Porous Photoelectrodes for Scalable Solar Fuel Production

H. Johnson, G. Zafeiropoulos, P. Varadan, , P. Kunturu, M. Lavorenti, M. Tsampas

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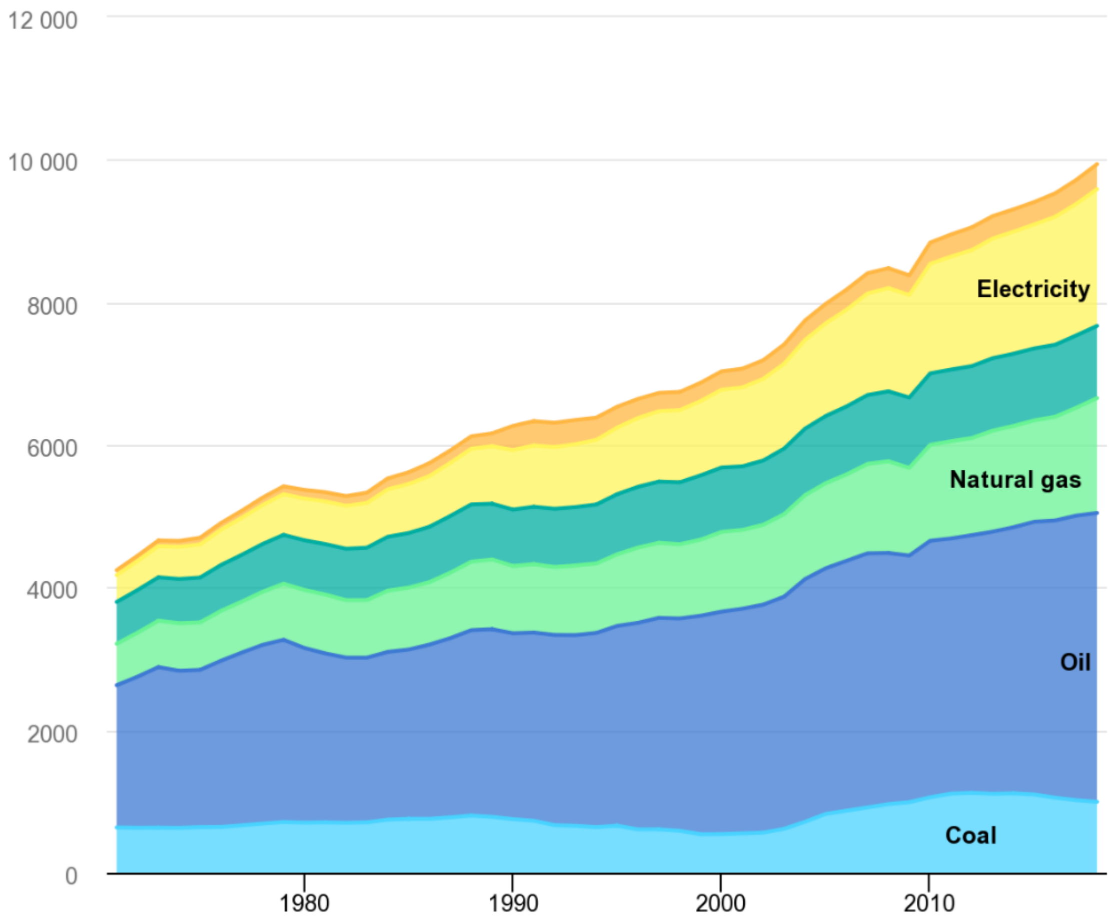
DIFFER TOYOTA

TOYOTA MOTOR EUROPE

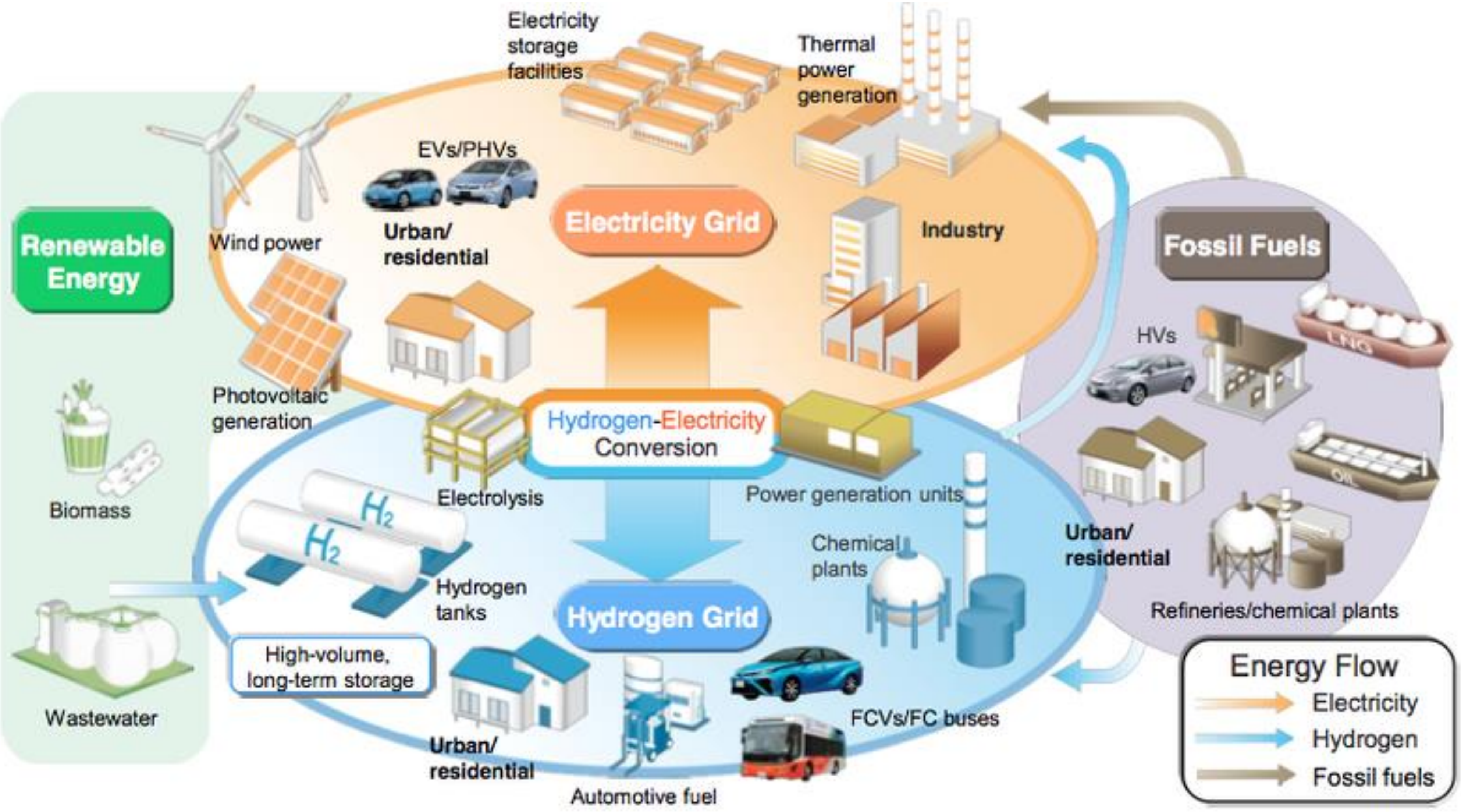
TOYOTA'S ENVIRONMENTAL VISION/ *Towards 2050*

MOTIVATION – SOLAR FUELS/ *Towards 2050*



- Only around 20% of the energy we use comes from electricity
- 80% is from 'chemical fuels' where energy is stored in chemical bonds
- Global energy consumption is still growing
- Need to replace conventional chemical fuels – fossil fuels – with renewable alternatives

TOYOTA'S ENVIRONMENTAL VISION/ *Towards 2050*



IMPORTANCE OF RENEWABLE HYDROGEN/ *Fuel Cell Electric Vehicles*

Mirai Lifecycle Assessment (Toyota Motor Corporation)

Direct use:

- In fuel cells (mobility – especially large vehicles, power supply)
- Direct combustion engine (mobility)

Fuel cell - Mirai

H_2 combustion - Yaris

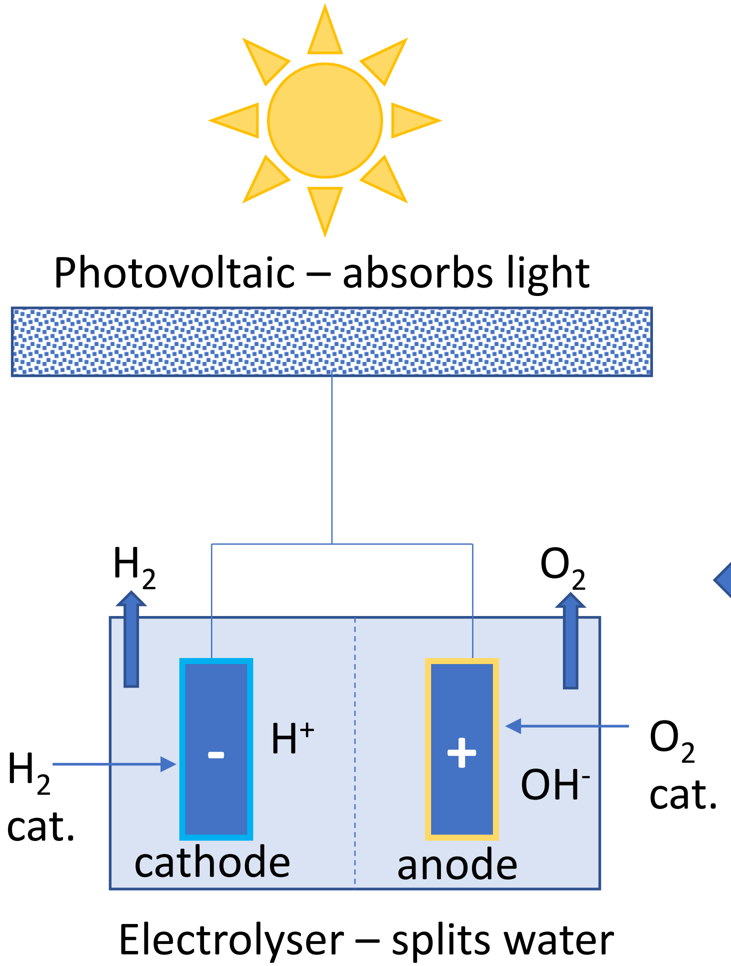
As chemical feedstock:

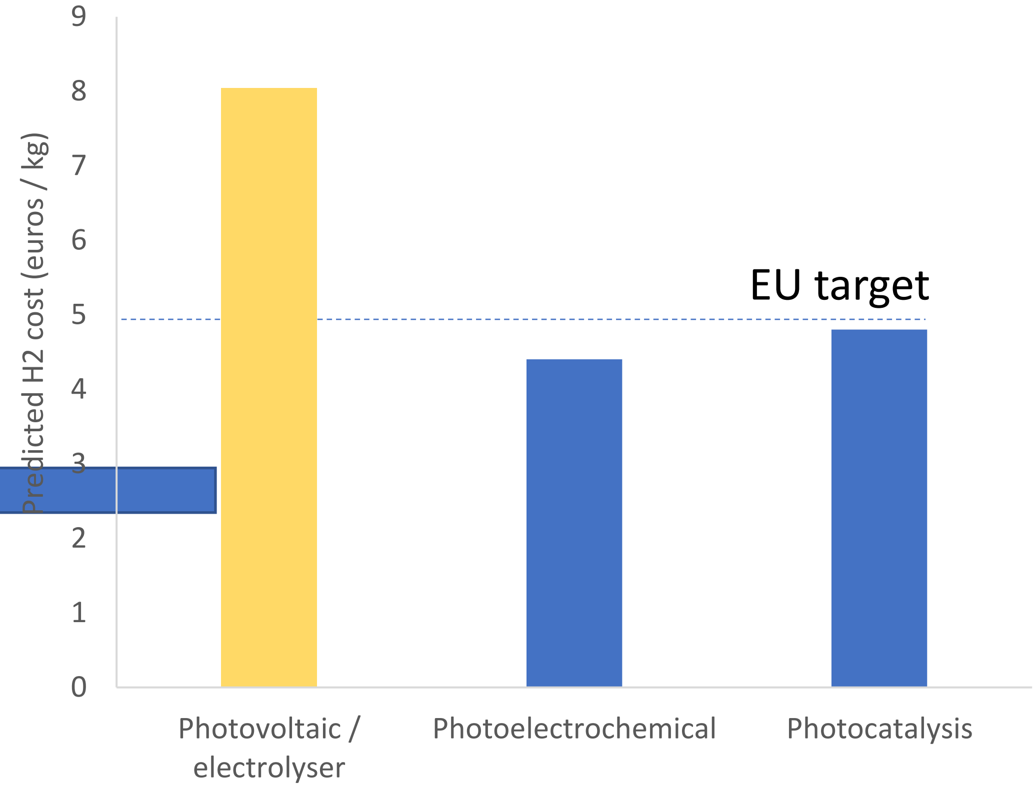
- Ammonia, hydrocarbon production (through Fischer-Tropsch reaction) for aviation and other hard to replace sectors

1. TOWARDS LOW COST RENEWABLE-H_2 - PHOTOVOLTAIC / ELECTROLYSER

Efficiency	**O (20 %)**
Scalability	**O**
Cost	**Δ**

Current status:
Small scale plants (DE, FR)
TRL: 9



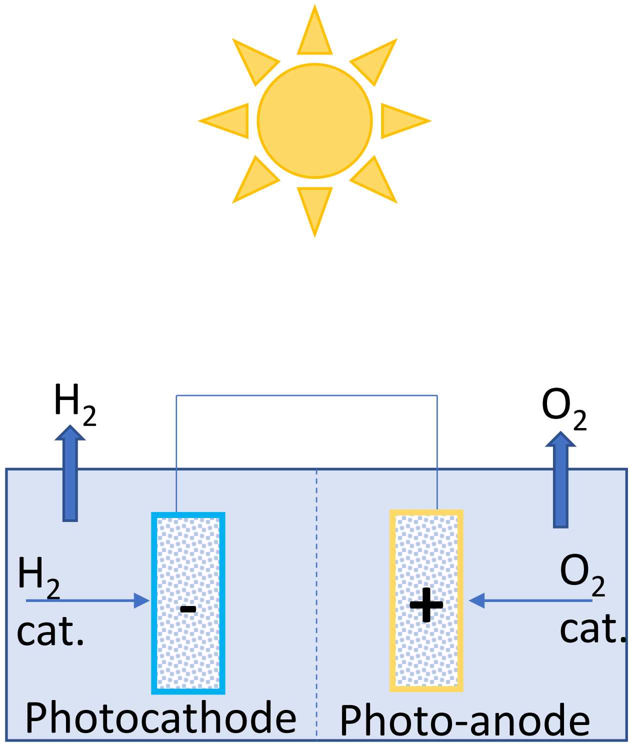


PHOTOVOLTAIC / ELECTROLYSER – main challenge = cost

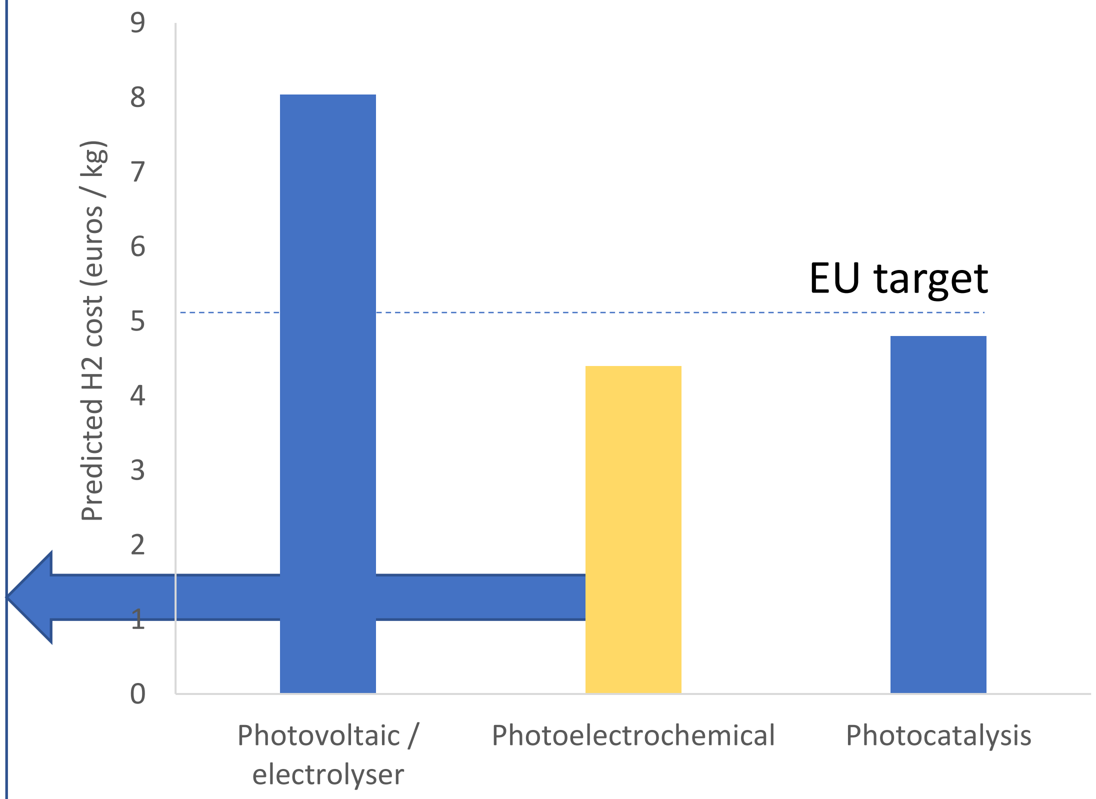
2. TOWARDS LOW COST RENEWABLE-H_2 - PHOTOELECTROCHEMICAL

Efficiency	**O (19 %)**
Scalability	**Δ**
Cost	**O**

Current status:
Lab-scale (1 – 100 cm^2)
TRL: 3 - 4

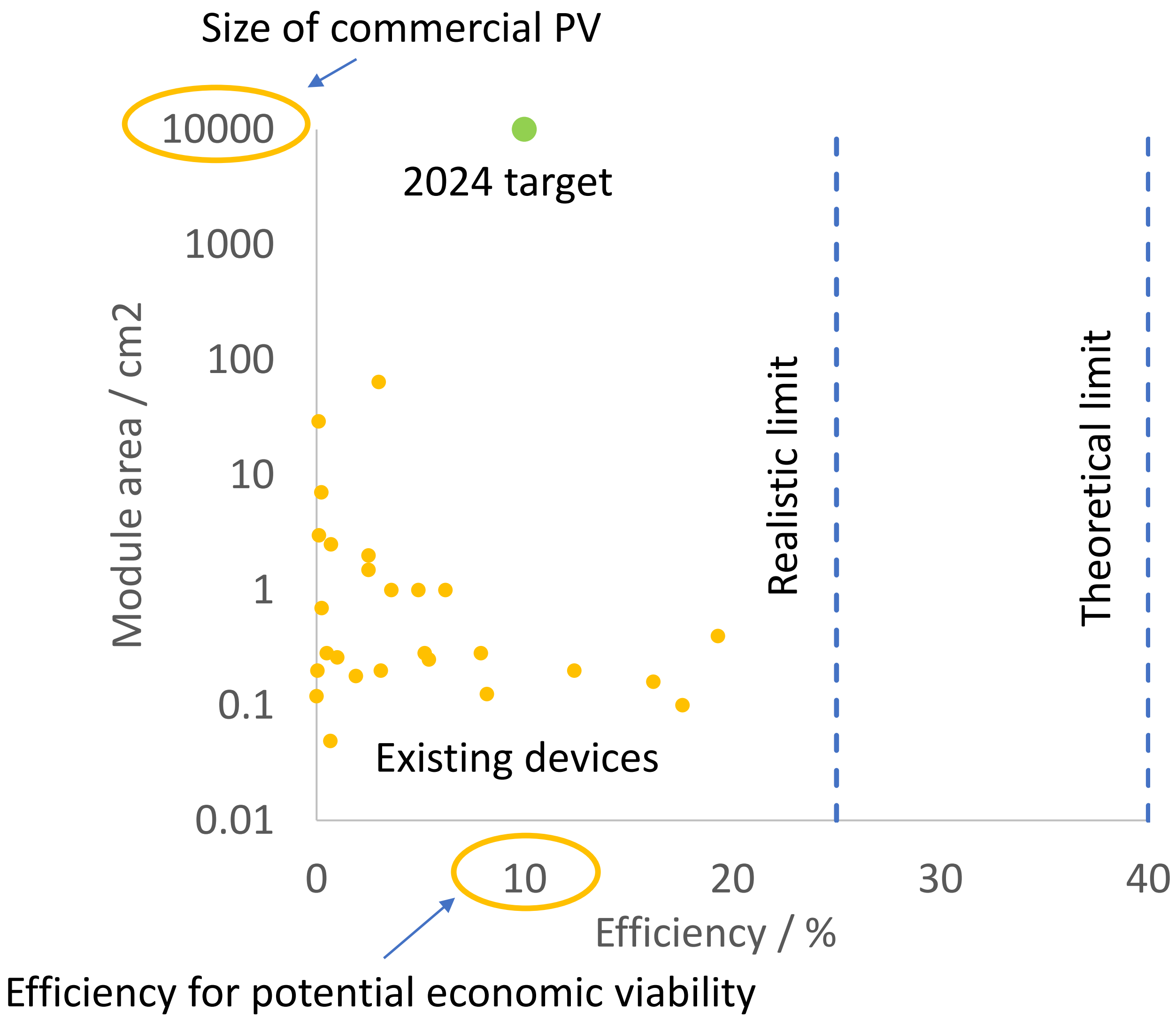


Photoanode / photocathode – absorb light and splits water



PHOTOELECTROCHEMICAL – main challenge = scalabilty

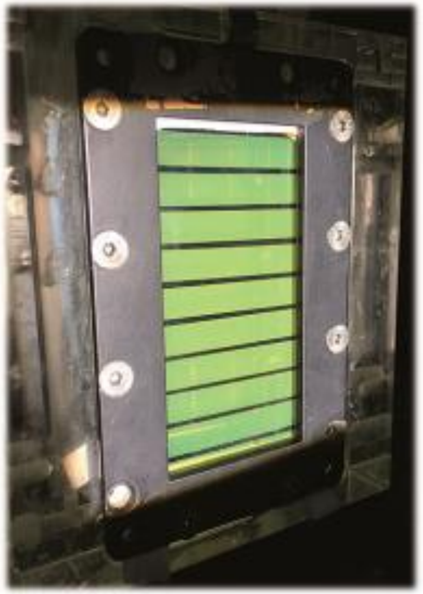
High Efficiencies Achieved but impractical sizes

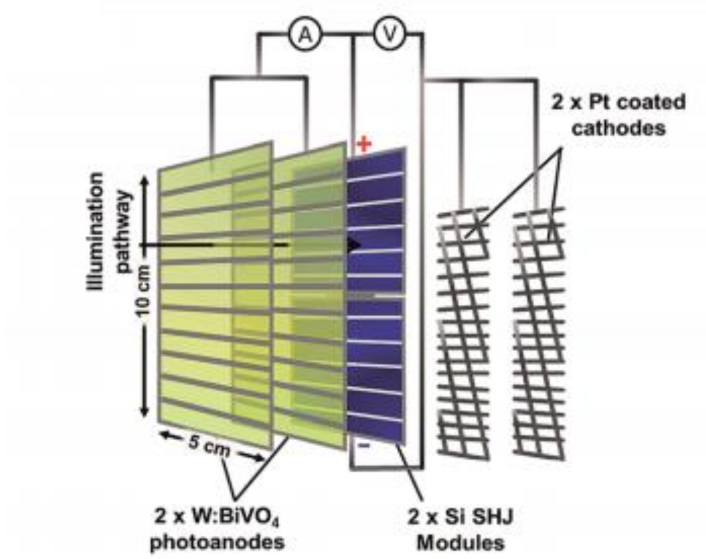


- Studies have shown that **PEC has the potential to be cheaper than PV/E** *(Energy Environ. Sci., 2016,9, 2354-2371)*
- **High efficiencies** achieved indicate technology potential
- More effort needed into **scale-up for practical implementation**

RESEARCH INTO SCALING */ 50 cm² $BiVO_4$*

HZB Helmholtz Zentrum Berlin



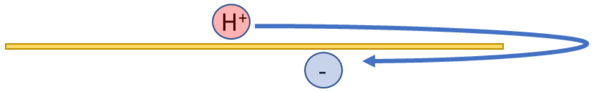


PEC–PV Configuration	Illum. Area (cm^2)	J ($mAcm^{-2}$)	*I* (mA)	Average. STH Efficiency. (%)
Pt/2-SHJ/Pt	50	0.02	1.0	0.03
CoP_i/W:$BiVO_4$(FSI)/2-SHJ/Pt	50	1.00	50.0	1.2
CoP_i/W:$BiVO_4$(BSI)/2-SHJ/Pt	50	1.50	75.0	1.9
Dual-CoP_i/W:$BiVO_4$/2-SHJ/Pt	**50**	**1.72**	**86.0**	**2.1**
Dual-CoP_i/H,W:$BiVO_4$(FSI)/2-SHJ/Pt	**0.24**	**4.45**	**1.07**	**5.5**
Dual-CoP_i/H,W:$BiVO_4$(FSI)/3-SHJ/Pt	0.24	5.12	1.23	6.3

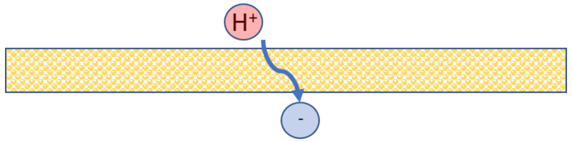
I. Y. Ahmet et al, Sustainable Energy Fuels, 2019, 3, 2366–2379

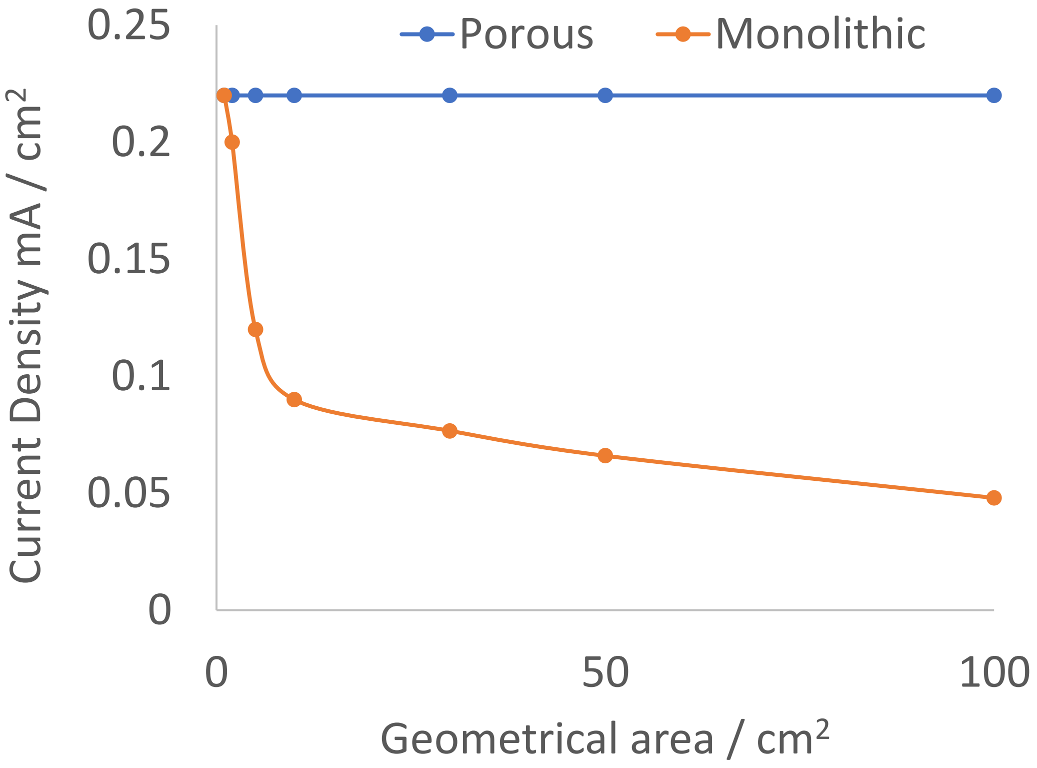
Porous Photoelectrodes *(For reduced ionic resistance)*

Monolithic approach



Porous approach





- Conventional devices use a 'monolithic structure'
- When the device is **increased in size, there is an increase in ionic resistance**
- **Our design uses porous photoelectrodes,** so species can travel ***through*** the electrode
- **Proof of concept porous photoelectrodes** demonstrated
- **Functionalisation with water absorbing materials** allows operation in liquid water or **ambient humidity**

DIFFER Dutch Institute for Fundamental Energy Research

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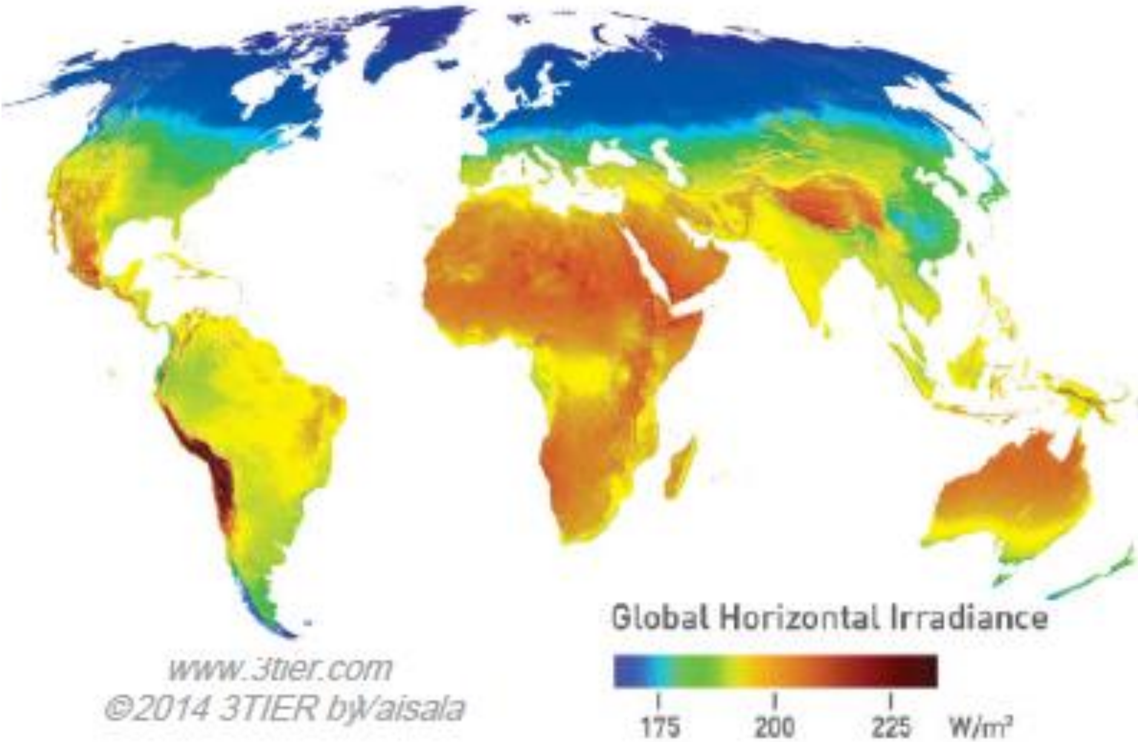
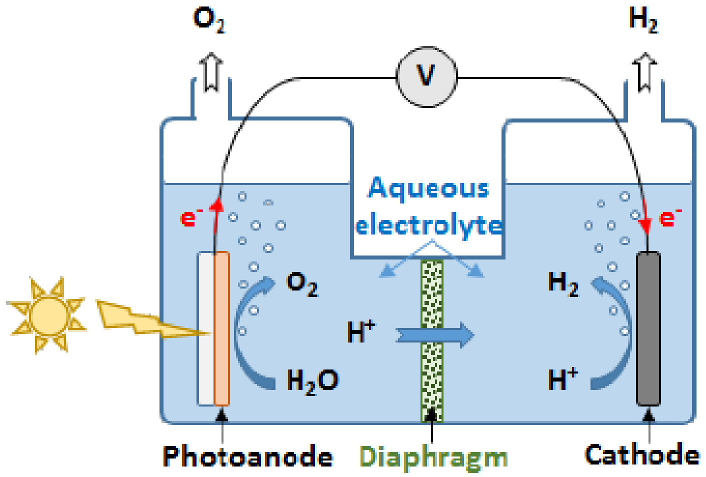
HUMIDITY AS WATER SOURCE */ Motivation*



- Inspired by the simplicity of PV installations, we are developing a humidity-absorbing solid electrolyte based hydrogen production
- This allows the decoupling of **solar irradiance and freshwater resources**
- Expands **geographical applicability** of PEC applications

OVERCOMING CHALLENGES OF PEC/ *Motivation*

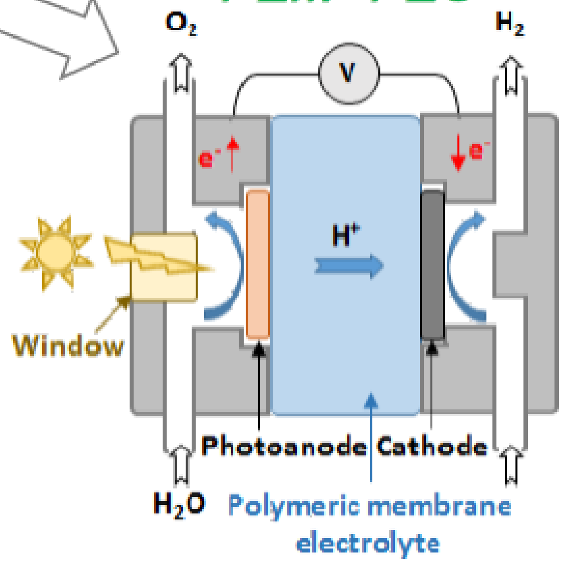
Conventional PEC



Conventional PECreactors

- *Input : light & (purified) water*
- *Dual use of water: reactant & electrolyte solvent*
- *Bubble formation → impede catalysis*
- *Safety issues H_2+O_2 mixing*

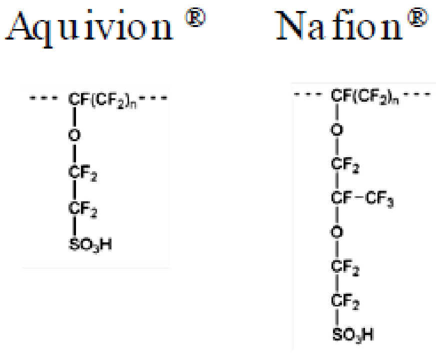
PEM- PEC



Alternative solid state PECreactor

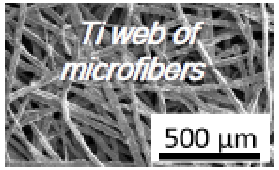
- *Input : light & humidified air (water source)*
- *Polymeric electrolyte membrane (PEM)*
  - *Direct product separation*
  - *Minimize water utilization*
- *Porous photoelectrodes*
  - *Compatible with PEM*
  - *Hinder bubble formation*

FUNCTIONALISATION FOR WATER ABSORPTION */ Porous electrodes*

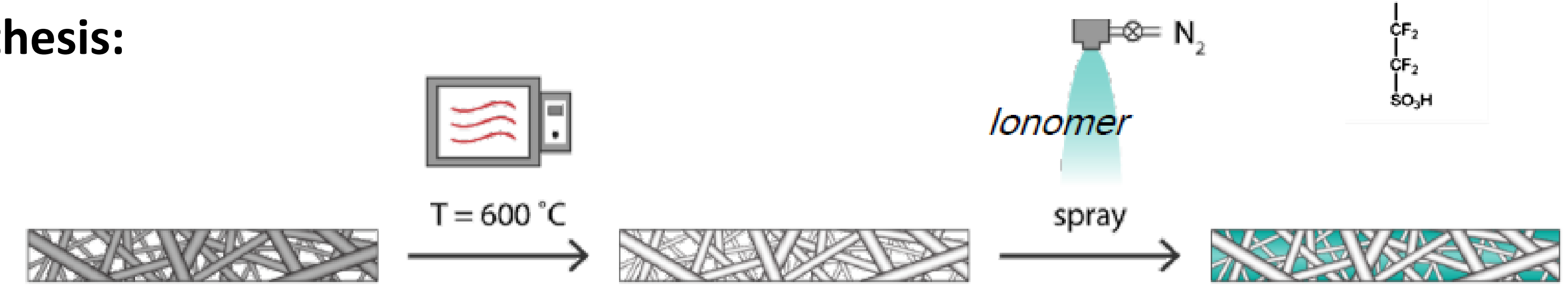


Procedure Ti / TiO_2 Electrode Synthesis:

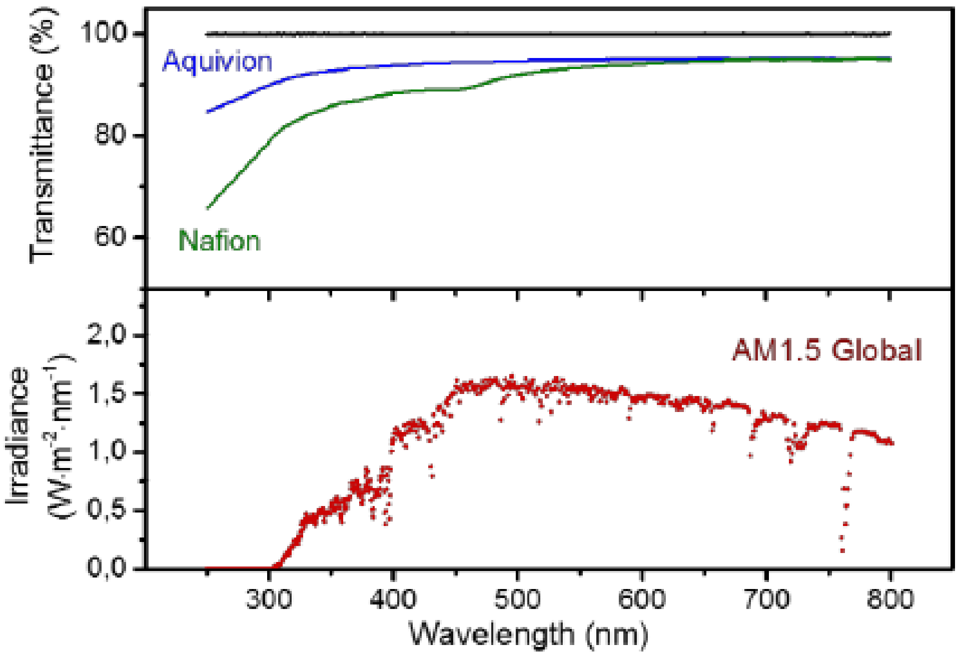
3D porous electrode back contact



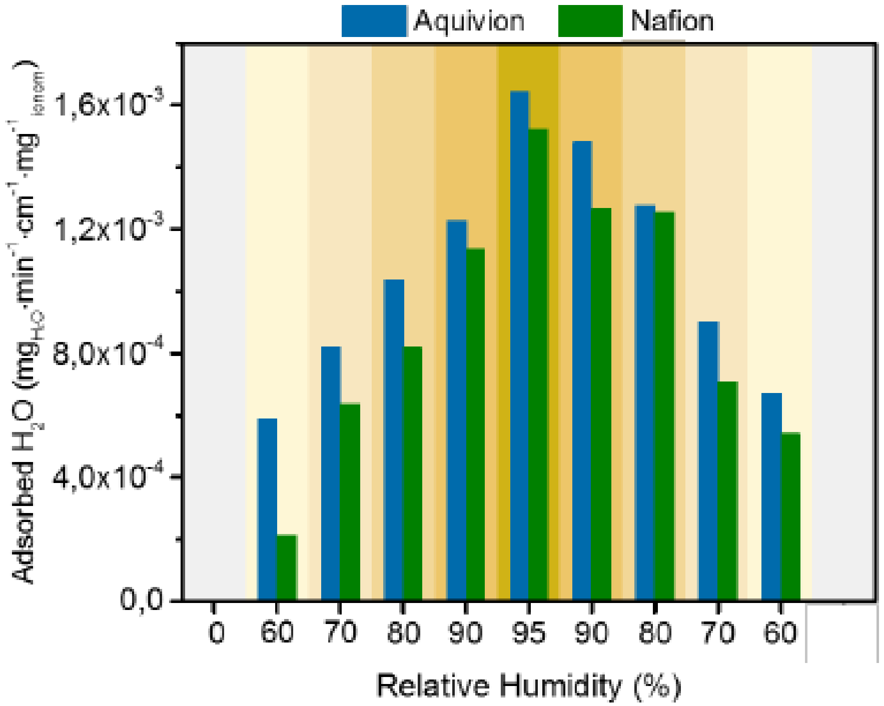
Fabrication and functionalization of porous photoanode



Transmittance:



Water Absorption:



- Ambient air flows into the device pores and humidity is absorbed by a functional coating
- Charge generated by light absorber reacts with **absorbed humidity** to form H_2 (and O_2 – released into air)
- Aquivion chosen for high transparency and water absorption

G. Zafeiropoulous et al, ACS App. Mater. Inter. 2019

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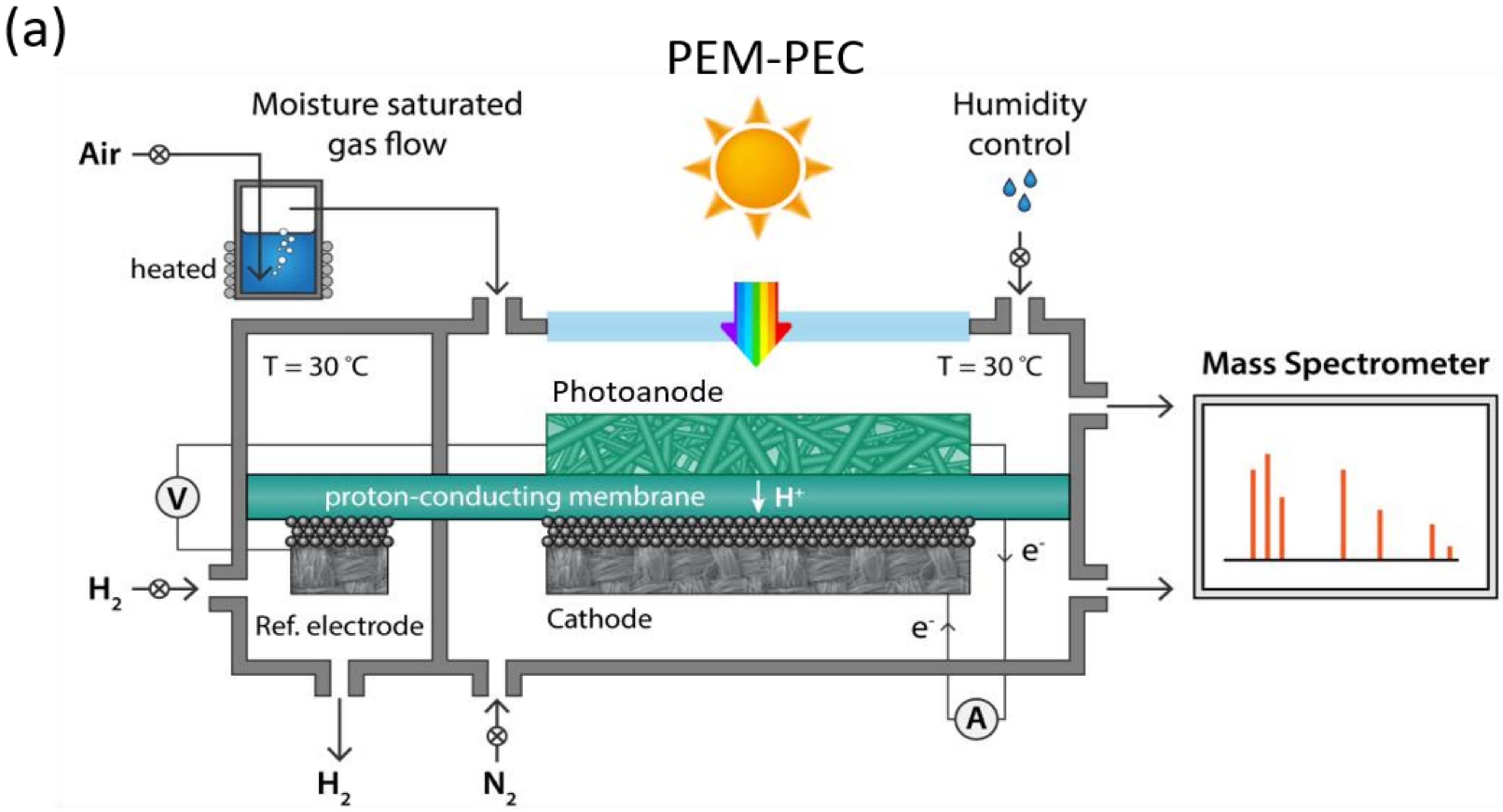
EXPERIMENTAL SET-UP/ *Porous electrodes*



G. Zafeiropoulous et al, ACS App. Mater. Inter. 2019

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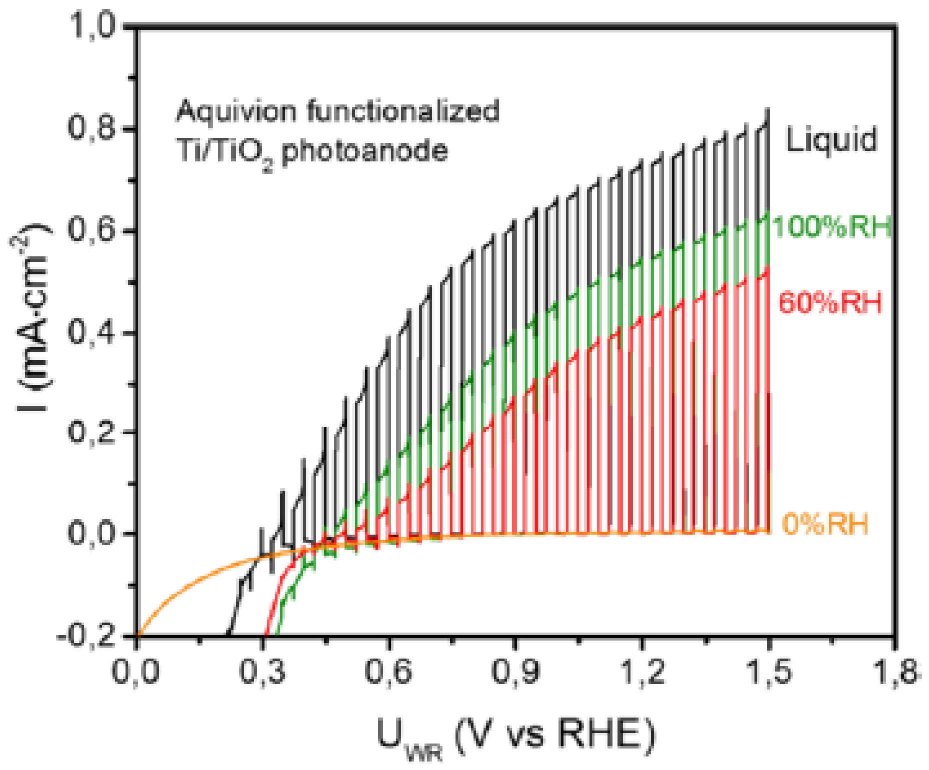
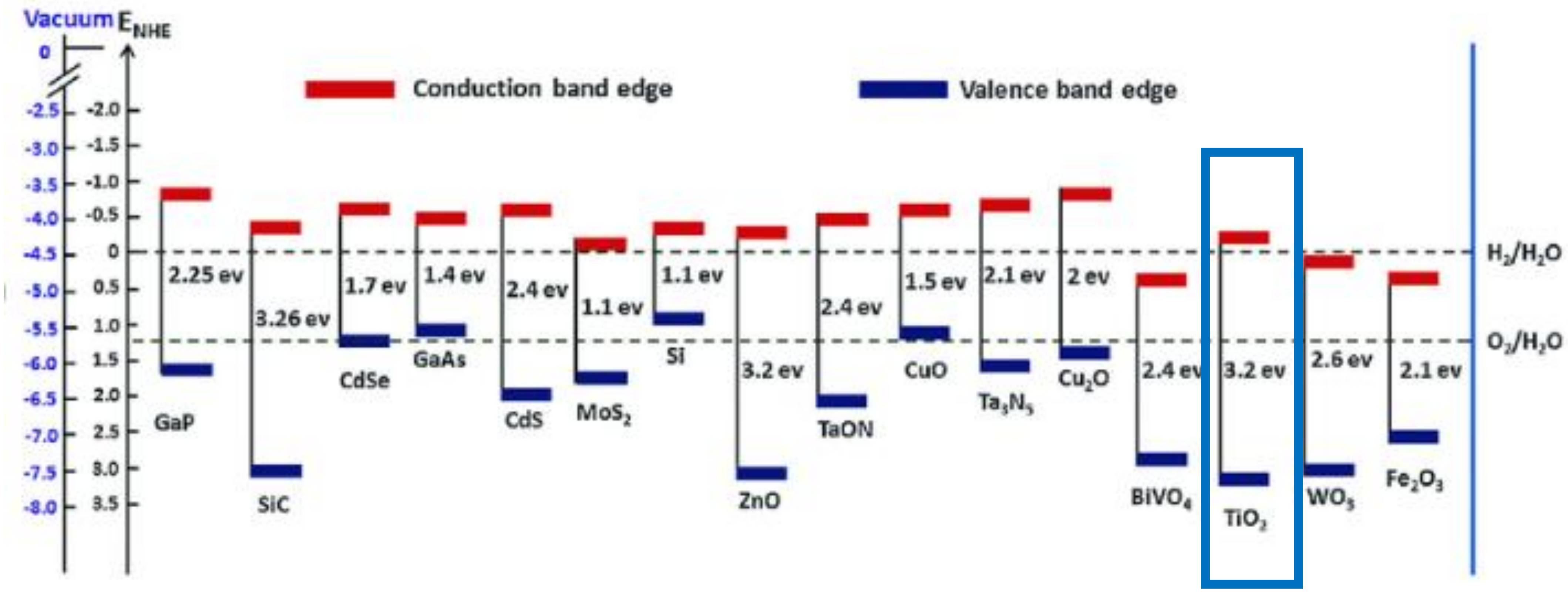
Performance under environmental conditions



- Performance was measured under various relative humidities and in liquid water
- At 60% RH (Madrid in summer) we have 70% of performance we achieve in liquid!
- However overall < 1% efficient

G. Zafeiropoulous et al, ACS App. Mater. Inter. 2019

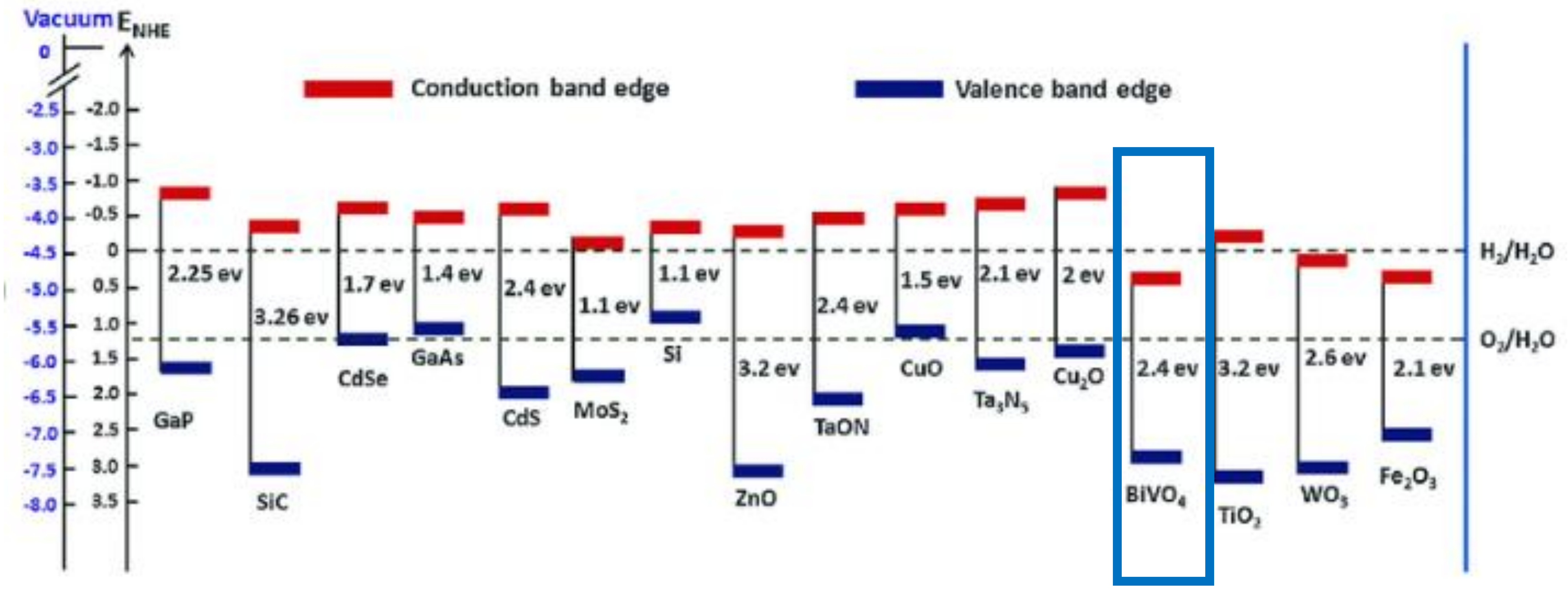
band-gap Materials/ *High Performance Material*



A. Gedamu, 2016, Nanoscale Horiz.. 1. 10.1039/C5NH00098J.

UV light
absorption

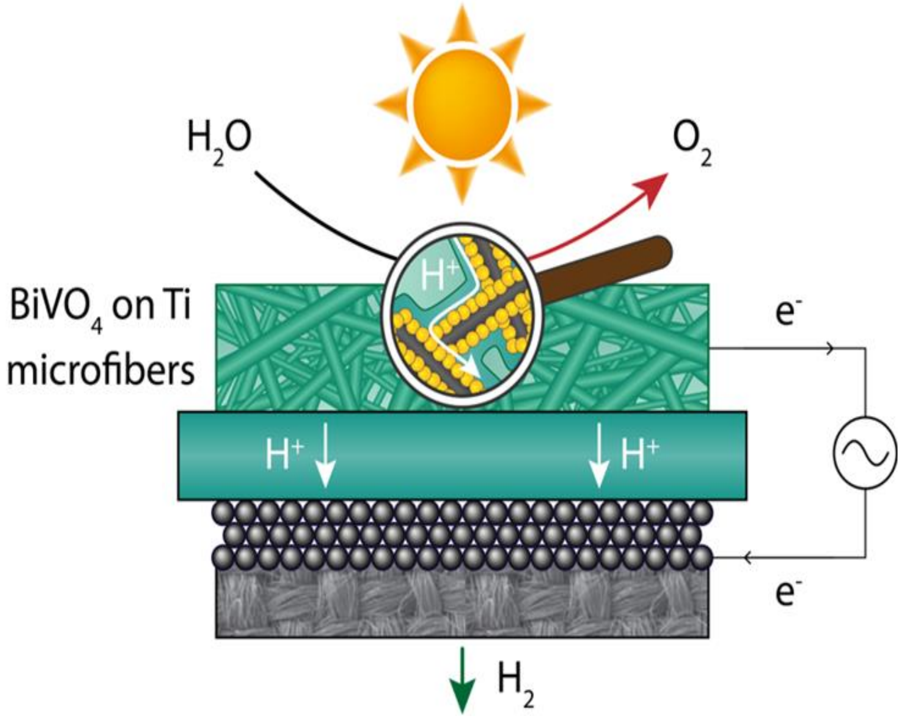
band-gap Materials/ *High Performance Material*



A. Gedamu, 2016, Nanoscale Horiz.. 1. 10.1039/C5NH00098J.

Visible light absorption

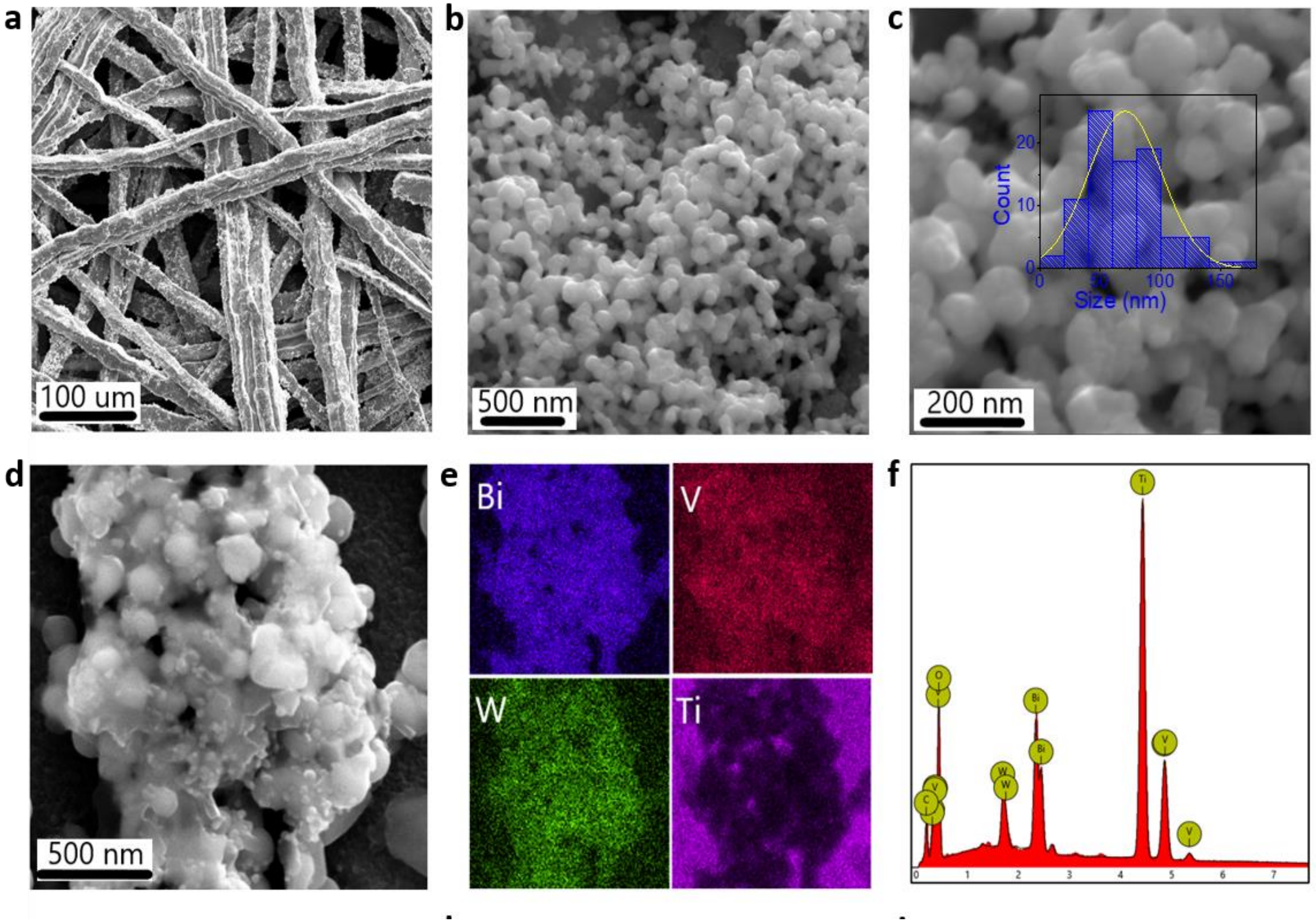
Deposition by SILAR and Performance



- $BiVO_4$ deposited by scalable SILAR technique on Ti felt electrodes

P. Varadan, G. Zafeiropoulous et al, ACS Energy Mater. 2021

W-DOPED BiVO$_4$ POROUS PHOTOELECTRODES */ High Performance Material*



- Electron microscopy indicates particle growth on Ti fibers
- With homogeneous particle size of around 90 nm

P. Varadan, G. Zafeiropoulous et al, ACS Energy Mater. 2021

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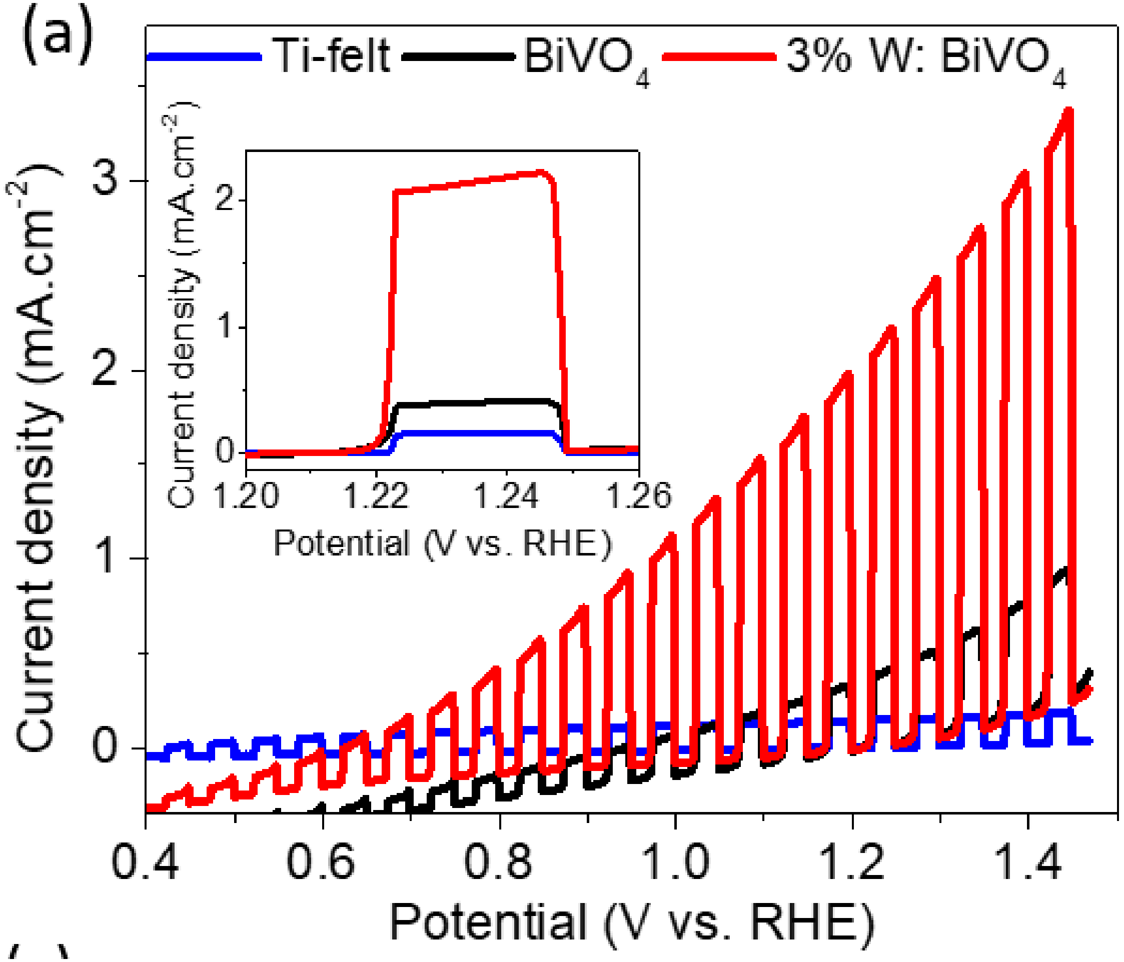
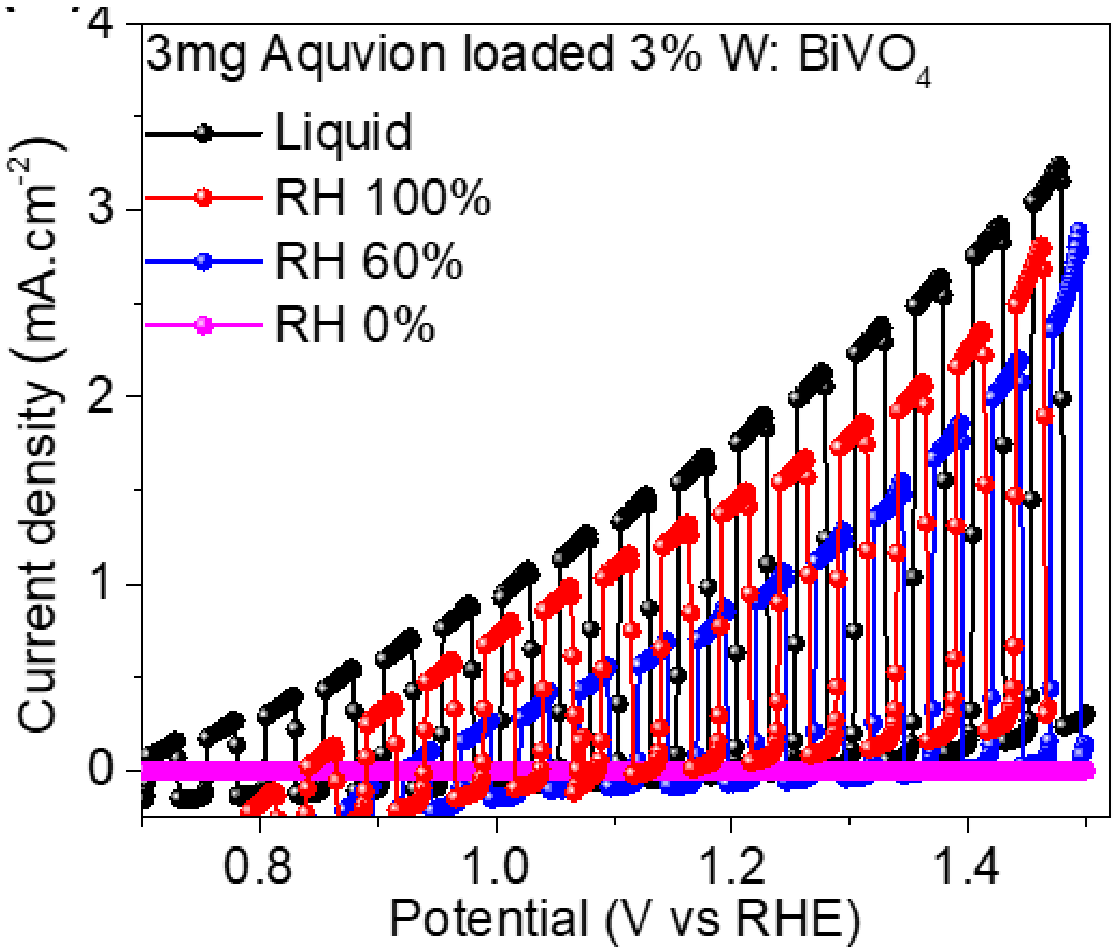


- In line with the literature, doping proved to be a highly effective strategy to increase photocurrent
- Doping percentages 1 – 5% were tested and 3% was found to be optimum

P. Varadan, G. Zafeiropoulous et al, ACS Energy Mater. 2021

Performance under environmental conditions

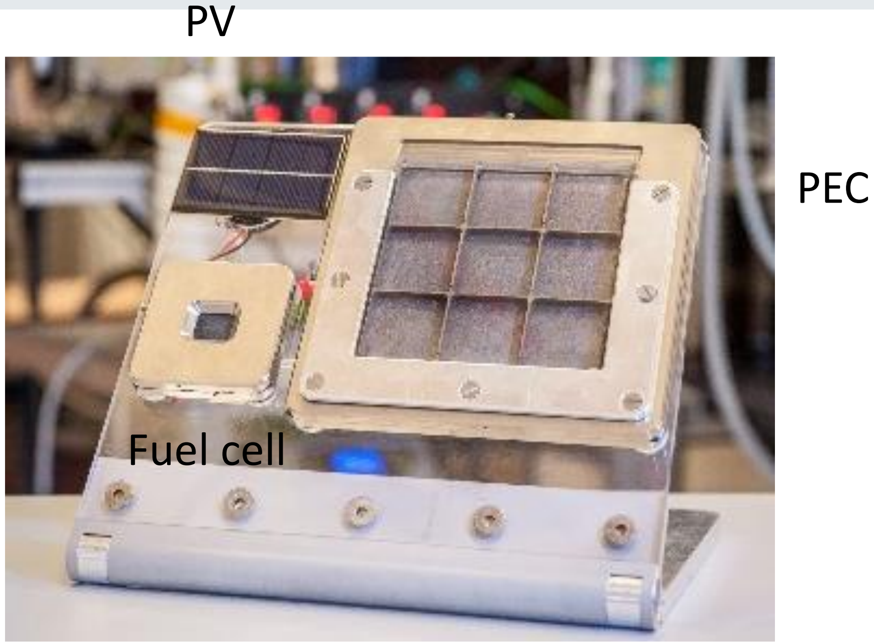


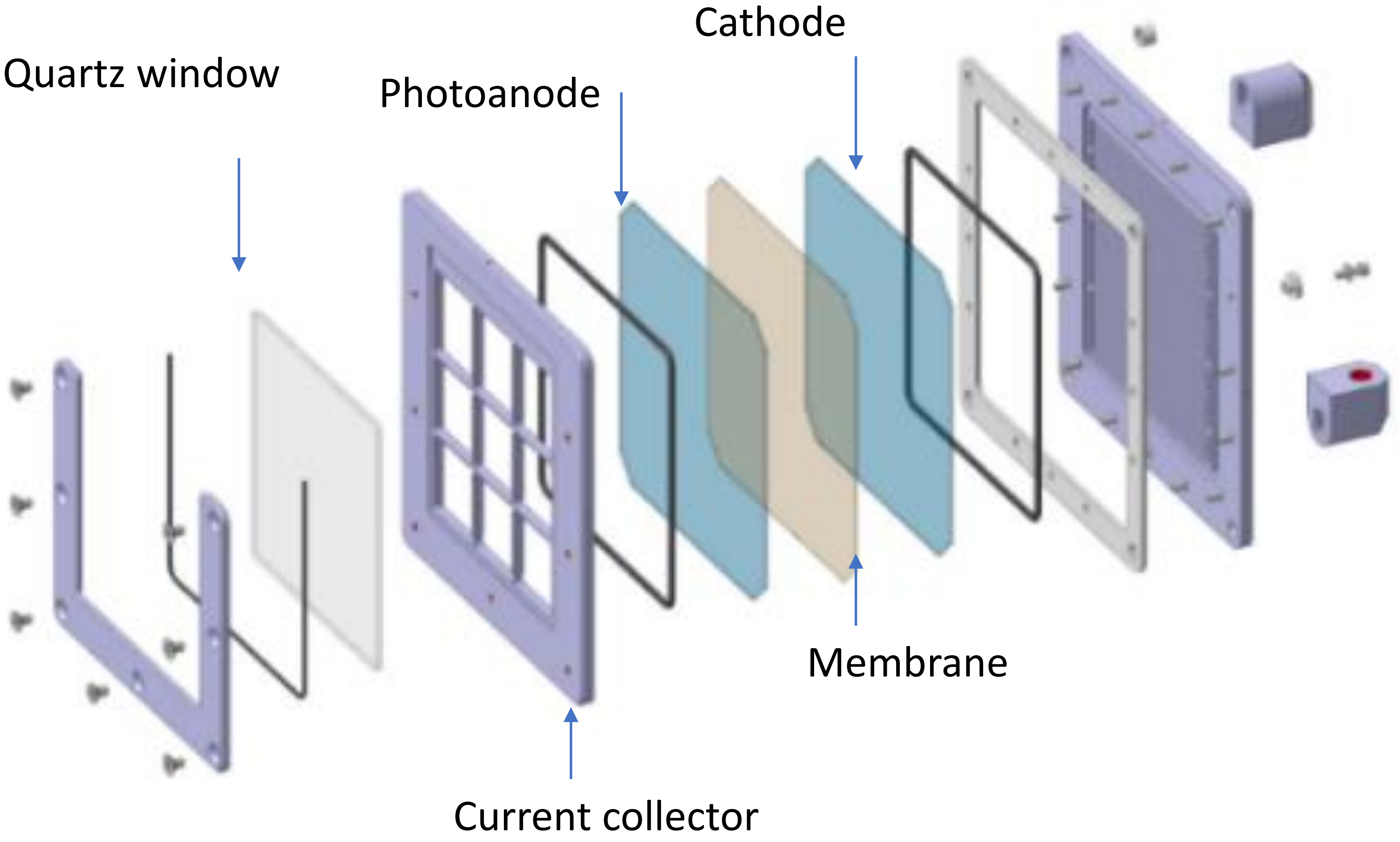
Photocurrents (at 1.23 V) up to:

- 2.05 mA cm^{-2} in liquid water
- 1.1 mA cm^{-2} at 60% RH

P. Varadan, G. Zafeiropoulous et al, ACS Energy Mater. 2021

PROTOTYPE





- Assembled working prototype of 100 cm^2

PERSPECTIVES FOR DIRECT SOLAR FUEL PRODUCTION BEYOND H_2

- The gas phase design based on porous photoelectrodes lends itself to use in electrochemical CO_2 conversion – avoids problem of low CO_2 solubility in liquid electrolyte

- Aim to produce fuels which cannot easily be replaced by hydrogen, for example, jet fuels

- We are now investigating the expansion of this research topic into this field, primarily related to the CO_2RR catalyst development

Sun-To-X

Solar Energy for Carbon-Free Liquid Fuel

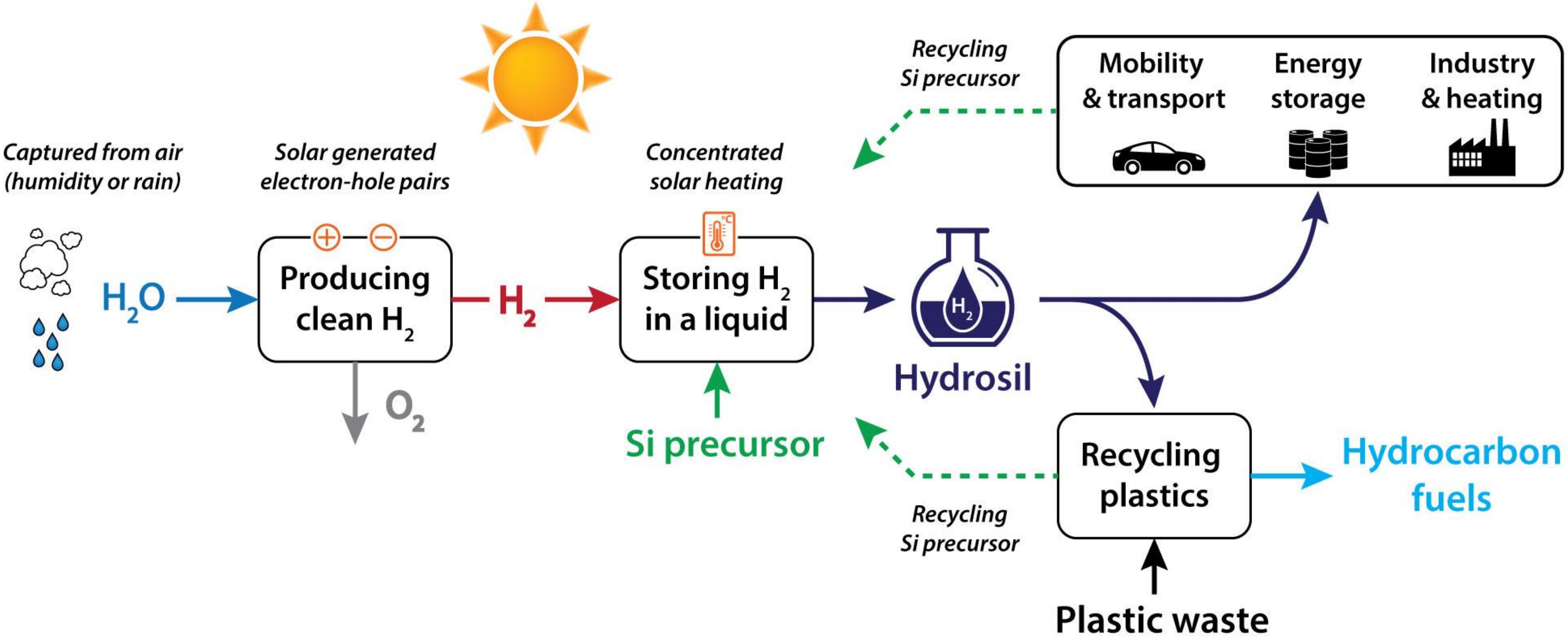
Scalable photoelectrochemical hydrogen production and storage in a liquid silicon hydride carrier

SUN to X
Solar Energy for Carbon-Free Liquid Fuel

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 883264.

An international consortium

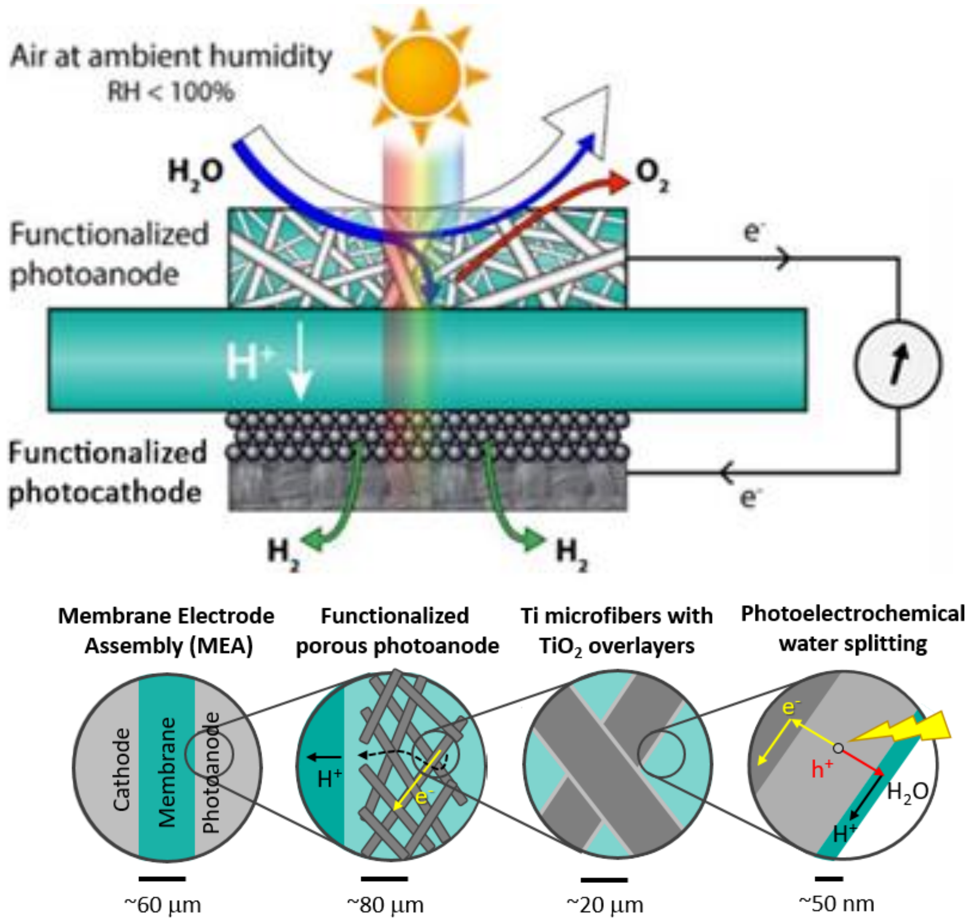
Project Overview



SUNtoX Solar Energy for Carbon-Free Liquid Fuel

Sun-To-X Concept

- Tandem configuration of photoanode / photocathode to maximise light absorption – target 8.2 mA cm^{-2} (10% solar hydrogen efficiency) – moving towards high efficiency photoelectrodes



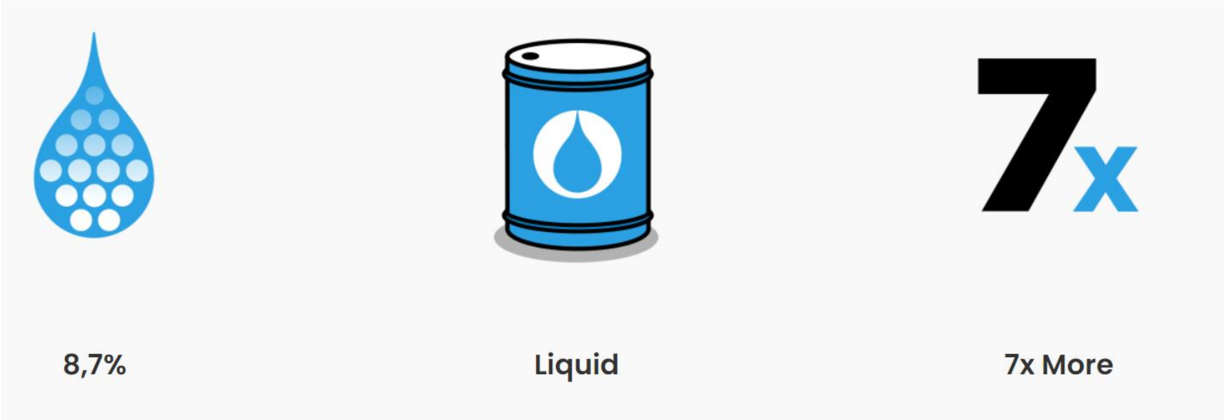
- Porous substrates with appropriate water absorbers to utilise ambient humidity as water source

Thermochemical H_2 Conversion to Hydrosil

Concept:

- Concentrated solar light (through specialised receiver) and electricity will convert H_2 to Hydrosil
- First time demonstration of concept and optimisation of process steps

What is Hydrosil?



H_2 storage capacity	At standard conditions	7 x more H_2 capacity than compressed gas

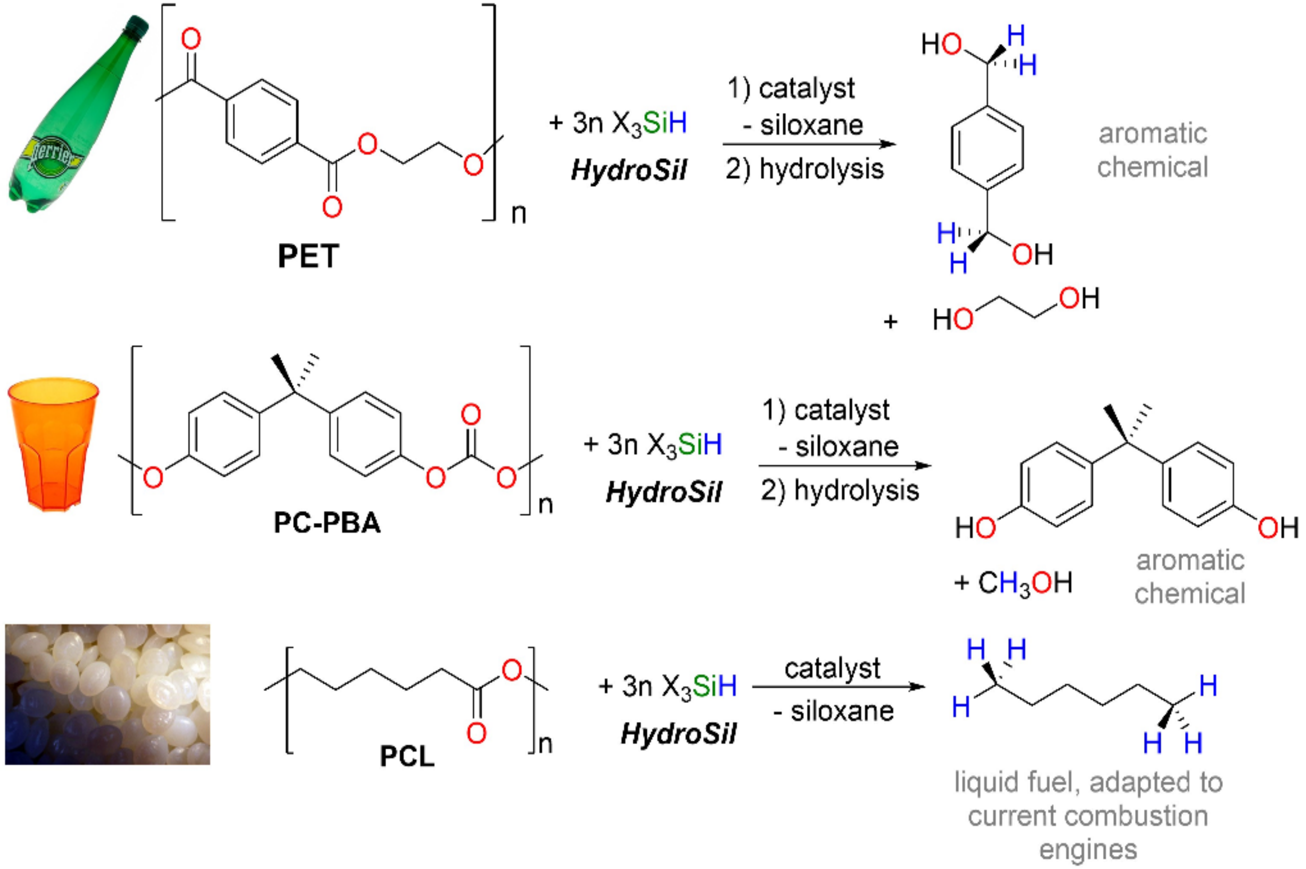
HySiLabs Hydrosil schematic

Recycling to Waste Plastics

Key targets:

- Reductive depolymerisation of plastics to monomers / valuable hydrocarbons through 'rechargeable' silicon hydride

- Production of hexane (0.1 mol scale) from PCL



Demonstration

Key Targets:

- Design and build a demonstrator to show the developed process
- 1 m^2 PEC device producing 29 g H_2 / day thermochemically converted into 320 g HydroSil / day

Existing Lightfuel PEC set-up at Engie

CONCLUSIONS */ Next Steps*

- Development porous photoelectrodes to improve photoelectrode scalability
- Functionalisation with water absorbing materials allows production of hydrogen from ambient humidity
- Deposition of W-doped $BiVO_4$ gives a performance of up to 2.05 mA cm^{-2} in liquid water, 1.1 mA cm^{-2} at 60% RH
- Prototype assembled
- Extension of this work – expansion to high efficiency photoelectrodes and development of liquid hydrogen storage material