

Challenges and Innovations in Photo/Electrocatalytic Energy Conversion

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9:00 am – 1:10 pm
27th of April 2021

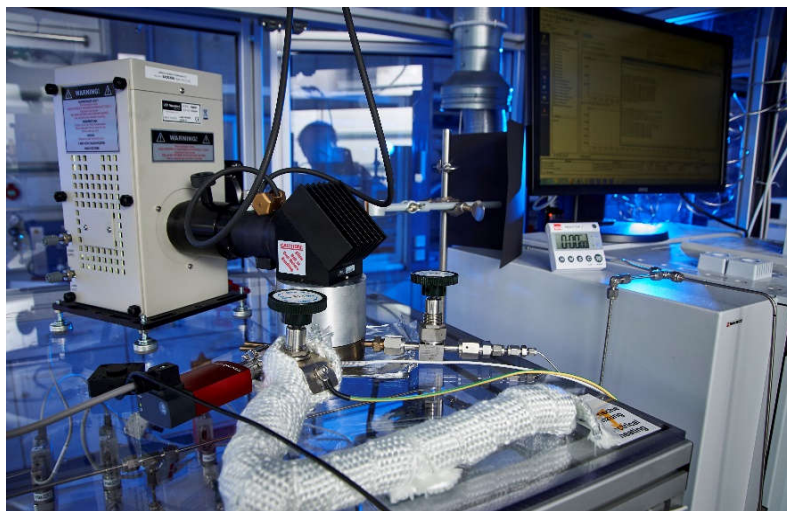


photo: laboratory department Strunk

Challenges and Innovations in Photo/Electrocatalytic Energy Conversion

Chemical reactions driven directly by (sun)light or by regeneratively produced electricity bear the potential to store renewable energy in chemical bonds. Examples are the production of hydrogen by the splitting of water, or reactions of carbon dioxide and water to hydrocarbons and oxygenates. This provides a convenient solution to store the energy for longer periods of time, and in such a way that it is compatible with current infrastructure for fuel transport and distribution (pipelines, gas stations etc.).

Although a large variety of approaches, materials and processes are intensively studied in world-wide initiatives, no industrial scale solution has yet been developed. This is not surprising, considering that the involved reactions are kinetically and thermodynamically highly challenging, and that they likely follow very complex reaction mechanisms.

In this workshop, renowned experts from Ulm University and the Leibniz Institute for Catalysis present their latest innovations in this intriguing scientific field, aiming to overcome persistent and newly found challenges to develop feasible chemical energy conversion processes.

You are welcome to join *via*

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Meeting-ID: [657 7356 1678](https://uni-rostock-de.zoom.us/j/65773561678?pwd=YnQ2dk5NVjB-SUFJGT2U1a3BOZzF4Zz09)
Kenncode: 999830

Scientific Program

- 9:00 am Prof. Radim Beránek (Planary)
P1 Photo(electro)catalysts with enhanced activity, selectivity, and stability: challenges and examples
Ulm University
- 9:50 am Hilario Huerta (Lecture)
L1 Development of catalyst/semiconductor assemblies for efficient photocatalytic CO₂ reduction
Leibniz Institute of Catalysis (Department Beller), Rostock
- 10:10 am Jun. Prof. Andrea Pannwitz (Keynote)
K Energy and Electron Transfer in Phospholipid Bilayers
Ulm University
- 10:40 am Break
- 10:50 am Prof. Sven Rau (Plenary)
P2 A new avenue for the optimization of molecular hydrogen evolving photocatalysts
Ulm University
- 11:40 am Dr. Nikolaos Moustakas (Lecture)
L2 How to influence product distribution in photocatalytic CO₂ reduction?
Leibniz Institute of Catalysis (Department Strunk), Rostock
- 12:00 pm Break
- 12:10 pm Dr. Annette Surkus (Lecture)
L3 Development of electrocatalysts for alkaline water electrolysis
Leibniz Institute of Catalysis (Department Francke), Rostock
- 12:30 pm Dr. Robert Francke (Planary)
P3 Combining Electrochemistry, Catalysis, and Modern Electrolyte Concepts for the Synthesis of Value-added compounds
Leibniz Institute of Catalysis, Rostock
- 1:10 pm End of Workshop

P1

**Photo(electro)catalysts with enhanced activity, selectivity, and stability:
challenges and examples**

Radim Beránek

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The development of photo(electro)catalytic systems capable of mimicking the natural photosynthesis by driving useful chemical transformations has attracted significant interest motivated by the need to meet various environmental concerns and to secure the future supply of clean and sustainable energy. The *activity*, *stability*, and *selectivity* of such systems is determined not only by the ability of materials to absorb light, but also by efficient separation of the photogenerated charges and their fast and selective reaction with substrates. The talk will discuss the challenges associated with the development of high-performance photo(electro)catalysts, based on selected examples from our recent work.^[1-3]

References:

- [1] C. Adler, D. Mitoraj, I. Krivtsov, R. Beranek, "On the Importance of Catalysis in Photocatalysis: Triggering of Photocatalysis at Well-Defined Anatase TiO₂ Crystals Through Facet-Specific Deposition of Oxygen Reduction Cocatalyst" *J. Chem. Phys.* **2020**, *152*, 244702.
- [2] I. Krivtsov, D. Mitoraj, C. Adler, M. Ilkaeva, M. Sardo, L. Mafra, C. Neumann, A. Turchanin, C. Li, B. Dietzek, R. Leiter, J. Biskupek, U. Kaiser, C. Im, B. Kirchhoff, T. Jacob, R. Beranek "Water-Soluble Polymeric Carbon Nitride Colloidal Nanoparticles for Highly Selective Quasi-Homogeneous Photocatalysis" *Angew. Chem. Int. Ed.* **2020**, *59*, 487.
- [3] C. Adler, I. Krivtsov, D. Mitoraj, L. dos Santos-Gómez, S. García-Granda, C. Neumann, J. Kund, C. Kranz, B. Mizaikoff, A. Turchanin, R. Beranek, "Sol–Gel Processing of Water-Soluble Carbon Nitride Enables High-Performance Photoanodes" *ChemSusChem*, **2021**, DOI: 10.1002/cssc.2021003

L1 Development of catalyst/semiconductor assemblies for efficient photocatalytic CO₂ reduction

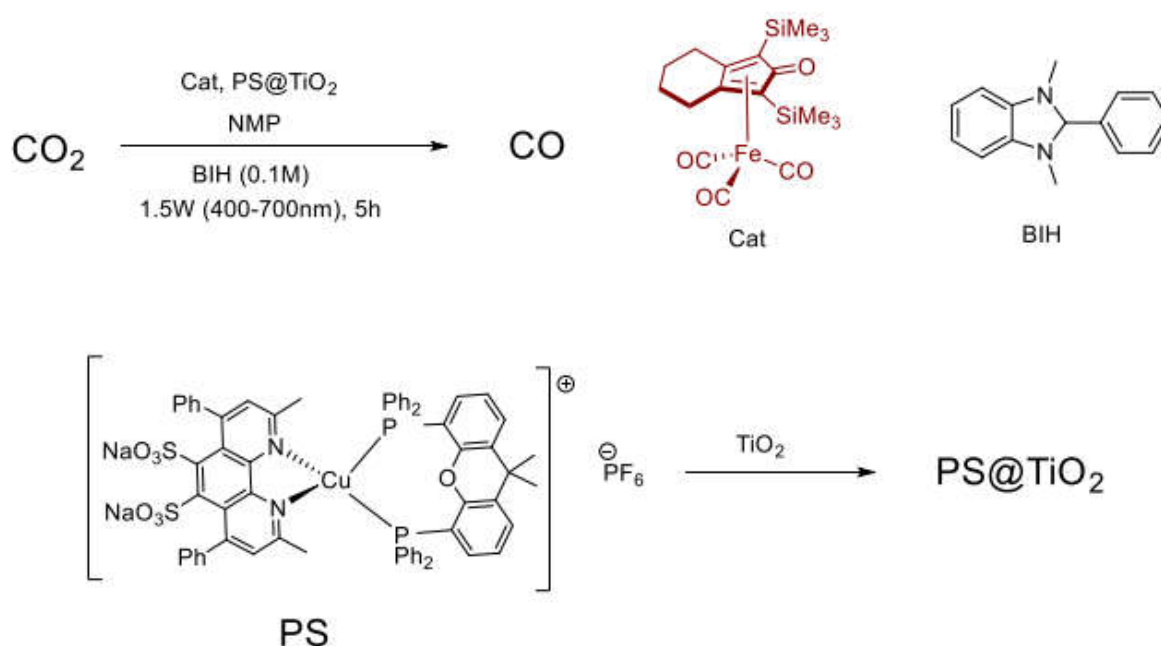
Hilario Huerta, Henrik Junge, Matthias Beller

Leibniz-Institut für Katalyse e. V., Albert-Einstein-Straße 29a, Rostock

Photocatalytic CO₂ reduction to valuable C1 and C2 chemicals has been a challenging task over the last decades. Efficient systems for this transformation using non-noble metal catalysts and photosensitizers are currently being investigated [1].

The use of heteroleptic copper (I) photosensitizers has been studied thoroughly and applied in proton photocatalytic reduction [2], furthermore, photosensitizer-Titanium dioxide composites have shown a positive outcome for this transformation [3].

Herein, we present the potential application of these heterogeneous materials as photosensitizers towards an efficient CO₂ photoreduction to CO using only non-noble metals and BIH as sacrificial reductant.



Heterogeneous photocatalytic system

[1] Green Chem. **2017**, 19, 2356

[2] Angew. Chem. **2013**, 125, 437

[3] ChemCatChem. **2014**, 6, 82

K

Energy and Electron Transfer in Phospholipid Bilayers

Andrea Pannwitz

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In natural photosynthesis the light harvesting complexes and photosystem I and II assemble in a in the thylakoid membrane to perform light harvesting, energy transfer, and electron transfer to a final catalyst. The assembly in the membrane enables for compartmentalization of reaction spaces and the establishment of transmembrane proton gradients. In this talk, the supramolecular functionalization of biomimetic phospholipid bilayers with light active and photoredox active molecular species will be shown using spectroscopic, microscopic and computational techniques.^[1,2]

References:

- [1] A. Pannwitz, H. Saaring, N. Beztsinna, X. Li, M. A. Siegler, S. Bonnet, *Chem. – A Eur. J.* **2021**, *27*, 3013–3018.
- [2] A. Pannwitz, D. M. Klein, S. Rodríguez-Jiménez, C. Casadevall, H. Song, E. Reisner, L. Hammarström, S. Bonnet, *Chem. Soc. Rev.* **2021**, DOI 10.1039/D0CS00737D.

P2

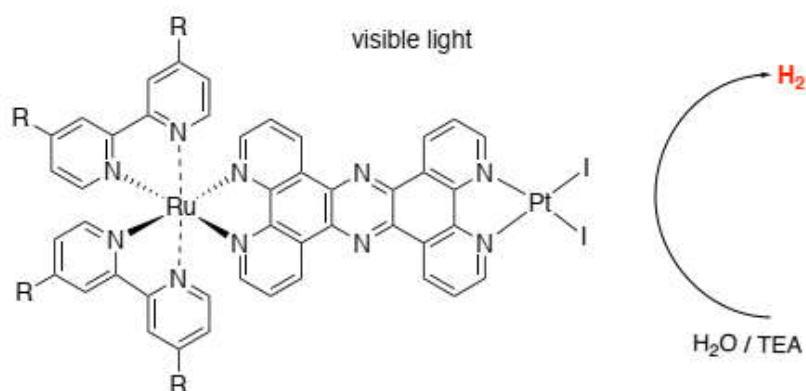
A new avenue for the optimization of molecular hydrogen evolving photocatalysts

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Benjamin Dietzek, Leibniz Institute of Photonic Technology, Albert-Einstein-Strasse
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Photocatalytic watersplitting can be utilised with molecular photocatalysts. Ruthenium complexes with related tpphz type ligands play an important role within this field. [1,2] Through a series of model catalysts we now can differentiate between several important structural aspects influencing the photocatalytic activity.

One very limiting factor for applying molecular catalysts is their propensity to loss of activity. Nature has devised elaborate repair systems restoring catalytic activity of biological molecular defined catalysts, i. e. enzymes. [3] We present here a new concept on repairing the below described molecular photocatalyst and thereby boosting catalytic performance.



Photocatalyst for hydrogen production which can be repaired

- [1] M.G. Pfeffer, T. Kowacs, M. Wächtler, J. Guthmuller, B. Dietzek, J.G. Vos S. Rau, *Angew. Chem. Int. Ed.* **2015**, 54(22), 6627-6631
- [2] D. Imanbaew, J. Lang, M. F. Gelin, S. Kaufhold, M. G. Pfeffer, S. Rau, C. Riehn, *Angew. Chem. Int. Ed.*, **2017**, 56(20), 5471-5474
- [3] M. Pfeffer, C. Mueller, E. Kastl, J. Habermehl, M. Wächtler, M. Schulz, D. Chartrand, F. Lavadière, P. Seeber, S. Kupfer, S. Gräfe, G. Hanan, J. Vos, B. Dietzek, S. Rau submitted **2021**

L2

How to influence product distribution in photocatalytic CO₂ reduction?

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The hydrocarbon yields in the photocatalytic reduction of CO₂ remain far from being considered attractive for any large-scale realization of the process.^[1] As the exact reaction pathway has not yet been conclusively illustrated,^[2] reliable and reproducible data should be collected to identify the products' yields and selectivity trends towards the unveiling of the underlying mechanism. This can only be achieved when considering and eliminating any source of carbon-containing impurities which can lead to an overestimation of the photocatalyst's performance. As an example, leftover solvents on the surface of the photocatalyst will potentially react faster than CO₂ under light irradiation as the latter exhibits higher thermodynamic stability than the adsorbed C-impurities.

While achieving high product yields is the main focus of most published studies (oftentimes not backed-up by blank measurements), product distribution and selectivity do not receive much attention. In the industrial realization of CO₂ photoreduction, a carefully selected set of conditions will have to be applied for the process to fulfill simultaneously high product yields and high selectivity towards the desired hydrocarbon for the respective application. High yields combined with low selectivity can lead to a more costly and more time-consuming process as gas separation techniques will have to be applied.

In this work, the necessity of applying high-purity conditions in CO₂ photoreduction and the influence of the experimental parameters (e.g., the addition of H₂ or H₂O in the reaction mixture) on product distribution will become evident through the presentation of a series of experiments of our group using metal-oxide based photocatalysts.

Development of electrocatalysts for alkaline water electrolysis

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Utilization of renewable energy sources such as wind or solar energy is strongly related with the issue of storage and transport of this intermittently provided energy. Transformation of this energy to hydrogen or synthetic natural gas is considered to possess the highest potential regarding long-term storage capacity as well as transportation over long distances. Moreover, the energy stored in hydrogen can be converted back to electricity by fuel cells on demand.

Water electrolysis represents the first and most essential step in conversion of electricity to hydrogen or synthetic natural gas. Currently, this key technology is accomplished with either alkaline or PEM electrolysis. Thereby, the performance is strongly dependent on the type of electrocatalyst used. As basic requirements, a low overpotential as well as high current densities and long-term stability are identified. However, noble metals as main components shall be replaced to conserve resources and to decrease the price.

Currently, great efforts have been achieved towards the replacement of noble metal-based materials by transition metal compounds containing iron, cobalt, or nickel. In this context, recent results concerning the development of such electrocatalysts for alkaline oxygen evolution reaction (OER) are presented.^[1] Material characterization and in-situ spectroelectrochemical studies have given advice to the active parts of the catalyst.^[2] A material based on cobalt and copper, could be patented by EVONIK.^[3]

While several active, noble metal-free materials have already been identified for alkaline water oxidation, acidic PEM electrolysis is still carried out with IrO₂ or RuO₂. The low pH value and the high anodic potential cause quick corrosion of the other materials.^[4, 5] Therefore, in two projects as part of the National Hydrogen Strategy 2020 ("Hydrogen Republic Germany"), we will try to significantly reduce the iridium content through methods such as aerogel formation and the targeted generation of single atom centers.

References:

- [1] M. Polyakov, A.-E. Surkus, A. Maljusch, S. Hoch, A. Martin, *ChemElectroChem* **2017**, *4*, 2109-2116; Impact of the Co:Cu Ratio in CoCu-Containing Oxidic Solids on their Activity for the Water-Splitting Reaction.
- [2] D. Hollmann, N. Rockstroh, K. Grabow, U. Bentrup, J. Rabeah, M. Polyakov, A.-E. Surkus, W. Schuhmann, S. Hoch, A. Brückner, *ChemElectroChem* **2017**, *4*, 2117-2122; From the Precursor to the Active State: Monitoring Metamorphosis of Electrocatalysts During Water Oxidation by In Situ Spectroscopy.
- [3] A. Maljusch, A. Martin, M. Polyakov, A.-E. Surkus, S. Hoch, M. Blug, W. Deis, Verfahren zur Herstellung eines in der Wasseroxidation einsetzbaren Elektrokatalysators, 2015E00266, EP2017/074926, WO2018/065339 A1.
- [4] A.-E. Surkus, N. Rockstroh, H. Junge, M. Beller; **2018**, Studie im Auftrag der Siemens AG; Studie zur weltweiten Verfügbarkeit von Iridium für Katalysatoren zur Sauerstoffentwicklung in Elektrolyseuren und Potentialabschätzung entsprechend des aktuellen Stands von Forschung und Entwicklung zur Reduzierung bzw. Verhinderung des Iridium-Einsatzes in Protonenaustauschermembran-Elektrolyseuren.
- [5] F. M. Sapountzi, J. M. Gracia, C. J. Weststrate, H. O. A. Fredriksson, J. W. Niemantsverdriet, *Progress in Energy and Combustion Science* **2017**, *58*, 1–35; Electrocatalysts for the generation of hydrogen, oxygen and synthesis gas.

P3

Combining Electrochemistry, Catalysis, and Modern Electrolyte Concepts for the Synthesis of Value-added compounds

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Electrosynthesis is frequently presented as an intrinsically sustainable, safe and efficient method [1]. While this is indeed often the case, this assessment cannot be easily generalized, since a number of challenges need to be addressed on the way to more efficient and truly sustainable processes. These challenges comprise the necessity for employing large amounts of supporting electrolyte additives along with the concomitant separation and waste issues [2]. A further problem is the kinetic inhibition of the heterogeneous electron exchange, which in many instances leads to a decreased selectivity and an increased energy consumption ('overpotential') [3]. Another challenge is the apparent restriction of electrosynthesis to redox reactions, which seems to exclude important redox-neutral processes such as rearrangements, cycloadditions and substitutions from the scope of applications [4]. In the present contribution, catalytic approaches and electrolyte concepts are discussed, which can help to overcome the abovementioned issues. For illustration of the principles, examples from our recent research activities are used [5]. These examples include applications of electrocatalysis and electrochemical catalysis, multifunctional electrolyte systems, and electrolysis carried out in microflow reactors.

References:

- [1] E. J. Horn, B. R. Rosen, Phil S. Baran, *ACS Cent. Sci.* **2016**, *2*, 302.
- [2] R. Francke, *Chimia* **2020**, *74*, 49.
- [3] R. Francke, B. Schille, M. Roemelt, *Chem. Rev.* **2018**, *118*, 4631.
- [4] R. Francke, R. D. Little, *ChemElectroChem* **2019**, *6*, 4373.
- [5] a) A. F. Roesel, M. Ugandi, N. T. T. Huyen, M. Majek, T. Broese, M. Roemelt, R. Francke, *J. Org. Chem.* **2020**, *85*, 8029.
b) A. F. Roesel, T. Broese, M. Májek, R. Francke, *ChemElectroChem* **2019**, *6*, 4229. c) B. Schille, N. O. Giltzau, R. Francke, *Angew. Chem. Int. Ed.* **2018**, *57*, 422–426. d) T. Broese, A. F. Roesel, A. Prudlik, R. Francke, *Org. Lett.* **2018**, *20*, 7483.