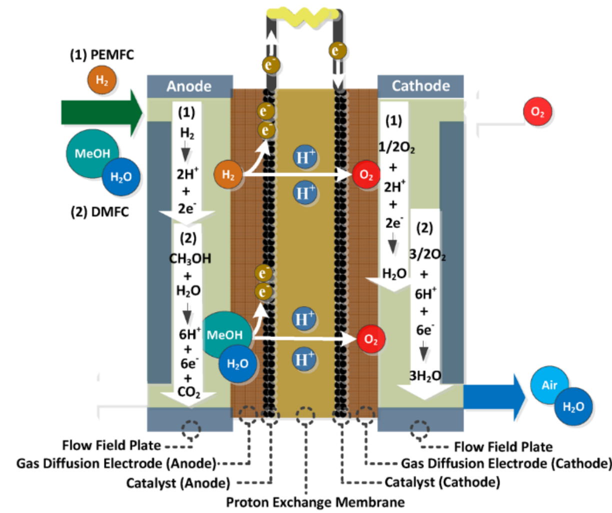


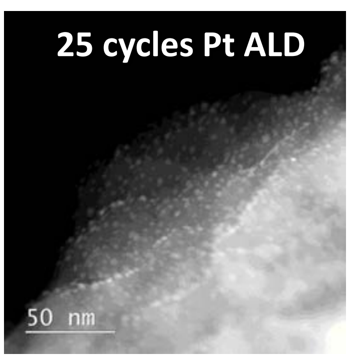
F. Fleming Crim, PNAS, 2008, 105, 12654

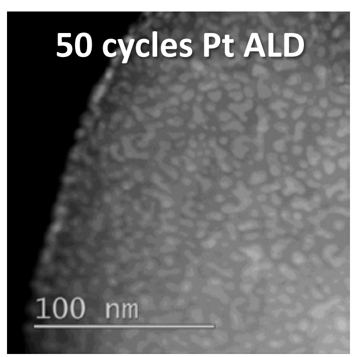
Plasmo-electrochemical nitrogen fixation: N_2 is activated by plasma → HER vs NRR ?

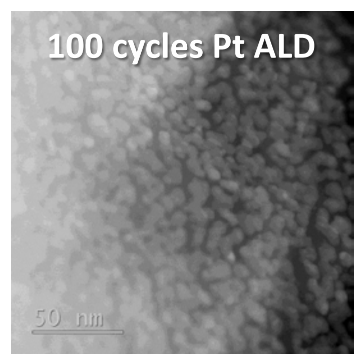
High surface area electrodes for PEMFC

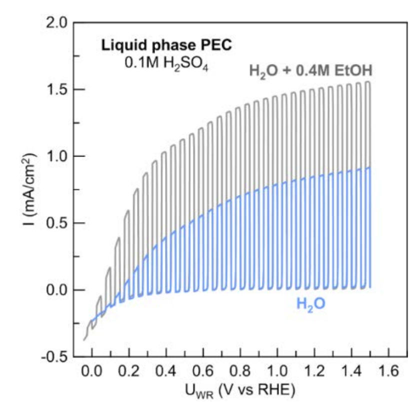
- Proton exchange membrane fuel cells PEMFCs represent a source of efficient and sustainable technology for the generation of energy.
- Conventional oxygen reduction reaction (ORR) catalyst is Pt deposited on a porous carbon support. Limitations → electrooxidation of C, agglomeration of Pt.
- Utilization of alternative supports based on a porous **3D web of titanium** microfibers for improving the performance via MSI.





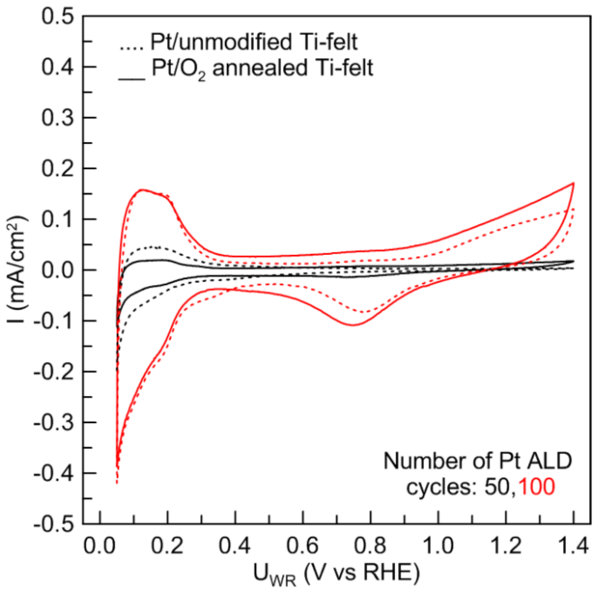


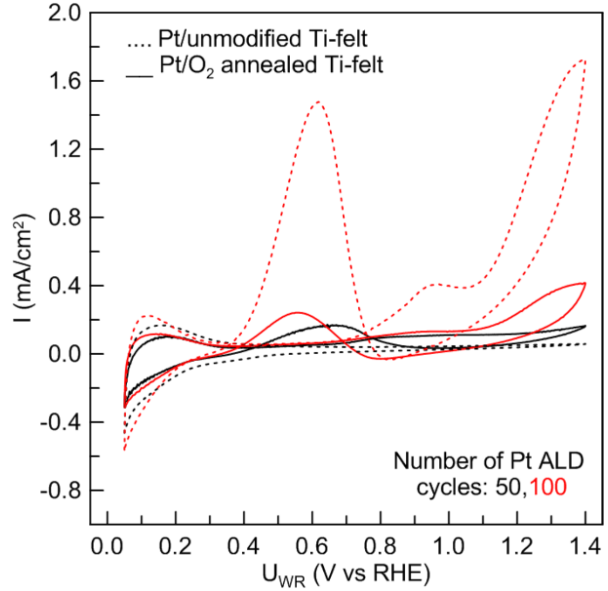


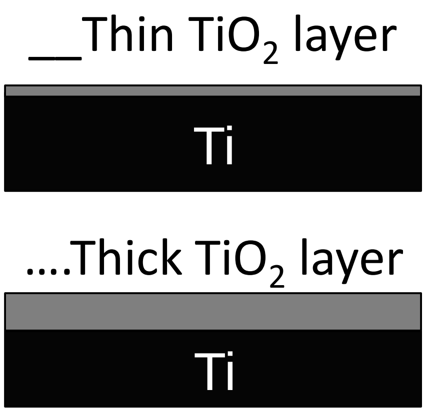


High surface area electrodes for PEMFC

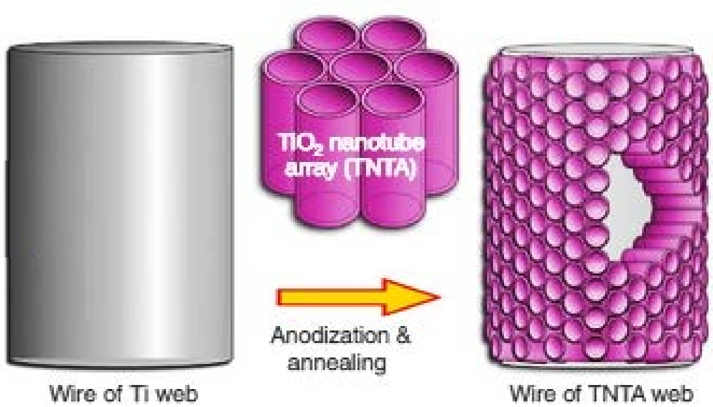
Cyclic voltammetry in H_2SO_4 without and with EtOH

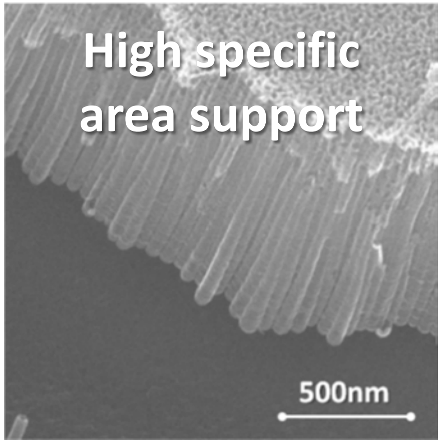






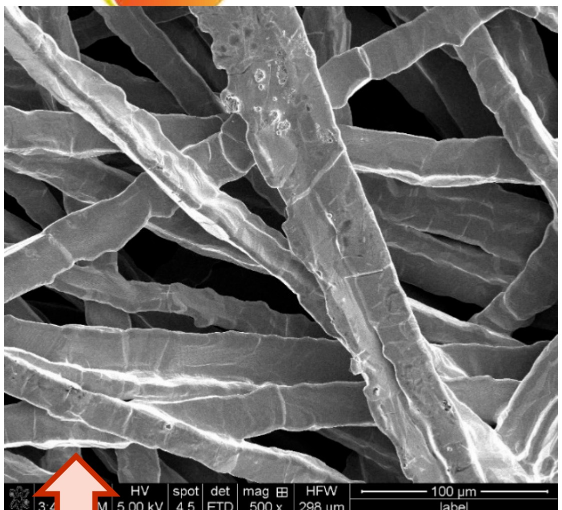
TiO_2 nanotube arrays





- Future plans Pt by ALD deposition on TiO_2 nanotube arrays for improving the surface area.

High ion flux He plasma treatment: 3D Ti-web nanostructuring



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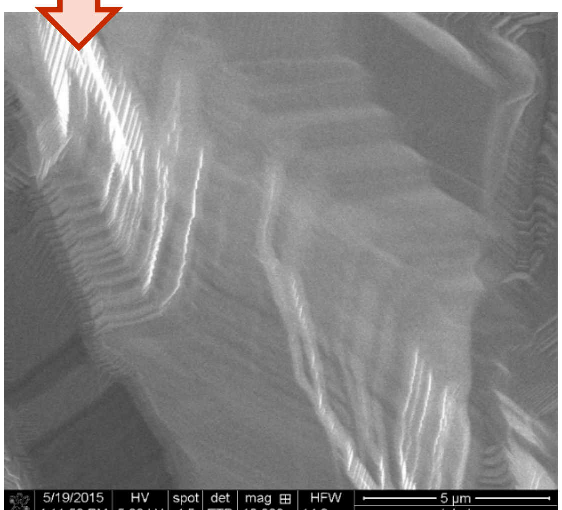
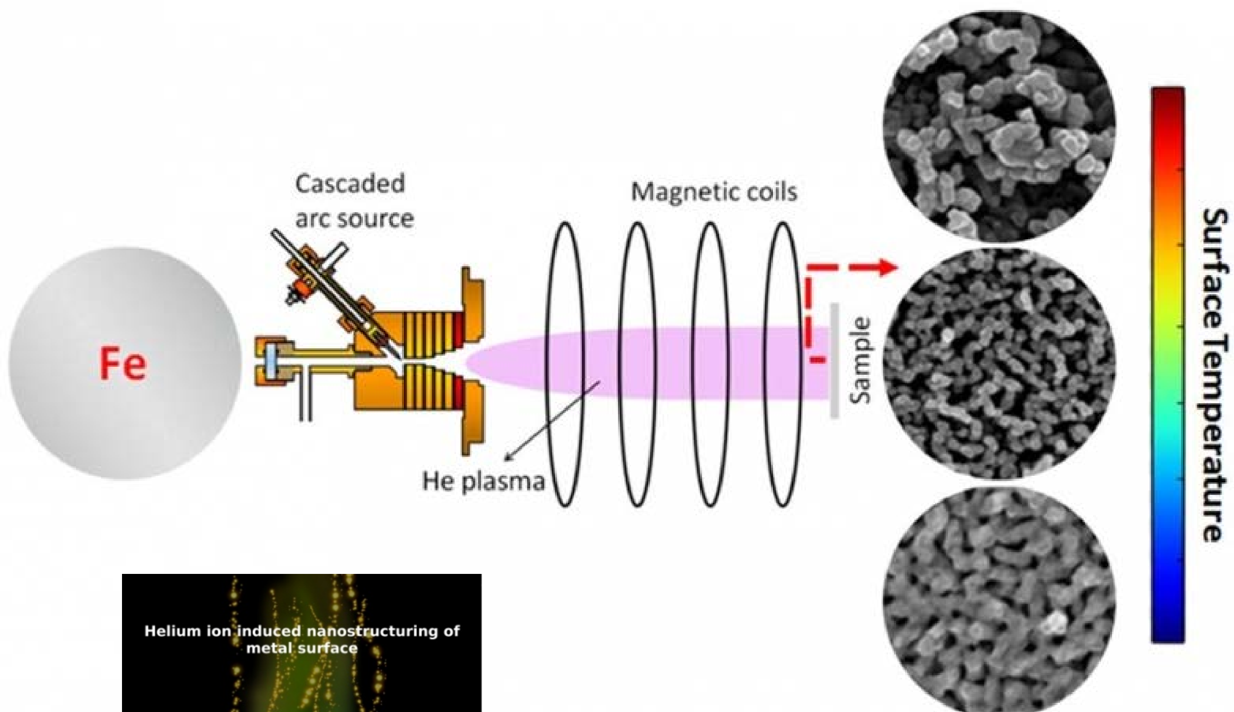
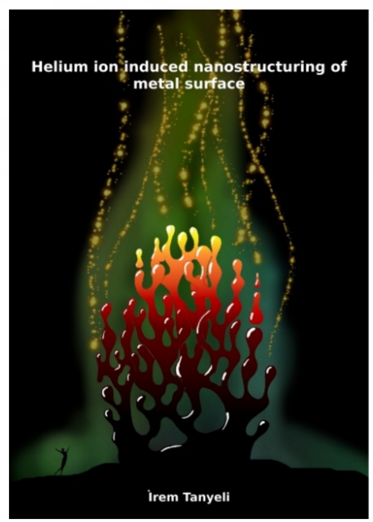
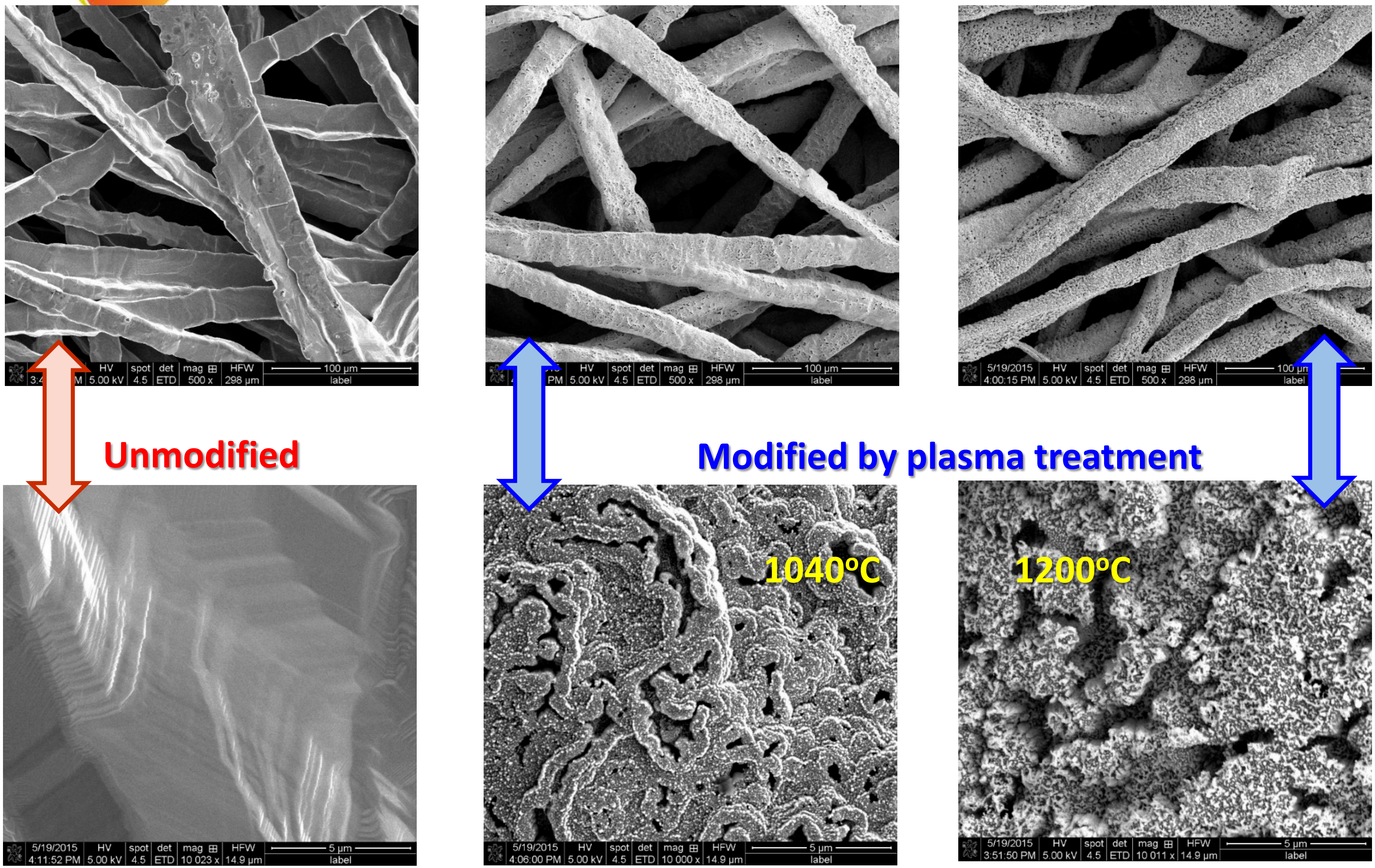






Tanyeli "Helium ion induced nanostructuring of metal surface", PhD thesis 2015

High ion flux He plasma treatment: 3D Ti-web nanostructuring



Thank you for your attention