

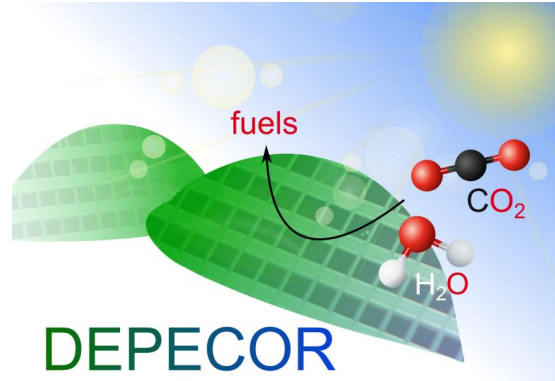
# CO<sub>2</sub> as a sustainable source of carbon - Pathways to industrial applications – CO<sub>2</sub>-WIN



Thomas Hannappel

TU Ilmenau

*Fundamentals of Energy Materials*



GEFÖRDERT VOM



Bundesministerium  
für Bildung  
und Forschung

## Direct efficient photoelectrocatalytic CO<sub>2</sub> reduction

### Project partners:

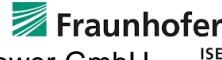
TU Ilmenau

TU München

Helmholtz-Zentrum Berlin

Fraunhofer ISE

AZUR SPACE Solar Power GmbH



Technische Universität München

### Associated partners:

Joint Center of Artificial Photosynthesis (JCAP)

École Polytechnique Fédérale de Lausanne (EPFL)

Evonik

BASF



We create chemistry



The **SPiRiT**  
of science



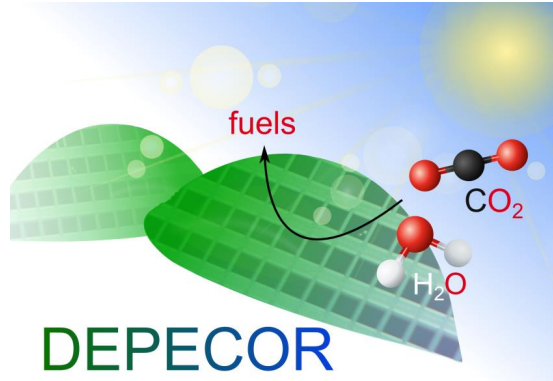
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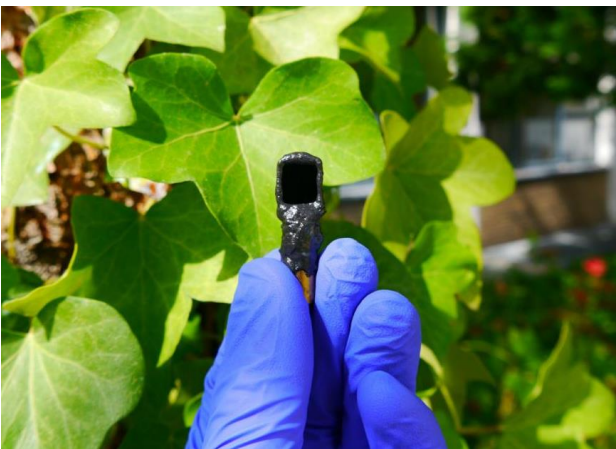
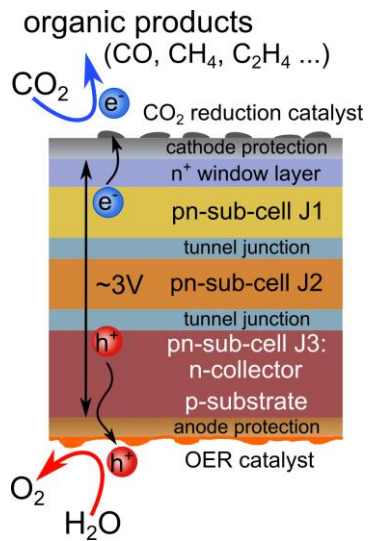
BASF



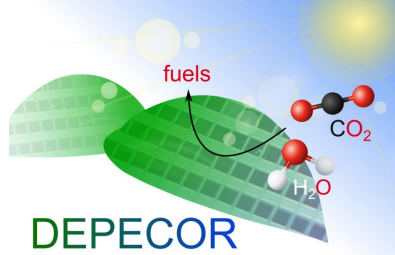
The **SPiRiT**  
of science



# Direct efficient photoelectrocatalytic CO<sub>2</sub> reduction



©Matthias M. May

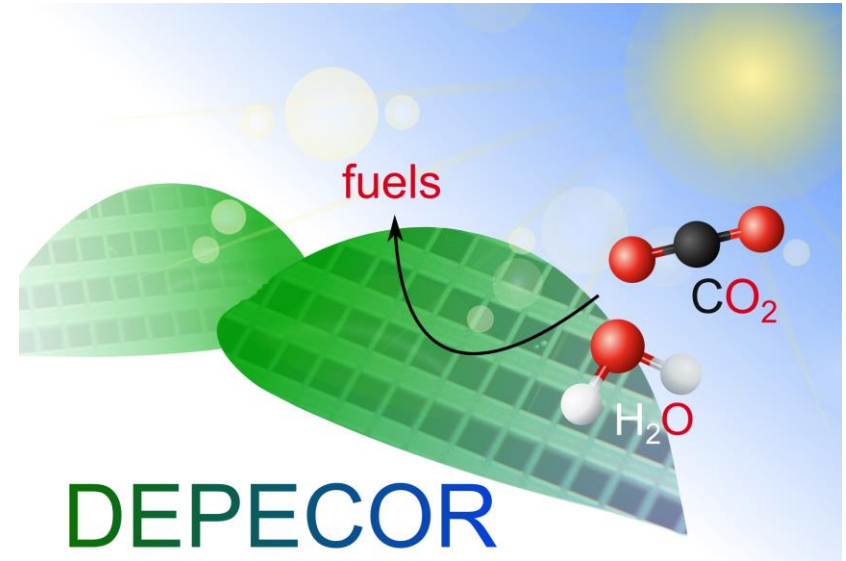


## Aims:

- realization of an **“artificial leaf”** in form of a multi-absorber structure,
- a **demonstrator** to efficiently reduce CO<sub>2</sub> through non-assisted, direct, **solar-driven photoelectrocatalysis**
- conversion into **hydrocarbons** as storable energy sources.

# Advantages of Photoelectrochemical Devices

- **No electric circuitry**, direct contact with electrolyte
- **No need of balance of 2 separate systems**
- Integration can **reduce systems costs**
- **Thermodynamically** and **dynamically** more **favorable**
- **Heat accelerates** reactions – in PV heat degrades PV performance
- Lower current densities, larger spectrum of **less precious catalysts** applicable
- **Scalable** at will
- .....

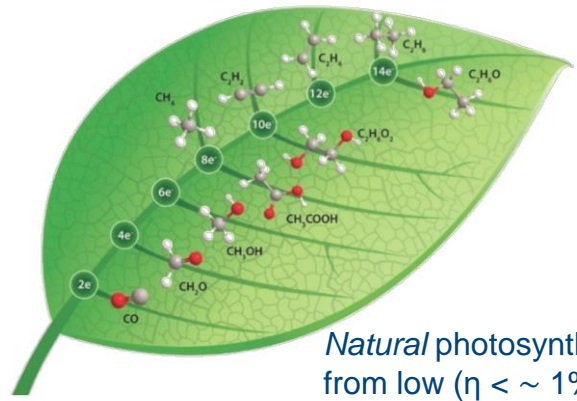
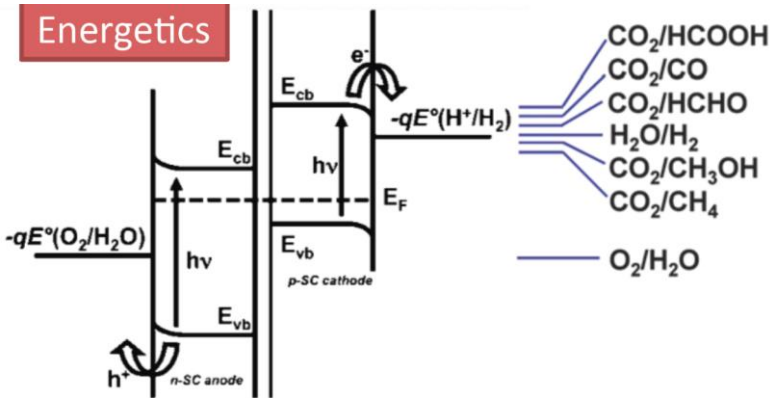
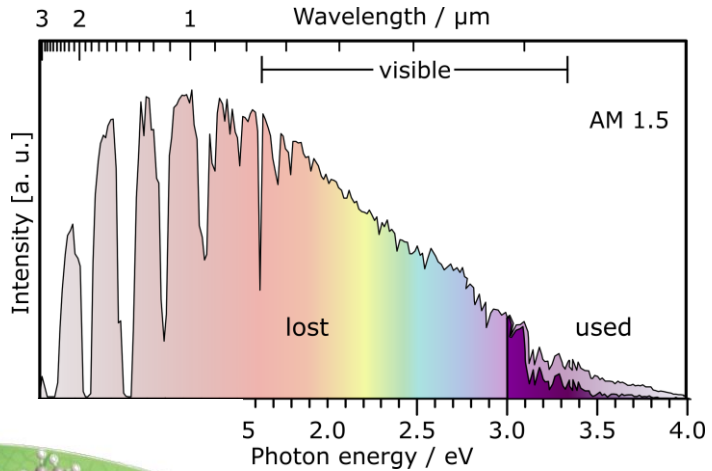


... an artificial leaf

# How to realize the “artificial leaf” - Photoelectrochemical cell structure

- Photo-absorbers
- Metal-oxide protective layers
- Electro-catalysts
- Prototype design

High potential needed ->  
**Band gap > ~ 3V**  
 required



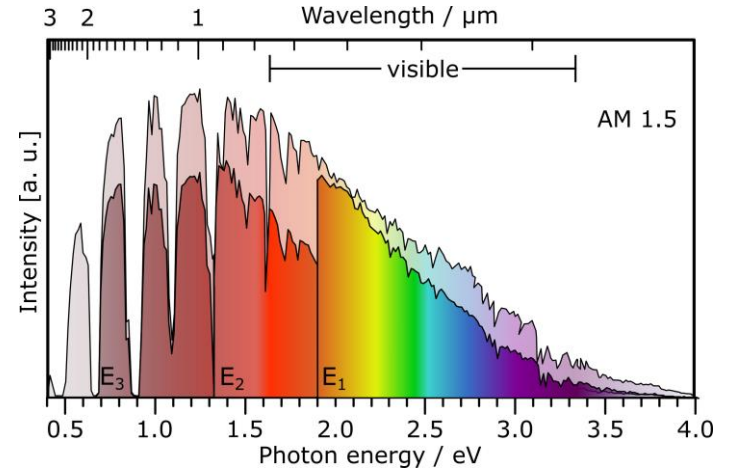
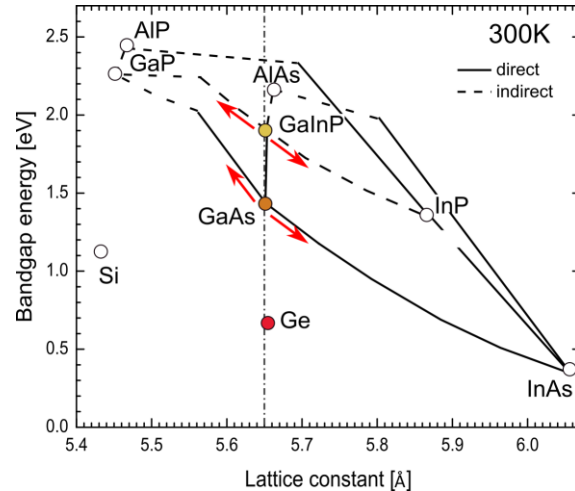
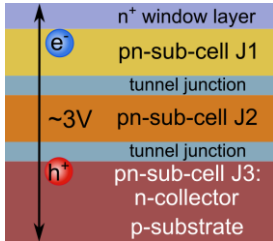
Natural photosynthesis suffers from low ( $\eta < \sim 1\%$ ) efficiency

➔ **not efficient!**  
 with single-junction photo-absorber

$E^\circ$  - Nernst potential vs. Normal Hydrogen Electrode at 25 °C and 1 atm gas pressure, pH=7

# How to realize the “artificial leaf” - Photoelectrochemical cell structure

- **Photo-absorbers**
- **Metal-oxide protective layers**
- **Electro-catalysts**
- **Prototype design**

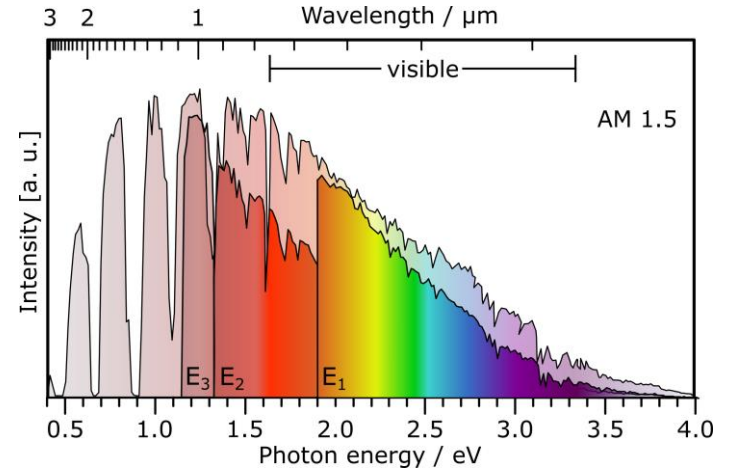
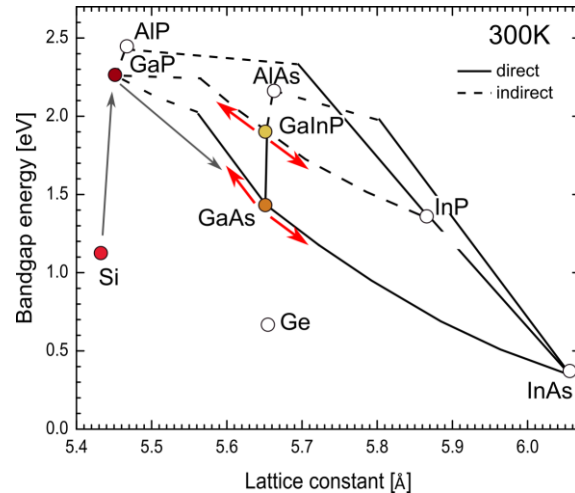
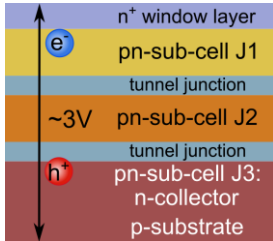


- **multi-absorbers** are required
- **high efficiency** and **optimal use** of solar photons
- III-V materials - **world-record** efficiencies
- **tunable** bandgaps



# How to realize the “artificial leaf” - Photoelectrochemical cell structure

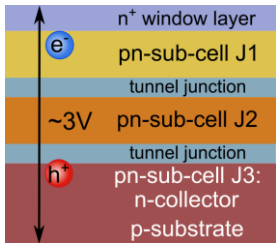
- **Photo-absorbers**
- **Metal-oxide protective layers**
- **Electro-catalysts**
- **Prototype design**



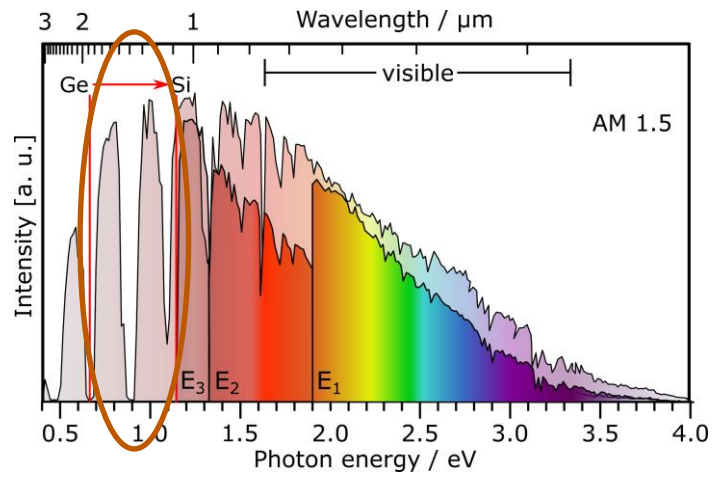
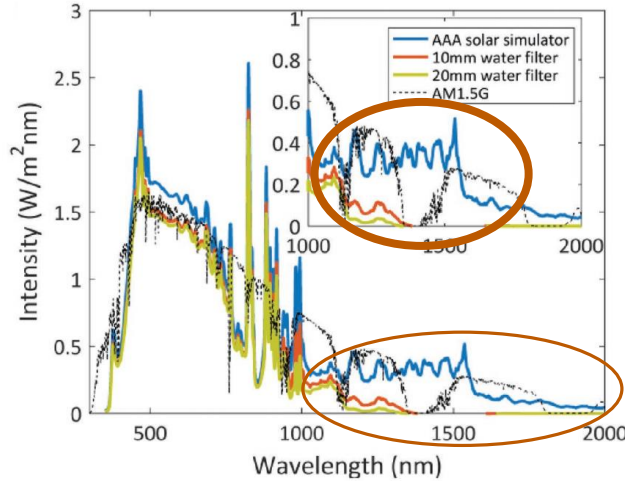
- **multi-absorbers** are required
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- Si – significant **costs reduction**

# How to realize the “artificial leaf” - Photoelectrochemical cell structure

- **Photo-absorbers**
- **Metal-oxide protective layers**
- **Electro-catalysts**
- **Prototype design**



the majority of the infrared light is absorbed by the aqueous electrolyte



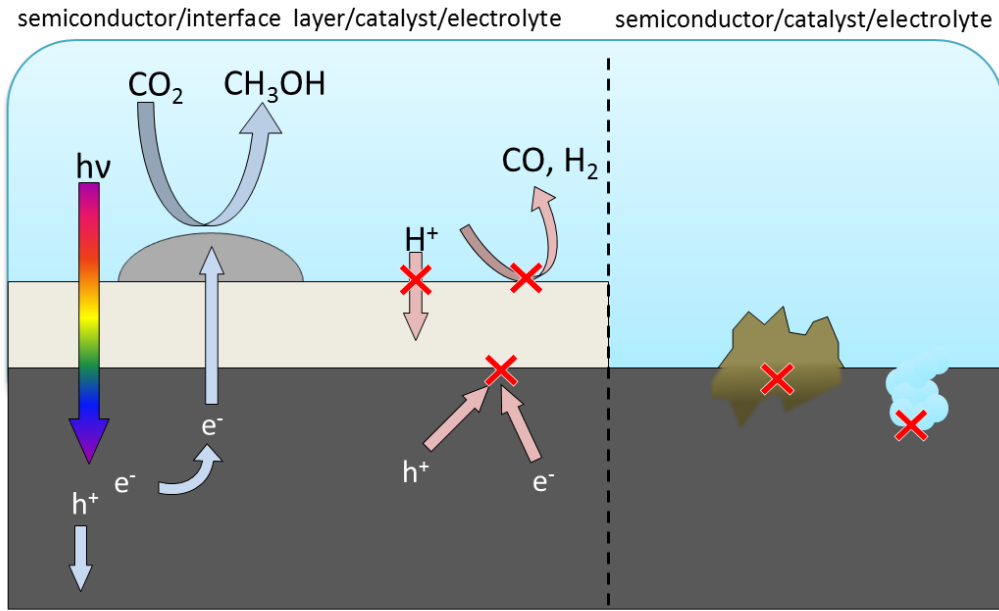
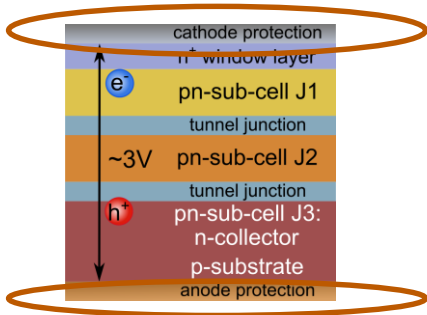
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Fig. taken from: K. A. Walczak et al., Adv. Energy Mater. 7 (2017) 1602791



# How to realize the “artificial leaf” - Photoelectrochemical cell structure

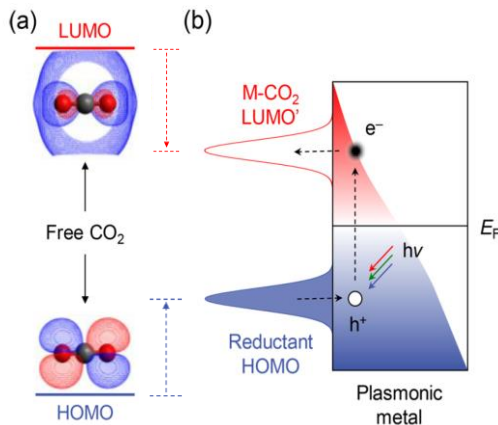
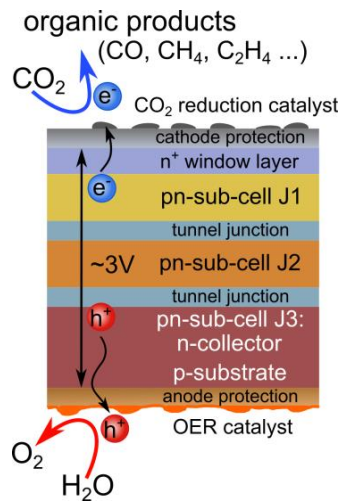
- Photo-absorbers
- Metal-oxide protective layers
- Electro-catalysts
- Prototype design



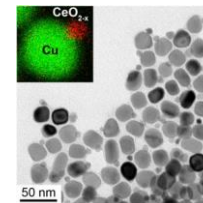
- |  |   |   |
|--|---|---|
| <p>Promoting:</p> <ul style="list-style-type: none"> <li>• Selective catalysis</li> <li>• <u>Carrier transport</u></li> <li>• Photovoltage generation</li> </ul> | <p>Inhibiting:</p> <ul style="list-style-type: none"> <li>• <u>Carrier recombination</u></li> <li>• Proton migration</li> <li>• Side-product formation</li> </ul> | <p>Eliminating:</p> <ul style="list-style-type: none"> <li>• <u>Corrosion</u></li> <li>• Undesired material interactions</li> </ul> |
|--|---|---|

# How to realize the “artificial leaf” - Photoelectrochemical cell structure

- Photo-absorbers
- Metal-oxide protective layers
- Electro-catalysts
- Prototype design



Catalysts:  
Ag, Cu, Sn



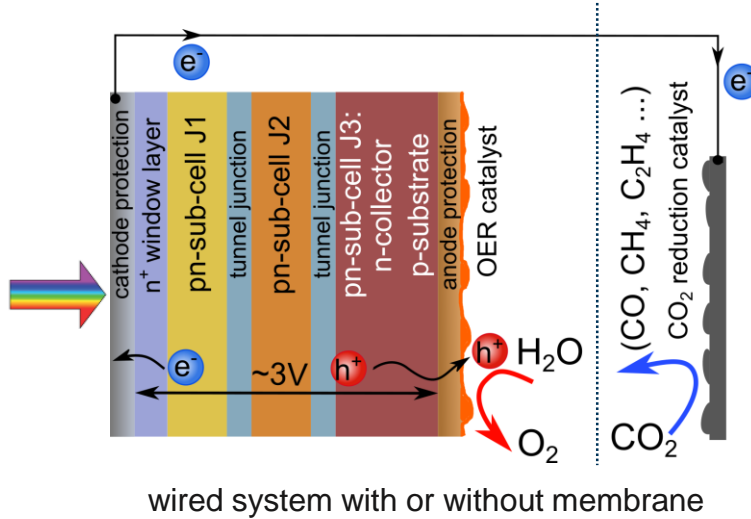
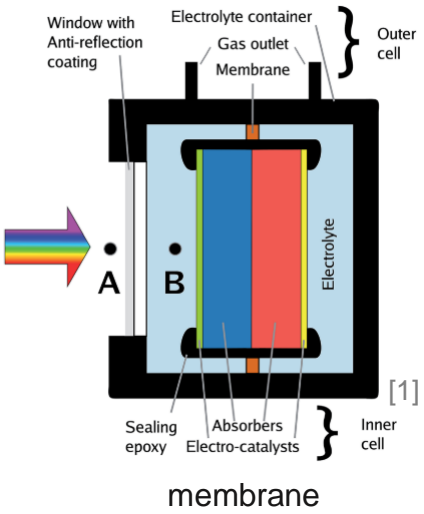
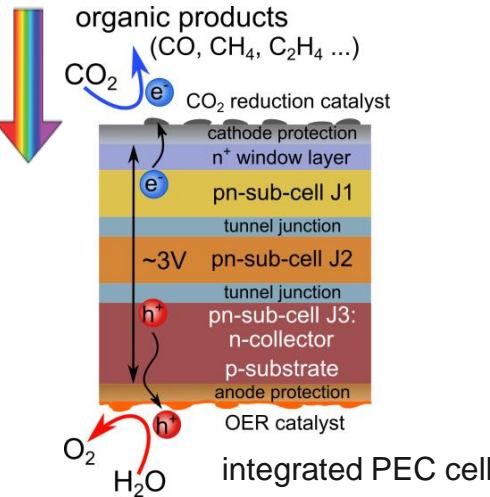
- Highly selective to promote CO<sub>2</sub> reduction
- Efficiency / activity
- Transparency
- Plasmonic effects enhance Fischer-Tropsch reactions (use of hot electrons)
- Shape, site and size of the nanoparticle will also influence the CO<sub>2</sub> electrochemical reaction

# How to realize the “artificial leaf” - Photoelectrochemical cell structure

- **Photo-absorbers**
- **Metal-oxide protective layers**
- **Electro-catalysts**
- **Prototype design**

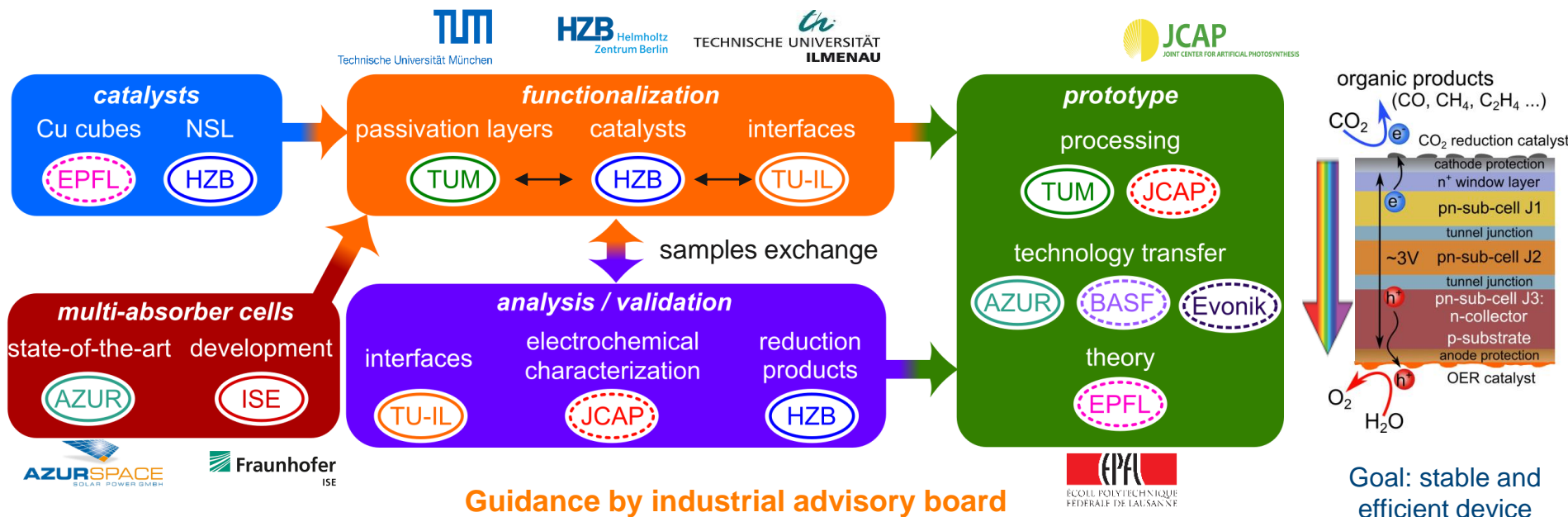
## Different designs must be considered:

- Ideally - an integrated device
- pH of solution impacts the product development and problem of product cross-over
- Problem of transparency of the catalyst



[1] M. M. May Sustainable Energy Fuels 1 (2017) 492

# Organization of collaboration



Goal: stable and efficient device  
**prototype** for CO<sub>2</sub> reduction

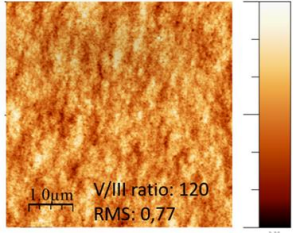
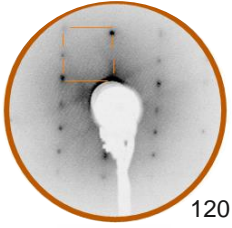
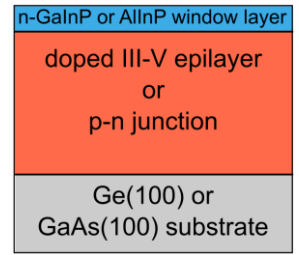
Long-term / short-term scientific visits at JCAP in the USA and the EPFL in Switzerland were not possible due to the COVID travel restrictions.

### Photo-absorbers

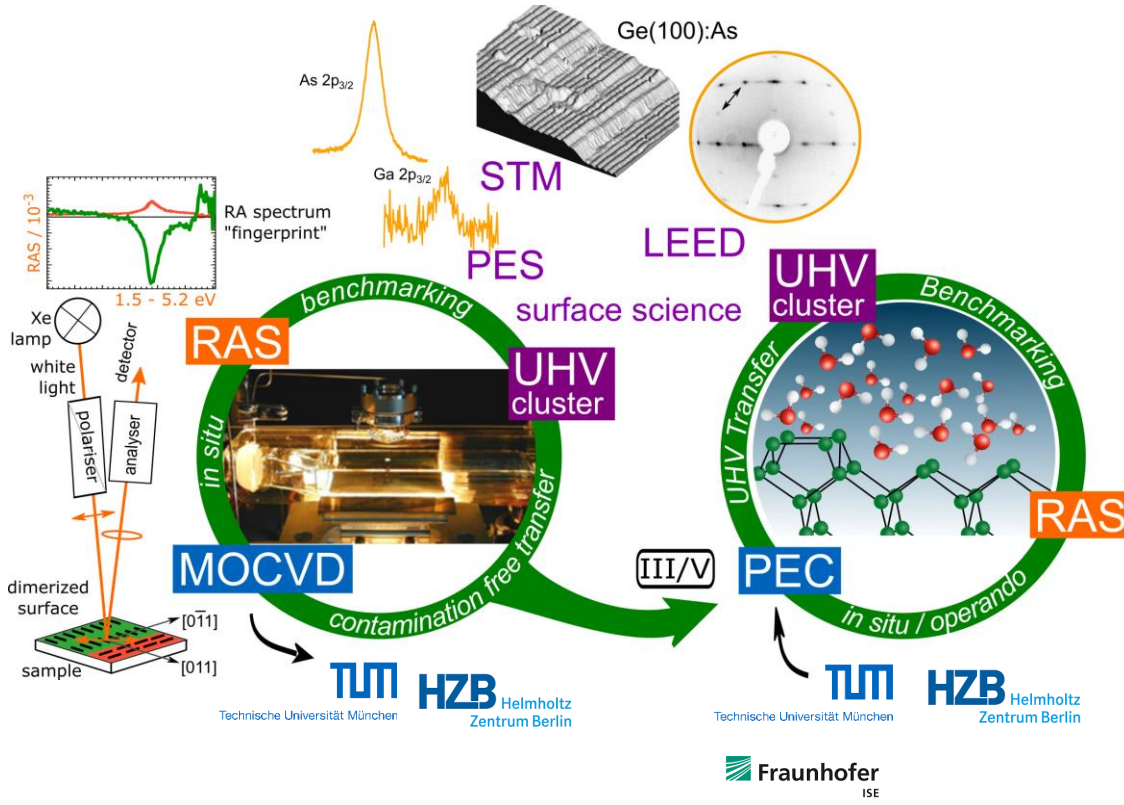


T. Hannappel   D. Ostheimer   M. A. Zare Pour   A. Paszuk

group-V or III-rich  
atomically ordered surface



III-V half-cells



## Metal-oxide protective layers



I. Sharp



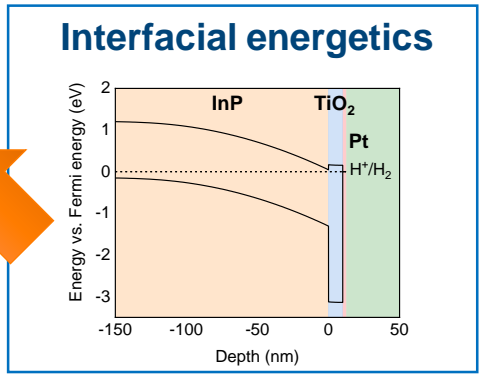
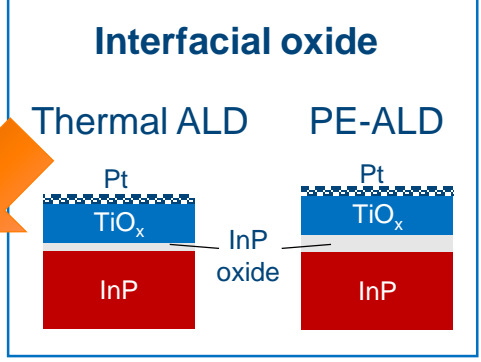
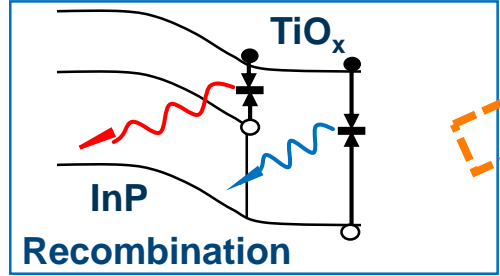
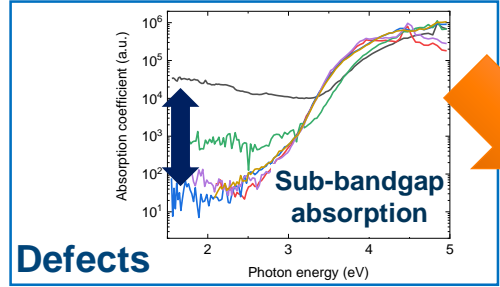
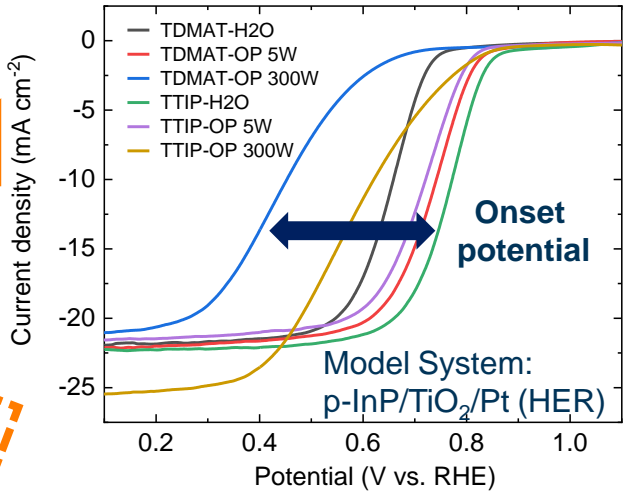
O. Bienek



J. Kühne



## Factors influencing photoelectrochemical performance





## Electro-catalysts



R. van de Krol P. Bogdanoff M. Mayer Y.-L. Tsai D. Aksoy

# Techniques for nano-structured thin layer preparation

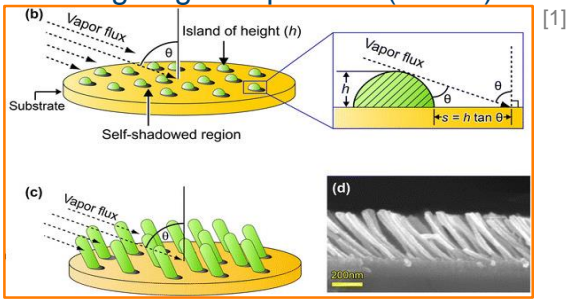
## Chemical-based synthesis

- Wet-chemical preparation
- Electrodeposition

## Physical deposition methods

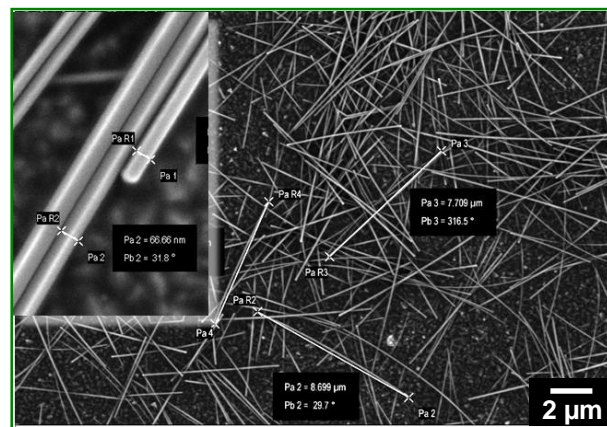
- Glancing Angle Deposition (GLAD)
- Nanosphere Lithography (NSL)

## Glancing Angle Deposition (GLAD)

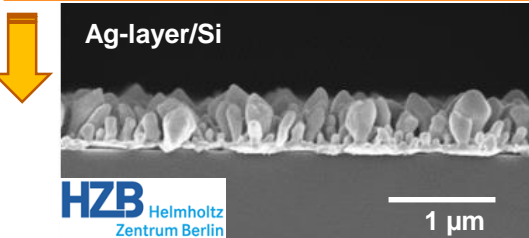
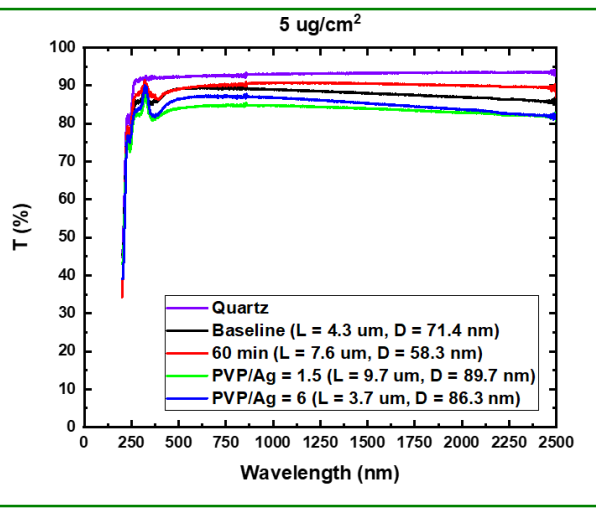


[1]

## Wet-chemical Poly(vinyl pyrrolidone)-mediated synthesis



Ag-nano needles with high transparency



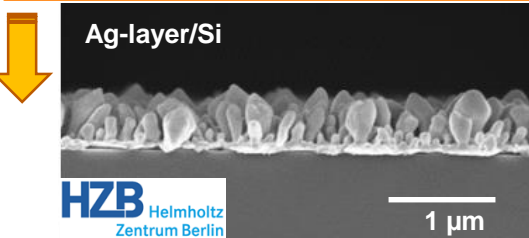
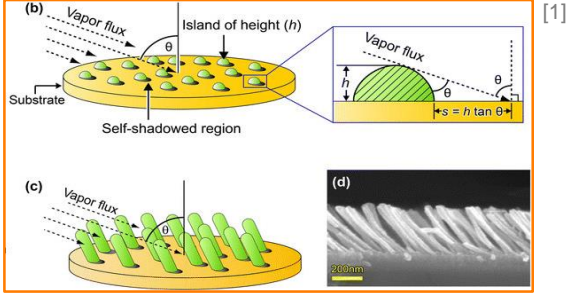
[1] Retrieved from Kwon et. al, *Nanoscale Res Lett* 10 (2015) 369

## Electro-catalysts



R. van de Krol P. Bogdanoff M. Mayer Y.-L. Tsai D. Aksoy

## Glancing Angle Deposition (GLAD)



# Techniques for nano-structured thin layer preparation

## Chemical-based synthesis

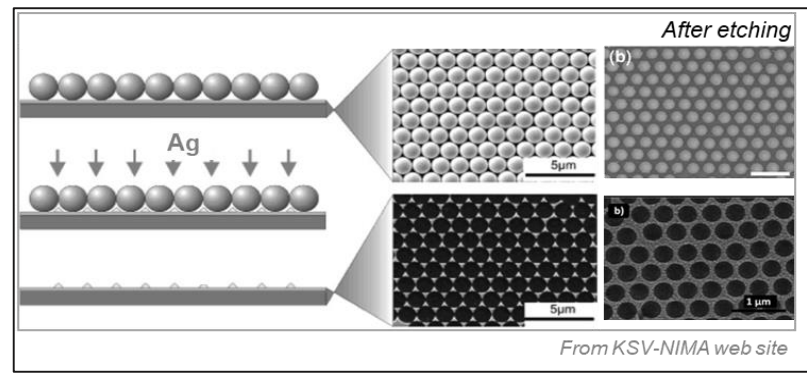
- Wet-chemical preparation
- Electrodeposition

## Physical deposition methods

- Glancing Angle Deposition (GLAD)
- Nanosphere Lithography (NSL)

in planning:

- Nanosphere Lithography (NSL)



- study CO<sub>2</sub>RR activity of the differently deposited nano-catalysts

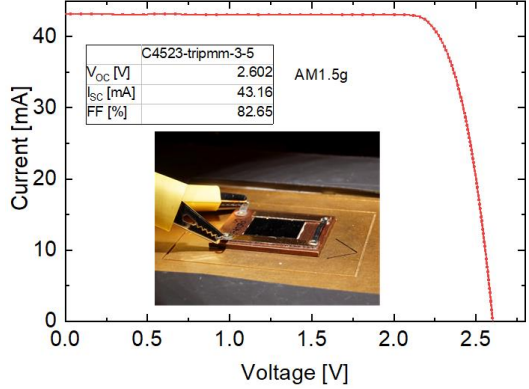
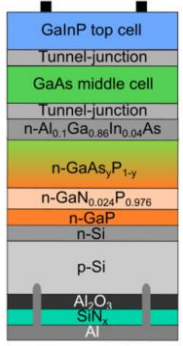
[1] Retrieved from Kwon et. al, *Nanoscale Res Lett* 10 (2015) 369

## III-V/Si photoabsorbers



F. Dimroth    M. Feifel

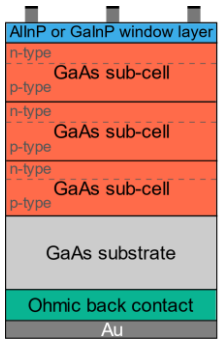
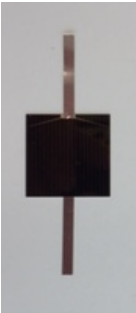
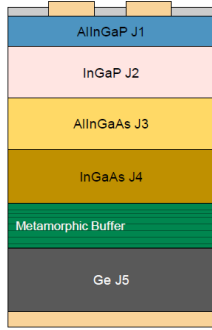
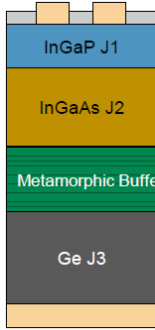
New cell structure must be established to achieve the high photovoltage



## III-V/Ge or GaAs test solar cells



G. Strobl    V. Khorenko



# DEPECOR Team – associated partners



H.A. Atwater

- support in the catalysts development, products quantification, membrane, models of mass transport of CO<sub>2</sub> to the active surfaces, device testing



R. Buonsanti



S. Haussener

- investigate the activity of specific Cu catalysts support in the modeling of the prototype



F. Menzel

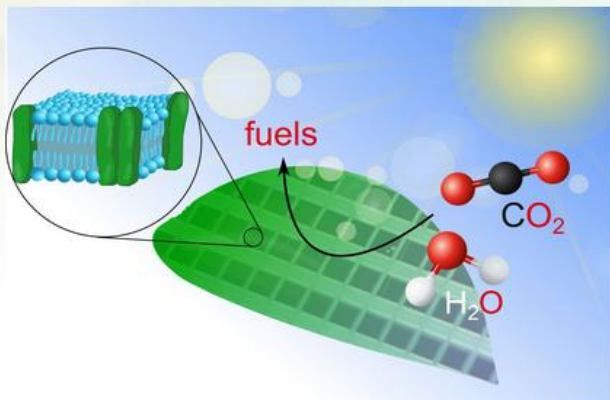
- advise on the prototype development regarding the technology transfer and commercial, relevant products



S. Bräuninger

**Student and PI exchange was planned previously in long- and short-term scientific visits at JCAP in the USA and the EPFL in Switzerland.**  
Not possible due to the pandemic, therefore .....

## US-German workshop series on artificial photosynthesis



Artificial Photosynthesis (AP) to generate useful chemicals and materials using only components of air and sunlight as inputs is a dream of visionaries and an active area of research. The AP research communities in Germany and the United States have many overlapping and complementary interests, and fruitful collaborations between them will help accelerate progress in the field. In the summer of 2020, a workshop sponsored by the BMBF in Germany and the DOE in the United States examined areas of opportunity for joint work, and recommended that an ongoing meeting series be launched to promote new connections between the scientific and engineering communities in the two countries.

This meeting series is now launched, organized by the German CO<sub>2</sub>-WIN consortium and a US-German steering committee.

The kick-off workshop took place on 25 May 2021. Below you will find the agenda and a link to register for the free event series. Registration will enable you to receive notices for future events.

**Kick-off: May 25<sup>th</sup>**

**Next workshops: June 29<sup>th</sup> and July 27<sup>th</sup> or August 3<sup>rd</sup>**

Thank you for your attention

