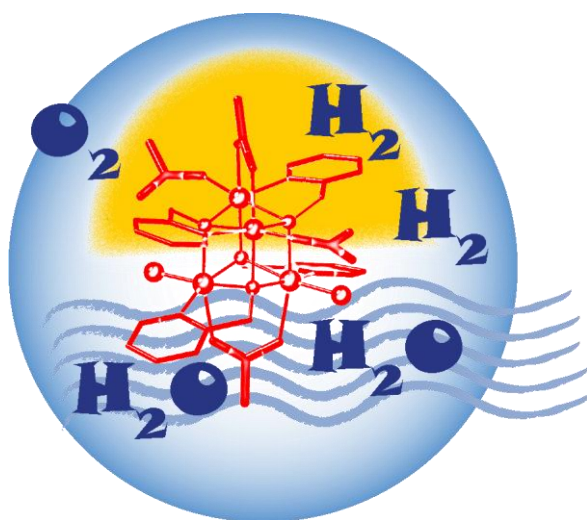




Progress Report 2020

URPP Solar Light to Chemical Energy Conversion



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1 Management Summary

The activities of LightChEC in the last year of the 2nd period were influenced by the contingencies imposed by the Covid crisis. Despite, progress was made throughout towards the objectives for 2020, albeit at a slower pace. Progress in heterogenization and electrocatalysis were substantial. For instance, it has been shown that the molecular catalysts from the Alberto group fully keep their integrity when grafted to electrodes and being subjected to electrocatalysis. The everlasting question about inherent instabilities of water reduction catalysts could thus be answered and a proof for their efficiencies and stabilities has been delivered. Substantial progress towards a full water splitting system was achieved in the Patzke group with transition metal chalcogenides based on Co, Fe and Mo nanocubes. These nanomaterials were prepared in a templated approach from Prussian Blue by exchanging parts of the cyanide anions with sulfide. They collaborated with Prof. Osterwalder on a different topic (molecular photoanodes). The materials showed excellent performance in the OE and in the HE reactions at low overpotentials, well comparable or even better than MoS₂ or RuO₂ systems. The Patzke group further rounded off their studies into the properties-performance parameters of cobalt-oxide-based water oxidation catalysts and obtained insight into their formation processes to explore optimal conditions for their fabrication. Time-resolved spectroscopy in the Hamm group enabled the detection of the laser-induced CO desorption from Pt and provided new insights in the various electron and energy transfer pathways of photocatalytic systems immobilized on surfaces. The Osterwalder group studied catalysts grafted to different surfaces by XPS (with Tilley and Alberto). Attempts to prepare epitaxial Ga₂O₃ overlayers on Cu₂O lead to some unexpected phenomena, which merit further investigations. Phosphonic acid catalysts grafted on TiO₂ gave insights into the stable dipole layer information in photocathodes. The highly promising Sb₂Se₃ photoelectrodes from the Tilley group progressed by doping studies. Photovoltages and photocurrents were improved, mechanisms are currently elucidated. The Tilley group also did first experiments towards biomass upgrading. This direction is an asset to LightChEC. Experimental studies were backed up by theory from the Hutter and the Luber groups. The Hutter group focused on calculations at the water/semiconductor interfaces by e.g. implementing machine-learning procedures for reproducing at ab initio quality the sampling of water at metallic surfaces, important for the interpretation of XPS results. Simulating time-resolved vibrational spectra at the interfaces was implemented with the Hamm group. The Luber group calculated adsorption modes of our main molecular catalysts on functional surfaces, important for re-designing their structures. Based on previous studies for H₂/CO₂ conversion/storage, a new kind of MOFs based on squaric acid has been implemented by the Ernst group. To provide evidence that a magnetic field acts on the electrochemical double-layer at electrodes, a magneto-optical device was set up by the Borgschulte group. It could be shown in pioneering experiments that magnetic properties and current densities correlate with applied potentials and magnetic fields.

The most substantial success in academic career development was the promotion of David Tilley to tenured Associate Professor. David occupied the Assistant Professorship that was created with LightChEC. His contributions to research and education will establish sustainable energy research as a core topic in the Department of Chemistry. Different members of LightChEC engaged in outreach activities, either via zoom or in written form. LightChEC became a member in the SUNERGY community and is now also active on Twitter.

Despite the impairments by Covid, LightChEC was very active and, for example, seminars continued. A large number of publications appeared, many with two internal or external PIs. Following the suggestions of the evaluators, LightChEC is not particularly aiming at devices but at excellent fundamental research. Still, as is obvious from the detailed research descriptions, working water splitting models have been achieved and will be pursued further.

2 Objectives

2.1 Objectives for the Reporting Year

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

Water / CO₂ Reduction Catalysts

- Grafting the pyrphyrin-based catalysts on solid phase materials or electrodes for studying their efficiencies in photo- and electrocatalysis.
- Exploring the established WRCs for CO₂ reduction in mono- and dinuclear complexes.
- Preparing new dual-core WRCs with conducting linking-ligands.
- Introducing different metal centres in the available ligand frameworks, structural characterization and assessing eventual catalytic activities.
- Mechanistic understanding of the processes leading to the formation of CO and H₂ respectively in the so-called "dual-core" complexes.
- Exploration of the bis-arene rhenium complexes [Re(η^6 -C₆H₅R)₂]⁺ as scaffolds for combining two differently active functions.
- Developing polymer-based photocathodes with the acyclic poly-pyridyl ligands
- Exploring the possibility of using atomic-precise molybdenum complexes as WRCs.
- Anchoring of WRCs in membranes.

Photosensitizers

- Switching from homogeneous to heterogeneous photosensitizers – grafting of catalysts to photoactive, semiconducting materials such as Sb₂Se₃ or organic photovoltaic cells.
- Using sulfides such as ZnS as carriers for anchored WRCs and exploring their efficiencies.
- Design and synthesize new cluster-like rhenium-based dyes and explore their suitability for photosensitizing proton reduction.

Electron relays and electrocatalysis

- Assess homogeneous electrocatalysis with mono- and dinuclear ruthenium complexes.
- Identify the electron transfer mechanisms in the CO₂ dual-core catalysts.

Photocatalysis in Membranes

Earlier, we have found that co-grafting of photosensitizer and WRC on reversed-phase particles resulted in very good H₂ formation rates. In 2019, co-adsorbing both on TiO₂ did not result in H₂ formation, probably due to reduced mobility of both components. With the improved catalysts in hand, we will resume non-covalent anchoring of single or multiple components in lipophilic (bi)layers and membranes. Resembling the natural system, such a heterogeneous photocatalytic setup will allow to study properties and mechanisms under conditions as in solution but still separated from other catalytic systems.

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

Transition Metal Chalkogenides and Phosphides for Water Splitting

We will intensify our activities in the development of nanostructured transition metal chalkogenides and phosphides as highly active, efficient and less explored electrocatalysts for water splitting. Special emphasis will be placed on the understanding of their surface reconstruction and structural stability under electrocatalytic conditions. Based on our studies on metal-Prussian blue nanocubes as bimetallic self-templated systems, we will extend our investigations upon a wider range of target compounds.

With our in-house easyXAFS system, we will conduct efficient ex situ pre-screening for further in situ XAS studies of these versatile catalysts over longer electrocatalytic operational periods.

Bifunctional alloy electrodes for overall water splitting

We will expand our research into heterogeneous water splitting systems with porous NiM alloy/stainless steel (M = Mn, Co, Fe) electrode systems as attractive low-cost materials. Their formation and optimization mechanisms will be monitored with in situ heating XRD/TEM. In the long term, we aim for integrated OER/HER systems constituted of the best alloys emerging from our screening.

Oxide WOCs

The challenging interplay between disorder, amorphous and crystalline features in transition metal oxides will be investigated for both a fundamental model system (cobalt oxide WOCs) and more complex, application-oriented perovskites, such as La-Sr-Mn/Co-oxides. PDF analyses in connection with advanced in situ TEM analyses and in house XAS methods will be applied to reveal the minimum structural requirements for high WOC performance of cobalt center models and the mechanistic principles of application-oriented perovskite electrodes for water splitting.

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

- Objective 1: Observe transient intermediates (e.g. Au-COO⁻ vs. Au-COOH) in CO₂ reduction on Au by transient IR spectroscopy.
- Objective 2: Develop and investigate a working hydrogen evolution system with a photosensitizer and a hydrogen evolution catalyst on an electron-donating semiconductor, such as NiO.
- Objective 3: Investigation of the effect of buried molecules on surfaces (in order to protect them) on electron-transfer steps.

2.1.4 Surfaces (Prof. J. Osterwalder)

- Growth of phosphonic acid layers on Sb₂Se₃(100) by ex-situ spin coating and characterization of the interface reaction and surface dipole formation.
- Continuation of the characterization of Ga₂O₃ mono- and multilayers on Cu₂O(111) grown by evaporating Ga in a low-pressure oxygen environment, in particular in terms of structure, band bending and band alignment.
- Continue the study of the charge transfer dynamics on Co-pyrphyrin loaded Cu₂O(111) surfaces.

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

- Photoelectrochemical Hydrogen Evolution: Improving the photovoltage of Sb₂Se₃, and investigation of Sb₂Se₃ for water splitting.
- Advanced Analytics: Further development of impedance modelling of multilayer semiconductor photoelectrodes. Development of Kelvin Probe Microscopy using the AFM for characterization of work function of our functionalized semiconductors (dipole project).
- (Photo)Electrosynthesis of Value-added Chemicals: Exploration of generating value added chemicals from renewable resources via (photo)electrochemistry.

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

- Implementation of machine learning procedure to train force fields that can reproduce with ab initio quality the sampling of water at metallic surfaces. This will make it possible to extend at least by one order of magnitude the timescale of molecular dynamics simulations even when nuclear quantum effects are included.

In collaboration with Osterwalder's group:

- Simulation of XPS at water-TiO₂ interface at different states of charge of the semiconductor
- Characterization of metal-oxide hosted hexagonal boron nitride and its functionalization
- Simulation of time resolved vibrational spectroscopy experiments at metal liquid interfaces

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

Single atom catalysts by formation of stable metalated extended ligand networks

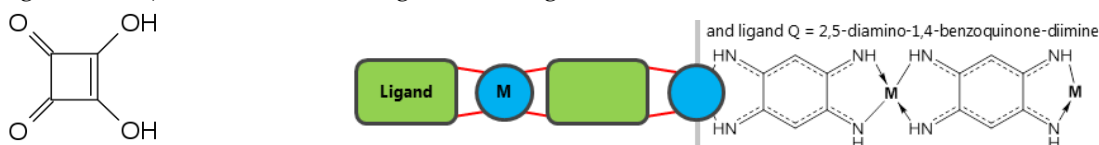
By 2D polymerization of melamine and cyanuric acid we plan to create a nitrogen-rich network which will be metalated with Fe, Co or Ni.

Metal-catalyzed H₂O, CO₂ and O₂ activation on metal-organic networks

The newly prepared catalysts will be tested for activation in ultrahigh vacuum and analyzed by infrared and photoelectron spectroscopies.

Single atom catalysts by formation of stable metalated extended ligand chains

Networks are often difficult to establish. Hence, we also aim at chain systems that are much easier to prepare. Close-packed self-assembly of chains are then considered as quasi-networks. As connecting ligands, we will try out squaric acid (see figure below), which should form linear chains with copper adatoms. A second approach will be using the ligand 2,5-diamino-1,4-benzoquinone-diimine (see figure below), which should also give metalorganic chains.



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

- Continuation of solar-water splitting probed by magneto-optics: Establishing the link between magneto-optics and magneto chemistry, case studies on Ni, Co-Pt, Fe-Pt; study of magneto-chemical materials from LightChEC materials.
- Photoemission studies on hydrogenation of hydrogen evolution reaction electrodes using the hydrogen membrane approach; characterization of LightChEC samples with HAXPES.
- Continuation of hydrogenation of gaseous organic compounds; setup of a hydrogenation reactor for liquid organic compounds.

2.1.9 Theoretical Chemistry (Prof. S. Luber)

- Investigation of preferred adsorption sites of phosphor-based linkers related to a water reduction catalyst at a functional surface.
- Study of the catalytic mechanism of a Co-based water reduction catalyst in collaboration with experimental groups.
- Development of an efficient approach for (Resonance)-Raman spectra for periodic systems.

2.2 Achieved Objectives and Milestones

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

Water / CO₂ Reduction Catalysts

A large variety of acyclic tetra-pyridyl complexes was decorated with multiple heterocycles at the methylene bridge between the two bipyridyl units. We unambiguously established that the hydroxy function at this position is crucial for fast hydrogen formation. We will continue with next generation acyclic catalysts accordingly. These catalysts showed for the first time that they are suitable for photocatalytic CO₂ reduction. Discerning between H₂ and CO is pH dependent but an advantage as far as syngas is produced directly at a correct pH value.

The adsorption of cyclic porphyrin-type WRCs on m-TiO₂@ITO was established in detail. We could in particular show in collaboration with the Osterwalder group by XPS that these catalysts are still intact after several days of operation but the m-TiO₂@ITO electrode decomposed. This confirmed our previous findings that the WRCs are much more stable than the typical running time of photocatalysis, with more than 500 kTON achieved in such a system. We prepared and fully characterized for the first time a dinuclear cobalt WRC. We could show that the two cobalt centres communicate through the bridge. Understanding electron transfer and electrochemistry has started with the Luber group.

Extension of water - and CO₂ reduction to mono- and dinuclear ruthenium complexes was assessed. Decorating the [Re(h⁶-C₆H₅R)₂]⁺ scaffold with bipyridyl unit carrying ruthenium-carbonyl moieties gave an efficient dinuclear catalyst for photo- and electrochemical CO₂ and proton reduction respectively. Deducing the mechanisms is planned with the Hamm group.

The acyclic poly-pyridyl ligands were bound on simple zinc sulfide. Proton reduction was not efficient but clearly ZnS mediated. The nature of the grafted catalyst is not clear yet, thus, a comparison to the free catalyst has to be undertaken.

Acyclic polypyridyl complexes were derivatized with vinyl and thiophene groups and polymerized for the production of polymer-based photocathodes, in cooperation with Empa. The polymers are available but key numbers such as the amounts of catalyst per polymer strand need to be quantified.

For extending the diversity of WRCs, we synthesized atom-precise [Mo₃S₄]⁴⁺ and did preliminary investigations with photo- and electrocatalysis. Since of molecular composition, detailed mechanistic studies are possible in contrast to the well-established and amorphous MoS₂.

Photosensitizers

For this year, we did not continue our search for new photosensitizers. We started preliminary research with a very new class of photosensitizers, namely octahedral Re₆ systems known to have long-lived triplet excited states. These new photosensitizers are of extreme stability but it is too early to report results.

Electrocatalysis

Relevant achieved objectives in electrocatalytic research are mentioned under the first point in this section. Generally, we could show for most of the newly developed WRCs that they are equally well able to produce H₂ in homogeneous solution or grafted to surfaces in an electrocatalytic setup. Most importantly, chronoamperometry experiments showed that the WRCs are much longer-lived than what we concluded from the photocatalytic studies, i.e. the photocycle limits the performance of H₂ production.

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

Transition Metal Chalkogenides and Phosphides for Water Splitting

We have published our study on transition metal sulphide nanoboxes as robust and bifunctional electrocatalysts [32]. This is a successful starting point for the further exploration of these versatile and promising materials for oxygen and hydrogen evolution reactions (OER/HER, respectively). We accessed metal sulfide nanoboxes (NBs) from convenient Co, Co/Fe and Ni/Fe Prussian blue (PB) nanocubes as templates for morphology control via an anionic exchange protocol for CN^- vs. S^{2-} to obtain the corresponding Co-S@PB, Co-Fe-S@PB, and Ni-Fe-S@PB NBs. Especially Co-Fe-S@PB NBs were subjected to detailed characterizations with a wide range of analytical methods, including X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS). Transmission electron microscopy (TEM) images demonstrated the hollow nanobox morphology with average sizes around 200 nm. Careful screening of the anion exchange parameters led to the optimization of the materials. The OER performance of Co-Fe-S@PB NBs was evaluated in 1 M KOH and compared to key references, including RuO_2 and IrO_2 as leading OER materials. Their performance was found to be superior to most related catalysts and to RuO_2 with a low overpotential of 286 mV at 10 mA/cm² along with a small Tafel slope value of 37.84 mV dec⁻¹. Furthermore, Co-Fe-S@PB NBs exhibited promising durability with stable performance over an operational period of 33 h at 10 mA/cm².

Furthermore, we developed our strategy towards the PB-templated synthesis of Co-Fe-Mo-S double-layered nanoboxes from Co-Fe-PB NC templates and $(\text{NH}_4)_2\text{MoS}_4$ as a Mo source. Their hollow box morphology gave rise to excellent OER performance when compared to leading metal chalcogenide catalysts (overpotential: 303 mV at 10 mA/cm², Tafel slope value: 42.06 mV dec⁻¹ in 1 M KOH). Moreover, their dual functionality was highly promising with efficient HER activity over the entire pH scale (e.g. small overpotential of 192 mV with Tafel slope of 57.57 mV dec⁻¹ in 0.5 M H_2SO_4) and superior over MoS_2 as a key reference. Current investigations are now focused on the dynamics of these catalysts and their true active species under operational conditions, which involve surface amorphization processes and in situ formation of Co/Fe oxide/hydroxides for Co-Fe-S@PB NBs. Once our in-house easyXAFS system is operational in 2021 (after an installation delay due to the global pandemic in 2020), we will focus on the mechanistic aspects of the new OER/HER catalysts to enable their further tuning for applications.

Bifunctional alloy electrodes for overall water splitting

In this project, we first focused on the optimization of low-cost Ni metal-based electrodes from industrial Ni sources which offer high potential for large scale water oxidation applications. To this end, a facile and scalable etching method was developed to introduce fluorine centers and the resulting activated F/Ni-based electrodes were analyzed in detail with respect to their structural features and their OER performance. A wide range of techniques were applied, including extended X-ray absorption fine structure (EXAFS), XPS, scanning electron microscopy (SEM), and high-resolution TEM. Electrochemical tests showed that the OER performance of the activated F/Ni-electrodes was competitive with leading OER catalysts (low overpotential of ca. 0.22 V, onset potential ~1.43 V (vs. Ag/AgCl) at ~20 mA cm⁻² and a low Tafel slope of ~37 mV dec⁻¹). The reasons for this high activity were investigated with electrochemical impedance spectroscopy (EIS) methods. Implementation of F centers into the electrode surface led to a drastic decrease of the charge transfer resistivity (R_{ct}) by a factor of approx. 10^{10} , which accounts for the notably improved performance through fluorination. Concerning the metal alloy electrodes for overall electrocatalytic water splitting, a series of highly active 3D porous Ni/Fe electrodes with different compositions were fabricated and investigated in detail (including SEM/TEM, Raman spectroscopy and EIS). High porosity of the electrodes was found to be the most important parameter and optimal performances for the porous Ni foam/stainless steel

electrodes reached overpotentials around 610 mV for OER and ~ -1.46 V (vs. Ag/AgCl) for HER to achieve a current density of 100 mA cm^{-2} . This is an excellent starting point for durable and low cost applications.

Oxide WOCs

Over the past year, we focused our attention on the long-standing problem of the influence of the synthetic history on the performance of a given water oxidation catalyst (WOC) and we made progress in our comprehensive parameter exploration of photocatalytic oxygen evolution with cobalt oxide catalysts. Although CoO_x catalysts keep attracting intense interest as photo-driven WOCs, rather little is known about the minimum preparative requirements to notably optimize their performance. We thus re-investigated pristine Co^{2+} cations, which are well known to exhibit a high WOC activity themselves (a continuous issue of decades of Co-WOC research since the early 1980s). To this end, we systematically studied the optimized transformation conditions of plain CoNO_3 as a salt precursor on the way to heterogeneous CoO_x catalysts, employing a wide range of analytical techniques, such as PXRD, TEM, along with extensive XAS and Raman/FT-IR spectroscopy studies. Photocatalytic activity was monitored over a wide timescale with a standard $\text{S}_2\text{O}_8^{2-}/[\text{Ru}(\text{bpy})_3]^{2+}$ assay, covering especially the very early stages of the initial CoNO_3 catalyst. The results show that the cobalt salt undergoes a “self-optimization” process to form CoOOH as the main active phase. The superior O_2 yield (ca. 91%) obtained from such catalysts when left to spontaneous rearrangement under optimized mixing conditions sheds new light on the fast and economic fabrication of photocatalytic Co-based WOCs. The results are currently under completion for submission.

Likewise, our in situ electrochemical XAS studies on $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ OER catalysts are now being completed for submission, and their self-reconstruction under electrocatalytic conditions was newly enlightened with further pair distribution function (PDF) analyses.

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

- As a step towards objective 1, observed laser induced desorption of CO [25], [21-7].
- As a step towards objective 2, understood better the electron transfer kinetics on a non-redox active substrate [20], [21-4].
- Accomplished objective 3 [21-3].

2.2.4 Surfaces (Prof. J. Osterwalder)

- Phosphonic acid layers were deposited on $\text{TiO}_2(110)$ surfaces rather than on $\text{Sb}_2\text{Se}_3(100)$ in order to better reflect the real situation in PEC cell electrodes. Surface dipole formation is observed via work function measurements.
- Ga_2O_3 layers of thicknesses up to 1 nm were grown on $\text{Cu}_2\text{O}(111)$. Attempts to form a single crystalline layer by annealing have failed, instead we observe diffusion of Ga into the bulk of $\text{Cu}_2\text{O}(111)$ at temperatures exceeding 400°C . Interestingly, deposition of Ga metal on $\text{Cu}_2\text{O}(111)$ leads to the formation of gallium oxide and a reduced Cu layer at the interface. Moreover, different band bending is observed on reconstructed and unreconstructed $\text{Cu}_2\text{O}(111)$ surfaces.
- Transient charge injection into the LUMO of Co-pyrphyrin molecules from the $\text{Cu}_2\text{O}(111)$ substrate could not be observed for reasons that are not entirely clear. Therefore, we switched to another pigment, PTCDA, where we observe interesting electron dynamics in the low picosecond range.

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

- Regarding the photovoltage improvement of Sb_2Se_3 , we have made good progress with etching and doping treatments. A Bachelor student discovered that etching of the as-deposited Sb_2Se_3 thin films with concentrated ammonium sulfide solutions gives an improvement in the onset potential by about 100 mV. Additional treatment with a CuCl_2 solution improves the photovoltage by a further 50 mV, in addition to record photocurrents for our lab thus far ($\sim 30 \text{ mA cm}^{-2}$). Current efforts are focused on elucidating the mechanism of these two treatments.
- Advanced analytics via impedance modelling is going very well, and we have published our first complete model of a multilayer photocathode (including capacitances) in January 2021 [21-7].
- We have also completed our first project in the synthesis of value-added chemicals, with the electrochemical oxidation of 5-hydroxymethylfurfural (a biomass derived compound) to 2,5-furandicarboxylic acid (a compound to make a renewable version of PET plastics). The manuscript is currently in revision and will be re-submitted in early 2021.

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

- We developed **the machine learning potential for the Pt-water** interface based on a deepMD model.
- We studied the reconstruction of the **$\text{Cu}_2\text{O}(111)$ surface covered by the hBN overlayer**, and the adsorption of single metal atoms at specific sites (promising trapping sites).
- We studied the competitive adsorption of **water and other molecules at the rutile $\text{TiO}_2(110)$ surface**, also considering different initial surface state by varying the surface hydroxylation. With the help of projected density of state, electrostatic potential profile, and core binding energy analysis, we could characterize the resulting band shift, surface dipole, electronic state alignment, and we could also refine the experiments interpretation.
- The project on **IR induced excitation** and subsequent dynamics for molecules at interface is still in a development phase. The main issue is that the direct accounting of tuneable time dependent fields and of nuclear-electronic couplings need some further software development.

2.2.7 Surfaces / H_2 and CO_2 Storage and Conversion (Prof. K-H. Ernst)

- Creation of squaric acid 2D metalorganic frameworks (MOFs): achieved.
- Metalorganic chains made 2,5-diamino-1,4-benzoquinone-diimine: achieved.
- Melamine and cyanuric acid networks: not achieved.

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

- Continuation of solar water splitting probed by magneto-optics: Setup fully functional. First paper using the method to evaluate the impact of magnetic fields on the hydrogen evolution on Pt published [21-5].
- Photoemission: HAXPES installation completed. First paper published [22]. Membrane approach applied on TiHx .
- Hydrogenation of organic compounds: New project acquired (Joined Empa-PSI project Synfuels).

2.2.9 Theoretical Chemistry (Prof. S. Luber)

We have studied in detail adsorption sites of phosphonate-linkers belonging to a water reduction catalyst on the surface via static methods. Moreover, solvent molecules have been included into the model in order to gain insight into the influence of the solvation environment. This has also been carried out in view of the subsequent study of the catalytic mechanism of this system. Aside from that, a novel approach for (Resonance) Raman spectra for the condensed phase has been developed and published.

2.3 Updated project planning

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

Water / CO₂ Reduction Catalysts

- Coupling two bis-bipyridyl moieties via different heterocycles into novel dual-core water reduction catalysts. Elucidating the mechanisms and performance with different electrochemical techniques. Profound electro- and photocatalysis since these are our best-performing WRCs.
- Derivatizing the cyclic pyrphin-based WRCs with groups different from phosphonates for embedding them into membranes or grafting them on sulfide or selenide materials (Tilley group).
- Benchmarking of polymerised vs monomeric WRCs in homogenous photocatalysis.
- Achieving a fully organic polymer-based photocathode (with Empa).
- Assessing the performance of $[\text{Mo}_3\text{S}_4]^{4+}$ WRCs coordinated to tridentate ligands and comprising a heterometal "M", i.e. $[\text{Mo}_3\text{M}(\text{L}^3)_3\text{S}_4]^{4+}$.

Photosensitizers

- Synthesis, physico-chemical studies of new water soluble photosensitizers with the core-cluster type $[\text{M}_6\text{E}_8]$, e.g. $[\text{Re}_6\text{S}_8]\text{Br}_6$.
- Graft best catalysts on the new semiconductors for preparing photocathodes.

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

In situ electrochemical TEM and XAS studies on perovskite-based OER electrocatalysts

We will investigate perovskite-type OER materials with outstanding electrochemical performance metrics and d-block metal cations other than Co (such as Mn or Fe) with the goal to substitute this relatively expensive metal component. For an in-depth understanding of their transformation under operational conditions, which is crucial for their efficient design in the first place, we will focus on the advanced combination of in situ electrochemical TEM investigations with operando XAS studies. With this knowledge at hand, we will also explore their corresponding HER activity for overall water splitting (e.g. through combination of perovskites and MoS_2 along the lines of our chalcogenide catalyst research).

Dynamic behaviour of spinel oxides and their structural evolution under OER conditions

Starting from our insight into the complex preparation-performance relations of spinel-type OERs (see 3.1.2 below), we will explore them parallel to the target perovskites with in situ electrochemical TEM and XAS techniques. Recent studies point to interesting operando dynamics of 3D transition metal spinel OER catalysts, which have been far less investigated than their perovskite counterparts have.

Long-term and large-scale performance of low cost manganese materials

To round off our investigations on an application-oriented note, we will aim to push the limits on manganese-based oxide OERs as representative materials for low cost technologies. Further mechanistic studies on our recently developed MnO_x electrodes with our operando repertoire will

create a feedback loop for the optimization of their coating procedures to significantly scale up their production dimensions (e.g. with convenient spray coating or thermal decomposition routes). This will promote the sought-after synchronization of mechanistic understanding and efficient production of oxide catalysts for water splitting.

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

- Observe transient intermediates in molecular CO₂ reduction systems.
- Continue towards a working hydrogen evolution system with a photosensitizer and a hydrogen evolution catalyst on an electron-donating semiconductor, such as NiO.
- Solvation of metal hydrides.

2.3.4 Surfaces (Prof. J. Osterwalder)

- Finishing the gallium oxide on Cu₂O(111) project and publish the results.
- Deposition of nickel metal on Fe₃O₄(001) surfaces to study the transition from a nickel single atom catalyst to the formation of a nickel ferrite surface.
- Preparation of hexagonal boron nitride layers on Cu(111) and Cu₂O surfaces and study of photoinduced charge dynamics in these systems.

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

- Sb₂Se₃: Elucidation of the origin of the photovoltage improvement by ammonium sulfide etching and CuCl₂ treatment. Investigations with anchored molecular catalysts.
- Impedance spectroscopy: Now that we have a realistic model and know how to analyze impedance spectra of multi-layer photocathodes, we will use this technique to identify problematic layers and the effect of certain treatments towards improving device performance.
- Immobilization of molecular catalysts via host-guest interactions: we will continue our work in this new area with new hosts (e.g. cucurbiturils) and new anchoring moieties for the guests (e.g. amino coumarin) that enable a control of the binding strength via pH.

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

- We are going to extend the generation of machine learning potentials for other water-metal interfaces, considering, for instance, Ni, Pd, Cu, Ag, and Au. Moreover, we aim at introducing nuclear quantum effects, implementing specific training of path-integral trajectories.
- Using ab initio molecular dynamics simulations, we will study reaction processes among molecules adsorbed at oxide interfaces. The conditions of electrified interface can be taken into account in DFT simulations by applying external electric fields or exploiting ad-hoc designed surface functionalization and periodic boundary conditions.
- 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.
- We will further investigate the hBN/Cu₂O system. The adsorption of metal atoms and metal clusters will be considered also as intercalated between the oxide and the overlayer. In this respect, we will focus on the formation of the oxygen vacancies, on possible reactive processes and on the effects on these latter of confinement at the interface.

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

- Creation of 2D MOFs on thin insulating films, such as MgO on Ag(100).
- Set-up of vacuum preparation / electrochemistry cell for testing of catalytic activity of MOFs.
- Creation of 2D MOFs with pentagonal symmetry.
- Creation of squarate-MOFs on HOPG.

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 hydrogenation of hydrogen evolution reaction electrodes using the hydrogen membrane approach focus on V, ZrV₂.
- Continuation of hydrogenation of gaseous organic compounds with focus on selective conversion ethylene to specific liquid alkanes (jet fuel).

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

- Continuation of the study of molecular Co-based water reduction catalysts on surface.
- Study of the redox potentials for mono- and dinuclear Co-based complexes in collaboration with experimentalists.
- Development of an approach for excited state dynamics of condensed phase systems.

3 Research

3.1 Overview of the Research Activities

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

A main part of 2020 was dedicated to finalizing structure-activity relationships with the tetrapyrrolyl ligands of the bis-bipyridyl type. Numerous functionalities were coupled to the bridging methylene groups and the performances in the hydrogen evolving reaction (HER) benchmarked. We can clearly conclude that the additional functionality is of minor importance. The most crucial factor is the availability of vicinal hydrogen donors such as simple $-OH$ groups.

The best catalyst is the keto-bis-bipyridyl ligand, which hydrolyzes in water to the corresponding hydrate offering two $-OH$ groups in a single WRC. This now assessed result is core for all further developments. The first steps towards a dinuclear WRC, already started in 2019, was continued. The HER is a two-electron process, therefore it seems obvious that two cobalt centers in one single molecule are better than mononuclear catalysts. Taking the need for proton donors into account, two keto-bis-bipyridyl ligands were coupled to a pyrazine moiety. Coordination to cobalt gave a structurally characterized CO_2 dual-core catalyst. This catalyst is electronically coupled via the pyrazine moiety, which makes the cobalt centers communicating with each other, thus enabling a two-electron process. Cyclovoltammetry clearly shows two separated reduction processes, which nature has to be established and is currently calculated in the Luber group.

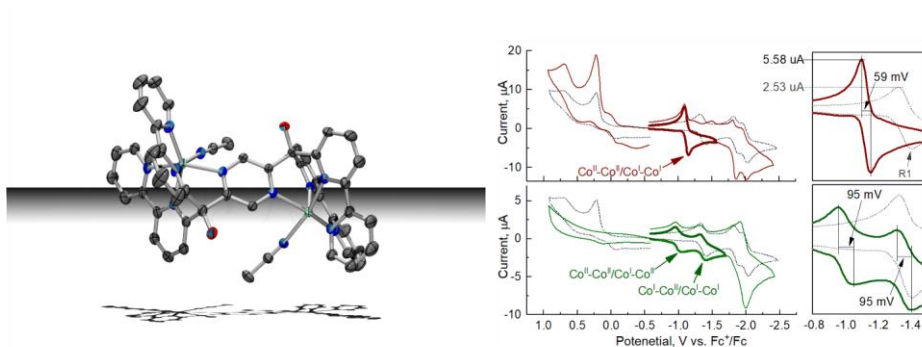


Figure 1: X-ray structure of a dinuclear, pyrazine-bridged WRC with two bis-bipyridyl ligands (left) and cyclovoltammetry of the same complex but bipyridyl- (top) and pyrazine-bridged (bottom).

Some of the structures, that were found to be best performing by benchmarking in homogenous solution, were incorporated in two different types of homopolymers: a conducting, polythiophene, based structure, and a polyvinyl based one. We have shown before that both polymers are still catalytically active in homogenous solution by photochemistry, and shift our focus now on the exact characterization, e.g. the number of repeating units. Furthermore, we devise heteropolymers to separate the catalytic units, introduce acid base functionalities and crosslinking. In terms of characterization not only the polymer size, but also the metal content are important merits under consideration. Ultimately, the polymers will be immobilized on semiconducting supports. First experiments with a standard bulk heterojunction organic solar cell based on P3HT/ C_{60} have shown promising photocurrents.

For the first time, we have evaluated the mononuclear acyclic tetrapyridyl complexes for CO₂ reduction in water. Still ongoing, we found that these classical catalysts perform well in CO₂ reduction albeit at different pH values than what was found for HER. This is probably the first time that photocatalytic CO formation was established with this type of catalysts and cobalt. How the catalyst behaves when grafted on surfaces is currently investigated. To stay with dinuclear catalysts, we explored the mode of action of mono- and dinuclear ruthenium catalysts known to be active in CO₂ reduction. We compared these catalysts in photo- and electrochemical settings. At low concentrations, the dinuclear catalyst was substantially better than the sum of the mononuclear ones. This indicates a concerted action what would be expected in this process. Cooperativity has to be assessed unambiguously though by mechanistic elucidation before a conclusion can be drawn.

This year we started electrocatalysis as a focus of research with the multitude of catalysts since we realized that the WRC stabilities are not performance limiting and they work much better than in a purely homogeneous system with a photocycle involved. For the coming years, the way to photocathodes will be more in the focus than pure homogeneous studies.

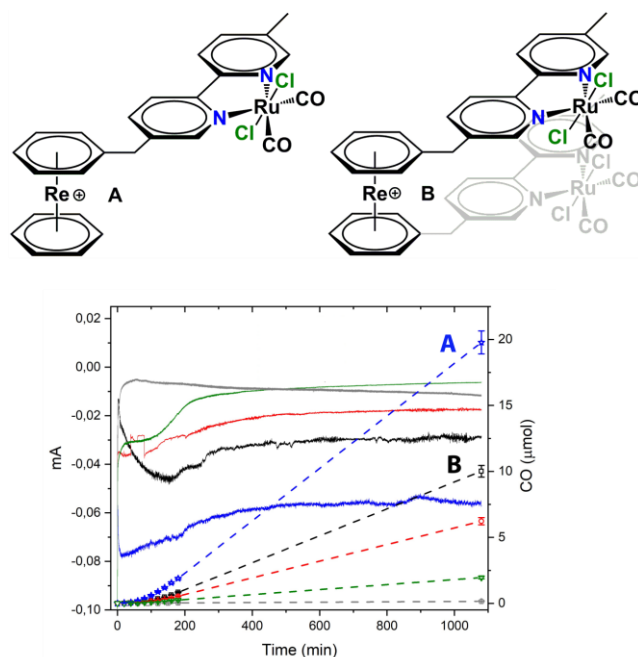


Figure 2: Mono- and dinuclear CO₂ reduction catalysts based on ruthenium (top) and performance in electrocatalysis. At equal Ru concentrations, the dinuclear catalysts (A) makes about double the amount of CO than the mononuclear one (B).

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

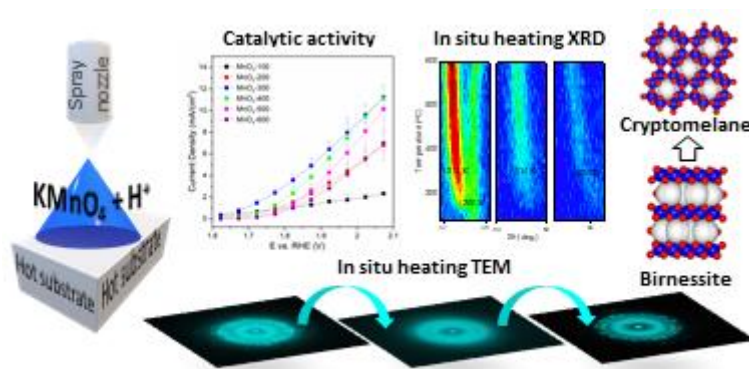


Figure 3: Facile production, in situ monitoring and electrochemical performance of MnO_x electrodes for the OER [21-2].

In the range of leading Mn-catalysts emerged from the convenient thermal decomposition of acidic KMnO₄ solution. This scalable technique furthermore offers very interesting opportunities to increase the electrode size for tapping into the potential of widely available Mn-resources. We monitored their formation with in situ heating TEM and related PXRD studies to shed new light on the structural evolution pathways (see Figure 3). The results also point to challenges in the in situ monitoring of precursor transformations under different analytical conditions [21-2].

In addition to the above-mentioned results, we elucidated fundamental aspects of oxide OER catalyst development. In search of abundant catalysts for large scale and facile preparation routes, we developed MnO_x electrodes with very promising OER performance and stability. These recyclable manganese oxide films with over 100 h of stable water electrolysis performance and overpotentials in

Along these lines, we also conducted comprehensive studies on the influence of synthetic methods and parameters on the properties and performance of spinel-type Co_3O_4 OER catalysts. Our long-time goal is to explain the complex synthesis-properties-performance relations systematically for a representative transition metal oxide-based catalyst system. To this end, we specifically focused on the parameter space of microwave-hydrothermal syntheses as a convenient and rapid technique to generate nanoscale Co_3O_4 materials. Our study demonstrated the key importance of careful synthetic parameter screening for identifying and optimizing the properties of OER catalysts, which are influential for their performance.

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

We will investigate molecular CO_2 reduction catalysts, whose intermediates are observed by transient IR spectroscopy with the help of a new laser system that can cover the relevant timescales from microseconds to seconds.

We now understand better the kinetics of the various electron and energy transfer steps between a Re carbonyl photosensitizer and co-adsorbed Cobalt(II) tetrapyrridyl catalyst on a non-redox active substrate (ZrO_2)^{[21-4], [20]}, which will be the basis of transferring the system to an electron-donating substrate (NiO). Several new Re complexes have been synthesized and characterized as potential photosensitizers^{[8], [21-1]}.

Various metal-hydride complexes were investigated by 2D IR spectroscopy to characterize the peculiarities of the Me-H chemical bond^[7]. Follow-up work will investigate solvation of these molecules and hence address the capability of metal-hydrides to accept or donate hydrogen bonds.

We investigated the vibrational energy transfer between Re-CO molecules on a surface in dependence of surface coverage, and found that is a collective phenomenon with a percolation threshold at a certain concentration^[6] (see Figure 4).

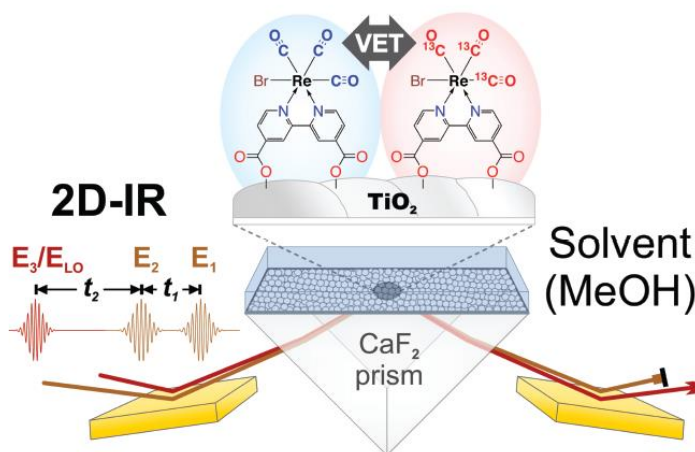


Figure 4: Experimental configuration to measure the vibrational energy transfer between Re-CO molecules on a surface.

3.1.4 Surfaces (Prof. J. Osterwalder)

The Tilley group recently showed that phosphonic acid (PA) layers provide stable dipole layers that allow the tuning of band alignments in semiconductor heterojunctions (R. Wick et al., *Energy Environ. Sci.* **2019**, *12*, 1901-1909). In order to obtain a fundamental understanding of this effect, we prepared PA layers of thicknesses up to 5 Å and measured the work function change to monitor the surface dipole formation (Figure 5). The layers were deposited by dipping the clean TiO₂(110) surface into dilute solution of PA in ethanol. While co-adsorbed ethanol reduces the work function, a monotonous increase is observed as a function of thickness of the PA layer. Recurring problems with our VG ESCALAB 220 surface science cluster tool slowed down the gallium oxide growth project which we plan to finish in spring 2021. The studies of charge injection into PTCDA molecules on Cu₂O(111) are almost finished and promise to shine light on relaxation processes at the semiconductor-molecule interface.

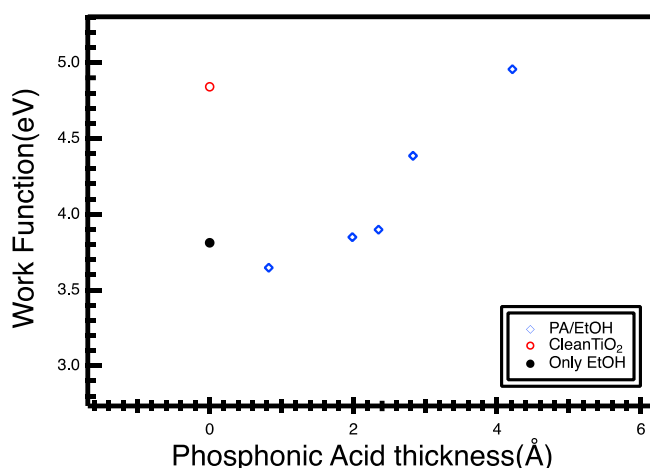


Figure 5: Work function values, measured by ultraviolet photoelectron spectroscopy, as a function of the thickness of the phosphonic acid layer.

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

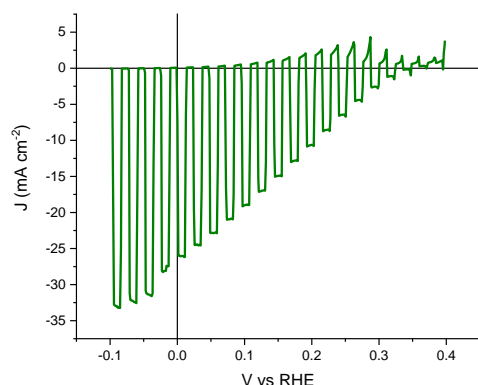


Figure 6: Sb₂Se₃-based photocathode for hydrogen evolution in pH 7 phosphate buffer solution under intermittent one sun illumination. Multilayer stack configuration: FTO/Au/Sb₂Se₃/TiO₂/Pt.

For the Sb₂Se₃, we have achieved record photocurrents for our lab, comparable with the best in the literature (> 30 mA cm⁻²). Moreover, we have improved the photovoltage to a respectable level with etching and treatment with CuCl₂ solution (Figure 6). The challenge now is to improve the fill factor, as there is clearly a resistive loss based on the slow rise of the photocurrent with applied voltage. Our impedance work will be invaluable in diagnosing the issues in these multilayer electrodes.

We have successfully demonstrated that molecular catalysts can be stably anchored to electrode surfaces via host-guest interactions, even in organic solvents. In fact, the binding with cyclodextrin hosts and naphthalene moieties on the guest is too strong to fully exchange the guests. We would

like to have better control of the binding, and we will therefore explore systems where we can modulate the binding strength using some orthogonal parameter, such as pH.

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

The work in our group aims at the atomistic understanding of structure/property relations as well as of processes and catalytic mechanisms involving functional materials of interest in photocatalysis and electrochemistry. To this purpose we employ electronic structure calculations also combined with ab initio molecular dynamics. Some of the projects are inspired by the collaboration with other groups in the consortium, e.g., Osterwalder's group. On the other hand, we also propose model systems that allow a more in-depth investigation of some fundamental aspects, as specific properties of interfaces, spectroscopic features of adsorbates, dynamics at surfaces.

The learning of efficient empirical potential for the water/Pt(111) has been obtained from an extensive set of configurations (energy and forces) which were generated by DFT AIMD during our previous project on this system. The resulting potential allows for molecular dynamics simulations 1000 times faster than standard ab initio methods, with

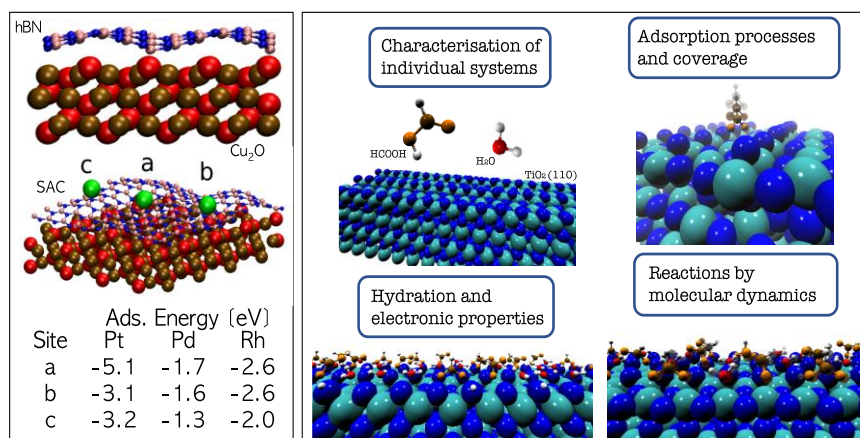


Figure 7 Left: Optimized hBN/Cu₂O system. The corrugated hBN offers different adsorption sites for single metal atoms (a,b,c). Some computed adsorption energies are summarized in the table. Right: Schematic representation of the strategy to investigate the functionalization of an oxide surface, including structural optimization, hydration, spectroscopy characterization and dynamics.

comparable accuracy in sampling the configuration space. The reliability has been assessed by comparing the water radial distribution functions and dipole orientations at the interface, with those generated by DFT-MD trajectories.

The Cu₂O/hBN interface has been optimized at different coincidence site lattices. Structural properties and energetics are obtained at the DFT level of theory. A promising feature of placing inert h-BN over cuprous oxide is that it can protect the substrate from degradation whilst potentially providing trapping adsorption sites for single atom catalyst (SAC) metals. Starting from the resulting most stable models, the formation energy of O vacancies at the interface and the adsorption of single metal atoms has been investigated. Preliminary studies of the dissociation of water on the adsorbed single metal atoms have been carried out.

The surface of oxide undergoes hydrophobic-hydrophilic photo-switch when illuminated with UV radiation under ambient conditions. The hydrophilic UV-induced effect is understood to be related to the oxidation of adsorbates on the surface. For instance, by exposing rutile (110) to air or solution, many studies report a (2x1) surface reconstruction on TiO₂. We already addressed the changes of the dipole layer and work function of oxides by the adsorption of dipolar molecules. Our goal is to employ DFT to study the competitive adsorption between water and other molecules under different conditions. In particular, we investigated the co-adsorption of formic acid and water (dissociated or intact). Different arrangements of the molecules on the surface are tested, and projected densities of states obtained are compared to experimental XPS to validate our results. Next, ab initio MD will be employed to take temperature and dynamic effects of the adsorbates into account.

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

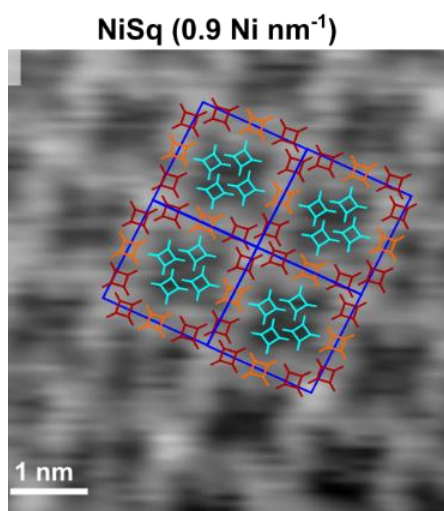


Figure 8: STM image of a 2D Ni/Cu-squarate MOF on Cu(100).

Metal-organic frameworks (MOFs) are a combination of inorganic constituents and organic ligands with a high degree of variability. The synthesis and thermal stability of monolayer thin Cu-, Ni- and Fe-squarate 2D MOFs is studied using X-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM) and temperature programmed reaction spectroscopy (TPRS) on a Cu(100) surface in ultrahigh vacuum. Highly ordered 2D squarate MOFs are obtained by mild annealing of squarate multilayers. Upon annealing at higher temperatures, the Ni- and Fe-squarate layers undergo autocatalytic surface explosion chemistry with carbon monoxide as desorbing product in a narrow temperature interval. Despite the different stabilities of Ni- and Fe-based MOFs, mixed {Ni+Fe}-MOFs also decompose in a single narrow temperature interval. Such behavior is explained by a numerical model which – unlike rate equation-based kinetics – explicitly considers the chemical nature of nearest neighbors.

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

Originally, we were aiming at applying a magneto-optical setup to probe material changes during electrochemistry operando. In addition, external magnetic fields affect various electrochemical processes directly, and can be used to enhance the efficiency of the electrochemical water splitting reaction. However, the driving forces behind this effect are poorly understood due to the analytical challenges of the available interface-sensitive techniques. The magneto-optical set-up developed within the LightChEC project allowed us to juxtapose the magnetic properties of the electrode with the electrochemical current densities in situ at various applied potentials and magnetic fields. On the example of an archetypal hydrogen evolution catalyst, Pt (Co/Pt superlattice), we provide evidence that a magnetic field acts on the electrochemical double layer affecting the local concentration gradient of hydroxide ions, which simultaneously affects the magneto-optical and magnetocurrent response.

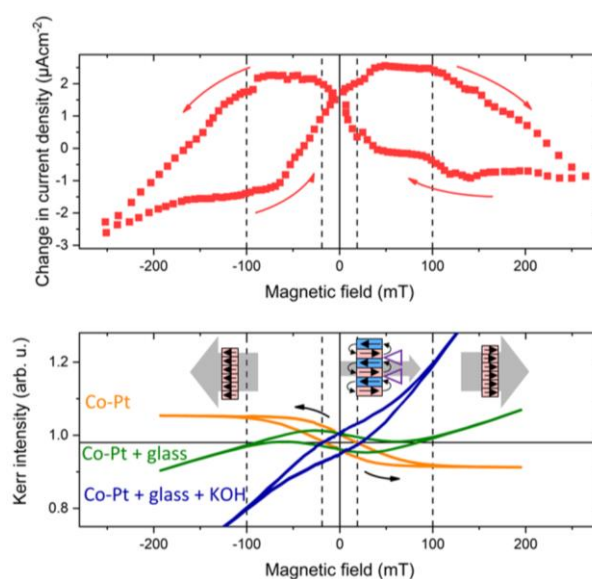


Figure 9: Top panel: Magnetocurrent density measured in 0.1 M KOH at -0.15 V and 3 s per measurement point. Bottom panel: MOKE hysteresis curves of Co/Pt in air (orange), with a glass optical window (green) and in 0.1 M KOH (blue). The sketches depict the magnetic domain structure causing magnetic stray fields and thus large local gradients near the interface even at low applied magnetic fields. The dashed lines are drawn at the MOKE coercive fields and saturation points.

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

We have worked in several directions in the context of the LightChEC URPP. On the one side, a thorough analysis of enhanced sampling methods (Blue moon, metadynamics) has been conducted where we could show that commonly used collective variables have certain shortcomings and may not describe the O-O bond formation, which is an essential step during water oxidation, in a proper and sophisticated manner. Based on this finding, we proposed a methodology for studying this reaction, which we applied to a water oxidation catalyst in solution. Thanks to this, we could illustrate the key role of the solvent environment and the influence of the intramolecular base in lowering the energetic barrier for this reaction. Moreover, we studied in detail a novel catalyst, which was designed in silico by us recently.

On the other side, our research has dealt with the adsorption behavior of a Co-based water reduction catalyst on surfaces. Moreover, properties such as redox potentials have been investigated with computational methods. Aside from that, excitation energies for a photosensitizer and modified version of it have been studied.

All this work has been conducted in close collaboration with experimental groups, in particular the group of R. Alberto.

3.2 Scientific Activities (Organized by URPP)

The URPP LightChEC serves as an exchange platform for all researchers working on the topic of water splitting at the University of Zurich, Empa and PSI. Researchers in positions not funded by the URPP regularly also take part in scientific activities of LightChEC. Around 60 people are part of this scientific community, ca. 19 of which were directly employed by the URPP in 2020.

As in the previous year, the URPP's science seminars were integrated into the department seminars and highlighted as **LightChEC Co-Seminars**.

Four speakers were invited on behalf of LightChEC to give a talk in 2020:

- 25 February: Prof. Dr. Arne Thomas, TU Berlin, DE
"Tuning Porosity and Backbone Chemistry of Covalent Organic Frameworks for (Photo)Catalytic Applications"
- 7 April: Prof. Dr. Curtis Berlinguette, The University of British Columbia, USA
postponed to 2021/2022
- 3 November: Prof. Dr. Mischa Bonn, Max Planck Institute for Polymer Research, DE
postponed to 2021/2022
- 8 December: Prof. Dr. Julia Kunze-Liebhäuser, Leopold-Franzens University Innsbruck, AT
"Active Equals Dynamic: The Secret of Copper Electrocatalysts"
postponed to 2021/2022

We also continued the well-established monthly **LightChEC Discussion Meetings**. This series of talks is meant to stimulate exchange and discussions within the LightChEC consortium. Members and associates are encouraged to present interesting research articles, methods or new concepts to the community, followed by a discussion about the topic.

Although voluntary, the meeting is usually well attended by 20 to 30 people, including most of the PIs. This discussion meeting not only gives researchers an opportunity to practice scientific presentations, but also teaches new concepts, establishes a culture of discussion and thus strengthens the joint spirit of the consortium across the different groups. When the Covid-19 pandemic rendered it impossible for in-person meetings to take place, the talks were continued in video call format.

The bi-annual **LightChEC Summer School** (including a symposium) was planned for August 2020. However, it had to be cancelled because of the pandemic. The summer school will be organized again in 2022.

From UZH Prof. Alberto and Prof. Tilley were planned to speak.

External speakers confirmed for the LightChEC Summer School 2020:

- Dr. Aaron Appel, Pacific Northwest Laboratory, USA
- Dr. Carolina Gimbert-Suriñach, Institute of Chemical Research of Catalonia, ES
- Prof. Dr. Evert Jan Meijer, University of Amsterdam, NL
- Prof. Dr. Richard Kramer Campen, Universität Duisburg-Essen, DE
- Prof. Dr. Carsten Streb, Ulm University, DE
- Dr. Lydia Petermann, Ulm University, DE
- Prof. Dr. Martin Sterrer, University of Graz, AT
- Dr. Elisabeth von Hauff, VU Amsterdam, NL

Some of the speakers have agreed to give a talk during the symposium in 2021 instead.

4 Academic Career Development

4.1 Activities in Academic Career and Development

Due to his enormous scientific contributions to research and education in the field of sustainable energy research, David Tilley was promoted to associate professor at the Department of Chemistry. This promotion asserts a continuation of this field at the University of Zurich. Tilley holds the assistant professorship that was created by the URPP LightChEC. He complements not only research at the department but also education, which is extended more specifically to semiconductors, green chemistry and electrochemistry. Since being promoted, he established the field of electrochemical biomass conversion, a topic not immediately related to the core topics of LightChEC but being a very important and well visible part of sustainable energy research.

Part of the budget (Education) is reserved for PhD students intending to attend a special conference. The board of directors selects the best applications, which are funded with the full costs. In 2020, four out of ten applications were funded. Due to cancellations, none of the awardees could finally attend the conference. The applicants benefitted in any case by writing a proposal and being awarded. If financially feasible, we will continue with this funding scheme.

To support the promotion of his academic career, Dr. Grigory Smolentsev from the division at PSI was made an associate member of LightChEC. This will give us access to SLS in the field of mechanistic elucidation of water splitting by e.g. XAS and give him the opportunity to get new catalysts and materials.

In total, eight PhD students finished their thesis during the reporting year.

Three PhD student graduated in the Alberto group in 2020. One (Nicolas Weder) remained as postdoc in the Tilley group and one (Daniel Hernández Valdés) became a postdoc to McMaster University CDN. One former PhD student (Peter Müller) joined a private company. Two Master student finished their thesis in 2020.

Prof. Patzke continued to host and to support Dr. Fabian von Rohr as an SNF Ambizione grant holder in her research group. He successfully applied for a SNSF professorship and will start his new and fully independent position in February 2021. One PhD student (Karla Lienau) defended her PhD thesis in 2020. For promoting excellent females in science, Dr. Sima Heidari applied for an Ambizione grant in the Patzke group.

Two students are about to graduate in the Hamm group (Ricardo Fernández Terán and Gökçen Tek), no PhD finished during the reporting year. One Master student (Jeanette Ruf) defended her MSc thesis and continues her PhD in this group.

Dr. Sourav Banerjee has left the Osterwalder group by the end of the reporting year to take a position as assistant professor in the department of chemistry of Central University Visva Bharati in India.

Dr. Zbynek Novotny is currently applying for an SNSF Eccellenza Professorial Fellowship that will be hosted by the Department of Chemistry of UZH and co-hosted by PSI and the Department of Physics. His project would be centered at the Swiss Light Source at PSI.

Prof. Tilley, as every year, had a 30-minute discussion with each student/postdoc regarding their career ambitions and feedback on their performance. One of his Master students, Dhananjeya Kumaar Venkatesababu Savitha, graduated in 2020 and is now a PhD student at ETH.

One postdoc from the Ernst group (M. Baljovic) has been sent to the Molecular Foundry Berkeley, USA in March 2020 for advanced experiments. Dr. Christian Wäckerlin from the group is currently applying for an SNSF Eccellenza Professorial Fellowship to be hosted by EPFL and co-hosted by PSI.

In the Borgschulte group, two students completed their PhD: Jasmin Terreni (defense in July 2020) has since started work as program director of the Master of Science in Life Sciences at ZHAW. Olga Sambalova defended her PhD in January 2021.

In the Lubber group, one PhD student (Mauro Schilling) defended his PhD thesis in 2020. He was part of an SNF project.

One PhD student from the Hutter group (Jinggang Lan) graduated in the reporting year.

4.2 Gender Equality Development

During the report period, Greta Patzke continued to serve as MNF representative of the UZH Gender Equality Commission. Furthermore, she was elected to serve for a new term as member of the MNF Gender Committee.

In most groups, the gender balance is somewhat established (LightChEC associated only), e.g. Tilley group with six males, five females, Alberto group three females and two males. In the Hamm group, two female postdocs are working on the project (Kathryn Tracy, Kerstin Oppelt). The Ernst group comprises two female students. From January 2021 on, one female PhD student will work in the frame of this project.

The unbalances are mainly due to the corresponding ratios of applications for which more males than females apply. In the Borgschulte group for instance, the group internal gender ratio fell from three females to three males at the beginning of 2020 down to one to three at the end of the year.

5 Publications

- [1] **Balaghi, S. E.; Triana, C. A.; Patzke, G. R.** Molybdenum-Doped Manganese Oxide as a Highly Efficient and Economical Water Oxidation Catalyst. *ACS Catal.* **2020**, *10* (3), 2074–2087. <https://doi.org/10.1021/acscatal.9b02718>.
- [2] Bolliger, R.; Meola, G.; Braband, H.; Blacque, O.; Siebenmann, L.; Nadeem, Q.; **Alberto, R.** Fully Solvated, Monomeric Re^{II} Complexes: Insights into the Chemistry of $[\text{Re}(\text{NCCH}_3)_6]^{2+}$. *Inorg. Chem.* **2020**. <https://doi.org/10.1021/acs.inorgchem.0c02819>.
- [3] **Borgschulte, A.; Terreni, J.; Billeter, E.**; Daemen, L.; Cheng, Y.; Pandey, A.; Łodziana, Z.; Hemley, R. J.; Ramirez-Cuesta, A. J. Inelastic Neutron Scattering Evidence for Anomalous H–H Distances in Metal Hydrides. *PNAS* **2020**, *117* (8), 4021–4026. <https://doi.org/10.1073/pnas.1912900117>.
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The following publications are referenced in the report but published (in print) only in 2021:

- [21-1] **Fernandez-Teran, R. J.**; **Sévery, L.** Coordination Environment Prevents Access to Intraligand Charge-Transfer States through Remote Substitution in Rhenium(I) Terpyridinedicarbonyl Complexes. *Inorg. Chem.* **2021**, 60 (3), 1325–1333. <https://doi.org/10.1021/acs.inorgchem.0c02914>.
- [21-2] **Heidari, S.**; **Balaghi, S. E.**; Sologubenko, A. S.; **Patzke, G. R.** Economic Manganese-Oxide-Based Anodes for Efficient Water Oxidation: Rapid Synthesis and In Situ Transmission Electron Microscopy Monitoring. *ACS Catal.* **2021**, 2511–2523. <https://doi.org/10.1021/acscatal.0c03388>.
- [21-3] **Oppelt, K. T.**; **Sévery, L.**; M. Utters, S. **D. Tilley**, and **Hamm, P.** Flexible to Rigid: IR Spectroscopic Investigation of a Rhenium-Tricarbonyl-Complex at a Buried Interface. *Phys. Chem. Chem. Phys.* **2021**. <https://doi.org/10.1039/D0CP06546C>.
- [21-4] **Oppelt, K. T.**; **Hamm, P.** About Control: Kinetics in Molecule Based Photochemical Water Reduction Investigated by Transient IR Spectroscopy. *Chimia* **2021**, in press.
- [21-5] **Sambalova, O.**; **Billeter, E.**; Yildirim, O.; Sterzi, A.; **Bleiner, D.**; **Borgschulte, A.** Magnetic Field Enhancement of Electrochemical Hydrogen Evolution Reaction Probed by Magneto-Optics. *Int. J. Hydrogen Energy* **2021**, 46 (5), 3346–3353. <https://doi.org/10.1016/j.ijhydene.2020.10.210>.
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- [21-8] Yang, W.; **Moehl, T.**; **Service, E.**; **Tilley, D.** Operando Analysis of Semiconductor Junctions in Multi-Layered Photocathodes for Solar Water Splitting by Impedance Spectroscopy. *Adv. Energy Mater.* **2021**, 2003569. <https://doi.org/10.1002/aenm.202003569>.

6 Structures

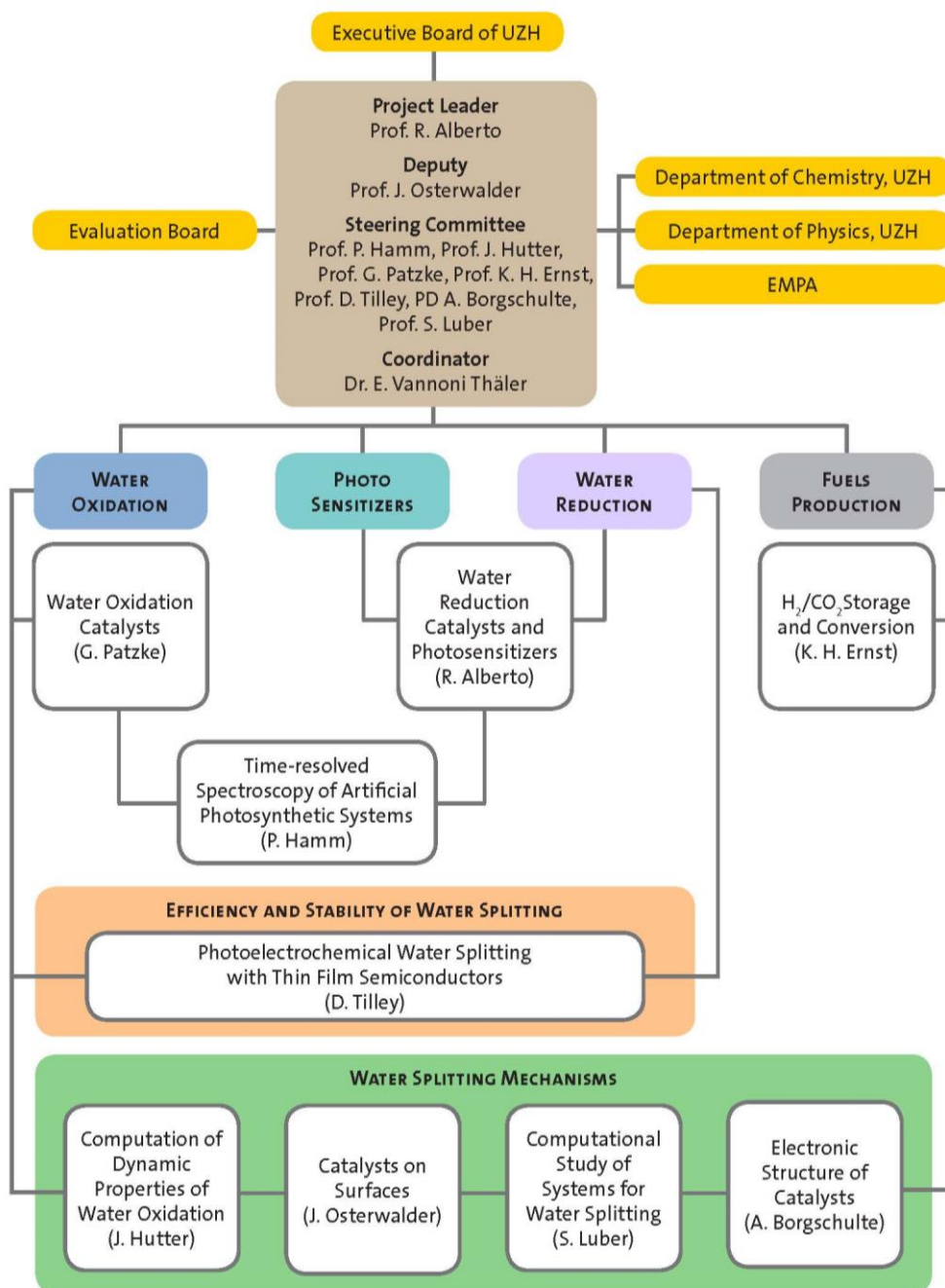


Figure 10: Organizational structure of the URPP LightChEC in 2020.

The URPP structure has remained the same as 2019. The coordinator Elisabetta Vannoni-Thäler left the program at the end of 2020 and was followed by Eva Stehrenberger.

For the last phase of the URPP, Prof. Patzke will become deputy project leader and then leader due to the upcoming retirement of Profs. Osterwalder/Alberto.

7 Third-Party Funds

7.1 Third-Party Funding of URPP Project Leaders

SNSF Divisions I to III

- Prof. Roger Alberto, Solar Light-driven Homogeneous Catalysis for Greener Industrial Processes with H₂ as Energy Source and CO₂ as C1 Building Block, 02.2017 – 01.2021, CHF 346'189.
- Prof. Peter Hamm, NCCR Molecular Ultrafast Science and Technology (MUST), 06.2018 – 06.2022, CHF 720'000
- Prof. Peter Hamm, 200020B 188694/1 (Extension: Ultrafast Vibrational Spectroscopy of Allosteric Proteins), CHF 773'577, 01.2020 – 12.2022
- Prof. Jürg Osterwalder, Surface Physics with Single-Layer Materials and Molecular Layers, SNSF Grant 200020 172641, CHF 839'027, 04.2017 – 03.2021.
- Prof. Karl-Heinz Ernst, Advanced chiral surface systems (10.2018 – 9.2022, CHF 530'768)
- Prof. Karl-Heinz Ernst, Metal cluster assemblies with a twist (01.2018 – 12. 2018, CHF 2'363'628, Sinergia w/UNIGE)
- Dr. Andreas Borgschulte, Ultra-High Pressure Hydride X-ray Photoelectron Spectroscopy, CHF 631'400, 2018 – 2022.
- Prof. Sandra Luber (SNSF Professorship), In Silico Investigation and Design of Bio-inspired Catalysts for Water Splitting (CHF 1.6 Mio., 02.2017 – 02.2021).

SNSF Divisions IV

- Prof. Jürg Osterwalder, NCCR Molecular Ultrafast Science and Technology (MUST), Phase III Project "Ultrafast Structural and Electron Dynamics in Surfaces", CHF 350'000, 07.2018 – 06.2022.
- Dr. Andreas Borgschulte, Mobiler Nachweis von Mikroverunreinigungen in Luft und Wasser mittels deep-UV Raman Spektroskopie, (BAFU, innovation fond), CHF 110'000, 2017 – 2019.
- Dr. Andreas Borgschulte, Spark Grant N° 190358, Cataluminescence, CHF 100'000, 12.2019 – 11.2020.
- Dr. Andreas Borgschulte, Requip N° 182987, Hard X-ray Photoelectron Spectrometer, CHF 700'000 (50% with Lars Juergens, Empa), 11.2019 – 11.2020.

Industry and Others

- CSC for Scholarship Hang Chen from 02.2019 – 02.2023 (project leader: G. R. Patzke), PhD salary paid to H. Chen
- Prof. David Tilley, Chinese Scholarship Council (CSC) Fellowship (Zhenbin Wang, project leader: SD Tilley); 10.2019 – 09.2023, allocated: CHF 100'800.
- Prof. David Tilley, Spanish Fellowship (Dr. Laxman Gouda, project leader: SD Tilley); 04.2019 – 03.2020, allocated ca. EUR 28'000.
- Prof. David Tilley, Photoelectrochemical Synthesis of Hydrogen Combined with Water Desalination, PERA Complexity Project, CHF 110'384, 09.2020 – 08.2021.
- Prof. Jürg Hutter, Sparse Tensor Linear Algebra Library, PASC, ETH Board: 07.2017 – 06.2020, CHF 428'640
- Prof. Jürg Hutter, Grant from Swiss National Supercomputing Center (ca. 8.4 Mio core hours per year 2019 – 2021).
- Dr. Andreas Borgschulte, Joined Empa-PSI project Synfuel, 6 Mio. CHF (Borgschulte group ca. CHF 300'000), Empa), ETH Board: 01.2021 – 12.2023.
- Prof. Sandra Luber, Two grants from Swiss National Supercomputing Center (until 2023)
- Prof. Sandra Luber, Grant from Platform for advanced computing in Europe

7.2 List of Funded Projects within Profit-Center (PC) of the URPP

- Prof. Greta Patzke, Forschungskredit Devi Prasad A S, 01.2021 – 09.2021, CHF 43'160
- Prof. David Tilley, Photoelectrochemical Synthesis of Hydrogen and Value-Added Chemicals for a Sustainable Chemical Industry, SNF Grant 200020_184737, CHF 900'000, 09.2019 – 08.2023.
- Prof. David Tilley, Forschungskredit to Dr. Wooseok Yang, CHF 73'515, 09.2019 – 08.2020.