CO₂ as a sustainable source of carbon - Pathways to industrial applications – CO₂-WIN

Thomas Hannappel
TU Ilmenau

*Fundamentals of Energy Materials*

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Direct efficient photoelectrocatalytic CO₂ reduction

**Project partners:**
- TU Ilmenau
- TU München
- Helmholtz-Zentrum Berlin
- Fraunhofer ISE
- AZUR SPACE Solar Power GmbH

**Associated partners:**
- Joint Center of Artificial Photosynthesis (JCAP)
- École Polytechnique Fédérale de Lausanne (EPFL)
- Evonik
- BASF

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**Institution:**
Technische Universität Ilmenau
Direct efficient photoelectrocatalytic CO$_2$ reduction

Aims:
- realization of an “artificial leaf” in form of a multi-absorber structure,
- a demonstrator to efficiently reduce CO$_2$ 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

\(E_0\) - Nernst potential vs. Normal Hydrogen Electrode at 25 °C and 1 atm gas pressure, pH=7

Xie et al., *Chemical Communications* 2016, 52 (1), 35
Walter et al., *Chemical Reviews* 2010, 110 (11), 6446
How to realize the “artificial leaf” - Photoelectrochemical cell structure

- Photo-absorbers
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- Electro-catalysts
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- multi-absorbers are required
- high efficiency and optimal use of solar photons
- III-V materials - world-record efficiencies
- tunable bandgaps
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- Si – significant costs reduction
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The majority of the infrared light is absorbed by the aqueous electrolyte.

- multi-absorbers are required
- high efficiency and optimal use of solar photons
- III-V materials - world-record efficiencies
- tunable bandgap
- Si – significant costs reduction

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

- Highly selective to promote CO₂ 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 CO₂ 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

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Organization of collaboration

**Goal:** stable and efficient device prototype for CO$_2$ reduction

**Guidance by industrial advisory board**

**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.
DEPECOR Team

III-V photoabsorbers: *in situ* surface control

- **Photo-absorbers**
  - T. Hannappel
  - D. Ostheimer
  - M. A. Zare Pour
  - A. Paszuk

Group-V or III-rich atomically ordered surface

- (2x1) InGaP surface grown on Ge(100)
- 120 eV
- 7.00 nm

- n-GaInP or AlInP window layer
- doped III-V epilayer
- or p-n junction
- Ge(100) or GaAs(100) substrate

III-V half-cells

- STM
- PES
- LEED
- UHV cluster
- UHV-Transfer
- Benchmarking

- MOCVD
- In situ contamination free transfer

- III/V
- PEC
- in situ / operando

- RAS
- RA spectrum "fingerprint"

- UHV cluster

- Fraunhofer ISE
- Technische Universität München
- Helmholtz Zentrum Berlin

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Factors influencing photoelectrochemical performance

Interfacial oxide
Thermal ALD
PE-ALD

Interfacial energetics

Defects
Sub-bandgap absorption

Recombination

Absorption coefficient (a.u.)
Photon energy (eV)
TDMAT-H2O
TDMAT-OP 5W
TDMAT-OP 300W
TTIP-H2O
TTIP-OP 5W
TTIP-OP 300W

Current density (mA cm$^{-2}$)

Potential (V vs. RHE)
TDMAT-H2O
TDMAT-OP 5W
TDMAT-OP 300W
TTIP-H2O
TTIP-OP 5W
TTIP-OP 300W

Onset potential

Model System: p-InP/TiO$_x$/Pt (HER)

Absorption coefficient (a.u.)

Photon energy (eV)
TDMAT-H2O
TDMAT-OP 5W
TDMAT-OP 300W
TTIP-H2O
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Onset potential

Model System: p-InP/TiO$_x$/Pt (HER)
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)

Wet-chemical Poly(vinyl pyrrolidone)-mediated synthesis

Ag-nano needles with high transparency

Techniques for nano-structured thin layer preparation

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in planning:
- Nanosphere Lithography (NSL)

- study CO$_2$RR activity of the differently deposited nano-catalysts
DEPECOR Team

- **III-V/Si photoabsorbers**
  - New cell structure must be established to achieve the high photovoltage

- **III-V/Ge or GaAs test solar cells**
DEPECOR Team – associated partners

- support in the catalysts development, products quantification, membrane, models of mass transport of CO$_2$ to the active surfaces, device testing

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

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

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 CO2-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 25th**

**Next workshops:** June 29th and July 27th or August 3rd
Thank you for your attention