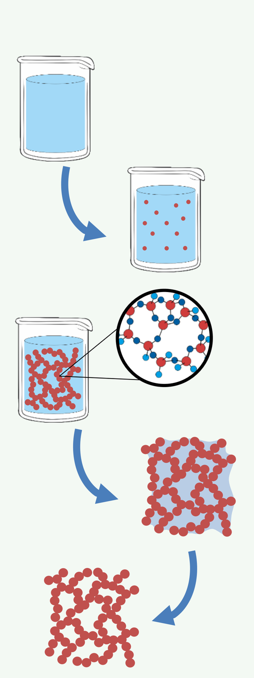
Ammonia on site: Separating charge generation from dark N_2 reduction on tailored TiO_2 aerogels

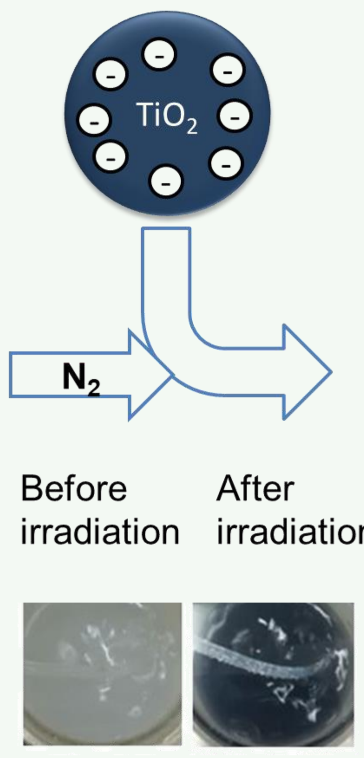
Roland Marschall, Barbara Milow, Dirk Ziegenbalg

Separating light-induced charge carrier generation from dark NRR catalysis

TiO_2 Aerogels FP1: synthesis optimization

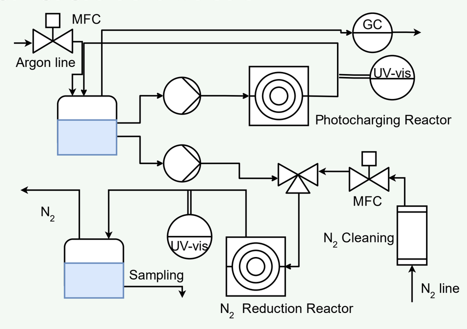
- tuning parameters: type of solvent, acid concentration, water concentration, and aging time
- specific surface area of up to 600 $m^2\,g^{-1}$
- controllable crystallinity from amorphous to 100%
- tunable phase composition: mainly anatase and up to 42% of brookite
- adjustable porous structure and pore size
- interconnected network leads to superior charge carrier separation

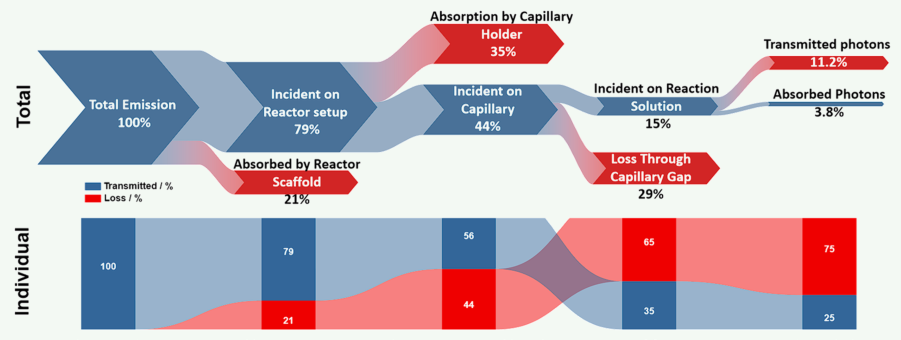




Separate photocharging and dark NRR

- two separate capillary reactors
- Taylor flow to increase mass transfer and control gas/liquid ratio
- fixed volume gas run

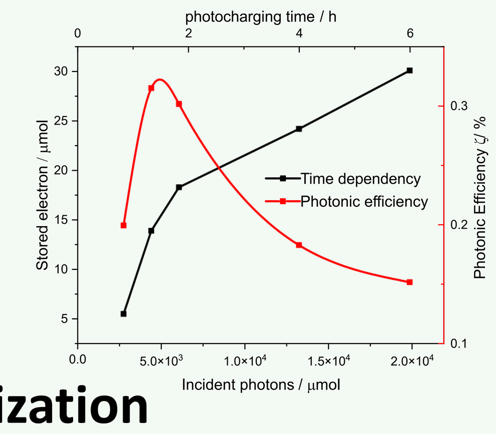


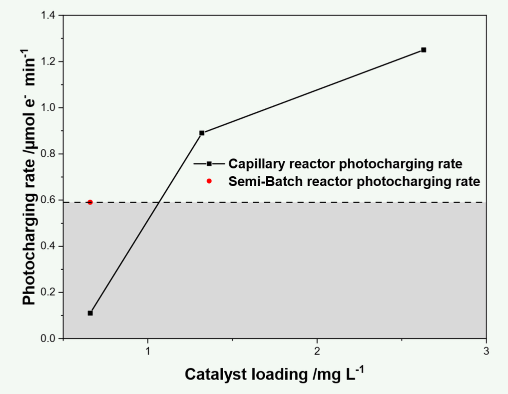


Sankey diagram illustrating the overall photon efficiency and Ribbon graph depicting individual photon losses within the system.

Reactor characterization

- photonic characterization
- adapted process parameters
- 3.8 % total photon absorption

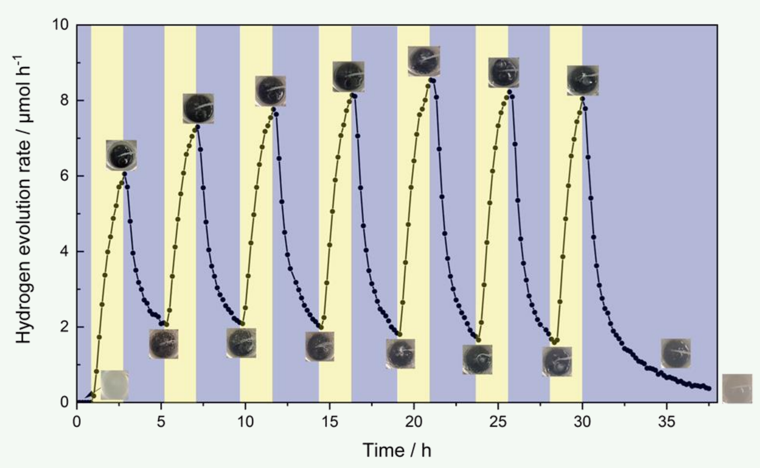




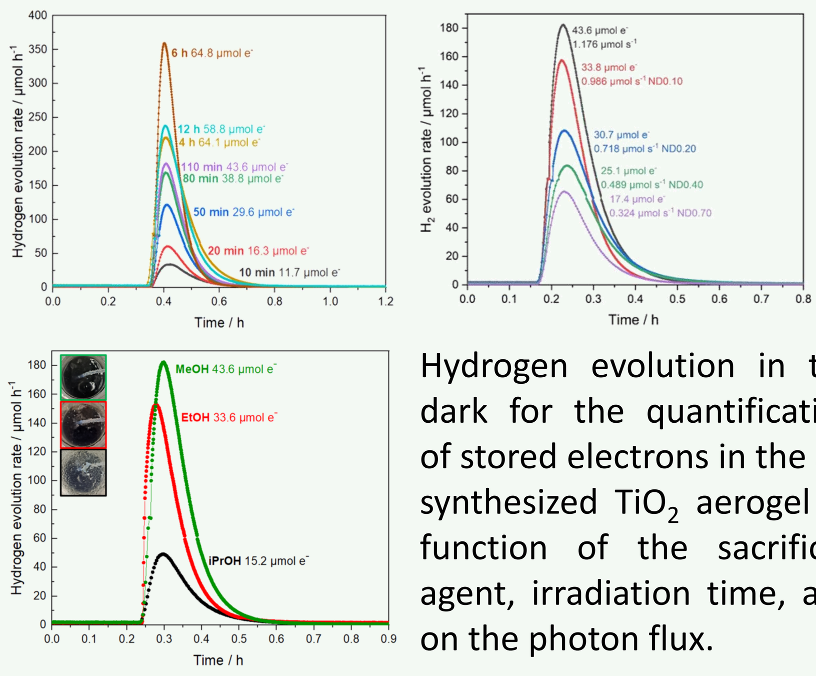
Gas phase photocharging & NRR

- fast photocharging
- no need for catalyst separation for NRR
- avoids N_2 solubility limitation

Photocharging batch results



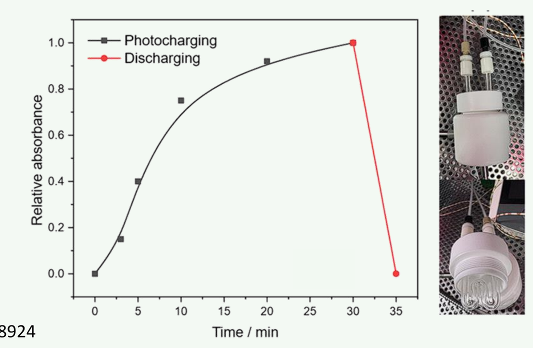
Hydrogen evolution rate during the periodic photocharging experiment to test cyclability.



Hydrogen evolution in the dark for the quantification of stored electrons in the as-synthesized TiO_2 aerogel as function of the sacrificial agent, irradiation time, and on the photon flux.

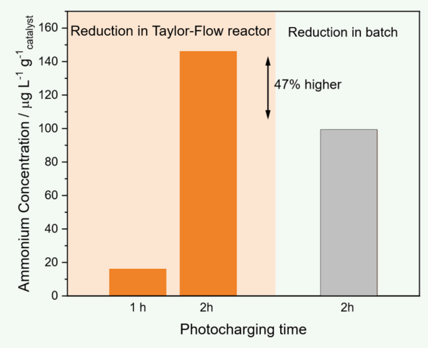
Process parameter optimization

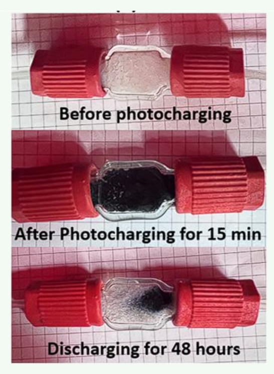
- faster photocharging with higher loading
- reduced suspension volume accelerates charging
- online UV/vis measurements using integrating sphere to follow photocharging and discharging

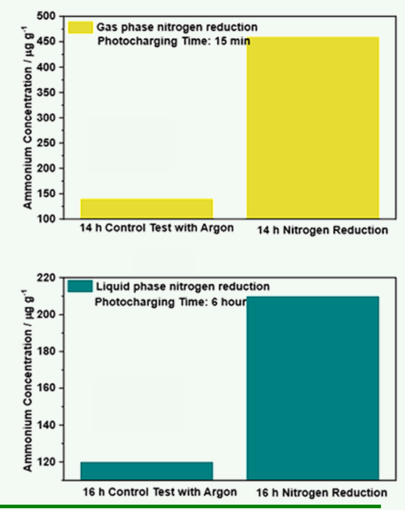


N_2 Reduction with Charged Aerogels

- increased N_2 reduction activity with longer photocharging time
- enhanced performance in Taylor flow reactor compared to batch mode





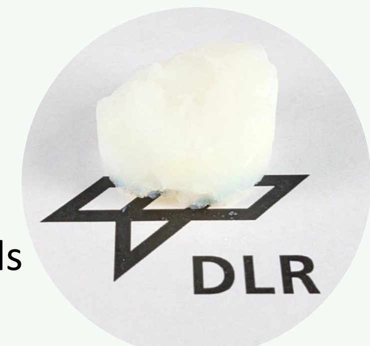


A. Valaei, A. Hofmann, A. Rose, P. Kuschmitz, P. Voepel, B. Milow, R. Marschall, D. Ziegenbalg, Chem. Eng. J., 2025, DOI: 10.1016/j.cej.2025.168924

Work Package 1

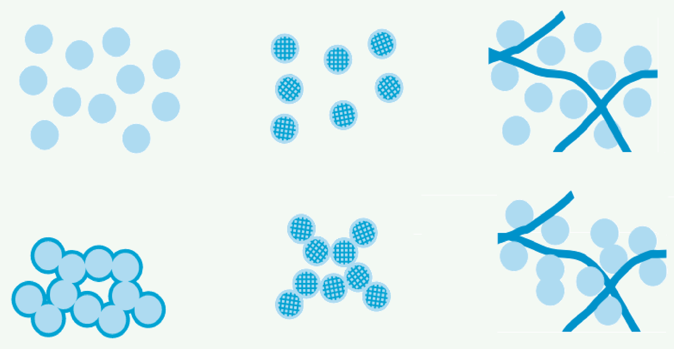
Aerogel tailoring for application

- mechanical stability: introducing spacers and scaffolding techniques to achieve stable monoliths, beads, films and mats
- fixation: developing deposition techniques for aerogel films on conductive substrates
- upscaling: investigating the influence of batch size and introducing continuous production methods
- band gap tuning: doping with metals and non-metals



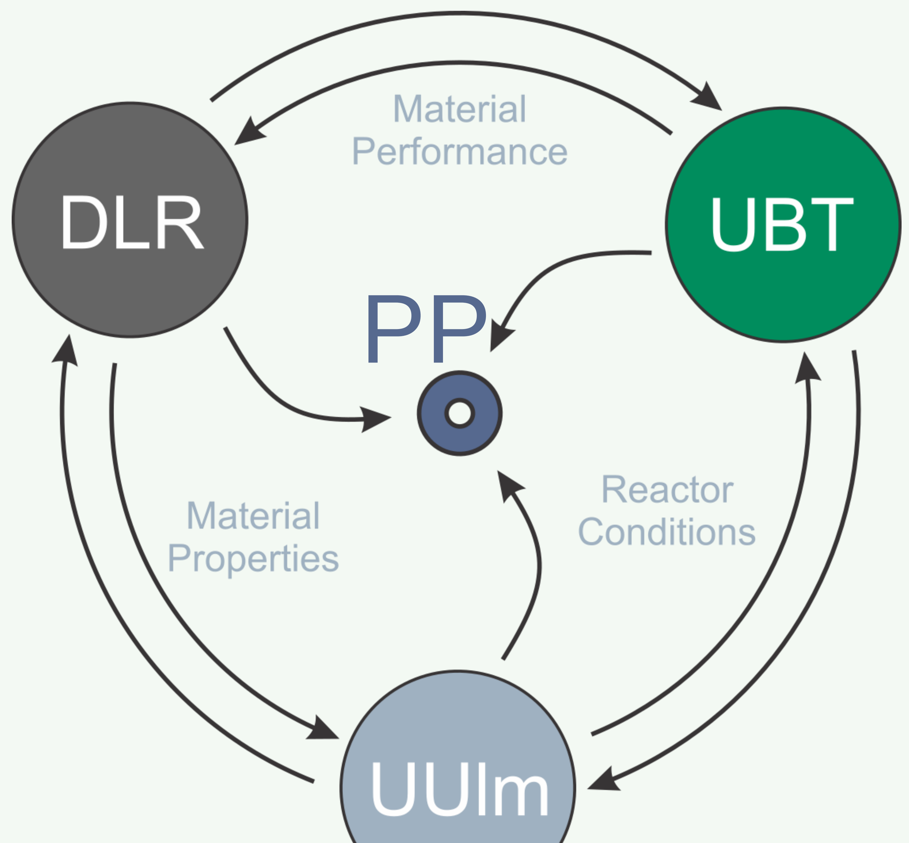
Comparison of different porous systems

- precursor based synthesis
- particle based synthesis
- fiber based synthesis
- combination of particle and fiber-based approaches with molecular precursor



Research Questions

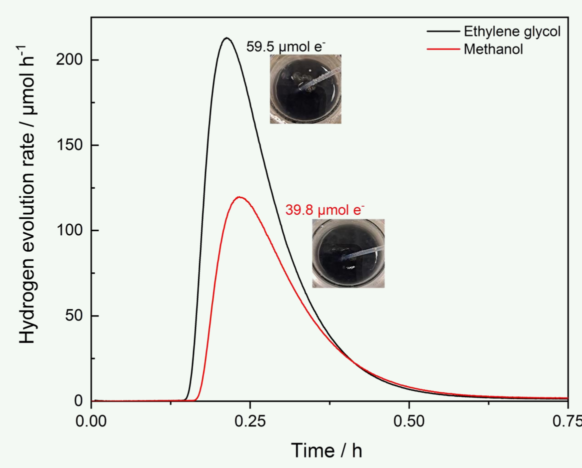
1. How to modify TiO_2-based materials for an increased efficiency of photocharging?
2. Which material properties determine the activity of dark N_2 reduction?
3. Which reactor types enable efficient photocharging and subsequent N_2 reduction?
4. Which reaction conditions enable efficient photocharging and N_2 reduction?

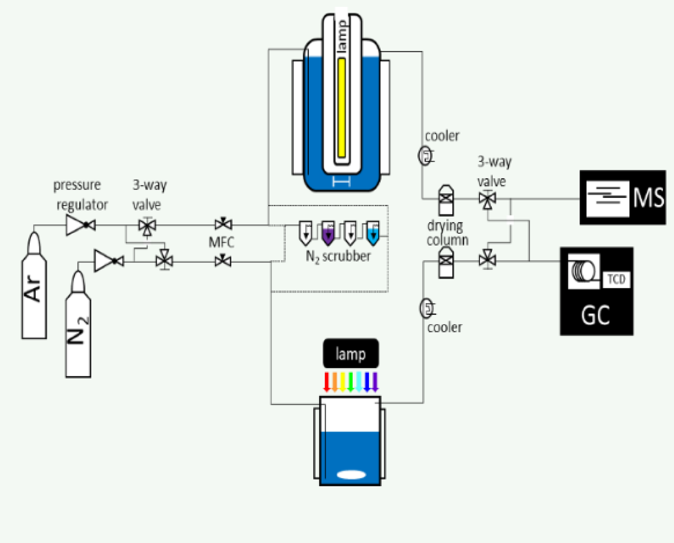


Work package 2

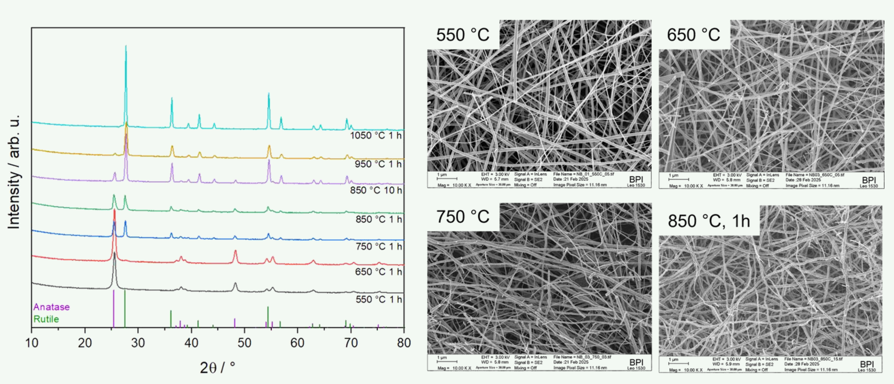
Photocharging, dark N_2 reduction

- systematic studies of charging conditions with different “waste” hole scavengers
- studying temperature (photothermal) effects
- investigating wavelength dependence, especially in cycling experiments





Photocharging / dark NRR of electrospun TiO_2 nanofibers



- Comparing aerogels with electrospun nanofibers
- Nanofibers will also be provided for gas phase photocharging and NRR: Open cell structure of the fiber mats beneficial compared to aerogels?

Work Package 5

Cooperation in the PP 2370

- Bloh/Streb/Strunk → Connecting with gas phase NRR/NOR
- Devi/Harms/Wark Apfel/Giusto/Oschatz → Charging other materials
- Klemm/Krüger/Risch → Connecting to electrocatalysis
- Jacob/Sharp/Zhang → Connecting to cathodes
- Streb/Ziegenbalg → Photoelectro-catalysis
- Browne/Exner/Oschatz → Porous Liquids
- Andronescu/KühneMazare → Exchange of materials / Reference data for PEC benchmarking

Research Objectives of FP2

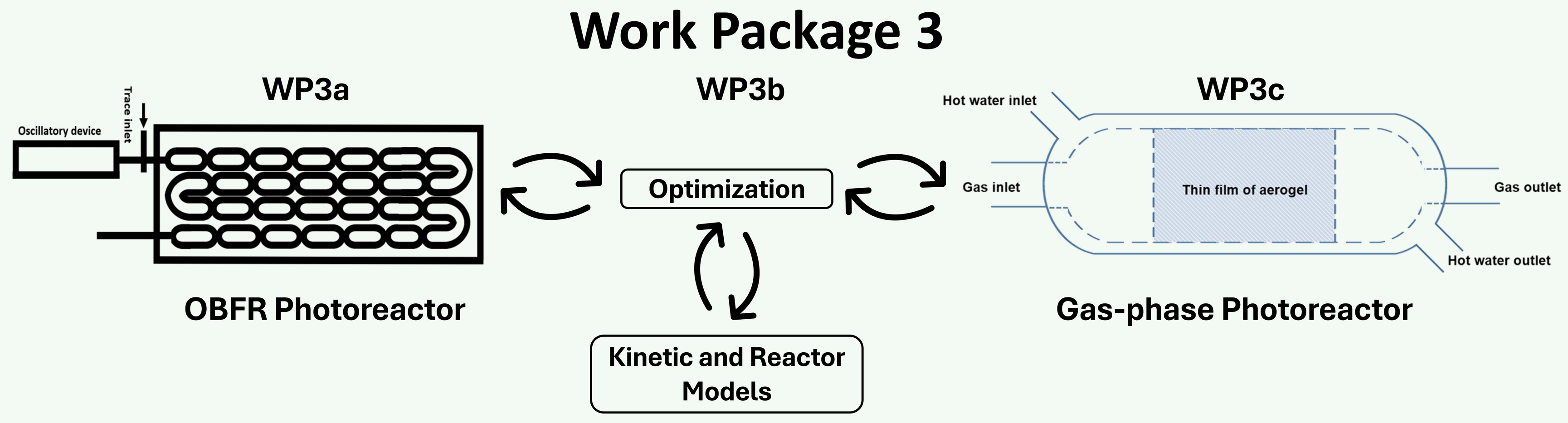
1. synthesis and characterization of photochargable TiO_2 aerogels with **adjustable properties**
2. development of **upscaling** and **shaping** procedures
3. synthesis and characterization of photochargable **TiO_2-fibers** with adjustable properties
4. systematic study of **influence of reaction conditions on different materials** for photocharging and nitrogen reduction efficiency
5. development and characterization of **liquid- and gas-phase** photocharging and N_2 reduction reactors
6. kinetic and reactor modeling for photocharging and nitrogen reduction
7. demonstration **of simultaneous reduction of N_2 and CO_2 towards urea**

Work Package 4

Feasibility study on urea production with photocharged TiO_2

- Is it possible to reduce CO_2 with photocharged TiO_2 aerogels?
- Thus, is it possible to simultaneously reduce CO_2 and N_2, to form urea?
- Compare gas phase vs. liquid phase operation.
- Study influence of CO_2/N_2 ratio, total system pressure, aerogel loading/mass, degree of initial photocharging, operation mode, reactor type etc.

Work Package 3



Liquid-phase solar photocharging reactors

- oscillatory baffled flatbed reactor for efficient solar photocharging
- online monitoring of photocharging

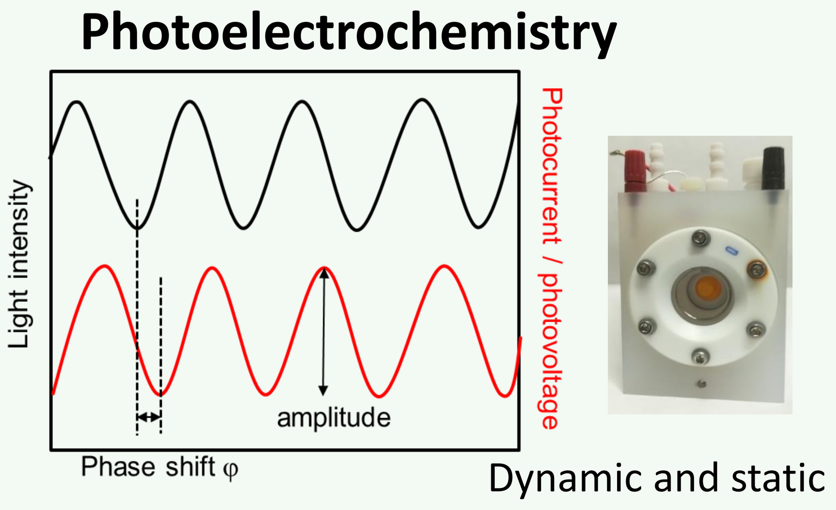
Model-supported optimization of process conditions

- kinetic and reactor models
- model-guided optimization

Gas-phase photocharging reactor

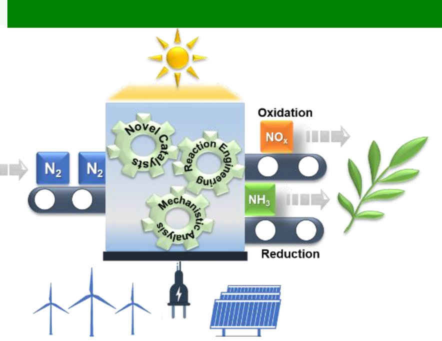
- systematic studies based on preliminary results from FP1
- investigating photocharging time, photon flux/photon irradiance, aerogel/fiber mats, and filling height

Photoelectrochemistry



Dynamic and static photoelectrochemical methods

Contact



Roland Marschall
Phone: +49-921-552776
www.marschall.uni-bayreuth.de
Roland.marschall@uni-bayreuth.de
Research Group Marschall

Barbara Milow
Phone: +49-2203-601-3537
www.dlr.de/fm
Barbara.Milow@dlr.de
Barbara Milow

Dirk Ziegenbalg
Phone: +49-731-50-25703
www.uni-ulm.de/ciw
Dirk.Ziegenbalg@uni-ulm.de
Dirk Ziegenbalg