



**University of
Zurich** ^{UZH}

URPP LightChEC

Progress Report 2022

URPP LightChEC - Solar Light to Chemical Energy Conversion



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Table of Contents

1 Management Summary	4
2 Objectives	6
2.1 Objectives for the Reporting Year	6
2.1.1 Photocatalytic Water Reduction WRC and Photosensitizers (Prof. R. Alberto)	6
2.1.2 Visible-Light-Driven Water Oxidation Catalysts (WOCs) (Prof. G. R. Patzke)	6
2.1.3 Time resolved Spectroscopy of Artificial Photosynthetic Systems (Prof. P. Hamm)	7
2.1.4 Surfaces (Prof. J. Osterwalder)	7
2.1.5 Molecular Approaches to Renewable Energies (Prof. D. Tilley)	7
2.1.6 Computational Studies of Dynamic Properties of Water Oxidation (Prof. J. Hutter)	7
2.1.7 Surfaces / H ₂ and CO ₂ Storage and Conversion (Prof. K.-H. Ernst)	8
2.1.8 Electronic Structure of Materials for Solar-Water Splitting (Dr. A. Borgschulte)	8
2.1.9 Theoretical Chemistry (Prof. Sandra Luber)	8
2.2 Achieved Objectives and Milestones	8
2.2.1 Photocatalytic Water Reduction WRC and Photosensitizers (Prof. R. Alberto)	9
2.2.2 Visible-Light-Driven Water Oxidation Catalysts (WOCs) (Prof. G. R. Patzke)	9
2.2.3 Time resolved Spectroscopy of Artificial Photosynthetic Systems (Prof. P. Hamm)	10
2.2.4 Surfaces (Prof. J. Osterwalder)	10
2.2.5 Molecular Approaches to Renewable Energies (Prof. D. Tilley)	10
2.2.6 Computational Studies of Dynamic Properties of Water Oxidation (Prof. J. Hutter)	11
2.2.7 Surfaces / H ₂ and CO ₂ Storage and Conversion (Prof. K.-H. Ernst)	11
2.2.8 Electronic Structure of Materials for Solar-Water Splitting (Dr. A. Borgschulte)	11
2.2.9 Theoretical Chemistry (Prof. Sandra Luber)	11
2.3 Updated project planning	12
2.3.1 Photocatalytic Water Reduction WRC and Photosensitizers (Prof. R. Alberto)	12
2.3.2 Visible-Light-Driven Water Oxidation Catalysts (WOCs) (Prof. G. R. Patzke)	12
2.3.3 Time resolved Spectroscopy of Artificial Photosynthetic Systems (Prof. P. Hamm)	12
2.3.4 Surfaces (Prof. J. Osterwalder)	13
2.3.5 Molecular Approaches to Renewable Energies (Prof. D. Tilley)	13
2.3.6 Computational Studies of Dynamic Properties of Water Oxidation (Prof. J. Hutter)	13
2.3.7 Surfaces / H ₂ and CO ₂ Storage and Conversion (Prof. K.-H. Ernst)	14
2.3.8 Electronic Structure of Materials for Solar-Water Splitting (Dr. A. Borgschulte)	14
2.3.9 Theoretical and Computational Chemistry (Prof. S. Luber)	14

3 Research	15
3.1 Overview of the Activities in Research	15
3.1.1 Photocatalytic Water Reduction WRC and Photosensitizers (Prof. R. Alberto)	15
3.1.2 Visible-Light-Driven Water Oxidation Catalysts (WOCs) (Prof. G. R. Patzke)	16
3.1.3 Time resolved Spectroscopy of Artificial Photosynthetic Systems (Prof. P. Hamm)	18
3.1.4 Surfaces (Prof. J. Osterwalder)	19
3.1.5 Molecular Approaches to Renewable Energies (Prof. D. Tilley)	19
3.1.6 Computational Studies of Dynamic Properties of Water Oxidation (Prof. J. Hutter)	20
3.1.7 Surfaces / H ₂ and CO ₂ Storage and Conversion (Prof. K.-H. Ernst)	20
3.1.8 Electronic Structure of Materials for Solar-Water Splitting (Dr. A. Borgschulte)	21
3.1.9 Theoretical and Computational Chemistry (Prof. S. Luber)	22
4 Scientific Activities and Outreach	23
4.1 Scientific Activities Organized by LightChEC	23
4.2 Outreach Activities	24
5 Academic Career Development	25
5.1 Activities in Academic Career and Development	25
5.2 Gender Equality Development	26
6 Publications	27
7 Structures	29
8 Third Party Funds	30
8.1 Newly Approved Third-Party Funding of URPP Project Leaders	30
8.2 Ongoing Third-Party Funding of URPP Project Leaders	30
8.3 Newly funded projects within Profit-Center (PC) of the URPP	31
8.4 Ongoing projects within Profit-Center (PC) of the URPP	31

1 Management Summary

The year 2022 was a period of fruitful growth and increased activity for LightChEC. The new lab space on the UZH Irchel Campus became fully operational and the excellent infrastructure along with the close proximity of most groups enhanced both the quality of research projects and collaborations. Considerable progress was achieved with respect to the goals that were set for 2022. The Alberto group obtained new insights into the key issues of catalyst nuclearity and electronic structure through the synthesis of two new dinuclear cobalt polypyridyl water reduction catalysts. Their cobalt centers were connected via bipyridyl and pyrazyl units, respectively, thus disabling or enabling electronic coupling of the active cobalt centers. Comprehensive mechanistic analyses pointed to a beneficial kinetic effect of electronic interaction between the metal centers, along with enhanced stability, when compared to mononuclear analogues. Unprecedented mechanistic insights into novel molecular CO₂ reduction catalysts, namely rhenium-based tricarbonyl complexes with specially designed P/As-containing quinolone-derived ligands, were obtained by the Hamm group. A unique combination of (spectro-)electrochemical and time resolved spectroscopy methods revealed that the new ligands induced different pathways, involving isomerization after electron transfer, that differ notably from conventional rhenium tricarbonyl catalysts. The Patzke group made progress in the mechanistic understanding and engineering of the most prominent bimetallic combination in heterogeneous water oxidation catalysis, namely mixed metal Ni/Fe-catalysts. They applied an anionic engineering strategy to design sulfur-substituted Ni/Fe-coordination polymers, which were analyzed with *operando* X-ray absorption spectroscopy, and a clear link between sulfur doping and enhanced performance via facilitated formation of high valent Ni^{III/IV}-O-Fe^{III/IV} will open the door to further low-cost water oxidation catalysts. The Osterwalder group advanced the field of heterogeneous Ni/Fe oxygen evolution catalysts from a different angle by growing nickel ferrite-related films on Fe₃O₄(001) surfaces through Ni deposition, followed by annealing. The so obtained highly active Ni-doped Fe₃O₄(001) surfaces were investigated in detail and the presence of a highly overstoichiometric nickel ferrite-related surface was established. A new record for copper(I) oxide photoanodes for water splitting was set by the Tilley group through applying a skillful protocol based on thermal oxidation and etching strategies. This resulted in morphologically diverse copper(I) oxide crystals, and detailed analytical investigations brought forward a new connection between the outstanding photon-to-current efficiency and the selective crystal orientations. Further impressive progress on the experimental and theoretical characterization of copper-based catalytic systems was presented by the Hutter group for h-BN/Cu_{2-x}O/Cu(111) heterostructures. The structural features of these interfaces were elucidated through comparison of simulated microscopy and spectroscopy data to experimental results, and the emerging “nano-reactor” catalyst model is very impactful for further applications. The Luber group presented important advances in the calculation of electric circular dichroism and absorption spectra through extending the real time propagation implementation in the CP2K software to velocity (and symmetric) gauge. This newly enabled excited state dynamic schemes also for periodic systems in CP2K, thereby adding key features to the program. In the field of on-surface syntheses, the Ernst group performed intense studies on metal-organic frameworks, which were characterized with a wide range of microscopic and spectroscopic techniques. Beyond these investigations, they explored a new system that had hitherto been proposed on a theoretical basis, namely 1D-potassium squarate salts. Major analytical progress was reported by the Borgschulte group, regarding the study of hydrogenation processes on electrodes for hydrogen evolution. Photoemission studies using a hydrogen membrane approach enabled unprecedented insights into reactive metallic materials based on zirconium and vanadium with impact on hydrogen storage and transport applications.

These intense scientific activities were complemented by the LightChEC seminar activities involving renowned international speakers and by the ongoing LightChEC discussion meetings. The networking and exchange highlight of 2022 was the very successful LightChEC Summer School in Les Diablerets in September. All external and internal participants were fascinated by the rich and highly interactive program that was offered by the prominent international speakers and teachers. We warmly thank them for their insightful presentations and very instructive teaching sessions.

Concerning the financial situation, the ongoing support of LightChEC through the regular budget of many involved PIs enabled the support of all prominent outreach events along with a high level of analytical instrumentation and experimental activities. The large number of young researchers associated with LightChEC shows its established “lighthouse” function for the participating institutes and for UZH in general. This prominent position is reflected by manifold career advances of LightChEC PIs and young researchers, encompassing board memberships and success in key funding schemes.

The year 2022 was finally a period of change for LightChEC. On the occasion of his retirement in 2022, we express our sincere gratitude to Prof. Osterwalder for being with LightChEC from the very beginning as an inspirational founder, leader and outstanding interdisciplinary scientist. We are very grateful for his strong support as our connection to the world of physics. Further, Prof. Patzke took on the LightChEC leadership in 2022 and keeps strengthening its ties with the SATW, the AEE Suisse and the Daylight Academy. We thank Prof. Alberto for many years of successful leadership that turned LightChEC into an internationally powerful consortium. His outstanding commitment and creativity brought us to the great prospects of 2022.

2 Objectives

2.1 Objectives for the Reporting Year

In the following, we resume our objectives for 2022 in condensed form and proceed with the results during the reporting year in the next section.

2.1.1 Photocatalytic Water Reduction WRC and Photosensitizers (Prof. R. Alberto)

Water / CO₂ Reduction Catalysts

- Extending dual-core WRCs to cyclic systems based on the pyrphrines and acyclic systems based on mono-anionic bis-pyridyl-nitrile ligands. Combination of advantages of acyclic poly-pyridyl and cyclic pyrphyrin-type ligands.
- Photocatalytic efficiencies of these catalysts for CO₂ and water reduction, electrochemical properties.
- Conjugating anchoring groups to terminal functionalities.

Photosensitizers

- Exchanging the apical halido or hydroxo ligands with electron acceptors and other functional systems.
- Assessing the photo- and electrochemical properties of these Re₆S₈-type clusters as a function of additional apical ligands, solvent, and other physico-chemical parameters.
- Determination of reductive and oxidative quenching with each photosensitizer.
- Introducing anchoring groups to the apical sites for surface grafting.

Further objectives

- Investigations of the full water splitting cell from the collaboration with the CFSO GmbH company.
- Using this setup for grafting our WRC on the photocathode side of the cell.
- Assessing efficiencies of the model and our own systems for H₂/O₂ formation.

2.1.2 Visible-Light-Driven Water Oxidation Catalysts (WOCs) (Prof. G. R. Patzke)

- We will further develop our operando methodology towards a precise understanding of the role of the non-metal centers in chalcogenide-based electrocatalysts for water splitting and the influence of anionic substitution will be investigated in particular, along with mechanistic and DFT studies.
- We will set out to develop new routes for the growth of transition metal carbodiimides as catalysts for the oxygen evolution and reduction reactions (OER/ORR) on conductive nanosheet substrates, especially reduced graphene oxide (rGO) or carbon nanotubes (CNTs).
- We will set out to functionalize and immobilize molecular transition metal water oxidation catalysts on electrode surfaces and we will also start to explore the potential of catalysts for urea oxidation or other alternative processes such as replacement of the OER half reaction with the catalytic decomposition of water pollutants (planned joint investigations with Ocean University of China (Quingdao) via a visiting CSC PhD scholarship in 2022 (Dan Zhang).
- We plan to strengthen the position of the URPP LightChEC in the Swiss academic and industrial landscape through G. R. Patzke's memberships in the Swiss Academy of Technical Sciences (SATW), in the Daylight Academy (DLA) and in the scientific advisory board of the AEE Suisse.

2.1.3 Time resolved Spectroscopy of Artificial Photosynthetic Systems (Prof. P. Hamm)

- In the upcoming year, we will focus on CO₂ reduction, continuing from the current stage of the project that is discussed below. That is, we will consider the second reduction step in the presence of CO₂, in which case CO₂ binds to the catalyst, gets reduced once, and forms a tri-carbonyl complex, according to proposals in the literature. All these intermediates should reveal very characteristic bands in the IR spectrum and should be detectable by transient IR spectroscopy. To that end, we will construct a measurement setup, in which the Ru-catalyst is pre-reduced once in an electrochemical cell. It then will be mixed with all other reaction components in a rapid-mixing device that will also serve as the IR measurement cell.
- Once established for the currently studied catalytic system, we will extend this approach to a wide variety of molecular CO₂ reduction catalysts that might also produce different products (e.g., CO, formate).

2.1.4 Surfaces (Prof. J. Osterwalder)

- Completion of the data analysis for the Ga₂O₃ growth study on Cu₂O(111) and paper writing.
- Growth study of Ga₂O₃ on Cu₂O(110) that should provide a better lattice match to β-Ga₂O₃.
- Continuation of the study of Ni monolayer and sub-monolayer films on Fe₃O₄(001) and the formation of the Ni-ferrite phase via annealing. Structural characterization is already advanced, measurements of the electronic properties are carried out in 2022.
- The two projects will constitute the main content of the PhD thesis of Mert Taskin who will finish his degree at the end of 2022.
- Measurements of the photoexcited charge transfer dynamics in the h-BN/Cu_{2-x}O/Cu(111) system grown by oxygen intercalation into h-BN/Cu(1111).

2.1.5 Molecular Approaches to Renewable Energies (Prof. D. Tilley)

- Sb₂Se₃: alternative synthesis methods for this material will be explored, such as hydrothermal synthesis, and selenization of thermally evaporated thin films of antimony metal. The improvement of the photovoltage will continue to be explored via various methods.
- Impedance spectroscopy: we continue to refine our model and understanding based on the study of different materials. This project will mesh more with the other group projects in the future, helping to understand different Sb₂Se₃ structures, as well as anchored molecular electrocatalysts.
- Immobilization of molecular catalysts via host-guest interactions: we will learn which solvent systems work best for the quartz crystal microbalance (QCMB) and investigate binding and de-binding of guest molecules in anchored hosts on both gold and oxide materials. We will begin our investigations on electrochemical QCMB, to measure mass changes during electrosynthetic reactions.

2.1.6 Computational Studies of Dynamic Properties of Water Oxidation (Prof. J. Hutter)

- We plan to use the generated machine learning potential for the metal-water systems to study water structure and dynamics under potential of zero charge for the different interfaces.
- We will apply path-integral molecular dynamics to address the probability of self-ionization events of water at the interface with metals like Rh, Pd, Ag, Ir, Pt, and Au (possibly also at electrified surfaces).

- The adsorption of metal atoms and metal clusters at the hBN/Cu₂O(111) interface will be considered also as intercalated between the oxide and the overlayer. We will focus on specific reactive processes and on the effects of confinement at the interface.
- We still aim at the simulation of the dynamics of molecules at the interface under the influence of time-dependent fields. The focus is on the application of excited state dynamics, which has been successfully applied in literature to study light-induced processes of aqueous metallic nanoparticles.

2.1.7 Surfaces / H₂ and CO₂ Storage and Conversion (Prof. K.-H. Ernst)

- Study the adsorption/desorption and coordination/activation of CO₂ and CO on MOFs by using FTIR spectroscopy, TDS and possibly ToF-SIMS: We will use isotopically labeled CO₂ and CO to distinguish the adsorbate from the CO-based MOF. Once the adsorption/desorption is understood, hydrogenation using atomic and molecular hydrogen.
- On-surface synthesis of MOFs on graphene/Ru(0001) and creation of 2D MOFs on thin insulating films, such as MgO on Ag(100), in order to understand the properties of the low-D MOFs unperturbed by the metal surface.
- Publication of the synthesis of MOFs on Au(111) along with the magnetism data: Quantitative analysis of the XAS/XLD/XMCD spectra using the real-space crystal-field software "multiX".

2.1.8 Electronic Structure of Materials for Solar-Water Splitting (Dr. A. Borgschulte)

- Continuation of solar water splitting probed by magneto-optics with focus on metal hydride forming electrodes.
- Photoemission studies on hydrogenation of hydrogen evolution reaction electrodes using the hydrogen membrane approach focus on reactive materials such as V, ZrV₂, and classical materials such as Ni and Fe, and Co (-oxides) using hard X-ray photoelectron spectroscopy combined with impedance spectroscopy.
- Continuation of hydrogenation of gaseous organic compounds with focus on selective conversion of ethylene to specific liquid alkanes (jet fuel).

2.1.9 Theoretical Chemistry (Prof. Sandra Luber)

- Extension of the excited state dynamics approach to include spin-orbit coupling.
- Study of excited state dynamics of molecules related to artificial photosynthesis.
- Implementation of efficient algorithms in order to improve convergence of the excited state calculations for non-adiabatic dynamics.

2.2 Achieved Objectives and Milestones

As indicated in the management summary, 2022 was a very fruitful year for LightChEC with exciting research results, so that the proposed objectives could be fulfilled to a large extent. Further details are then provided in section 3 of this report.

2.2.1 Photocatalytic Water Reduction WRC and Photosensitizers (Prof. R. Alberto)

Water / CO₂ Reduction Catalysts

- Two bis-bipyridyl moieties were coupled via bipyridyl and pyrazyl moieties. The mechanisms have been elucidated. TONs unexpectedly did not increase substantially but the overpotential was reduced by 150 mV [15].
- A wide variety of polymerized and monomeric WRCs were prepared and investigated in homogenous and heterogeneous photo- and electrocatalysis (Rahn, F. *Photo- and Electrocatalysis with Polymerised Water Reduction Catalysts*, Universität Zürich, 2022).
- Cooperation with CFSO GmbH was initiated for the preparation of a full water-splitting cell. Project is continuing with Empa.
- The performance of [Mo₃S₄]⁴⁺ WRCs coordinated to tridentate ligands and comprising a heterometal "M", i.e. [Mo₃M'(L₃)₃S₄]⁴⁺ was not achieved due to the complexity of the synthesis (MSc thesis Iva Walz).

Photosensitizers

- Challenging high temperature syntheses of core-cluster type [M₆E₈], e.g. [Re₆S₈Br₆]⁴⁺ were achieved and structurally characterized.
- Physico-chemical properties were established showing that these clusters would be excellent photosensitizers.
- Due to time constraints, grafting of these photosensitizers on the (new) semiconductors as photocathodes was not achieved.

Further objectives

- The full water-splitting cell from the collaboration with CFSO GmbH was not yet achieved but it is ongoing. The dielectricum is the main problem. Accordingly, the other objectives in this context are delayed as well.

2.2.2 Visible-Light-Driven Water Oxidation Catalysts (WOCs) (Prof. G. R. Patzke)

Design and understanding of chalcogenide-based electrocatalysts for water splitting

- Based on our published study on cobalt phosphide-based catalysts for the oxygen and hydrogen evolution reactions (OER/ORR) [16], we proceeded with the exploration of structure-activity relationships and their underlying reactions mechanisms. New insights into mixed transition metal coordination polymer catalysts for the OER were obtained. As planned, we further developed our *operando* studies along with an in-depth investigation of sulfur tuning of the target materials to assess the influence of non-metal centers on the OER activity [17] (cf. section 3.1). Concerning the hydrogen evolution reaction (HER) performance of transition metal sulfides, we have launched *operando* studies and progress has been made in their operational stabilization through structural design (see objectives for the coming period).

Exploration of transition metal carbodiimides as catalysts for the oxygen evolution and reduction reactions (OER/ORR)

- We have optimized cobalt carbodiimide (CoNCN) catalysts with respect to synthetic and structural parameters for competitive OER performance (section 3.1). Further results have been obtained with respect to their combination with carbon nanotubes (CNTs) for the ORR. A complete account of this research field will be given in the forthcoming report.

Immobilization and exploration of molecular catalysts for water oxidation and alternative oxidative processes

- Instead of molecular photoelectrodes, our focus in 2022 was placed on the planned research of Dan Zhang (visiting CSC PhD Scholarship from Ocean University of China (Qingdao)) on the catalytic removal of acrylamide as a representative organic pollutant in combination with energy saving HER processes. Progress was made in the synthesis of Ag-doped Ni₂P nanosheets on Ni foam as a bifunctional catalyst that drives both processes with promising performance (cf. section 3.1.2).

2.2.3 Time resolved Spectroscopy of Artificial Photosynthetic Systems (Prof. P. Hamm)

- We investigated the photophysics and photochemistry of a series of molecular CO₂ reduction catalyst with the help of time-resolved IR spectroscopy and accompanying, more “traditional” electrochemical methods. The compounds include trans(Cl)-[Ru(bpy)(CO)₂Cl₂] as well as **Re-P** and **Re-As**, the latter of which are described in more detail below.
- Regarding the construction of a measurement setup, in which the CO₂ catalyst is pre-reduced in an electrochemical cell before it enters the time-resolved experiment, little progress has been achieved.

2.2.4 Surfaces (Prof. J. Osterwalder)

- The data analysis for the Ga₂O₃ growth study on Cu₂O(111) has been completed and figures for a publication have been prepared.
- The Ga₂O₃ growth study on Cu₂O(110) has been completed, and photoelectron diffraction data indicate higher crystalline order than for growth on Cu₂O(111).
- Ni-ferrite-like films were grown on Fe₃O₄(001) by depositing Ni metal onto the bare magnetite surface and subsequent annealing. A paper focusing on the temperature-dependent interdiffusion has been submitted, a second paper on the evolution of the electronic structure is in preparation.
- The PhD thesis of Mert Taskin is close to completion.
- A paper on the measurement of photoexcited charge transfer dynamics in the h-BN/Cu₂O/Cu(111) system grown by oxygen intercalation into h-BN/Cu(111) has been submitted.

2.2.5 Molecular Approaches to Renewable Energies (Prof. D. Tilley)

- Sb₂Se₃: objectives were achieved. Both hydrothermal synthesis and selenization of thermally evaporated thin films of antimony metal yielded photoactive material with decent performance. Both works will yield a paper in the next year.
- Impedance spectroscopy: objectives were achieved. We are still trying to conclusively assign an RC element from the data, but we are able to advance and understand our materials even without this detailed knowledge. The impedance work has expanded onto other projects such as the Sb₂Se₃ photocathodes as well as the anchored molecular electrocatalysts.
- Immobilization of molecular catalysts via host-guest interactions: objectives were achieved. We carried out extensive investigations with the quartz crystal microbalance (QCMB) with regards to stability in different solvents as well as binding and de-binding of guest molecules in anchored hosts on both gold and oxide materials. Fundamental investigations of the ALD TiO₂ layer with QCMB are still underway.

2.2.6 Computational Studies of Dynamic Properties of Water Oxidation (Prof. J. Hutter)

- We generated and applied model interaction potentials for large scale simulation of liquid water/solid material interfaces.
- We refined the characterization of the h-BN/Cu_{2-x}O/Cu(111) heterostructure thus providing a reliable model consistent with the experimental findings.
- We concluded the work on the dynamic processes triggered by the co-adsorption of formic acid and water on the rutile TiO₂ surface.

2.2.7 Surfaces / H₂ and CO₂ Storage and Conversion (Prof. K.-H. Ernst)

- Due to substantial repair of apparatus the FTIR studies on CO₂ adsorption were postponed into 2023. Instead, we studied 1-dimensional chiral metal-organic MOFs.
- The on-surface synthesis of metal-organic frameworks has been intensively studied. In addition, we studied a new materials system, namely the salt potassium squarate. These form 1-dimensional salts which had been only theoretically predicted before.
- The publication of the synthesis of MOFs on Au(111) along with the magnetism data: Quantitative analysis of the XAS/XLD/XMCD spectra is in preparation and will be submitted in spring 2023.

2.2.8 Electronic Structure of Materials for Solar-Water Splitting (Dr. A. Borgschulte)

- Continuation of solar water splitting probed by magneto-optics with focus on metal hydride forming electrodes: new results on magneto-chemical effects on Ni-electrodes for water splitting.
- Photoemission studies on hydrogenation of hydrogen evolution reaction electrodes using the hydrogen membrane approach focus on reactive materials such as V, ZrV₂: various papers published, highlight is "Bulk Thermodynamics Determines Surface Hydrogen Concentration in Membranes", published in *Adv. Inter. Mat.* [1].
- For classical materials such as Ni and Fe, and Co (-oxides) using hard X-ray photoelectron spectroscopy combined with impedance spectroscopy: Paper on Ni-electrodes submitted (see 3.1.8)
- Continuation of hydrogenation of gaseous organic compounds with focus on selective conversion of ethylene to specific liquid alkanes (jet fuel): Project running, first papers in preparation

2.2.9 Theoretical Chemistry (Prof. Sandra Luber)

- Extension of the excited state dynamics approach to include spin-orbit coupling: this objective has been achieved and was tested already on various small molecules.
- Study of excited state dynamics of molecules related to artificial photosynthesis: this work has been postponed since focus was shifted more to method development and implementations.
- Implementation of efficient algorithms to improve convergence of the excited state calculations for non-adiabatic dynamics: various algorithms have been implemented already and work in this direction is partly still ongoing.
- In addition to the points mentioned in 2.1.9, the real time propagation implementation in CP2K was extended to velocity (and symmetric) gauge, allowing now novel excited state dynamic schemes also for periodic systems in CP2K. This implementation has been made available in the CP2K program [6].

2.3 Updated project planning

The manifold research results of 2022 led to some new aspects of the project planning, as outlined below. Specific directions were newly emerging with high priority, but the general lines of research are continued on a very promising trajectory.

2.3.1 Photocatalytic Water Reduction WRC and Photosensitizers (Prof. R. Alberto)

Since the PI is retiring by the end of the spring semester 2023 and the group shrunk essentially to one PhD student who will start writing in the second half of 2023, the project planning is limited. A major task will consist in the knowledge and equipment transfer to the remaining groups, especially to Tilley's since it is closest to the project.

Water / CO₂ Reduction Catalysts and Photosensitizers

- Further support to the coworkers of CFSO GmbH to finalize a full water-splitting device.
- Preparing a full series of 3d, 4d and 5d complexes with our new tetradentate, mono- and di-anionic ligands. Explore their photophysical properties as new and more light-stable photosensitizers.
- Electro- and photocatalytic studies with selected examples of these complexes. Aim is to lower the overpotential.
- Finalize the exploration of dinuclear rhenium-bridged WRCs for communication between the two metal centers.

2.3.2 Visible-Light-Driven Water Oxidation Catalysts (WOCs) (Prof. G. R. Patzke)

- We plan to investigate **cobalt sulfide catalysts** for water splitting with special emphasis on regulating their restructuring processes during HER via carbon protection strategies. A **feedback loop between operando monitoring and economic catalyst design** will be created to optimize performance and metal contents.
- We will construct Co- and higher, biphasic/layered metal organic framework (MOF)-**derived nanomaterials** with mixed 3d transition metals. Their post-treatment in combination with **non-metal (P, S) doping** will generate interesting electrocatalysts with tunable electronic structures and coordination environments.
- Our MOF-derived and related 3d transition metal-containing electrocatalysts will be subjected to **ultra long-time electrocatalytic tests** in combination with operando XAS characterizations at suitable intervals for **feedback loops** to connect **restructuring** processes with economic catalyst design.
- We will complete and publish our studies on phosphide-based bifunctional electrocatalysts for **acrylamide oxidation and hydrogen evolution catalysis**.

2.3.3 Time resolved Spectroscopy of Artificial Photosynthetic Systems (Prof. P. Hamm)

- As a methodological development, we plan to synchronize two existing laser setups in a way that all relevant timescales from picoseconds to seconds can be covered in one and the same instrument.
- We will continue to investigate the full (!) reaction cycle of molecular CO₂ reduction catalyst, predominantly with the help of time-resolved IR spectroscopy on all relevant timescales from picoseconds to seconds.

- This will include pre-reducing the CO₂ reduction catalyst in an electrochemical cell in order to be able to investigate the time-evolution of each individual electron separately in these multi-electron processes.

2.3.4 Surfaces (Prof. J. Osterwalder)

- Submission of a paper on the evolution of the electronic structure in Ni-ferrite-like films grown on Fe₃O₄(001).
- Completion of the PhD thesis of Mert Taskin.

2.3.5 Molecular Approaches to Renewable Energies (Prof. D. Tilley)

- Sb₂Se₃: improve the photovoltage through both interface and bulk treatments. We will investigate the combination of sulfurization (targeting bulk defects) and metal ion treatment (targeting surface/interface defects) to improve the photovoltage of Sb₂Se₃/TiO₂ heterojunction photocathodes.
- Impedance spectroscopy: we will gain insight into the unknown process (RC element) by carrying out impedance spectroscopy in the dual working electrode configuration, which is highly novel and could be a powerful technique for assignment of different elements in multi-process thin films.
- Immobilization of molecular catalysts via host-guest interactions: novel molecular catalysts and host molecules will be synthesized for improved stability and/or recycling. Fundamental studies regarding charge transfer between electrodes and host-guest bound molecular electrocatalysts will continue.

2.3.6 Computational Studies of Dynamic Properties of Water Oxidation (Prof. J. Hutter)

- 2D/Metal-oxide-catalyzed reactions studied in confined space underneath hexagonal boron nitride on Cu(111): We will address the oxygen spillover phenomena, i.e., the diffusion of oxygen to the metal's surface from either the gas phase adsorbs on the oxide which then spill over, or from the oxide, resulting in a further reduction. We will determine the relative stability of activated reactants and intermediates at the interface, investigating the dynamics of the active sites. The identified species will be characterized by calculating electronic properties, and the spectroscopic signatures, to be compared with experimental data. By combining AIMD with metadynamics, we will study processes like the carbon monoxide oxidation, selectivity and activity of carbon dioxide reduction, and the oxidative dehydrogenation of alcohols to carbonyl compounds. The method is able to discriminate among competitive reaction pathways, estimate the underlying free energy surfaces and thus disclose the fundamental aspect that determine functionality, performance, selectivity.
- Investigation of MoS₂/g-C₃N₄, a 2D/2D heterostructures, which have shown to be composite catalyst with enhanced photocatalytic activity: In particular, we will characterize the band-edge position with respect to the lattice match, and its influence on the efficiency in light absorption and promotion of the segregation of photogenerated electrons from the hole at the interface. For this study we will use DFT-based electronic structure calculations in the ground and in the excited state.

2.3.7 Surfaces / H₂ and CO₂ Storage and Conversion (Prof. K.-H. Ernst)

- Synthesis of MOFs with even smaller ligands and magnetic atoms in order to enhance the magnetic exchange between the atoms.
- Formation of homochiral MOFs by using chiral ligands for enantioselective chemistry.
- Interaction of gases with MOFs.

2.3.8 Electronic Structure of Materials for Solar-Water Splitting (Dr. A. Borgschulte)

- Continuation of solar water splitting probed by magneto-optics with focus on metal hydride forming electrodes.
- Photoemission studies on classical materials such as Ni and Fe, and Co (-oxides) using hard X-ray photoelectron spectroscopy combined with impedance spectroscopy.
- Continuation of hydrogenation of gaseous organic compounds with focus on selective conversion of ethylene to specific liquid alkanes (jet fuel).

Structural and organizational objectives: application for projects

- SWEET (Renewable Fuels and Chemicals for Switzerland - reFuel.ch)
- SNSF Advanced Grants (Quantitative hydrogen surface imaging by high resolution electron recoil)

2.3.9 Theoretical and Computational Chemistry (Prof. S. Luber)

- Extend real time propagation schemes to the calculation of magnetic spectroscopic properties
- Derive schemes to study in detail conical intersections
- Apply our excited state dynamics approaches to systems of interest in the condensed phase

3 Research

3.1 Overview of the Activities in Research

3.1.1 Photocatalytic Water Reduction WRC and Photosensitizers (Prof. R. Alberto)

Molecular photosensitizers are still the limiting factor in homogeneous light-induced water reduction. In the course of a specialized Master thesis (*Iva Walz*), we finalized the full characterization of a series of $[\text{Re}_6\text{S}_8\text{X}_6]^-$ type clusters ($\text{X}=\text{halides}, \text{H}_2\text{O}$ or HO^-) with X -dependent charges. These clusters have excited state lifetimes in the microsecond-range and absorb light up to 540 nm, both depending on the nature of "X". Reductive quenching with various sacrificial electron donors is extremely fast, e.g. for 1-Methyl-4-phenylpyridinium $9.9 \cdot 10^9 \pm 5.2 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ or even $2.1 \cdot 10^{10} \pm 1.2 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]\text{Cl}_4$. Quenching is oxidative, i.e., the electron should be transferred to a WRC such as the Mo cluster or our standard cobalt complexes. Photocatalytic experiments under non-optimized conditions showed very slow H_2 evolution. However, in contrast to experiments with the common $[\text{Ru}(\text{bpy})_3]^{2+}$ photosensitizer where H_2 evolution ceases after a couple of hours, the activity only very slowly decreased over 60 h, underlying the light-stability of this PS. Although we did not pursue this study, it is an excellent entry point into long-term stable systems, probably not with our usual WRCs but with new ones. In addition, the apexes in the cluster can easily be substituted with anchoring groups for grafting them to semiconductor materials. Thus, the perspective of such multinuclear complexes is obvious and they have probably just not been studied in more detail since the preparations are not at all routine and were very new for us.

We finalized the study with the dual-core WRCs (see progress report 2020) in detail with electrochemical simulations, extensive experimental electrochemistry, and photo-electrocatalytic studies. The results were published and the paper [15] became labelled a "very important paper" by the editor. A series of further dual-cores has been prepared but their catalytic activities did not exceed the ones of the published catalysts. One example is given in Figure 1. Although active over quite some time, the reaction profile requires an interpretation, which we do not have at this moment.

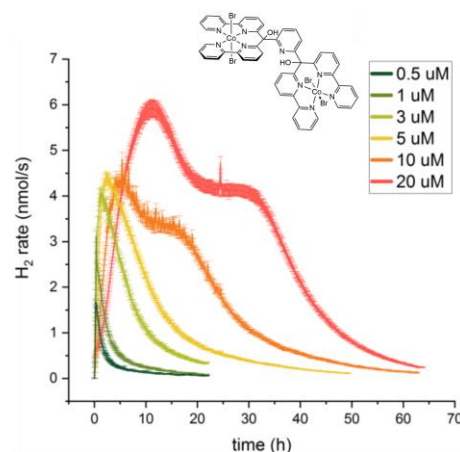


Figure 1: Photocatalysis with dual core WRC and $[\text{Ru}(\text{bpy})_3]^{2+}$ as PS.

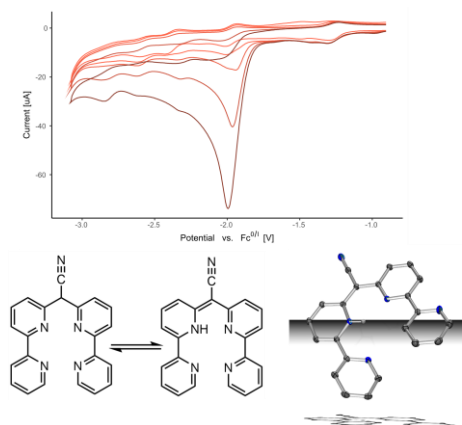


Figure 2: Tautomerism of open cycle anionic tetrapyrrolyl ligand and X-ray structure displaying the proton at one of the pyridine rings.

In extension to the macrocyclic porphyrin systems, we have synthesized an open-cycle porphyrin ligand, having only one CH-CN group between the bipyridyl units (Figure 2). Tautomerism should make the first coordination sphere electronically flexible and allow for a proton in the direct vicinity of the cobalt center. Since the corresponding complexes have a low overpotential, we will further explore this kind of WRC for the rest of the period (see updated project planning).

3.1.2 Visible-Light-Driven Water Oxidation Catalysts (WOCs) (Prof. G. R. Patzke)

During the previous reporting period, we had obtained substantial insight into the restructuring processes and structural moieties that account for the outstanding overall water splitting activity of cobalt phosphide-based electrocatalysts (Yonggui Zhao, [16]). With this knowledge about the powerful role of non-metal centers and our enhanced monitoring methodology at hand, we completed and published an in-depth and *operando* study into the productive influence of sulfur tuning on mixed metal Ni/Fe-catalysts for the OER [17]. The particular 3d metal center combination of Ni and Fe is well known as powerful. However, Ni/Fe synergisms raise fundamental mechanistic and design questions with respect to the optimal environments for both metal centers, especially in their high valent states during OER, and the systematic structure-activity relationships. In our study, we specifically addressed two key issues, namely (1) *facilitating the formation of high valent Ni and Fe states* and (2) *ideal conditions and energetic relations for dual oxygen-bridged Ni-Fe moieties for efficient O-O bond formation*. Based on our previous works, we selected coordination polymers (CPs) as attractive target materials that offer manifold organic/inorganic linking options in combination with interesting structural features and high surface areas. Specifically, we started from reduced NiFe-based CPs with a structural motif

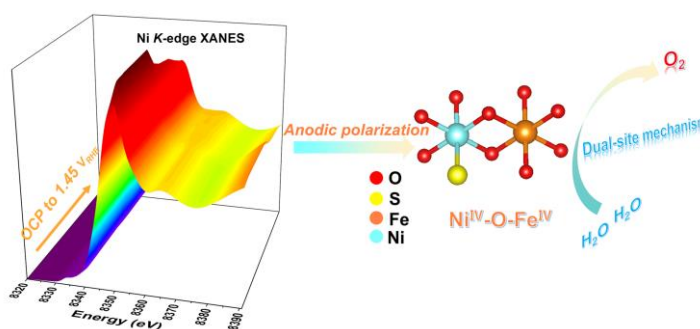


Figure 3: Unraveling the active Ni-O-Fe OER moieties of S-R-NiFe-CP catalysts with *operando* XAS monitoring (taken from *ACS Nano* **2022**, *16*, 15318).

related to layered double hydroxides and a high content of oxygen deficiencies (O_d -R-NiFe-CPs). They were subjected to our anionic engineering strategy in order to produce S-R-NiFe-CP catalysts through controlled introduction of sulfur atoms. *Ex situ* X-ray absorption spectroscopy (XAS) investigations revealed that the newly added sulfur atoms preferably refill the oxygen deficiencies in the vicinity of the Ni atoms instead of substituting O atoms. These engineered S-R-NiFe-CP displayed notably enhanced OER performance (overpotential 245 mV at 20 mA/cm² and Tafel slope of 30.28 mV/dec) when compared to the precursor O_d -R-NiFe-CPs (271 mV and 49.10 mV/dec), and they were superior to most current NiFe-containing electrocatalysts. The reasons for this highly productive influence of our sulfur engineering strategy were systematically unraveled with a combination of analytical and theoretical (DFT) investigations. *Operando* X-ray absorption near edge structure (XANES) spectra at the Ni- and Fe-K edges, respectively, showed that both metal centers were oxidized to high valent species (oxidation states > +3) and thereby both played a key role in the O-O bond formation process. Next, *operando* extended X-ray absorption fine structure (EXAFS) spectra at both Ni/Fe absorption edges under OER conditions clearly demonstrated the formation of in situ formed oxygen-bridged S-Ni^{IV}-O-Fe^{IV}-O moieties with highly oxidized metal centers during O₂ evolution. Most importantly, further *operando* investigations on non-substituted, pristine O_d -R-NiFe-CP catalysts showed that the formation of these crucial Ni^{III/IV}-O-Fe^{III/IV} units is hindered in the absence of sulfur doping. These insights are in line with complementary electrochemical impedance spectroscopy tests and DFT calculations. They showed, along with pH dependent tests, that both catalysts generated oxygen indeed via a dual site mechanism, which was energetically favorable for S-R-NiFe-CPs due to the remarkably low energy barrier of 0.44 eV to initiate the O-O bond formation atop Ni-O-Fe sites. Our results highlight the conceptual power of mechanism- and heteratom-based engineering of OER catalysts through smart control over their sublattices and defects. This will pave the way to many more low cost CP catalysts for energy conversion.

In line with our strategies to tune non-oxidic transition metal-based OER towards lower metal contents, we made considerable progress in the optimization of cobalt carbodiimide (CoNCN) nanoparticles (*Chong Huang*). We developed different gas phase and flux-assisted preparative approaches to differentiate between highly- and low-crystalline (LC- and HC-) CoNCN nanomaterials, which both underwent a self-optimization process during cyclic voltammetry tests. Their already promising overpotentials were further improved through iron doping strategies, especially for LC-CoNCN. Optimization of the Fe content brought forward LC-Fe_{0.25}Co_{0.75}NCN (341 mV @ 10 mA cm⁻²) that outperforms commercial RuO₂ standards (360 mV @ 10 mA cm⁻²) and displays a stable performance during prolonged chronopotentiometry tests. Further analytical and operando-tests are now planned, including our recently developed carbon nanotube composites of HC-CoNCN that display competitive performance in the oxygen reduction reaction (ORR) catalysis.

Furthermore, our development of silver doped, nickel phosphide (Ni₂P) based-catalysts proved successful in the coupling of the HER with acrylamide oxidation as a valuable replacement of the OER by the oxidative removal of aqueous pollutants (*Dan Zhang*). The synthesis of these bifunctional catalysts proceeds in three steps: first, Ag-Ni hydroxide was grown uniformly on nickel foam (NF) in a hydrothermal process, followed by thermal phosphorization to generate Ag-Ni₂P/NF. Next, Ag-Ni₂P/NF was reconstructed in situ through cyclic voltammetry (CV) tests. Current data show that these reconstructed nanosheets (CV-Ag-Ni₂P /NF) excelled through a low voltage of 1.82 V to drive a current density of 100 mA/cm² with substantial removal of acrylamide (79.34%) after 24 h of stable performance at 50 mA/cm². Furthermore, post-catalytic analyses demonstrated the integrity of the bifunctional catalyst after this extended application period. This promising study is now completed for joint publication with Ocean University China (Quingdao).

3.1.3 Time resolved Spectroscopy of Artificial Photosynthetic Systems (Prof. P. Hamm)

We focused on CO₂ reduction in the reporting year, one example of which will be described in more detail in the following. That is, we investigated newly available Re tricarbonyl compounds, that are structurally quite similar to the well-established CO₂ reduction catalyst Re(bpy)(CO)₃Cl, to establish a combined method of electrochemical/spectroelectrochemical measurements and time resolved spectroscopy over a very large range of timescales (1ps-1s). This multi-method approach led to a deeper understanding of the complex electrochemical processes the new compound shown below.

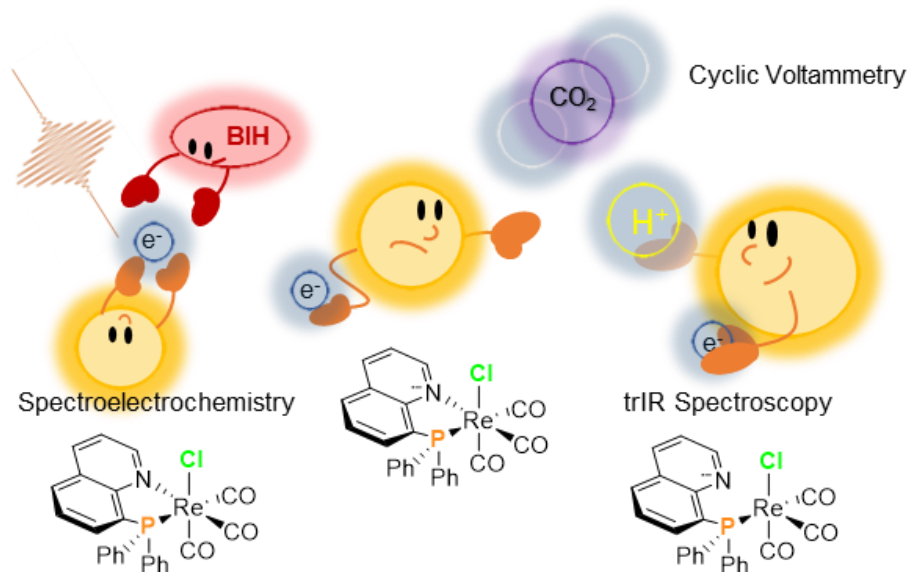


Figure 4: Molecular structure of one the rhenium tricarbonyl complex **Re-P∩N**, (**Re-As∩N** is isostructural) and representation of the investigated reactions.

The new compounds (Figure 4) **Re-P∩N** and **Re-As∩N** are tricarbonyl complexes bearing 8-(diphenylphosphanyl)quinoline or 8-(diphenylarsanyl)quinoline as ligands and to our knowledge it was the first time these type of ligands have been tested for electrocatalytic CO₂ reduction. These ligands in **Re-P∩N** and **Re-As∩N** have a bidentate binding motif similar to the bipyridine ligand in the established rhenium diimine complexes. Despite structural similarity of the compounds, the electrochemical behavior was very different for the new molecules. We found that instead of typical axial ligand loss upon (2e⁻) reduction the complex as would be the case for Re(bpy)(CO)₃Cl **Re-P∩N** and **Re-As∩N** likely undergo an isomerization after single electron reduction. The equilibrium of this reaction is influenced by the presence of a proton donor/and or CO₂ in the reaction solution.

Visible pump IR probe experiments on the 20 ps-1 μs timescale of **Re-P∩N** and **Re-As∩N** show a high quantum yield for light induced reduction with different electron donors. Electrochemical studies at different scan rates of **Re-P∩N** in presence of CO₂ and/or a proton donor suggest that the singly reduced **Re-P∩N** complex undergoes further chemical transformation on timescales shorter than 1-2s. This motivated the time resolved IR spectroscopic study of **Re-P∩N** in presence of CO₂ and a sacrificial electron donor over 12 orders of time (picoseconds-seconds), which was only possible with a quite recently built trIR setup with a 100 kHz laser. This combination of transient absorption spectroscopy with cyclic voltammetry, "the spectroscopy of the electrochemist" opens up unique possibilities to unravel new reaction mechanisms. A publication on this work has been submitted and is currently under revision.

3.1.4 Surfaces (Prof. J. Osterwalder)

Prof. Osterwalder has retired in August 2022 but was given extension of his right to confer a PhD by the Faculty of Science until mid-2023. The three remaining PhD students will defend their thesis in early spring 2023. They all work on LightChEC related projects.

During this last year Mert Taskin focused mainly on the experimental study of Ni-ferrite-like films grown on $\text{Fe}_3\text{O}_4(001)$. He was motivated by a recent electrochemical characterization of such films during the oxygen evolution reaction (F. Mirabella et al., *Electrochimica Acta* **2021**, 389, [138638](#)), where the catalytic activity was tuned via the Ni concentration. His XPS and photoelectron diffraction experiments showed that the systems with maximum activity are highly overstoichiometric in Ni, reaching compositions close to Ni_2FeO_4 while still preserving an inverse spinel-like structure.

Jan Beckord was able to grow a monolayer of Cu_2O on $\text{Cu}(111)$, covered by a monolayer of hexagonal boron nitride, by oxygen intercalation into the h-BN/ $\text{Cu}(111)$ system. The thus protected Cu_2O layer shows a band gap of 1.8 eV and defect states in the mid-gap region. Relaxation times of hot electrons excited in the underlying copper metal are strongly reduced in this region due to the efficient trapping in the defect states.

Nicolo Comini has studied the interaction of the formate-covered $\text{TiO}_2(110)$ surface with water vapor in view of the hydrophilic-to-hydrophobic switching of this surface. Even though formate binds more strongly due to the bidentate bonding to this surface, he could show that exposure to clean water vapor at near-ambient pressures could lead to a replacement of formates by hydroxyls. Fernanda Nunes and Marcella Iannuzzi of the Hutter group have identified a pathway for this replacement reaction by means of metadynamics simulations, and a joint paper has been submitted.

3.1.5 Molecular Approaches to Renewable Energies (Prof. D. Tilley)

Currently, eight out of the ten PhD students and postdocs in the Tilley group work on LightChEC related projects. The most significant change in our group's activities is a new research direction in photocatalytic sheets, where we will also strengthen our ties with the Patzke group. Our main idea is to translate the thin films under investigation in our group to particle sheets, which have the potential to generate solar hydrogen at a lower cost than fossil hydrogen.

We continue work on Sb_2Se_3 thin film photocathodes with a primary goal of improving the voltage (Pardis Adams). Successful treatments can then be applied to Sb_2Se_3 particle sheets to improve the efficiency (Ramon Schnyder). We also had a record-breaking performance with our Cu_2O photocathodes, which was reported in *Energy & Environmental Science* [10]. We also began work with BiVO_4 and investigated thick TiO_2 overlayers that nevertheless allow charge transfer (water oxidation) (Sanghyun Bae). These strategies, too, can be applied to BiVO_4 photocatalytic sheets (David Yong Sam). Erin Service is developing a novel in situ characterization technique that combines impedance spectroscopy and dual working electrode, which is high risk-high reward project. Işık Tunçay is leading the project on anchored molecular electrocatalysts for solar fuel applications, and will focus this year on developing new molecular electrocatalysts for reduction reactions that are compatible with anchoring to electrode surface via host-guest interactions.

3.1.6 Computational Studies of Dynamic Properties of Water Oxidation (Prof. J. Hutter)

Studies on understanding the structure in the nanoscopic region of water that is in direct contact with solid surfaces, so-called **contact layer**, which is key to quantify macroscopic properties that are of interest. We have addressed two fundamental questions by means of extensive MD simulations: i) How are **intermolecular correlations of the water contact layer** influenced by different chemical composition and crystal orientation of the substrate? ii) How does the microscopic structure of the contact layer in turn influence macroscopic properties relevant to hydration, to slippage, and to osmotic transport? We focused on model surfaces that are of special interest for reaction **processes occurring in electrochemical cells**, namely Au(100) and Au(111), and for transport processes occurring in nanofluidic membranes and energy storage devices, namely graphene and MoS₂. We found that the intermolecular correlations of the water contact layer vary dramatically on each substrate.

In the context of our research on **2D material/metal-oxide interfaces**, we have provided a model structure, which was used for simulating diffraction features with the electron diffraction in atomic clusters code (*Phys. Rev. B* **2001**, 63 (7), [075404](#)) for comparison with XPD measurements. The comparison of simulated STM images and XAS to experiments was used to validate the assignment of the structural features at the interface. We could characterize the structural and electronic properties of the resulting ordered h-BN/Cu_{2-x}O/Cu(111) heterostructure, a model “**nano-reactor**” catalyst with a broad range of potential catalysis applications.

We did follow-up of the study on the immobilization of molecular catalysts via host-guest interactions. In particular, we performed large scale simulation at the hybrid functional DFT level, to compare the different binding functions of the naphthalene and adamantane guests inserted in the cyclodextrin as free standing as well as anchored to an oxide material (TiO₂). This work is related to the previous studies made by binding the cyclodextrin on a metallic support. The equilibration of the structures is based on ab initio molecular dynamics simulations where the oxide surface is saturated by a liquid water film. By analyzing the electronic density of states, we conclude that there is a different coupling of the catalyst with the supporting oxide material, which is also expected to affect the catalytic activity.

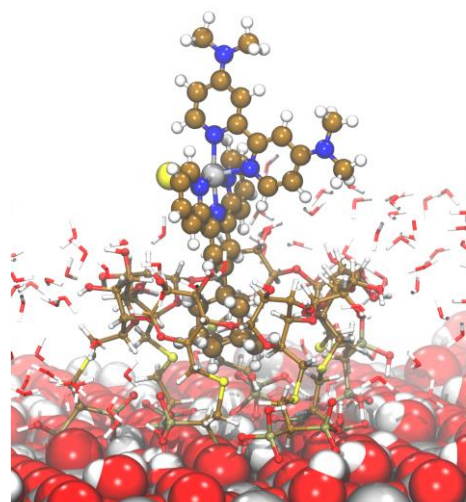


Figure 5: Host-guest complex anchored at the rutile TiO₂(110)/water interface. The displayed structure corresponds to a snapshot extracted from the AIMD trajectory.

3.1.7 Surfaces / H₂ and CO₂ Storage and Conversion (Prof. K.-H. Ernst)

We have continued our studies on low-dimensional metal-organic frameworks (MOFs) as a very versatile class of nanomaterials. Their electronic, magnetic, and catalytic properties can be tuned by choice of the metal atom and the ligand. Previous studies used imines and diols. Now oxocarbons, a class of ligands consisting only of oxygen and carbon, represent ideal molecules to produce metal-rich MOFs which have a high density of active metal sites. We moved now from squarate ligands to pentagonal and hexagonal oxocarbons (Figure 6) with magnetic atoms such as nickel and erbium.

The Ni and Er-based MOFs on Au(111) were studied by STM (Scanning Tunneling Microscopy), XPS (X-ray Photoelectron Spectroscopy) and XAS/XLD/XMCD (X-ray Absorption Spectroscopy, X-ray Linear Dichroism, X-ray Magnetic Circular Dichroism) and TDS (Thermal Desorption Spectroscopy).

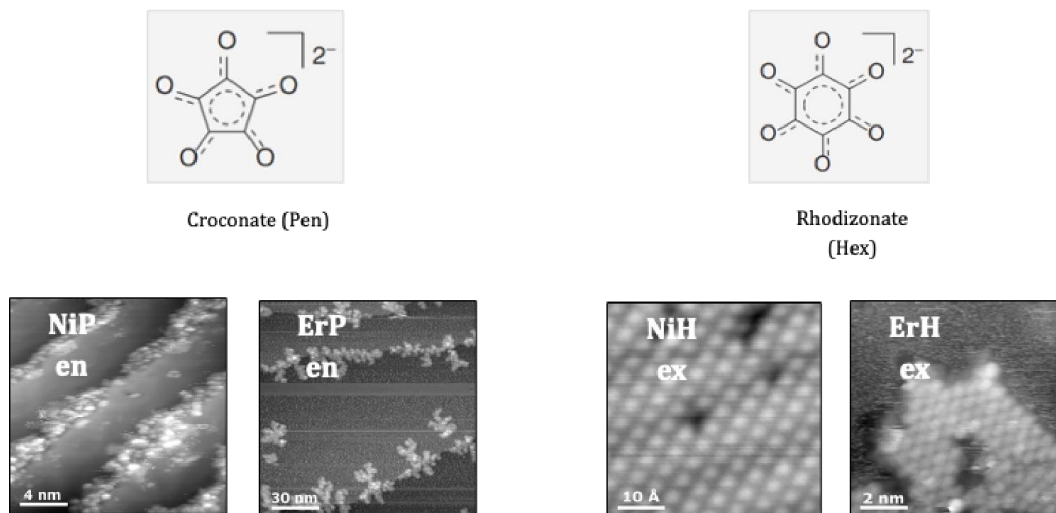


Figure 6: STM images of MOFs with pentagonal and hexagonal ligands grown on gold with nickel and erbium as coordinating atoms. Only the rhodizonate MOFs form a regular lattice while the pentagonal croconate forms only dendritic structures.

The magnetic exchange coupling has been studied with synchrotron-based XMCD but was found to be very small. By using even smaller ligands such as tetracyanoethylene we hope to create MOFs with large magnetic exchange that is expected to enhance the probability of stabilizing a bent CO_2^- anion after adsorption of neutral carbon dioxide. Such bent species are expected to be prone to easier hydrogenation.

3.1.8 Electronic Structure of Materials for Solar-Water Splitting (Dr. A. Borgschulte)

The overall aim of the Borgschulte group within LightChEC is to study the connection between electronic structure of an electrocatalyst and its electrochemical performance. To forward the current state-of-the-art, new characterization methods are needed. Supported by various funding sources, we established a new methodology based on a combination of soft- and hard X-ray photoelectron spectroscopy (XPS/HAXPES), coupled with electrochemical impedance spectroscopy (EIS).

As benchmark material we studied Ni used in alkaline water electrolysis. The outstanding properties of Ni-materials do not arise from the metallic host, rather from the surface passivated with various oxidized compounds formed during the electrochemical process. This newly formed layer is responsible for the catalytic properties of the system, therefore the investigation of its evolution as function of potential and time is crucial for a deeper understanding of the overall electrochemical process. However, the characterization of the chemical environment at the topmost layer, as well as the underlying layers, is complex and requires surface sensitive techniques. Here, we show that while ambient pressure soft X-ray photoelectron spectroscopy (APXPS) allows to follow the changes of the topmost layer, characterization of the deeper layers' modifications occurring during electrocatalysis requires a combination of soft- and hard X-ray photoelectron spectroscopy (XPS/HAXPES), coupled with electrochemical impedance spectroscopy (EIS).

The findings show how the high electrocatalytic activity of Ni (oxy)-hydroxides is directly related to the increasing water intercalation into the passivation layer, which supports the long-debated

hypothesis of a water mediated OH^- diffusion mechanism. High performance of the electrode is promoted by the peculiar structure of the surface, which self-organizes during the initial formation of the passivation layer enabling self-healing during electro-catalysis. The results are submitted and currently under review.

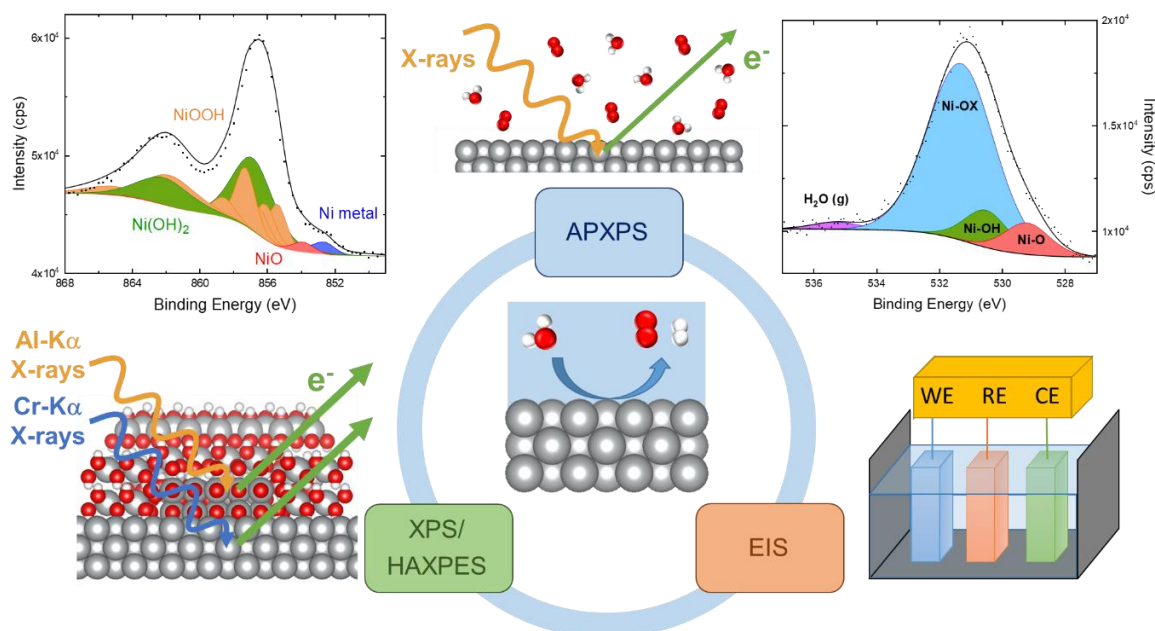


Figure 7: Schematic representation of the techniques developed within LightChEC to investigate the oxidation of clean metal surfaces upon exposure to O_2 and/or H_2O (APXPS, blue), the electrochemical evolution of the system over time in different conditions (EIS, orange) and the surface/bulk modifications after alkaline water splitting (XPS/HAXPES).

3.1.9 Theoretical and Computational Chemistry (Prof. S. Luber)

In the course of this project, the theoretical description and simulation of UV/VIS and electric circular dichroism spectra with real-time time-dependent density functional theory (RT-TDDFT) was extended to formulations within different gauges: The velocity gauge allows to include the electric field in terms of a uniform vector potential. This formulation is advantageous for applications with periodic boundary conditions, which is usually the case for "real world" problems as this is a standard way to include the environment of the molecule of interest, be it liquids, solids, or interfaces. The symmetric gauge allows simulations driven by a constant, uniform magnetic field.

Both methods have been implemented in the high-performance program package CP2K, using pseudopotentials for additional speed-up of the calculations. Their availability can advance the theoretical investigation of more complex chemical systems such as homogeneous and heterogeneous catalysts alike.

Aside from that, important progress has been made for efficient excited state dynamics in the condensed phase. Important properties have been derived and implemented such as the calculation of spectroscopic properties and spin-orbit couplings. Moreover, challenges with respect to convergence of excited state calculations and their consistent calculation during density functional theory-based molecular dynamics have been tackled such as the extension of the orbital transformation method to certain excited states and derivation of orbital tracking schemes. First applications to small molecules, also modelled in a realistic manner with full explicit solvation, have successfully demonstrated the usefulness of these developments, paving the way for future research to obtain highly desirable insight into light-driven processes during water splitting catalysis.

4 Scientific Activities and Outreach

4.1 Scientific Activities Organized by LightChEC

LightChEC Summer School

After the previous Summer School in 2020 had to be cancelled, the 2022 edition was successfully held in Les Diablerets in early September. Most talks and teaching sessions were a great success, and the organization did not encounter any major issues.

The participants as well as the speakers invited gave very positive feedback. We also received a few suggestions for improving the event (e.g. tweaking the schedule and the poster session) and are planning to implement them for the final LightChEC Summer School in 2024.

Invited speakers and teachers:

- Prof. Theodor Agapie, Caltech, USA
- Dr. Aaron Appel, Pacific Northwest National Laboratory (PNNL), USA (remote talk)
- Dr. Gabriele Colombo, Casale SA, Switzerland
- Prof. Sascha Ott, Uppsala University, Sweden
- Prof. Oleg Prezhdo, University of Southern California, USA
- Prof. Sven Rau, CataLight, Ulm University, Germany
- Prof. Ludmilla Steier, University of Oxford, UK
- Prof. Carsten Streb, Johannes Gutenberg University Mainz, Germany
- Prof. Jenny Y. Yang, University of California, Irvine, USA

Scientific Seminars

The URPP science seminars were held as an integrated part of the Department of Chemistry seminars and highlighted as "LightChEC Co-Seminars". During the day, seminar speakers were available for scientific discussions, and a meet-greet-lunch was specifically organized for students.

Three speakers were invited on behalf of LightChEC in 2022:

- 24 May: Prof. Dr. Siegfried R. Waldvogel, Johannes Gutenberg-University Mainz, DE
"Electrifying Organic Synthesis"
- 9 November: Prof. Dr. Victor Mougel, ETH Zurich
"Bio-Inspired Small Molecule Activation: A Journey Across Multiple Scales"
- 22 November: Prof. Dr. Mischa Bonn, Max Planck Institute for Polymer Research, DE
"A Molecular View of Water Interfaces"

Discussion Meetings

Our long-standing series of internal LightChEC Discussion Meetings was again held monthly during the reporting year. These meetings are meant to stimulate exchange and discussions within the consortium. Members and associates present interesting research articles, methods, or new concepts to the community, followed by a discussion about the topic.

In addition to giving young researchers an opportunity to practice scientific presentation skills, the discussion meeting also introduces new concepts and establishes a culture of discussion, strengthening the joint spirit of the consortium between the different groups.

To increase the participation above the level of 2022, we identified several reasons. Most importantly there was some feedback about certain topics not being well suited for everyone invited. We have encouraged the next speakers to again provide topics that are of general interest to all groups in LightChEC and that contain suitable background information.

4.2 Outreach Activities

The **LightChEC website** recorded about 5720 visits in the reporting year, which is 18% more than in the previous year. The average visit duration, however, has decreased by 30% compared to 2021. About 55% of the visitors registered are from Switzerland, followed by 14% from the USA.

The LightChEC **Twitter** account, while obviously remaining a niche outlet, expanded followership by around 33% in 2022. Interaction was highest during the time around the Summer School but has slightly decreased over the full year compared to 2021.

In the upcoming year, we will connect with other international research centers and attract more followers through broader advertising our planned public talks and symposium along with new publications and highlights from ongoing LightChEC activities.

Greta R. Patzke was elected a member of the **Daylight Academy** (<https://daylight.academy>). She gave a talk at the Daylight Awareness Week 2022 in May on the topic of artificial photosynthesis ([youtube.com/watch?v=pkexmIHYiUM](https://www.youtube.com/watch?v=pkexmIHYiUM)). She furthermore contributed an expert section to the SATW report "Forschungslandschaft Schweiz: Ein technologisches Panorama" on the topic of "Künstliche Photosynthese" ([SATW Forschungslandschaft Schweiz SBFI-Studie Lang 2022 DE.pdf](#)).

She continues to serve on the advisory boards of several internationally acknowledged scientific journals and she actively participated in recently published position papers of the scientific advisory board of the AEE Suisse.

The group of Dr. Borgschulte has started an **industry collaboration** with H2 Solar (<http://h2solar.ch>) called MeRuCath.

They also organized and supported various conferences and **public events**, such the Powerfuel Week 2022 (<https://powerfuel.ch>) or the PhD symposium 2022 at Empa.

5 Academic Career Development

5.1 Activities in Academic Career and Development

Prof. **Luber** joined the editorial board of *Helvetica Chimica Acta* in winter 2022 and later in the year was appointed associate editor of WIREs *Computational Molecular Science*. She also was elected to the board of the Platform Chemistry of the Swiss Academy of Sciences.

In June, Fabrizio Creazzo, a postdoc in the Luber group, was awarded the UZH Forschungskredit PostDoc Grant. Eva Vandaele has received a poster award at the 58th Symposium on Theoretical Chemistry in Heidelberg, Germany.

Yonggui Zhao from the **Patzke group** completed his PhD thesis entitled "*Development and Characterization of Transition Metal-Based Nanomaterials for Electrochemical Water Splitting*" and started a LightChEC postdoc position a successor of Dr. Benjamin Probst. He was furthermore awarded a *Chinese Government Award for Self-Financed Students Abroad* in 2022.

Devi Prasad from the Patzke group has been granted a *Researcher Development Grant* from the Royal Society of Chemistry, to participate on the 44th International Conference on Coordination Chemistry in Rimini, Italy. Daniel Civettini joined the Patzke group as a new PhD candidate.

From the **Alberto group**, Dr. Benjamin Probst left university for the electrochemistry division of the company Sensirion. Dr. Franziska Rahn accomplished her PhD thesis entitled "*Electrocatalysis with Polymerised Water Reduction Catalysts*". Iva Walz finished her MSc with a thesis entitled "*Alternative Sulphur Bridged Clusters for Solar Water Splitting*", and Nathalie Decrausaz accomplished her MSc with a thesis entitled "*Reactivity and Photophysical Behavior of Bipyridine Derivatives and their fac-[Re(L)(CO)₃(bipy)]ⁿ⁺ Complexes*".

Emanuel Billeter successfully completed his PhD in the **Borgschulte group**. He has since started a postdoc position at DTU Copenhagen with Prof. Ib Chorkendorff, who had been an invited speaker at the LightChEC Summer School 2014.

Three PhD candidates and one Master student have their projects ongoing.

Christian Wäckerlin, former postdoc in the **Ernst group**, has successfully applied for a SNSF Eccellenza Professorial Fellowship, starting in January 2023.

Prof. Ernst himself in October received the "JVSS-Microbeam Analysis Award" from the Division of Microbeam Analysis (MBA) of the Japan Society of Vacuum and Surface Science (JVSS) for outstanding research results in the field of microbeam analysis.

Mert Taskin, Nicolò Comini, and Jan Beckord from the **Osterwalder group** are close to finishing their PhD. Jürg Osterwalder, who officially retired in July 2022, has made sure they are well coached and is still supervising them until they can finish their respective thesis.

Two new PhD candidates have started their position in with LightChEC in the **Tilley group**: David Yong Sam and Ramon Schnyder.


In the **Hamm group**, Luka Tatarashvili and Sergio Aranda Ruiz started their PhD projects in 2022.

5.2 Gender Equality Development

In 2022, Prof. Patzke continued her services as MNF representative of the UZH Gender Equality Commission and as a member of the MNF Gender Equality Committee.

In the whole consortium, of the 59 researchers who were at least loosely part of LightChEC during most of the year, 40 were male and 19 were female, which is a similar ratio compared to the two previous years.

6 Publications

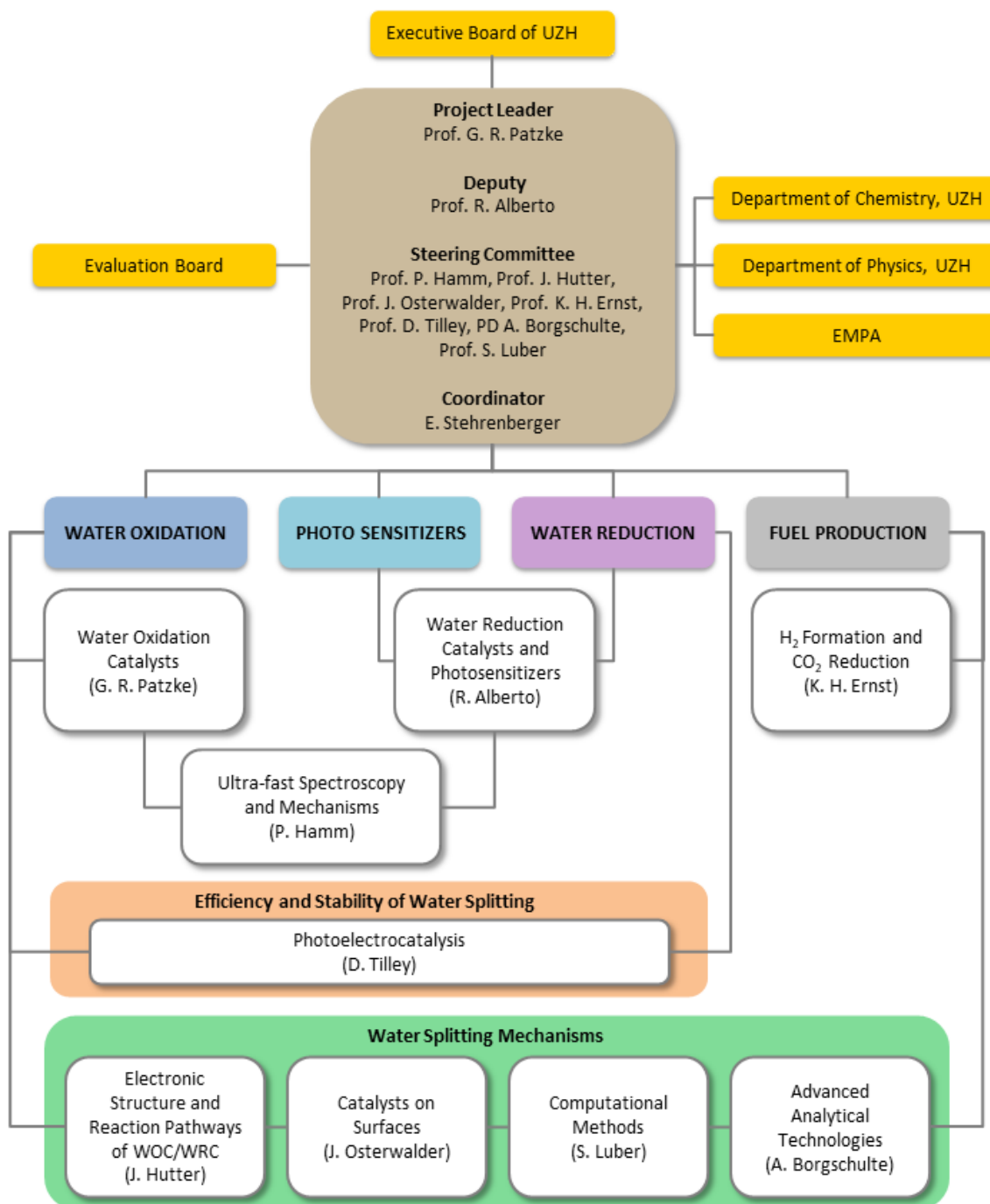
10 open access publications 

- [1] **Billeter, E.; Kazaz, S.; Borgschulte, A.** Bulk Thermodynamics Determines Surface Hydrogen Concentration in Membranes. *Adv. Mater. Interfaces* **2022**, *9* (23), 2200767. <https://doi.org/10.1002/admi.202200767>. 
- [2] **Borgschulte, A.; Terreni, J.; Fumey, B.; Sambalova, O.; Billeter, E.** Short-Lived Interfaces in Energy Materials. *Front. Energy Res.* **2022**, *9*, 830. <https://doi.org/10.3389/fenrg.2021.784082>. 
- [3] **Bühler, J.; Zurflüh, J.; Siol, S.; Blacque, O.; Sévery, L.; Tilley, S. D.** Electrochemical Ruthenium-Catalysed C-H Activation in Water through Heterogenization of a Molecular Catalyst. *Catal. Sci. Technol.* **2022**. <https://doi.org/10.1039/D1CY01999F>. 
- [4] **Kazaz, S.; Billeter, E.; Borgschulte, A.** Sorption Kinetics in Metal Hydrides by Leaky Coating. *Int. J. Hydrogen Energy* **2022**, *47* (78), 33403–33409. <https://doi.org/10.1016/j.ijhydene.2022.07.248>.
- [5] **Lan, J.; Yamamoto, Y.; Suzuki, T.; Rybkin, V. V.** Shallow and Deep Trap States of Solvated Electrons in Methanol and Their Formation, Electronic Excitation, and Relaxation Dynamics. *Chem. Sci.* **2022**, *13*, 3837–3844. <https://doi.org/10.1039/D1SC06666H>. 
- [6] **Mattiat, J.; Luber, S.** Comparison of Length, Velocity, and Symmetric Gauges for the Calculation of Absorption and Electric Circular Dichroism Spectra with Real-Time Time-Dependent Density Functional Theory. *J. Chem. Theory Comput.* **2022**. <https://doi.org/10.1021/acs.jctc.2c00644>.
- [7] **Müller, P.; Probst, B.; Spingler, B.; Blacque, O.; Alberto, R.** Polar Substituents Enable Efficient Catalysis for a Class of Cobalt Polypyridyl Hydrogen Evolving Catalysts. *Helvetica Chimica Acta* **2022**, *105* (3), e202100237. <https://doi.org/10.1002/hlca.202100237>. 
- [8] **Naik, J. M.; Bulfin, B.; Triana, C. A.; Stoian, D. C.; Patzke, G. R.** Cation-Deficient Ce-Substituted Perovskite Oxides with Dual-Redox Active Sites for Thermochemical Applications. *ACS Appl. Mater. Interfaces* **2022**, *15* (1), 806–817. <https://doi.org/10.1021/acsami.2c15169>.
- [9] **Nikolic, M.; Longo, F.; Billeter, E.; Cesarini, A.; Trtik, P.; Borgschulte, A.** Combinatorial Neutron Imaging Methods for Hydrogenation Catalysts. *Phys. Chem. Chem. Phys.* **2022**, *24* (44), 27394–27405. <https://doi.org/10.1039/D2CP03863C>.
- [10] **Niu, W.; Moehl, T.; Adams, P.; Zhang, X.; Lefèvre, R.; Cruz, A. M.; Zeng, P.; Kunze, K.; Yang, W.; Tilley, S. D.** Crystal Orientation-Dependent Etching and Trapping in Thermally-Oxidised Cu₂O Photocathodes for Water Splitting. *Energy Environ. Sci.* **2022**. <https://doi.org/10.1039/D1EE03696C>. 
- [11] **Prabhakar, R. R.; Moehl, T.; Friedrich, D.; Kunst, M.; Shukla, S.; Adeleye, D.; Damle, V. H.; Siol, S.; Cui, W.; Gouda, L.; Suh, J.; Tischler, Y. R.; van de Krol, R.; Tilley, S. D.** Sulfur-Treatment Passivates Bulk Defects in Sb₂Se₃ Photocathodes for Water Splitting. *Adv. Funct. Mater.* **2022**, *32* (25), 2112184. <https://doi.org/10.1002/adfm.202112184>. 
- [12] **Shao, F.; Wong, J. K.; Low, Q. H.; Iannuzzi, M.; Li, J.; Lan, J.** In Situ Spectroelectrochemical Probing of CO Redox Landscape on Copper Single-Crystal Surfaces. *PNAS* **2022**, *119* (29), e2118166119. <https://doi.org/10.1073/pnas.2118166119>.
- [13] **Scheffe, J. R.; Haussener, S.; Patzke, G. R.** Solar Hydrogen Production. *Energy Technology* **2022**, *10* (1), 2101021. <https://doi.org/10.1002/ente.202101021>. 
- [14] **Wäckerlin, C.; Cahlík, A.; Goikoetxea, J.; Stetsovych, O.; Medvedeva, D.; Redondo, J.; Švec, M.; Delley, B.; Ondráček, M.; Pinar, A.; Blanco-Rey, M.; Kolorenč, J.; Arnau, A.; Jelínek, P.** Role of the Magnetic Anisotropy in Atomic-Spin Sensing of 1D Molecular Chains. *ACS Nano* **2022**, *16* (10), 16402–16413. <https://doi.org/10.1021/acsnano.2c05609>.

- [15] **Weder, N.; Grundmann, N. S.; Probst, B.;** Blacque, O.; **Ketkaew, R.; Creazzo, F.; Luber, S.; Alberto, R.** Two Novel Dinuclear Cobalt Polypyridyl Complexes in Electro- and Photocatalysis for Hydrogen Production: Cooperativity Increases Performance. *ChemSusChem* **2022**, *15* (17), e202201049. <https://doi.org/10.1002/cssc.202201049>. 
- [16] **Zhao, Y.; Dongfang, N.; Triana, C. A.; Huang, C.;** Erni, R.; **Wan, W.;** Li, J.; Stoian, D.; Pan, L.; Zhang, P.; **Lan, J.; Iannuzzi, M.; Patzke, G. R.** Dynamics and Control of Active Sites in Hierarchically Nanostructured Cobalt Phosphide/Chalcogenide-Based Electrocatalysts for Water Splitting. *Energy Environ. Sci.* **2022**, *15* (2), 727–739. <https://doi.org/10.1039/D1EE02249K>. 
- [17] **Zhao, Y.; Wan, W.;** Dongfang, N.; **Triana, C. A.;** Douls, L.; **Huang, C.;** Erni, R.; **Iannuzzi, M.; Patzke, G. R.** Optimized NiFe-Based Coordination Polymer Catalysts: Sulfur-Tuning and Operando Monitoring of Water Oxidation. *ACS Nano* **2022**, *16* (9), 15318–15327. <https://doi.org/10.1021/acsnano.2c06890>.

7 Structures

The URPP structure has remained the same as in 2021. After the retirement of Prof. Osterwalder in 2022, his very successful line of research will result in at least five further publications and three completed PhD theses.



8 Third Party Funds

8.1 Newly Approved Third-Party Funding of URPP Project Leaders

- Andreas Borgschulte, industry project “Efficiency of mercapto-Ru based membrane photocathodes”, 10.2022 – 04.2023, financed by H2 Solar, CHF 50'000.
- Prof. Karl-Heinz Ernst, Advanced chiral surface systems, 10.2022 – 09.2024, CHF 157'878.

8.2 Ongoing Third-Party Funding of URPP Project Leaders

SNSF - Divisions I to III

- Prof. Peter Hamm, 200020B 188694/1 (Extension: Ultrafast Vibrational Spectroscopy of Allosteric Proteins), 01.2020 – 12.2022, CHF 773'577.
- Prof. Karl-Heinz Ernst, Advanced chiral surface systems, 10.2018 – 09.2022, CHF 530'768.
- Dr. Andreas Borgschulte, Ultra-High Pressure Hydride X-ray Photoelectron Spectroscopy, 172662, 03.2018 – 02.2022, CHF 463'400.
- Prof. Jürg Osterwalder, Model systems for single-atom catalysts and 2D-confined catalysis studied by in situ surface science methods, SNSF Grant 200020 200303, 04.2021 – 07.2022, CHF 365'644.
- Prof. David Tilley, Photoelectrochemical Synthesis of Hydrogen and Value-Added Chemicals for a Sustainable Chemical Industry, SNF Grant 200020_184737, 09.2019 – 08.2023, CHF 900'000.
- Prof. Sandra Luber, Forefront approaches for modelling of compounds and their application to water reduction catalysis, SNSF Project 204265, 10.2021 – 09.2025, CHF 620'000.

SNSF - Division IV

- Prof. Peter Hamm, NCCR Molecular Ultrafast Science and Technology (MUST) Phase III, 06.2018 – 06.2022, CHF 720'000.
- Prof. Jürg Osterwalder, NCCR Molecular Ultrafast Science and Technology (MUST), Phase III Project "Ultrafast Structural and Electron Dynamics in Surfaces", 07.2018 – 06.2022, CHF 350'000.
- Prof. Sandra Luber, NCCR Catalysis “Pushing the boundaries of dynamic understanding of water splitting catalysts”, 04.2021 – 02.2024, CHF 247'640.
- Prof. Sandra Luber, Sinergia “Degradation mechanisms in photoelectrochemical devices”, 05.2022 – 04.2026, CHF 2'232'908 in total for all three groups involved.

EU

None

Industry

None

Others

- CSC for Scholarship Hang Chen from 02.2019 – 02.2023 (project leader: G. R. Patzke), PhD salary paid to H. Chen.
- CSC Fellowship for Zhenbin Wang, 10.2019 – 09.2023 (project leader: S.D. Tilley), CHF 100'800.
- CSC Scholarship for Zeyi Zhang from 11.2021 – 10.2025 (project leader: G. R. Patzke), PhD salary paid to Z. Zhang.
- CSC Scholarship Han Zhao from 11.2021 – 10.2025 (project leader: G. R. Patzke), PhD salary paid to H. Zhao.

- Dr. Andreas Borgschulte, Joined Empa-PSI project Synfuel, ETH Board, 01.2021 – 12.2023, CHF 6 Mio. (Borgschulte group ca. CHF 400'000), Empa).
- Prof. Sandra Luber, Two grants from Swiss National Supercomputing Center, until 2023.

8.3 Newly funded projects within Profit-Center (PC) of the URPP

None

8.4 Ongoing projects within Profit-Center (PC) of the URPP

- Sponsoring LightChEC Summer School, financed by Swiss Industry Science Fund and SCS, 03.2018 – 12.2023, CHF 14'000.