



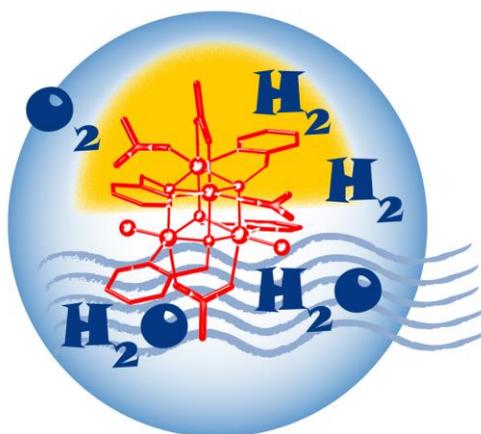
University of
Zurich^{UZH}

URPP Solar Light to Chemical Energy Conversion

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URPP LightChEC

Scientific Report **2019**



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1 Management Summary

An important event during the reporting period was the evaluation of the URPP LightChEC by the external board of evaluators (Profs. Stenbjörn Styring, Uppsala, Hubert Girault EPFL and Hans Geerlings, U Delft). The two day evaluation included presentations, discussions with the individual PIs, PhDs and students and a poster exhibition. The report by the evaluators was very positive, recommending to continue in the third phase and some changes in the management structure. A quotation from the report mirrors the progress of the URPP very well: "*The unpublished work presented during the evaluation was of extremely high level showing a large diversity building on the well-developed close collaborations*". Indicative for the URPP LightChEC is the intense collaborations between the groups. About 50% of all papers are collaborative works, i.e. they could only be realized on a high level due to the cooperations, mirroring the spirit of LightChEC very well. The third phase was then confirmed by the board of the University by the end of 2019. In extension to the data of the previous reports, it should be emphasized that the number of publications in 2019 exceeded those of 2018. All cooperations are being pursued and an additional interaction with a group at PSI complements the available analytical instrumentation. Different outreach activities were undertaken to inform the public about our program and the importance of artificial photosynthesis.

As every second year, a symposium under the umbrella of LightChEC was a further highlight in interactivity. Six international, leading scientists from artificial photosynthesis reported about their research. They discussed with the PhDs and Post docs during a poster session at which the young researchers presented their results. Regular science discussion meetings and LightChEC department seminars together with the Department of Chemistry assured a continuous exchange in house and externally. These seminars are very welcome, in particular for the students. A certain amount of the regular budget was reserved for competitive applications from inside LightChEC to attend conferences. This gives PhDs and Post Docs the opportunity to go to conferences outside of the regular budget. The PIs obtained many invitations to international conferences (appendix).

The process to promote David Tilley to associated professorship was started, final decision will be in 2020. Prof. Tilley contributes substantially to LightChEC and fills a gap in education and research. Sandra Luber was promoted to an associated professorship and she will thus be full member of LightChEC until the end of the third phase.

The budget for 2019 was met, a small excess will be carried over to 2020 and is reserved for the summer school and other activities. Since the third phase will rely on half of the budget of previous phases, the URPP will reduce its contributions to the PIs accordingly. A good amount of third party funds could be acquired, which support continuation of LightChEC to a great extent.

The past year was thus with regard to science, collaborations, career opportunities for young researchers and the promotion of female scientists successful and fulfilled in these respects the requirements from UZH. The very positive feedback from the evaluators but also recognition by the international community does power our efforts for the forthcoming years.

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:** Improving the performance of WRCs and adsorbing them on solid supports, either for photoelectrocatalysis or for electrocatalysis. Generating dinuclear WRCs with concerted action. Combining WRCs with photosensitizers on solid phase support and evaluating their stabilities. Investigation about the option of applying the catalysts also for CO₂ reduction. Introducing additional functions at the bridgehead position in cyclic and acyclic tetrapyrrolyl systems (pyrphyrins).
- **Photosensitizers:** Polymerization of WRCs for grafting them to organic solar cells. Evaluation if electron transfer takes place for the organic photosensitizer to the WRCs. Investigations about the convenience of using the bis-arene rhenium complex as scaffold for photosensitizers and WRCs. Exploring Ir-based photosensitizers
- **Electron Relays - Electrocatalysis:** Elucidating the stabilities of the water reduction catalysts by switching from photocatalysis to electrocatalysis. Replacing the photocycle by an electrocycle. Exploring further sacrificial electron donors apart from ascorbic acid.

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

- **Molecular WOCs:** We will proceed from Co/Ni-based molecular WOCs to the development of Cu-based dinuclear and oxocluster WOCs through mechanistically founded synthetic concepts. Next, their immobilization on oxide semiconductor surfaces for high performance hybrid photoanodes will be implemented and monitored.
- **Composite and nanoscale WOCs:** We will develop our research on nanoscale transition metal/carbon composites further towards single atom catalysts. Preferred target systems will include phthalocyanines of Co, Ni and Fe on graphene oxide sheets. This further size reduction and exposure of the active size will enable us to study catalytic mechanisms in detail with operando techniques. Activities will be complemented with studies on the application of InP/ZnS quantum dot systems for H₂ generation from biomass.
- **Oxide vs. metallic catalysts:** In-depth in situ TEM studies on high performance complex perovskite-type WOCs will be compared to binary and doped low cost Mn-based oxide materials. Their performance will be compared to corresponding transition metal alloy catalysts on stainless steel electrodes.

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

- Finalize pump-probe spectroscopy of hydrogen-evolution on Pt@TiO₂. If we fail to unambiguously identify Pt-H as a transient intermediate, e.g. since the Pt-H vibration is too weak or since its transient population is too small, we will move to CO₂ reduction on Au@TiO₂, whose proposed intermediates (e.g., Au-COO⁻ or Au-COOH) must have strong IR marker modes.
- Finalize surface dilution experiments to understand the distance dependence of vibrational energy transfer on surfaces.
- Continue with a complete water splitting system on surfaces.

2.1.4 Surfaces (Prof. J. Osterwalder)

- Controlled growth of MoS₂ on Sb₂Se₃(100) and characterization of structure, band alignment and band bending, as well as stability in water.
- Controlled growth of Ga₂O₃/Cu₂O(111) and characterization of structure, band alignment and band bending.
- Measurement of excited state lifetime of Co-porphyrin on Cu₂O(111).
- Measurement of semiconductor-water interface with ambient pressure XPS.

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

- Investigate guest-host approach for transiently heterogenized molecular catalysts-based electrocatalysis.
- Publish initial work on dipole strategy for improved performance in semiconductor-based solar energy conversion systems.
- Publish follow up paper to our Sb₂Se₃ discovery, further solidifying our international standing with this promising material.

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

- Investigation of nuclear quantum effects (NQE) for molecules on the Pt(111) surface. We investigate if NQE contribute to electrochemical properties at interfaces, i.e. band alignments or computational standard hydrogen electrode.
- Further investigation of rhenium and ruthenium dyes on ultrathin alumina.
- Band alignment of thin phosphonic acid films on Al₂O₃ and TiO₂.
- Investigation of CO₂ activation on CeO₂.

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

- Synthesis of special graphene with targeted defects ("nanographene").
- Modification of carbon systems with noble metals as hydrogenation catalysts.
- Studying the activity of carbon-metal systems towards hydrogenation.

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

- Continuation of the solar water splitting membranes development for *in-situ* XPS measurements of heterogeneous solar water splitting catalysis.
- Solar-water splitting probed by magneto-optics: magneto-optical hysteresis of Co-electrodes during (photo-) electrochemistry.
- Hydrogenation reaction of organic compounds facilitated by metal hydrides.

2.1.9 Theoretical Chemistry (Prof. Sandra Luber)

- Elucidation of the oxygen-oxygen bond formation and related environmental effects in water oxidation with different protocols based on enhanced sampling methods.
- Beyond density functional theory: investigation of importance of correlation effects for nucleophilic water attack in water oxidation.
- Development of efficient approach for electronic (circular dichroism) spectra.

2.2 Achieved objectives and milestones

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

- Water / CO₂ Reduction Catalysts:** Based on our cyclic and acyclic poly-pyridyl ligands and complexes, we have introduced a wide variety of additional coordinating groups for improving the overpotential and the stability. The fifth group covers heteroaromatic rings such as pyrrole, imidazole, pyrazole and others. The objective of diversifying the basic ligand frameworks made progress since some complexes displayed improved physico.-chemical properties. Furthermore, all basic structures were conjugated to phosphonate groups for grafting them on electrodes or photoactive semiconductor materials. We assessed the stabilities of the grafting as a function of condition parameters and established the hydrogen production. Different new mono- and dinuclear cobalt and ruthenium complexes / WRCs were prepared and investigated towards CO₂ and water reduction. Of particular interest was to discern between the two in electrocatalytic systems. Tuning the potential, a high selectivity for CO or H₂ was achieved (paper submitted). Electropolymerization of vinyl bearing catalysts and grafting on organic photovoltaic cells is established (together with Empa) but efficiency needs to be assessed. A novel kind of dinuclear catalysts was synthesized and fully characterized. Since H₂ formation is a two electron process, concerted action should lead to more rapid catalysis. Mechanisms of electron transfer dynamics on surfaces have been explored successfully with the Hamm group. Catalysts and photosensitizers were also transferred to the Osterwalder group. Extended electrochemical characterization with all available catalysts was completed.
- Photosensitizers:** The development of new photosensitizers based on the pyrphyrin framework has not been pursued further in this year since a focus was put on electrocatalysis. A new collaboration with University of Basel has though been established and their photosensitizers will be evaluated in our photocatalytic systems.
- Electron Relays - Electrocatalysis:** Several other, organic electron relays have been investigated (e.g. TDAE or hydroquinones) but only hydroquinones in presence of phosphines were successful. They do not offer advantages but may be suited for some special systems. For grafting catalysts and photosensitizers on surfaces to move from homo- to heterogeneous catalysis, we have synthesized different multi-phosphonate anchors. Two different catalysts, one acyclic and a pyrphyrin-type macrocyclic framework have been conjugated to these anchors. The resulting complexes were successfully grafted on nanoparticles and on an ITO type electrode. Electrocatalysis run for days without decrease of current (paper submitted), clearly showing for the first time the persistent stability of the hydrogen evolving catalyst based on cyclic tetrapyrrolyl systems and as confirmed by XPS (Osterwalder group). The milestone of further stable WRCs was thus achieved.

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

- Molecular WOCs:** In 2019, we published our major progress in the understanding of the formation pathways of Co-cubane molecular WOCs. With a series of systematic experiments, we elucidated the assembly two structurally different Co-cubane types from key building blocks in solution. Along these lines, the presence of counteranions was identified as a hitherto unknown crucial parameter for the predictive design of Co/Ni-cubane WOCs, and several more new compounds emerged from this strategy. In parallel, we finished and published our study on Co-cubane cocatalysts on hematite photoanodes and contributed significantly to their understanding. For the first time, we revealed a functionality transition of the {Co(II)₄O₄}-type cocatalysts from predominant hole reservoirs to catalytic centers as a function of the applied bias. To this end, we combined photoelectrochemical

and rate law analyses, and we confirmed the newly observed trends for different Co-based molecular and heterogeneous catalysts. These results generate significant impact in the understanding of cocatalyzed photoelectrode systems that combine tailored molecular WOCs and optimized semiconductors into new hybrid systems. After establishing these new guidelines, our development of Cu-complexes as WOCs is still ongoing, new compounds have now emerged, and their immobilization on BiVO₄ and hematite photoanodes is scheduled for the coming months.

- **Composite and nanoscale WOCs:** We are now in the process of submitting our first study on single atom catalysts, namely a new soft landing strategy of Co-, Ni- and Fe-phthalocyanines on graphene oxide sheets. They were successfully synthesized in pure and exceptionally well-defined form (see below) and their electrocatalytic oxygen evolution and reduction performance was found to be excellent when compared to commercial RuO₂ and Pt/C references. Our study addresses two fundamental questions in the emerging field of SACs, namely (a) achieving synthetic control over the precise coordination of the active sites and (b) the exact influence of the coordination on the catalytic activity. In addition to a wide range of analytical characterizations and DFT calculations, in situ X-ray absorption spectroscopy (XAS) measurements under operational conditions were performed, and the results provided a coherent interpretation of the observed OER and ORR trends. Activities on the use of InP/ZnS nanoparticles for biomass reduction are still in progress.
- **Oxide vs. metallic catalysts:** We have concluded and published our study on the synthesis and in-depth characterization/assessment of low-cost Mo-doped manganese oxides for electrocatalytic water oxidation. This work generated progress in the understanding and optimization of this promising economic source of catalysts through straightforward doping strategies. In situ TEM studies on the perovskite-type WOCs have been performed and they are now in the process of being backed up with pair distribution function (PDF) measurements to acquire a comprehensive concept of the operational stability of these important perovskite catalysts. Preparation and characterization of NiFe electrodes for overall water splitting has been conducted in parallel and the results are written up for publication. The excellent performance in alkaline media was traced back to the formation of a thin oxy/hydroxyl layer over the inner alloy core, thus generating new insight into the mechanistic pathways of these promising economic electrode materials

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

- For the time being, we gave up the idea of detecting Pt-H as transient species in water evolution, since all our attempts in that direction were not successful. We now concentrate on CO₂ reduction.
- Surface dilution experiments on vibrational energy transfer on surfaces haven been finalized. We currently model the 2D-IR spectra theoretically in order to extract microscopic information on the surface morphology.
- Towards a complete water splitting system on surfaces, we have co-immobilized a Re-based photosensitizer with a Co-based hydrogen evolution catalyst on various semiconductor surfaces and performed transient IR and transient VIS experiments. While the system is not evolving hydrogen, we start to understand why, as a basis of a more rational design of such systems.

2.2.4 Surfaces (Prof. J. Osterwalder)

- Continued attempts to grow MoS₂ on Sb₂Se₃(100) under UHV conditions failed. Unlike Au(111), where highly ordered growth of MoS₂ could be demonstrated, similar recipes did not work on Sb₂Se₃(100). Therefore, the project was abandoned.
- Monolayers of Ga₂O₃ on Cu₂O(111) could be grown by evaporating Ga in low-pressure oxygen environment and were characterized by XPS. The characterization of structure, band alignment and band bending is underway.
- The electron dynamics on clean Cu₂O(111) surfaces was characterized by time-resolved two-photon photoemission. Hot carrier dynamics in the conduction band and exciton formation could be observed on defect-free surfaces, while these effects are completely suppressed on surfaces with high defect densities. The adsorption of Co-porphyrin appears to have a similar suppressing effect, but the influence of surface defects and adsorbed molecules still needs to be disentangled.
- The decomposition of well-defined RuO₂(110) films in acidic solution could be studied under OER operando conditions with ambient pressure XPS at the Swiss Light Source.

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

- Investigation of guest-host achieved; final experiments are underway before submission of the manuscript.
- Dipole strategy achieved and a follow up Master project was initiated.
- Follow up paper to Sb₂Se₃ not yet achieved, although the manuscript should be submitted in the next few months.

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

- Ab initio MD simulations of water at the Pt(111) and at the Au(111) interfaces, including nuclear quantum effects, which show how the quantum delocalization might affect the ionization of water as catalyzed by the metallic surface.
- More catalysts anchored at the thiol terminated beta-cyclodextrine have been characterized. Electronic structure properties, adsorption energies, and STM images have been calculated to add insight to the experimental findings (group Tilley).
- First principles simulations of different adsorption species of carbon dioxide on the stoichiometric and reduced ceria (CeO₂) (111) surface. The observed configurations were compared in terms of geometry, stability, charge transfer, and vibrational modes.
- Study on the modulation of the dipole layer by adsorption of atomic F at the alumina surface, changing adsorption site and coverage.
- No further investigations on Re and Ru dyes on alumina have been carried out.

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

- Synthesis of special graphene with targeted defects (“nanographene”). Structural defects in graphene are of high interest for metal-free catalysis and sensing of small gaseous molecules. Using special precursor molecules, we prepared special defects in graphene layers. The transformation of two different molecular precursors pentaindenocorannulene (PIC, C₅₀H₂₀) and coronene (CR, C₂₄H₁₂) on a copper surface into defective graphene has been studied. Unlike CR, which consists of seven hexagons and can be considered (after dehydrogenation) as a subunit of graphene, PIC is a geodesic polyarene which also has 6 pentagons in its carbon backbone. The defects were clearly characterized with scanning tunneling microscopy. Deposition of either PIC and CR on hot Cu(111) surfaces leads to carbon layers which can be qualitatively described as porous carbon aggregates (350°C), dense carbon layers (400 °C–450 °C), defective graphene

consisting of nanometer sized graphene domains (500 °C–550 °C) and extended graphene (600 °C). In view of the different appearance, only in the porous aggregate regime (350°C) the precursors are still partly preserved.

- Modification of carbon systems with noble metals as hydrogenation catalysts. In order to achieve a defined surface functionalization with convex carbon caps, the buckybowl pentaindenocorannulene (PIC) was used for modification of a copper surface and studied by means of scanning tunneling microscopy (STM), scanning force microscopy (AFM) as well as dispersion-enabled density functional theory (D-DFT). A major fraction of isolated PIC molecules stands 'bowl-cavity-up' at low-temperatures. PIC is thereby partly submerged into the surface by creating a four-atom vacancy underneath the pentagonal center ring. Only a minority fraction stands convex side-up, pointing with the pentagonal centered C5 ring away from the surface. This minority system was the goal of the modification.
- Studying the activity of carbon-metal systems towards hydrogenation. We have studied the transfer of atomic hydrogen between surface-adsorbed molecules during thermally induced chemical reactions. The hydrogen transfer can lead to desorption of species or C–C bond cleavage and hydrogenation of PAHs. The interaction with hydrogen was studied for the PIC-modified surface. A vast majority of PIC became indeed hydrogenated (+2H and +4H), as clearly identified by time-of-flight secondary ion mass spectrometry (ToF-SIMS). However, these steps involved (undesired) C–C bond cleavage at the corannulene core. Both reaction products are planar, as identified with carbon monoxide-tip-modified AFM (CO-nc-AFM). By theoretical means it was evaluated that one of the hydrogenated products would have an open shell character, that is quenched in the adsorbed state on the surface. On gold the same reactions were identified with ToF-SIMS. If in this case the open-shell character survives is still subject of ongoing work.

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

- Continuation of the solar water membranes development for *in-situ* XPS measurements of heterogeneous solar water splitting catalysis: The objective was only partially achieved; main technical challenge barrier is the high partial pressure of water. New strategy is the study of *in-situ* hydrogenation of electrodes for water splitting by XPS such as NiO_x; this mimics the electronic structure changes of the electrode under real water splitting conditions, while being compatible to XPS.
- Solar-water splitting probed by magneto-optics: magneto-optical hysteresis of Co-electrodes during (photo-) electrochemistry: The objectives were fully achieved: the main milestones was the successful setup of magneto-optical spectrometer with parallel measurements of the magneto-current for electro-chemical studies for both water splitting half reactions. As scientific results: we confirmed the recently published great magneto-chemical effect of Ni-electrodes on oxygen evolution reaction. Time-resolved measurements as possible with our setup brought to the fore that the built up of nickel oxides during oxygen evolution is influenced by the magnetic field, which is possibly the origin of the magneto-chemical effect. To establish the link between magneto-chemistry and magnetization of an electrode, we investigated Co-Pt electrodes due to its peculiar magnetic properties. This electrode material shows a magneto-chemical effect on both hydrogen and oxygen side.
- Hydrogenation reaction of organic compounds facilitated by metal hydrides: We evidenced that bulk hydrogen in LaNi₅H_x reduces C₂H₄ to C₂H₆.

2.2.9 Theoretical Chemistry (Prof. Lubser)

- All the objectives mentioned in 2.1 were achieved. In more detail, enhanced sampling methods were applied to the oxygen-oxygen bond formation step of a Ru-based water oxidation catalyst which has allowed novel insight, also regarding various steps of the reaction network. The importance of correlation effects in the nucleophilic water attack was studied with a novel protocol relying on complete active space calculations along reaction pathways. An efficient protocol for the calculation of electronic (circular dichroism) spectra was published.

2.3 Updated project planning

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

- **Water / CO₂ Reduction Catalysts:** Having efficient and long-term stable WRCs in hand, we will continue to develop our di- and multinuclear catalysts. The ones we have prepared over the reporting period are so promising that their design will be fine-tuned and subjected to photo- and electrocatalysis. The communicative interaction of two or more metal centres will be the base for a new class of WRCs (and CO₂ reduction catalysts) unprecedented so far. We will introduce metals different from cobalt, aiming at a water oxidation catalyst but with the same ligand framework. For anchoring on surfaces, we will use the strategy developed over the reporting period. The mono- and dinuclear complexes developed for CO₂ to CO reduction are working efficiently in photo- and in electrocatalysis. Assuming a concerted mechanism, the reaction mechanisms will be scrutinized for optimizing the basic structures. These catalysts will also be derivatized with the aforementioned anchoring groups. We aim at a new water oxidation and CO₂ reduction catalyst by the end of the 2020 period. We should then have a full water splitting system in hand.
- **Photosensitizers:** Since moving from homo- to heterogeneous catalysis, the development of new homogeneous photosensitizers will be postponed. The current photosensitizers based on Ru or Re are sufficient for studying electron transfer dynamics on surfaces. We will thus switch to photocathodes (and anodes) as light absorbing materials as investigated in the Tilley group. In addition, we will study the covalent binding of WRCs to sulphides and selenides based nanoparticles and quantum dots. They have absorbing properties superior to homogeneous molecules and satisfy the heterogeneous condition. Along this path, we should achieve a photocathode with the molecular WRCs mentioned before. If molecular water oxidation catalysts become available, a comparable design for photoanodes will be developed. Establishing photocathodes with polymerized WRCS and grafting on photovoltaic cells with organic light absorbers will be pursued as a further important step towards a device.
- **Electron relays and electrocatalysis:** As for photosensitizer development, new electron relays will not be a focus for the next period. Since under heterogeneous conditions, the focus will be shifted on electrocatalysis or photoelectrocatalysis. All catalysts available so far will be functionalized with anchoring groups and be adsorbed on photoactive supports or electrodes, replacing electron relays by electrons. Electrocatalysis will assess performance and allow as to fine-tune the molecular structures of the catalysts without interference from a photocycle.
- **Photocatalysis in Membranes:** In an earlier study, we have found that co-grafting of photosensitizer and WRC on reversed-phase particles resulted in very good H₂ formation rates. In the reporting period 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. This will be an extension to ongoing homogeneous and nanoparticle-based heterogeneous systems.

2.3.2 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 investigations.
- **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.

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

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

2.3.4 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.

2.3.5 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.

2.3.6 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.

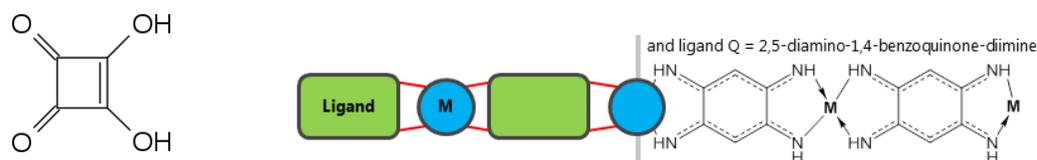
- Simulation of XPS at water-TiO₂ interface at different states of charge of the semiconductor (collaboration with Osterwalder's group)
- Characterization of metal-oxide hosted hexagonal boron nitride and its functionalization (collaboration with Osterwalder's group)
- Simulation of time resolved vibrational spectroscopy experiments at metal liquid interfaces (collaboration with Hamm's group)

2.3.7 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 atoms. A second approach will be using the ligand 2,5-diamino-1,4-benzoquinone-dimine (see figure below), which should also give metalorganic chains.



2.3.8 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 (installation summer 2020).
- Continuation of hydrogenation of gaseous organic compounds; setup of a hydrogenation reactor for liquid organic compounds.

2.3.9 Theoretical and Computational 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.

3 Research

3.1 Overview of the activities in research

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

The core of our activities in this period was the preparation of highly stable, macrocyclic ligands, derivatized for irreversible adsorption on oxidic surfaces such as TiO₂ or ZrO₂. The complexes of the ligands shown in Figure 1 represent excellent catalyst to be assessed for photo- and electrocatalytic performance in all details and in collaboration with the other groups ATR-IR spectroscopy as outlined in the Hamm report is just one example. Functionalized macrocyclic tetra-pyridine and acyclic tetra- or penta-pyridyl ligands were grafted on electrodes and on nanoparticles.

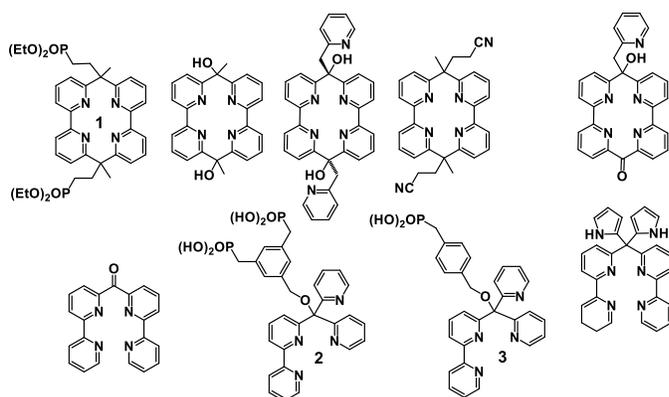


Figure 1. Ligands and corresponding complexes in the focus of this part of the URPP.

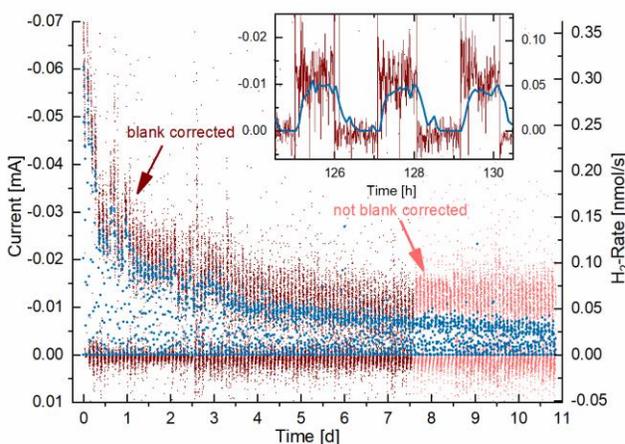


Figure 2. Chronoamperometry over 10d confirming the high stability of electrode bound porphyrin systems.

Synergistic interaction allowed a mechanistic understanding of electron transfer dynamics. Since the syntheses were unexpectedly long and multi-step, this part of the project was more time consuming than assumed (thesis of Peter Müller). We found in the last year studies that single phosphonate anchoring groups do not bind WRCs or PSs very stably to oxidic surfaces under photocatalytic conditions, as often reported in literature, but not investigated in detail. We undertook therefore a detailed study about the pH dependence and found that at least two phosphonate groups are necessary to keep the catalysts bound in the acidic branch of the pH scale. Above pH 10, even two phosphonates were not sufficient to retain the grafting. These results are important for the future design of anchoring groups.

Catalyst 1 was grafted on ITO electrodes and H₂ formation under a bias studied. We found an extraordinarily stability for this catalyst and H₂ formation could be observed over days. We realized that electrocatalytic H₂ formation did not cease because the catalyst decomposed but due to instability of the ITO support. It was also found that sequential application of a voltage and switching off the voltage allowed the ITO electrode to recover. Under this experimental conditions, electrocatalysis did run for 10 days, which means 5 days of electrocatalysis (Figure 2). XPS measurements before and after catalysis exhibited the catalyst to be still intact.

To develop these architectures even farther, so-called dual core ligands were developed. Since H₂ formation is a two electron process, two metal centres in close contact to each other may accelerate the rate of H₂ formation. The dual core might even open the option of introducing two different metal centres,

which will be investigated in the next phase. In addition, two potentially oxidizing metals may open a path into water oxidation with principally the same ligand framework (Figure 3)

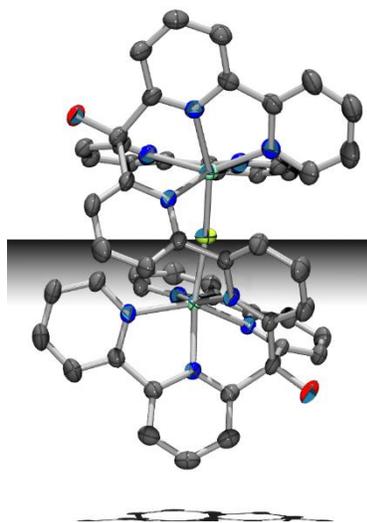


Figure 3. A dual core Co-complex of acyclic tetrapyrrolyl ligands, bridged by an additional bipyridyl ligand.

We stepped also in the field of CO₂ reduction with our ligand scaffolds. One of the approaches was to combine two metal centres on a [Re(η^6 -arene)₂]⁺ scaffold, in a ferrocene-like conformation. Due to the structural flexibility of the ligands (rotation around the arene-Re-arene axis, tilting along the Re-ligand axis) we expected an ideal situation for intermetallic communication. The complexes with one or two ruthenium centres were subjected to photo- and electrocatalysis and compared to their mono-metallic congeners. Highly selective CO over H₂ formation was found in case of electrocatalysis with the catalysts in solution and not grafted on the electrode, a distinct acceleration of CO formation was found, confirming the communication between the two metals. Initial theoretical and experimental studies indicate that one metal serves as the electron reservoir while the other one is doing catalysis. These excellent systems will be pursued further.

In addition to these "regular" activities with PhD students, a series of MSc theses complemented this ongoing research. Regarding PhD thesis, Peter Müller investigated all aspects of the acyclic ligands, Nicola Weder is responsible for the dual-core system and Daniel Hernandez-Valdes for CO₂ reduction. All three will finish their thesis in 2020. Mathias Mosberger accomplished his PhD in 2019.

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

During the report period, we completed a coherent research program on the design and understanding of different WOC types with Co-based materials as a methodological thread.

(1) In the upcoming field of **hybrid molecular photoanodes**, we presented the first comprehensive investigation of the functionalities of molecular cocatalysts on photoanodes. To this end, we first combined the molecular cubane WOC [Co^{II}₄(dpy{OH}O)₄(OAc)₂(H₂O)₂](ClO₄)₂, that had emerged from our previous studies, with well-characterized hematite photoanodes prepared in our lab. The selected {Co(II)₄O₄}-type cocatalyst furthermore features the key {H₂O-CO₂(OR)₂-OH₂} edge site motif, which has been identified as the *sine qua non* moiety of the most efficient heterogeneous Co-based WOCs. We discovered a dynamic functionality of the cocatalysts first with intensity modulated transient photocurrent spectroscopy (IM-TPS). At moderate potentials (0.9 – 1.1 V), the surface cocatalysts mainly store a large amount of photogenerated holes, while at potentials above 1.1 V their role changes towards hole transfer without significant storage. The results were backed up with further photoelectrochemical impedance spectroscopy (PEIS) and kinetic studies, and we confirmed the dynamic cocatalyst behavior for two additional molecular cocatalysts and heterogeneous cobalt oxide. Our study provided substantial progress in understanding the controversially debated role of cocatalysts on photoelectrodes.

(2) Furthermore, we discovered the first disordered 1D cobalt coordination polymer catalyst (Co-dppeO₂) that opened up a new type of **disordered hybrid organic-inorganic catalysts** for outstanding and durable water oxidation catalysis. Co-dppeO₂ had been outperforming a wide range of other Co-based catalysts in key electrocatalytic processes during previous studies and technical applications, but its highly disordered features after synthesis from dppe and Co₂(CO)₈ rendered the elucidation of its structural motif an

outstanding challenge. We tackled this with an innovative two pillar strategy, based on in situ FT-IR monitoring of its formation pathway accompanied by computational modeling of experimental X-ray scattering and absorption spectra combined with complementary analytical techniques (Figure 4). These methods in their entirety revealed the presence of hydrated $\{H_2O-Co_2(OH)_2-OH_2\}$ edge-site motifs embedded within a flexible organic matrix of bridging hydrophobic dppeO₂ ligands. This new, highly disordered architecture transfers principles of the self-repairing OEC embedment in PSII to a new class of applied electrocatalysts. Moreover, we made substantial methodological progress in the highly relevant but widely unresolved challenge of structurally characterizing disordered materials with fundamentally new motifs.

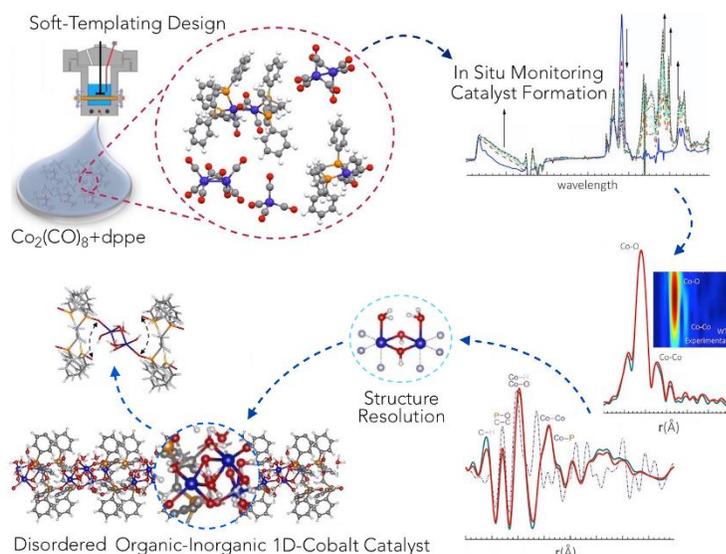


Figure 4. Two-pillar strategy for elucidating the new disordered hybrid organic-inorganic electrocatalyst Co-dppeO₂.

increasing disorder and surface area together with lower oxidation states. In contrast, no such clear property-dependent trends were observed for photochemical water oxidation, and all samples showed related electrochemical WOC activity. This study underscored the importance of catalytic assays and precise preparative protocols for establishing structure-performance guidelines in WOC design.

(3) Moreover, we reported on new insights into a key factor that is widely underexplored in the **design of heterogeneous WOCs**, namely the influence of their preparative history on the resulting catalytic activity. To this end, we selected cobalt spinel Co₃O₄ as a representative model system to apply a three-step methodology. We investigated (a) the influence of the preparative method on the materials properties, (b) their correlations with the WOC performance and (c) the latter as a function of the catalytic test method (photochemical, chemical and electrochemical water oxidation tests). This systematic study revealed a striking dependence of the Co₃O₄ WOC activity on the applied test method. Key parameters for high chemical water oxidation activity were identified as

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

- We now consider Au@Sb₂Se₃ as system for CO₂ reduction, optically pumping the semiconductor, which then injects charges into Au-nanoparticles that reduce CO₂. We are currently optimizing the experimental configuration to make intermediates detectable by transient IR spectroscopy.
- We investigated the interaction and desorption of small-molecule adsorbates, such as CO, from thin metal films in water by time-resolved IR spectroscopy.
- Surface dilution experiments on vibrational energy transfer was investigated both experimentally and theoretically
- Investigated the reaction cycle of a Re carbonyl photosensitizers and co-adsorbed Cobalt (II) tetrapyrridyl catalyst on ZrO₂ and TiO₂ (see Figure 5), and related the kinetics of the various electron and energy transfer steps to the distance distribution of both molecules on the surface.
- As a new subproject, started to look at various metal-hydride complexes by 2D IR spectroscopy to characterize the peculiarities of the Me-H chemical bond.

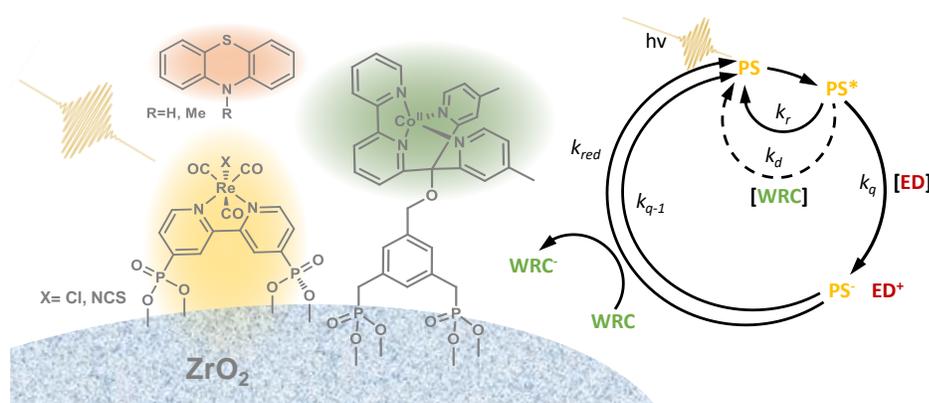


Figure 5. A Re-based photosensitizer and a Co-based hydrogen evolution catalyst co-immobilized on a ZrO₂ surface with the reaction cycle indicated.

3.1.4 Surfaces (Prof. J. Osterwalder)

We report the successful measurement of the temporal evolution of hot electron populations near the Cu₂O(111) surface (Figure 6). Cuprous oxide is a promising electrode material for water reduction which is also studied in the Tilley group. The introduction of oxygen vacancies in the surface strongly suppresses the number of electrons that reach the surface directly via the conduction band, which links such defects to the limited photovoltage often observed in such devices. Empirically, this effect can be counteracted by forming Ga₂O₃/Cu₂O heterojunctions. We have successfully grown Ga₂O₃ monolayers on top which will allow us to shed further light on the mechanism behind this improved performance.

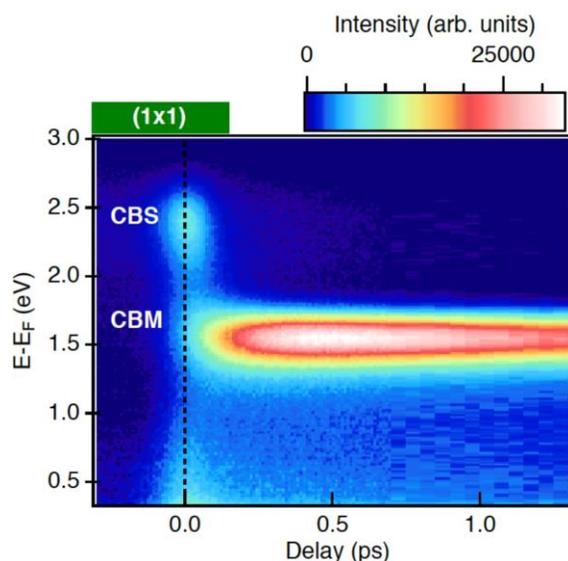


Figure 6. Electron energy distribution after excitation with a 3 eV pump pulse, color-coded as function of time delay (horizontal axis) and energy (vertical axis) for the defect-free (1x1) surface of $\text{Cu}_2\text{O}(111)$, showing initial excitations into a higher conduction band state (CBS) and ultrafast relaxation to the conduction band minimum (CBM) and concomitant exciton formation (downward shift).

Again inspired by the results obtained in the Tilley group, we have started to study the formation of phosphonic acid layers on $\text{Sb}_2\text{Se}_3(100)$ surfaces. Using an ex-situ spin coating approach, we were able to form layers in the monolayer range where XPS spectra suggest significant charge transfer at the interface. Using our ambient pressure XPS instrument at the Swiss Light Source, we have studied the in situ oxidation of $\text{Ir}(001)$ films, as well as the decomposition of a $\text{RuO}_2(110)$ catalyst under OER operando conditions.

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

New Materials for Photoelectrochemical Water Splitting: We continued our work on Sb_2Se_3 photocathodes, investigating the causes of the low photovoltage with advanced characterization techniques such as time-resolved microwave conductivity and low temperature photoluminescence to identify traps. In addition, we began work on solution processed semiconductors such as Cu_2S and SnS in a newly purchased glovebox.

Advanced Analytics: We developed a new impedance-based methodology for characterizing multilayer photocathodes by analyzing how the observed resistances change depending on applied potential. This analysis helped us to identify problematic interfaces in the promising cuprous oxide-based $\text{Cu}_2\text{O}/\text{Ga}_2\text{O}_3/\text{TiO}_2/\text{RuO}_x$ photocathode. Current work is expanding this methodology to new material systems such as Sb_2Se_3 .

Host-Guest Approach to Anchored Molecular Catalysts: We have successfully demonstrated electrocatalytic activity of molecular catalysts that are bound to a surface via host-guest interactions. A conducting surface is modified with cyclodextrins, and then a molecular catalyst that is appended with a naphthyl group docks inside the pore. Current efforts are focused on visualizing the host-guest structures on the surfaces with AFM and STM (in collaboration with Prof. Osterwalder).

3.1.6 Computational Studies of Water Oxidation/Reduction Systems (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., Tilley's group and 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 electronic properties of an aluminum oxide slab with a dipole layer made out of fluorine atoms have been studied by means of DFT calculations. We use a standard model for alumina, constituted by a 3x3x1 slab where each aluminum atom on the top and on the bottom surfaces is replaced by three hydrogen atoms. The hydroxyl groups on the top surface are then subsequently replaced by fluorine atoms in steps of 1/3 of the total OH coverage. The results show that both the valence and the conduction band edges are shifted towards more negative values on the vacuum scale when increasing the fluorine coverage of the surface, thus maintaining roughly the same band gap.

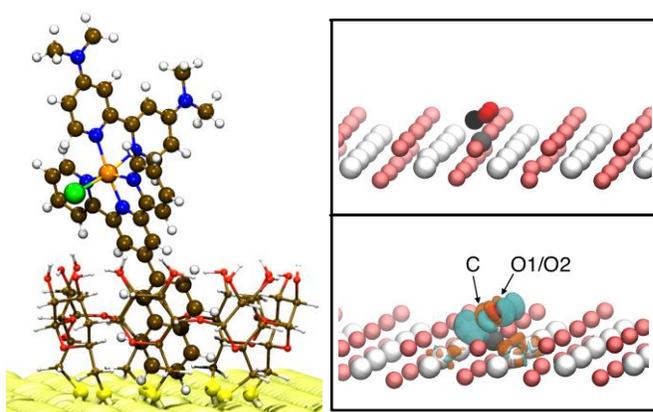


Figure 7. Left – Optimized geometry of the Ru catalyst bound to the thiolated cyclodextrin on Au(111). Right – One possible CO₂ adsorption site on reduced ceria, and charge density difference illustrating the resulting redistribution of electrons.

We studied four different molecular catalysts modified by naphthyl group to be host into a thiolated beta-cyclodextrin grafted on Au(111). Our calculations show that the host-guest binding is strengthened by the presence of the metallic surface, even though no covalent bond is formed between the catalyst and the metal. Moreover, the distribution of the frontier orbitals of the catalyst suggest that electron transfer between the electrode and the active site is possible. We also simulated the STM images of the grafted host and host-guest complexes to be compared with experimental images to confirm the trapping of the molecular

The electronic structure of the reduced ceria (111) surface is modelled by introducing oxygen vacancies on the topmost or the subsurface oxygen layer. Numerous local minima can be found on the potential energy surface for both, the bare reduced surface, and CO adsorptions on the reduced surface. In particular we isolated unexpected bent CO configurations in close vicinity to the surface oxygen vacancy, which partially reoxidize the reduced ceria surface. Moreover, our simulations show that the oxygen vacancy concentration has a direct impact on the relative stability of possible adsorption configurations. The vibrational analyses of the adsorbates on both the pristine and reduced surface show promising accordance with previous theoretical and experimental results.

By using state-of-the-art path-integral ab-initio molecular dynamics, we have shown that nuclear quantum effects play a decisive role in the ionization of water at the Pt interface, thus providing new physical insight on proton hopping at aqueous metal electrode interface under ambient condition. In particular, from our results an unexpected picture of the Pt-water interface emerges, as it is generally assumed that water does not dissociate when no bias potential is applied. We instead observe that the formation of hydronium and adsorbed hydroxyl at the interface, though rare, is plausible and reversible.

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

Structural defects in graphene on the other side are of high interest for metal-free catalysis and sensing of small gaseous molecules. Using special precursor molecules we prepared special defects in graphene layers (Figure 8). Different types of defects have been observed, in part previously only proposed theoretically. Next steps would be pinning metals to these defects for stable catalysts.

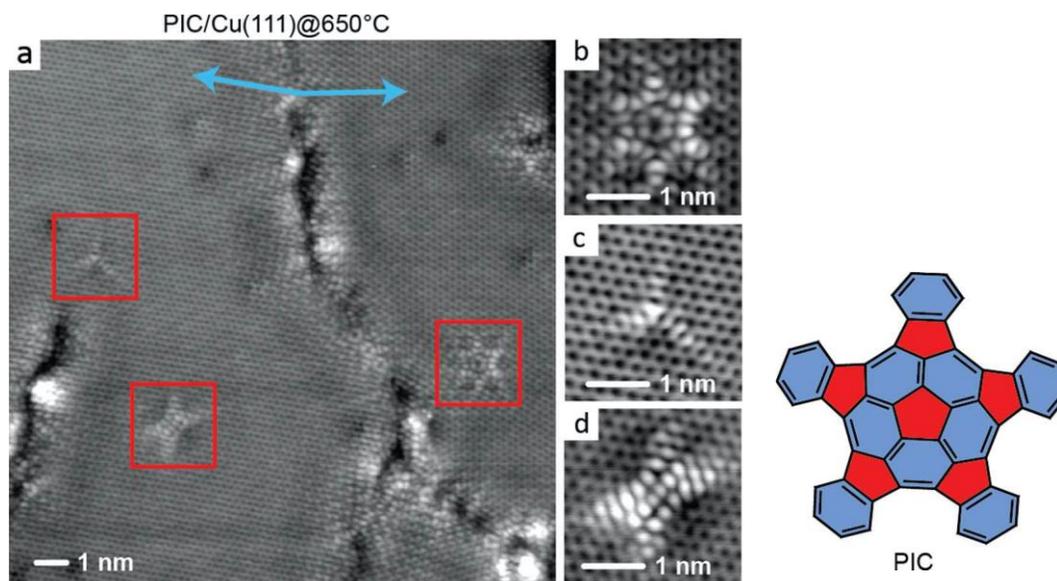


Figure 8. STM images of graphene layers grown from pentaindenocorannulene (PIC, right) containing localized defects. Images (a-d) were obtained after deposition of PIC onto Cu(111) kept at 650 °C and subsequent annealing at 600 °C for one hour without further evaporation of molecules. Blue arrows label two rotational domains of graphene separated by grain boundaries. Three red boxes label the locations of three different local defects, shown in images (b-d) respectively.

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

A side project of the URPP is the reduction of CO₂ to synthetic fuels by renewable hydrogen enhanced by adsorption of the products and by absorption of the reactant hydrogen in metal hydride. While the former is very promising, we observed a diminished CO₂ reduction on palladium hydride surface. We studied the same reaction on the hydride LaNi₅H_x. However, this hydride is completely oxidized within the first reaction cycle, and thus not suitable as a catalyst. We were thus looking for hydrogenation reactions without aggressive products such as water, and we made a find in the hydrogenation of ethine to ethene, and further to ethane. LaNi₅H_x is stable under reaction conditions, and thus allows a variety of experiments. One striking outcome is the evidence that bulk hydrogen and not surface hydrogen (although present, too) in LaNi₅H_x reduces C₂H₄ to C₂H₆ (see Figure 9). We will continue this very promising research direction in 2020, as it has interesting fundamental as well as technical prospects.

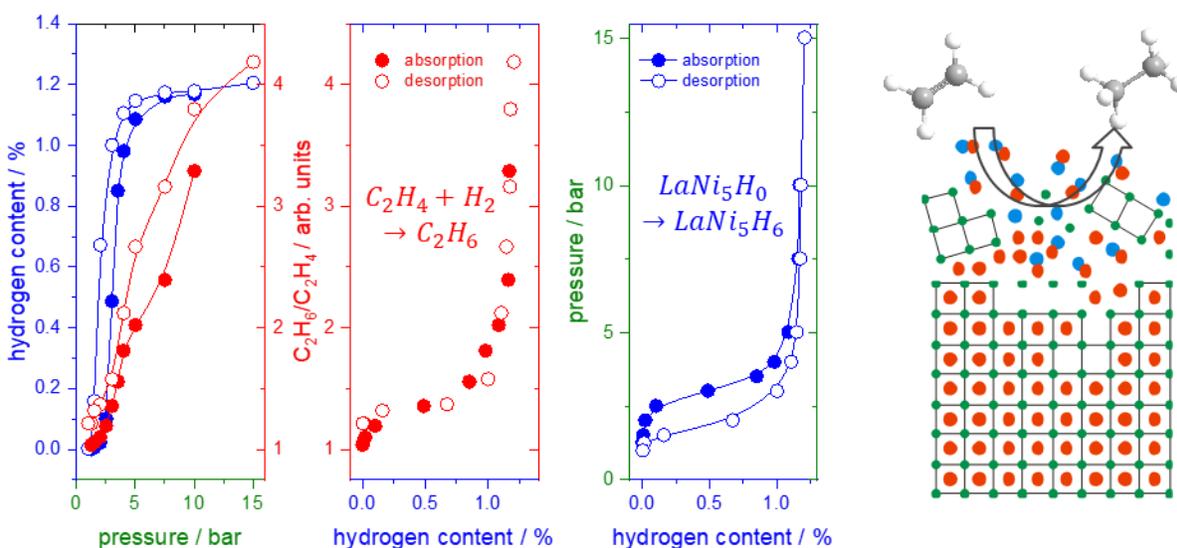


Figure 9. Evidence that bulk hydrogen in LaNi₅H_x reduces C₂H₄ to C₂H₆ is provided by the fact that the conversion (ratio of C₂H₄ to C₂H₆) is better described by hydrogen content in the material than by the applied pressure. The right picture is a sketch illustrating the atomistic mechanism of the reaction at a LaNi₅ surface, which is complex due to oxygen induced segregation (red/blue spheres: La₂O₃ and Ni (green) phases are formed). It is surprising that although Ni is catalytically active for ethene reduction, bulk hydrogen is the reactant.

The difficulties with finding a suitable water permeable membrane for XPS studies were mentioned above. We are therefore planning to use the hydrogen permeable membranes approach to mimic materials properties during hydrogen evolution. A typical example to be studied is Ni as hydrogen evolution electrode. Although a metal, the active electrolyte-electrode interface is a Ni-oxide. It is known from literature that the amount of hydrogen in the oxide interface controls the performance of the electrode. We will study the electronic structure changes of NiO_x upon hydrogen intercalation by our hydrogen membrane method using synchrotron photoemission (@ELETTRA, Trieste). Great results are expected from the implementation of the new hard X-ray photoelectron spectrometer open to samples from the LightCheC consortium. In addition to specific materials science challenges of making renewable chemical carriers from light, we worked on superordinated concepts for their implementation into daily life. Alternative to concepts based on future technologies, we proposed a combination of largely existing technologies to use solar energy to recycle atmospheric CO₂ into a liquid fuel. The research, which was published in PNAS, caused great media coverage.

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

In a collaboration with the experimental group of G. R. Patzke, we have contributed to a detailed study about the synthesis and formation of cubane oxo clusters, which are of high interest as (potential) bio-inspired water oxidation catalysts. Computational protocols beyond standard approaches have been elucidated for the oxygen-oxygen bond formation, which is an essential step in water oxidation catalysis and often assumed to be the rate-limiting step. On the one hand, fully ab initio molecular dynamics-based calculations for entire free energy surfaces including sophisticated treatment of environmental effects at ambient conditions have been performed, which has allowed novel insight into this key step. For instance, the role of specific water molecules and ligands in this reaction could be clarified. Further investigations regarding functional ligands are ongoing, which is of interest for informed catalyst design. Moreover, highly accurate complete active space calculations have been carried for an entire reaction path based on a novel computational procedure, which has complemented the picture obtained from density functional theory for the oxygen-oxygen bond formation. Aside from that, computational approaches for inclusion of the effects of electronically excited states have been studied for electronic circular dichroism spectroscopy. Last but not least, computational protocols for the calculation of pKa values via ab initio molecular dynamics have been examined and applied to a water oxidation catalyst for the first time.

3.2 Scientific activities (organized by URPP)

The URPP serves as an exchange platform for all researchers working on the topic of water splitting at the University of Zurich. All the researchers, including those on positions not funded by the URPP, take part regularly at the scientific activities of the URPP. The community counts ca. 50 researchers (-19 directly employed by the URPP in 2019).

LightChEC Co-Seminars

For the first time this year, the previously known LightChEC science seminars were integrated into the Department Seminars and highlighted as LightChEC Co-Seminars organized by the scientific responsible (Prof. Sandra Luber). Four speakers have been invited and gave a talk:

- 16.04.2019 **Prof. Inke Siewert**, Georg-August University of Göttingen: *Metal complex with proton responsive ligands as molecular electrocatalysts in energy conversion reactions*
- 21.05.2019 **Prof. em. Jean-Michel Saveant**, University Paris Diderot, France: *Toward intelligent design of molecular catalysts of electrochemical reactions*
- 30.10.2019 **Dr. Gerald Meyer**, The University of North Carolina at Chapel Hill, USA: *Mechanisms of Dye-Sensitization at Molecular-Semiconductor Interfaces*
- 10.12.2019 **Dr. Hisatomi Takashi**, Shinshu University, Japan: *Photocatalyst materials and reaction systems for large-scale renewable solar hydrogen production by water splitting*

LightChEC Discussion Seminars

LightChEC Discussions is a monthly series of talks to stimulate exchange and discussions within the LightChEC consortium, and is organized by Dr. Benjamin Probst. Participants of the URPP LightChEC are encouraged to present once a year an interesting research article, a method or a new concept to the broader community, followed by a discussion about the topic. LightChEC Discussions is an informal meeting, and there is snacks and drinks available. With 20 to 30 persons, including PIs, the voluntary meeting is usually quite well attended. Talks are two times 20', and are followed by vivid discussions. LightChEC Discussions do not only give the presenter an opportunity to practice presentations, but it also teaches new concepts, established a culture of discussions and thus strengthens the joint spirit of the consortium.

Additional events

- The PhD students of the URPP LightChEC are affiliated with the “Graduate School of Chemical and Molecular Sciences Zurich” and they all present their research work in its framework.
- **29.11.2019 URPP LightChEC Symposium 2019**
Irchel Campus, University of Zurich

The LightChEC Symposium 2019 was attended by more than 80 people. Six external speakers were invited to give a presentation on one aspect of the broad field of solar fuels. The program of the Symposium also included three poster sessions during which 35 posters were presented and discussed by LightChEC researchers.

Invited Speakers Symposium

Dr. Marie-Noëlle Collomb, Université Grenoble Alpes, Saint-Martin-d’Heres, France

Photo-induced redox catalysis for hydrogen production with molecular and hybrid system

Prof. Jörg Libuda, Friedrich Alexander University, Erlangen, Germany

Model interfaces in catalysis and energy science: from surface science to electrochemistry and photoelectrochemistry

Prof. Erwin Reisner, University of Cambridge, UK

Interfacing nature’s catalytic machinery with synthetic materials for semi-artificial photosynthesis

Prof. Märten Ahlquist, KTH Royal Institute of Technology, Sweden

Simulating molecular catalysts at interfaces and in explicit solvent

Dr. Etsuko Fujita, Brookhaven National Laboratory, USA

CO₂ reduction and hydrogenation using metal complexes with pyridinol-type ligands

Prof. Tanja Cuk, University of Colorado at Boulder, USA

Resolving chemical bond dynamics at an electrode surface

4 Academic career development

4.1 Activities in academic career development

Roger Alberto: Mathias Mosberger accomplished his PhD thesis, working now at Siegfried.

David Tilley: In 2019 René Wick-Joliat, Wei Cui, Laurent Sévery, and Rajiv Prabhakar defended their Ph.D. theses. René is now a postdoc at ZHAW, Wei is expected to take up a faculty position in China after receiving the Ph.D. degree, Laurent will begin a postdoc at UC Berkeley (Prof. T. Don Tilley) and Rajiv will begin a postdoc at Lawrence Berkeley National Lab (Prof. Joel Ager). Also, Jonas Zurflüh and Casey Beall defended their Masters theses in 2019. Jonas has a job in Basel, and Casey has begun her Ph.D. in PSI. In 2019 I hired 3 new Ph.D. students working within the framework of the URPP, two of which happen to be female (Erin Service, Pardis Adams, and Zhenbin Wang). I also engaged a female Bachelor's student (Isik Tuncay), and she is now a Masters student in my group.

Andreas Borgschulte: The group consist of three PhD-students and one Postdoc (two female, two male). All members were encourages to take part and highlight their research results on national and international conferences. We reorganized the work of one PhD-student to bridge her absence during motherhood to allow her finishing in time.

Greta Patzke: In 2019, I continued to support the team of Dr. Fabian von Rohr as a SNF Ambizione grant holder. He is currently taking further steps towards his independent academic career development with proposals for the ERC and SNF Eccellenza programs. Dr. Sima Heidari successfully implemented her research ideas supported by the UZH Forschungskredit.

Karl-Heinz Ernst: One female PhD student obtained doctoral title in 2019. LightChEC postdoc (C. Wäckerlin) has been sent abroad (Prague) for advanced studies for the entire year.

4.1 Gender equality development

Peter Hamm: Two female postdocs are working on the project (Kathryn Tracy, Kerstin Oppelt), as well as two female Master student (Mirjam Utters, Jeanette Ruf) and one female Bachelor students (Aleksandra Dimitrieva).

Greta Patzke: With respect to gender equality development, I continued to serve in 2019 as MNF representative of the UZH Gender Equality Commission as well as member of the MNF Gender Committee.

5 Publications

1. **Alberto R**, Iannuzzi M, Gurdal Y, **Probst B** (2019). [Coll(BPyPy₂COH)(OH₂)₂]²⁺: A Catalytic Pourbaix Diagram and AIMD Simulations on Four Key Intermediates. *Chimia*, 73(11): 906-912.
2. **Cui W**, **Moehl T**, Siol S, **Tilley SD** (2019). Operando electrochemical study of charge carrier processes in water splitting photoanodes protected by atomic layer deposited TiO₂. *Sustainable Energy & Fuels*, 3: 3085-3092.
3. **Billeter E**, **Terreni J**, **Borgschulte A** (2019). Hydride Formation diminishes CO₂ Reduction Rate on Palladium. *Chem Phys Chem*, 20: 1-7.
4. Han R, Rempfer K, Zhang M, Dobbek H, Zouni A, Dau H, **Luber S** (2019). Investigating the structure and dynamics of Apo-Photosystem II. *ChemCatChem*, 11: 4072-4080.
5. Hemmi A, Cun H, Tocci G, Epprecht A, Stel B, Lingenfelder M, de Lima LH, Muntwiler M, **Osterwalder J**, Iannuzzi M, Greber T (2019). Catalyst Proximity-Induced Functionalization of h-BN with Quat Derivatives. *Nano Lett*, 19(9): 5998-6004.
6. **Karageorgaki C**, Mutombo P, **Ernst KH** (2019). Interaction of Chiral and Achiral Dimethylsuccinic Acid Diastereomers with a Cu(110) Surface. *J Phys Chem*, 123(4): 2329-2335.
7. **Karageorgaki C**, Mutombo P, Jelinek P, **Ernst KH** (2019). Chiral Surface from Achiral Ingredients: Modification of Cu(110) with Phthalic Acid. *J Phys Chem*, 123(4): 9121-9127.
8. Kliuiev P, Zamborlini G, Jugovac M, Gurdal Y, von Arx K, Kay W, Schnidrig S, **Alberto R**, Iannuzzi M, Feyer V, Hensberger M, **Osterwalder J**, Castiglioni L (2019). Combined orbital tomography study of multi-configurational molecular adsorbate systems. *Nat Commun*, 10(1): 5255.
9. **Li J**, **Wan W**, **Triana CA**, **Novotny Z**, **Osterwalder J**, Erni R, **Patzke GR** (2019). Dynamic Role of Cluster Cocatalysts on Molecular Photoanodes for Water Oxidation. *J Am Chem Soc* 141: 12839-12848.
10. Li JY, Lampart S, Siegel JS, **Ernst KH**, **Wackerlin C** (2019). Graphene Grown from Flat and Bowl Shaped Polycyclic Aromatic Hydrocarbons on Cu(111). *Chem Phys Chem*, 20(18): 2354-2359.
11. **Luber S** (2019). Recent progress in computational exploration and design of functional materials. *Comp Mat Sci*, 161: 127-134.
12. Mairena A, Zoppi L, Lampart S, Baldrige KK, Siegel JS, **Ernst KH** (2019). Fivefold Symmetry and 2D Crystallization: Self-Assembly of the Buckybowl Pentaindenocorannulene on a Cu(100) Surface. *Chem Eur J*, 25: 11555-11559.
13. Mairena A, Baljovic M, Kaweck M, Grenader K, Wienke M, Martin K, Bernard L, Avarvari N, Terfort A, **Ernst KH**, **Wackerlin C** (2019). The fate of bromine after temperature-induced dehydrogenation of on-surface synthesized bisheptahelicene. *Chem Sci*, 10: 2998.
14. **Mattiat J**, **Luber S** (2019). Vibrational (resonance) Raman optical activity with real time time dependent density functional theory. *J Chem Phys*, 151: 234110.
15. **Mattiat J**, **Luber S** (2019). Electronic circular dichroism with real time time dependent density functional theory: Propagator formalism and gauge dependence. *Chem Phys*, 527: 110464.
16. **Mavrokefalos C**, **Patzke GR** (2019). Water Oxidation Catalysts: The Quest for New Oxide-Based Materials. *Inorganics*, 7: 29.
17. **Moehl T**, **Cui W**, **Wick-Jolat R**, **Tilley SD** (2019). Resistance-based analysis of limiting interfaces in multilayer water splitting photocathodes by impedance spectroscopy. *Sustainable Energy & Fuels*, 3: 2067-2075.
18. Moradi M, Opara NL, Tulli LG, **Wackerlin C**, Dalgarno SJ, Teat SJ, Baljovic M, Popova O, van Genderen E, Kleibert A, Stahlber H, Abrahams JP, Padeste C, Corvini PFX, Jung TA, Shahgaldian P (2019). Supramolecular architectures of molecularly thin yet robust free-standing layers. *Sci Adv*, 5: eaav4489.

19. **Mosberger M, Probst B**, Spingler B, **Alberto R** (2019). Influence of Hetero-Biaryl Ligands on the Photo-Electrochemical Properties of [Re^INCS(N^IN)(CO)₃]-Type Photosensitizers. *Eur J Inorg Chem*, 30: 3518-3525.
20. Ni L, Güttinger R, **Triana CA**, Spingler B, Baldrige KK, **Patzke GR** (2019). Pathways towards true catalysts: computational modelling and structural transformations of Zn-polyoxotungstates. *Dalton Trans*, 48: 13293-13304.
21. **Oppelt K, Fernández-Teràn R**, Pfister R, **Hamm P** (2019). Geminate Recombination versus Cage Escape in the Reductive Quenching of a Re(I) Carbonyl Complex on Mesoporous ZrO₂. *J Phys Chem C*, 123(32): 19952-19961.
22. Patterson BD, Mo F, **Borgschulte A**, Hillestad M, Joos F, Kristiansen T, Sunde S, van Bokhoven JA (2019). Renewable CO₂ recycling and synthetic fuel production in a marine environment. *PNAS*, 116(25): 12212-12219.
23. **Reith L, Lienau K, Triana CA**, Siol S, **Patzke GR** (2019). Preparative History vs Driving Force in Water Oxidation Catalysis: Parameter Space Studies of Cobalt Spinets. *ACS Omega*, 4(13): 15444-15456.
24. **Schilling M, Luber S** (2019). Determination of pK_a Values via ab initio Molecular Dynamics and its Application to Transition Metal-Based Water Oxidation Catalysts. *Inorganics*, 7: 73.
25. **Schilling M, Luber S** (2019). Insights into artificial water oxidation - A computational perspective. *Adv Inorg Chem*, 74: 61-114.
26. Siol S, Beall C, Ott N, Döbeli M, González-Castaño M, **Wick-Jolat R, Tilley SD**, Jeurgens LPH, Schmutz P, Cancellieri C (2019). Anodizing of Self-Passivating WxTi1-x Precursors for WxTi1-xOn Oxide Alloys with Tailored Stability. *ACS Appl Mater Interfaces*, 11: 9510-9518.
27. **Song F**, Al-Ameed K, **Schilling M**, Fox T, **Luber S, Patzke GR** (2019). Mechanistically Driven Control over Cubane Oxo Cluster Catalysts. *J Am Chem Soc*, 141: 8846-8857.
28. **Terreni J**, Trottmann M, Franken T, Heel A, **Borgschulte A** (2019). Sorption-Enhanced Methanol Synthesis. *Energy Technol*, 7: 1801093.
29. **Tilley SD** (2019). Recent Advances and Emerging Trends in Photo-Electrochemical Solar Energy Conversion. *Adv Energy Mater*, 9: 1802877.
30. **Totani R**, von Rohr FO, Zhao J, **Novotny Z, Zabka WD**, Soluyanov A, **Osterwalder J** (2019). Sb₂Se₃(100): A strongly anisotropic surface. *Phys Rev Materials*, 3: 125404.
31. **Triana CA, Moré R**, Bloomfield AJ, Petrović PV, Ferrón SG, Stanley G, Zarić SD, Fox T, Brother EN, Sheehan SW, Anastas PT, **Patzke GR** (2019). Soft Templating and Disorder in an Applied 1D Cobalt Coordination Polymer Electrocatalyst. *Matter*, 1: 1354.
32. Vijselaar W, Kunturu PP, **Moehl T, Tilley SD**, Huskens J (2019). Tandem Cuprous Oxide/Silicon Microwire Hydrogen-Evolving Photocathode with Photovoltage Exceeding 1.3 V. *ACS Energy Lett*, 4: 2287-2294.
33. **Zabka WD, Musso T, Mosberger M**, Novotny Z, **Totani R**, Iannuzzi M, **Probst B, Alberto R, Osterwalder J** (2019). Comparative Study of the Different Anchoring of Organometallic Dyes on Ultrathin Alumina. *J Phys Chem C*, 123(36): 22250-22260.
34. **Wan W**, Wei S, Li J, Zhou Y, **Patzke GR** (2019). Transition metal electrocatalysts encapsulated into N-doped carbon nanotubes on reduced graphene oxide nanosheets: efficient water splitting through synergistic effects. *J Mater Chem A*, 7(25): 15145-15155.
35. **Wick-Jolat R, Musso T, Prabhakar RR**, Löckinger J, Siol S, Cui W, **Sévery L, Moehl T, Suh J, Hutter J, Iannuzzi M, Tilley SD** (2019). Stable and tunable phosphonic acid for band edge engineering of photoelectrochemical and photovoltaic heterojunction devices. *Energy Environ Sci*, 12(6): 1901-1909.
36. **Yang W, Prabhakar RR**, Tan J, **Tilley SD**, Moon J (2019). Strategies for enhancing the photocurrent, photovoltage, and stability of photoelectrodes for photoelectrochemical water splitting. *Chem Soc Rev*, 48(19): 4945-5178.

6 Structures

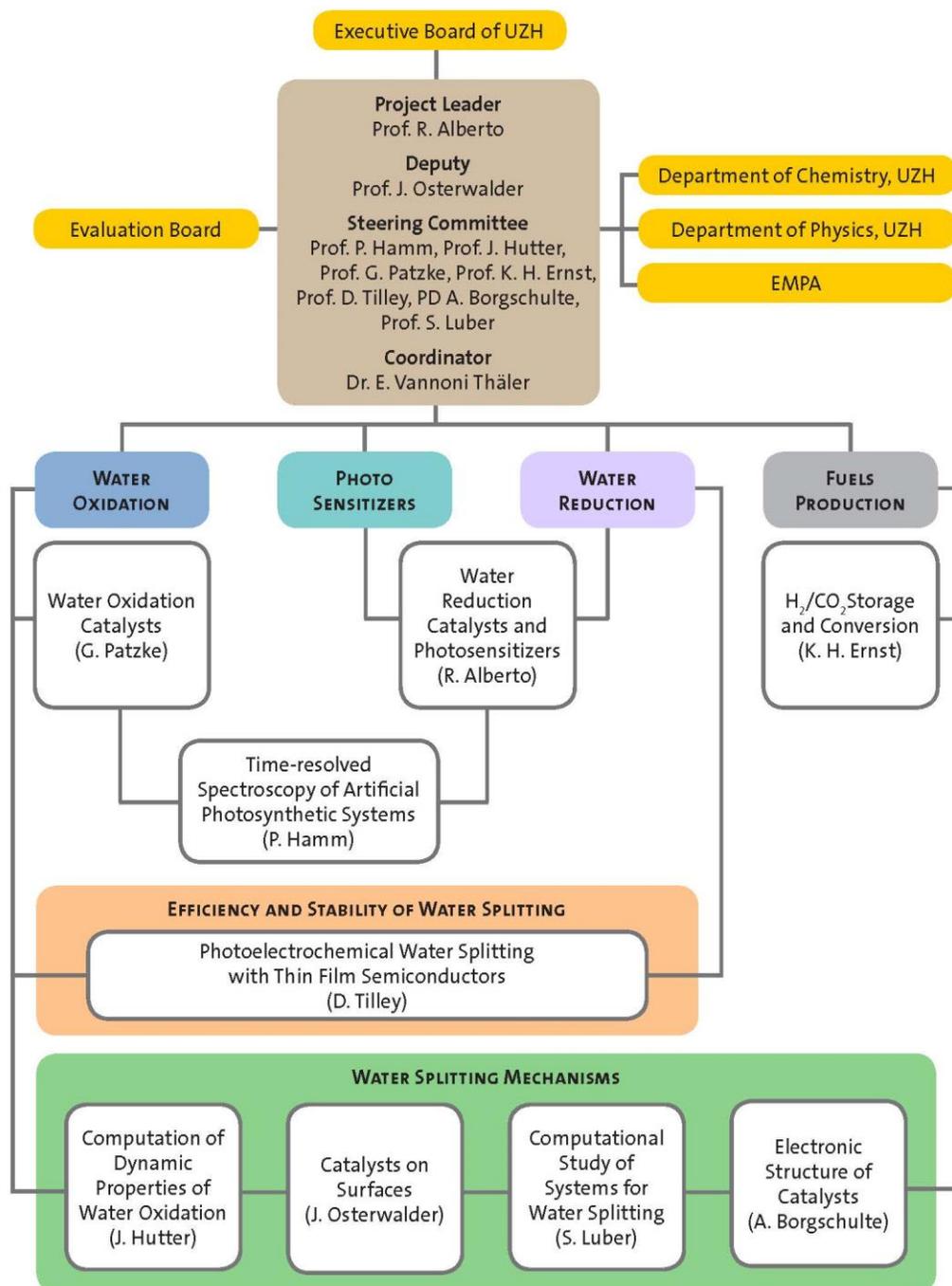


Figure 9. URPP organization.

7 Third party funds

7.1 Third-party funding of URPP project leaders

- SNSF - Divisions I to III

- Prof. Sandra Luber (SNSF Professorship), In Silico Investigation and Design of Bio-inspired Catalysts for Water Splitting (1.6 Mio. CHF, Feb 2017- Feb 2021).
- Prof. Jürg Osterwalder, Surface Physics with Single-Layer Materials and Molecular Layers, SNSF Grant 200020 172641, 839'027 CHF, 04.2017 – 03.2021.
- Prof. Peter Hamm, Ultrafast Vibrational Spectroscopy of Allosteric Proteins; SNSF Division II, 773'577 CHF, 01.2017-12.2019.
- Prof. Roger Alberto, Prof. Peter Hamm, Prof. Jürg Hutter, and Prof. Greta Patzke, Sinergia CRSII2_160801/1, SNSF Division II, total amount for the 3 PIs 1'593'704 CHF, 02.2015-12.2019.
- Prof. Peter Hamm, NCCR MUST, 06.2018-06.2022, CHF 720'000.
- Prof. Roger Alberto, Solar Light-driven Homogeneous Catalysis for Greener Industrial Processes with H₂ as Energy Source and CO₂ as C1 Building Block, 01.02.2017 - 31.01.2021, 346'189 CHF.
- Dr. Andreas Borgschulze, Ultra-High Pressure Hydride X-ray Photoelectron Spectroscopy, 4631'400 CHF, 2018-2022.

- SNSF - Division IV

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

- EU

- None

- Industry and Others

- Prof. Sandra Luber, Two grants from Swiss National Supercomputing Center (ca. 85 Mio. core hours, till 2020).
- Prof. Greta R. Patzke, Chinese Scholarship Council (CSC) Fellowship (Wenchao Wan, project leader: GR Patzke); 01.2017-12.2019, allocated: 68'400 CHF.
- Prof. Jürg Hutter, Sparse Tensor Linear Algebra Library, PASC, ETH Board 01.07.2017 - 30.06.2020, CHF 428'640.
- Prof. David Tilley, Chinese Scholarship Council (CSC) Fellowship (Zhenbin Wang, project leader: SD Tilley); 10.2019-09.2023, allocated: 100'800 CHF.
- Prof. David Tilley, Spanish Fellowship (Dr. Laxman Gouda, project leader: SD Tilley); 04.2019-03.2020, allocated ca. 28'000 €.
- Dr. Andreas Borgschulze, BAFU, deepUV Raman spectrometer for water analysis, 130'000 CHF, 02.2017-08.2019.

7.2 List of funded projects within Profit-Center (PC) of the URPP

- 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.
- Prof. Greta Patzke, Forschungskredit to Dr. Sima Heidari, 02.2019-09.2019.

8 Specific tasks and problems

Instrumentation: Alberto, Patzke and Tilley could acquire a XAS instrument from a special budget request from "Investitionskredit der Universität", about 350 kFr. This will complement our instrumentation to a great extent.

9 Appendix

Scientific Presentations Prof. Alberto

- R. Alberto at the Humboldt University zu Berlin, May 22, 2019: "Homo- and heterogeneous light-induced proton reduction with cyclic and acyclic polypyridyl complexes" (invited GDCh lecture)
- R. Alberto, Sasol company South Africa, October 28, 2019: "Cobalt, Rhenium, Technetium and some other elements, research at the Alberto lab" (invited lecture, focusing mainly on CO₂ reduction)
- R. Alberto, University of Bloemfontein, South Africa, November 1, 2019: "Organometallic Rhenium chemistry in photocatalysis" (invited lecture)
- R. Alberto, University of Auckland, New Zealand, December 5, 2019: "Photocatalysis with cobalt complexes" (invited lecture for a distinguished award)
- R. Alberto, Scientifica, August 31, 2019, U Zurich, "Auf dem Weg zur Wasserstoffgesellschaft" (Outreach lecture)
- R. Alberto, Lions Club, November 6, Winterthur: "Die Energie der Zukunft, Sonnenenergie ohne Photovoltaik" (Outreach lecture)

Scientific Presentations Prof. Patzke (Invited)

- G. Patzke, Institute of Neuropathology USZ, March 19th 2019: "Materials design for current challenges: from artificial photosynthesis to bioactive oxoclusters" (talk)
- G. Patzke, MPI for Chemical Energy Conversion, Symposium on Applied Chemistry, Berlin, Germany, 2-3 May 2019: "Bio-Inspiration, nanoscience and solar power: new roads to artificial photosynthesis" (talk)
- G. Patzke, 235th ECS Meeting, Dallas/TX, USA, 26-30 May 2019: "Monitoring and preparation-performance trends of co-based electrocatalysts for electrochemical water oxidation" (talk)
- G. Patzke, F2Cp2 2019 Joint Conference, Lausanne, Switzerland, 14-19 July 2019: "Solar thermochemical vs. electrocatalytic energy conversion: key materials parameters" (talk)
- G. Patzke, Joint Annual Meeting of SPG and OPG, Zurich, Switzerland, 26-30 August 2019: "Economic materials design for clean energy: artificial photosynthesis" (talk)
- G. Patzke, Transregio (SFB/TRR) 234 "CataLight" Summer School, Masserberg, Germany: "Concepts for clean energy materials: from bio-inspiration to solar power" (talk)
- G. Patzke, 3rd ICTC on Translational Chemistry, Caparica, Portugal, 2-5 December 2019: "Bio-inspired water oxidation catalysts: formation pathways and design perspectives" (talk)

Scientific Presentations Group Prof. Hamm

- R. Fernández-Terán, UZH Doktorandentag 2019, July 4th 2019: "Distance dependence of vibrational energy transfer: calibrating a molecular ruler with 2D ATR-IR spectroscopy" (talk)
- R. Fernández-Terán, Time Resolved Vibrational Spectroscopy meeting (TRVS), Auckland, New Zealand, 8-13 September 2019: "Calibrating a surface-sensitive molecular ruler with 2D ATR-IR spectroscopy" (talk)
- R. Fernández-Terán, SCS Fall Meeting 2019, September 6th 2019: "Re(I) \square^2N -tricarbonyl and \square^3N -dicarbonyl complexes with terpyridine ligands: unusual substituent effects and photocatalytic properties" and "Calibrating a surface-sensitive molecular ruler with 2D ATR-IR spectroscopy" (posters)
- R. Fernández-Terán, NCCR-MUST Meeting 2019, 14-16 January 2019: "Distance dependence of vibrational energy transfer: calibrating a molecular ruler with 2D ATR-IR spectroscopy" (poster)
- R. Fernández-Terán, 23rd International Symposium on the Photochemistry and Photophysics of Coordination Compounds (ISPPCC), Hong Kong, 14-19 July 2019: "Re(I) \square^2N -tricarbonyl and \square^3N -"

dicarbonyl complexes with terpyridine ligands: unusual substituent effects and photocatalytic properties" (poster)

- R. Fernández-Terán, LightChEC Symposium, Zurich, Switzerland, November 29th 2019: "Transition metal hydrides: unexplored aspects of organometallic complexes relevant for catalysis" and "Calibrating a surface-sensitive molecular ruler with 2D ATR-IR spectroscopy" (posters)
- K. Oppelt, Time Resolved Vibrational Spectroscopy meeting (TRVS), Auckland, New Zealand, 8-13 September 2019: "Geminate Recombination versus Cage Escape - Quenching of a Re(I) Carbonyl Complex on Mesoporous ZrO₂" (talk)
- K. Oppelt, LightChEC Symposium, Zurich, Switzerland, November 29th 2019: "Design Strategies for Heterogeneous Photochemical Water Splitting Systems from Time Resolved Spectroscopy" (poster)

Scientific Presentations Prof. Tilley

- S. D. Tilley, 10th International Conference on Materials for Advanced Technologies (ICMAT), Singapore, 23-28 June 2019: "Earth-abundant Thin Film Materials for Photoelectrochemical Water Splitting" (invited)
- S. D. Tilley, NanoGe Fall Meeting 2019, Berlin, Germany, 5 Nov 2019: "*Operando* Electrochemical Methods for a Deeper Understanding of Photoelectrochemical Water Splitting Systems" (invited)
- Laurent Severy, SCS Fall Meeting 2019, Zurich, Switzerland, 06 September 2019: Host-Guest Interactions on Electrode Surfaces for Immobilization of Molecular Catalysts (talk)
- X. Zhang, LightChEC Symposium 2019, Zurich, Switzerland 29 November 2019: Solution processed stoichiometric Cu₂S thin films for hydrogen evolution (poster)
- J. Suh, European Materials Research Society (EMRS) 2019 Spring, Nice, France 27.-31.05.2019: Solution Phase Deposited SnS Thin Films: Photocathode for Water Splitting (talk)
- J. Suh, LightChEC Symposium 2019, Zurich, Switzerland 29.11.2019: Bismuth Sulfur Iodide (BiSI) Thin Film Photoanode for Water Oxidation (poster)
- R. Wick-Joliat, SCS Fall Meeting 2019, Zurich, Switzerland, 06 September 2019: Stable and tunable phosphonic acid dipole layer for band edge engineering of photoelectrochemical and photovoltaic heterojunction devices (talk)
- R. Prabhakar, EMRS Spring meeting, Nice, France, 27-31 May 2019: Enhanced charge carrier transport in sulfurized Sb₂Se₃ investigated by in-situ potential sensing and time-resolved spectroscopy (talk)
- R. Prabhakar, SCS Fall meeting, Zurich, Switzerland, 6 Sept 2019: Enhanced charge carrier transport in sulfurized Sb₂Se₃ investigated by in-situ potential sensing and time-resolved spectroscopy (talk)
- L. Gouda, LightChEC Symposium 2019, Zurich, Switzerland, 29 November 2019: Electrochemical conversion of biomass to value-added products (poster)
- L. Gouda, Electrochemical Approach to Chemical Synthesis, summer school, Gottingen, Germany, 06 - 09 October 2019: Electrochemical conversion of biomass to value-added products (poster)

Scientific Presentations Prof. Osterwalder

- Z. Novotny, Symposium on Surface Science, Baqueira Beret, Spain, 10-16 March 2019: "Probing Solid-Liquid Interfaces with Tender X-Rays" (poster)
- L. Grad, DPG Frühjahrstagung, Regensburg, Germany, 31 March - 5 April 2019: "Electronic Properties of Cobalt-Porphyrin on Cuprous Oxide"
- Z. Novotny, Joint Annual Meeting of the SPS and ÖPG, Zürich, 26-30 August 2019: "Probing Solid-Liquid Interfaces with Tender X-Rays" (invited)

- R. Totani, Joint Annual Meeting of the SPS and ÖPG, Zürich, 26-30 August 2019: "Characterization of Sb₂Se₃ single crystals for photocatalysis" (contributed talk)
- R. Totani, FisMat 2019, Catania, Italy, 30 September - 4 October: "Sb₂Se₃(100): A Strongly Anisotropic Surface for Photocatalysis" (contributed talk)
- Z. Novotny, AVS 66th International Symposium & Exhibition, Columbus, OH, 20-25 October 2019: "Probing Solid-Liquid Interfaces with Tender X-Rays"
- N. Comini, AVS 66th International Symposium & Exhibition, Columbus, OH, 20-25 October 2019: "Probing Solid-Liquid Interfaces with Tender X-Rays" (poster)
- Z. Novotny, PSI Condensed Matter Retreat, FHNW Brugg, 29 October 2019: " Probing Solid-Liquid Interfaces with Tender X-Rays" (poster)
- Z. Novotny, 6th Annual Ambient Pressure X-Ray Photoelectron Spectroscopy Workshop, Lund, Sweden, 10-13 December 2019: "Oxidation of Ir(001) Towards IrO₂ Studied by Ambient Pressure X-ray Photoelectron Spectroscopy"

Scientific Presentations Group Prof. Hutter

- Y. Al-Hamdani, 14th MolCh Surf Meeting 2019, Bern, Switzerland, 21 June 2019: "Establishing reference adsorption energies in low dimensional materials using computational methods" (talk)
- Y. Al-Hamdani at al., WE-Heraeus Seminar on "Operando surface science - Atomistic insights into electrified solid/liquid interfaces", Physikzentrum Bad Honnef, Germany, 21 June 2019: "Computational Materials Science at the University of Zurich" (talk)
- J. Lan, WaterEurope, Multiscale simulations and coarse-grained models for water and aqueous systems, Lausanne, Switzerland, 22 October 2019: "Ionization of Water as an Effect of Quantum Delocalization at Aqueous Electrode Interfaces" (poster)
- J. Lan, Theoretical Chemistry and Computational Modeling: 20 years promoting Excellence in Science, Donostia, Spain, 31 May 2019: "Water-Metal Interfaces from Ab-initio Molecular Dynamics" (poster)
- J. Lan, The Fifth Competence Center for Computational Chemistry meeting, Zurich, Switzerland, 17 January 2019: "Insights into the interface CO/Pt(111) with water from First-Principles Simulations" (poster)
- J. Lan, Spring Meeting of Swiss Association of Computational Chemists, Geneva, Switzerland, 7 January 2019: "Insights into the interface CO/Pt(111) with water from First-Principles Simulations" (poster)
- J. Lan, Operando Surface Science ? Atomistic Insights into Electrified Solid/liquid Interfaces, Physikzentrum Bad Honnef, Germany, 9 December 2019: "Ionization of Water as an Effect of Quantum Delocalization at Aqueous Electrode Interfaces" (talk)
- J. Lan, EPFL, Summer School, Advanced Electronic Structure Methods in Condensed Matter Physics, Lausanne, Switzerland, 9 July 2019: "Self-ionization of water at aqueous Pt interface" (talk)
- J. Lan, Mainz Materials Simulation Days, Mainz, Germany, 7 June 2019: "Self-ionization of water at aqueous Pt interface" (talk)

Scientific Presentations Group Prof. Ernst

- K-H Ernst, Atomic Level Characterization, Kyoto, Japan, 20-25 October 2019: “Chirality and the emergence of molecular structure” (invited)
- K-H Ernst, National Meeting of the American Chemical Society, San Diego, USA, August 26th 2019: “On-surface topochemistry of helicenes” (invited)
- K-H Ernst, International Workshop on Nanomaterials and Nanodevices (IWNN), Beijing, CN, July 5th 2019: “On the density of racemic and homochiral crystals: Wallach, Liebisch and Sommerfeld in Göttingen” (invited)
- K-H Ernst, International Workshop on Nanomaterials and Nanodevices (IWNN) Beijing, CN, 1-3 July 2019: “Surface topochemistry of helicenes” (invited)
- K-H Ernst, SSNS'19 Shizukuishi, Iwate Prefecture, Japan, 14–18 January 2019: “Stereospecific chemistry and self-assembly of carbohelicenes on surfaces” (invited)
- A. Mairena et al., International Conference on Chirality, Bordeaux, France, 14-17 July 2019: “On the validity to call Wallach’s rule Wallach’s rule” (talk)
- A. Mairena et al., 3 S' 19 Symposium on Surface Science, Baqueira-Beret, Spain: “Bis-, tris- and monohelicenes: 2D self-assembly and on-surface chemistry” (talk)
- K-H Ernst, Chirality@The Nanoscale Symposium, CSF, Monte Verità, Ascona, CH, 14th October 2019: “On the density of racemic and homochiral crystals: Wallach, Liebisch and Sommerfeld in Göttingen” (poster)
- K-H Ernst et al., Chirality@The Nanoscale Symposium, CSF, Monte Verità, Ascona, CH, 14th October 2019: “Spin filtering by helical molecules” (poster)

Scientific Presentations Group Dr. Borgschulte

- E. Billeter & A. Borgschulte, 35th SAOG Meeting, Fribourg, Switzerland, January 31st 2019: “Pressure-composition isotherms of PdHx by electron energy loss spectroscopy” (poster)
- E. Billeter et al., Hydrogen Metal Systems Gordon Research Conference, Castelldefels, Spain, 30 June to 5 July 2019: “Ethyne Hydrogenation by Pd-PdHx” and “Small bulk changes - big surface effects” (posters)
- E. Billeter et al., 18th European Conference on Application of Surface and Interface Analysis, Dresden, Germany, 15-20 September 2019: “Electronic Structure of HxMoO3 and HxWO3” (talk)
- E. Billeter et al., Extreme Rays Workshop, Rome, Italy, 6-7 July 2019: “Operando Soft X-Ray Photoemission Spectroscopy reveals chemochromic mechanism in HxWO3 bronzes” (poster)
- E. Billeter et al., Empa PhD Day, St. Gallen, Switzerland, November 28th 2019: “Electronic Structure of HxMoO3 and HxWO3” (talk)
- E. Billeter et al., LightChEC Symposium, Zurich, Switzerland, November 29th: “Electronic Structure of HxWO3 and HxMoO3” (poster)
- A. Borgschulte Andreas et al., 13th Int. Symposium Hydrogen & Energy Seoul, Republic of Korea, 20-25 January 2019: “Repulsive interaction diminishes H-uptake and catalysis” (talk)
- A. Borgschulte et al., Hydrogen Metal Systems Gordon Research Conference, Castelldefels, Spain, 30 June to 5 July 2019: “Hydrogen on and in Catalysts” (posters)
- A. Borgschulte et al., SCS Fall Meeting 2019, Zurich, Switzerland, September 6th 2019: “Hydrogen on Cu/ZnO catalysts” (poster)
- A. Borgschulte, Komatsu Technology IAB 2019, Amsterdam, The Netherlands, September 30th 2019: “What is the fuel of tomorrow?” (talk)
- O. Sambalova, WE-Heraeus-Seminar. Operando Surface Science – Atomistic Insights into Electrified Solid/Liquid Interfaces, Bonn, Germany, 9-13 December 2019: “Magneto-optical Kerr effect set-up for operando probing of electrode surfaces” (talk)

- O. Sambalova et al., Extreme Rays Workshop, Rome, Italy, 6-7 July 2019: “Hard and soft X-ray photoelectron spectroscopy for selective probing of surface and bulk chemical composition in a perovskite-type Ni catalyst” (poster)
- O. Sambalova, Empa PhD Day, St. Gallen, Switzerland, November 28th 2019: “Magneto-optical Kerr effect set-up for electrochemistry” (talk)
- O. Sambalova et al., LightChEC Symposium, Zurich, Switzerland, November 29th 2019: “Magneto-optical Kerr effect set-up for electrochemistry”(poster)
- O. Sambalova et al., SCS CHanalysis conference, Beatenberg, Switzerland, 11-12 April 2019: “HAXPES-XPS combination reveals surface structure changes of La_{0.30}Sr_{0.55}Ti_{0.95}Ni_{0.05}O_{3-x}” (poster)
- O. Sambalova, UZH Graduate School Seminar, Zurich, Switzerland, March 11th 2019: “Water splitting: the quest for developing operando surface-sensitive analytical techniques” (talk)
- O. Sambalova et al., SCS Fall Meeting 2019, Zurich, Switzerland, September 6th 2019: “Magneto-optical Kerr effect set-up for in situ probing of oxygen evolution electrodes” (talk)

Scientific Presentations Prof. Sandra Luber

- S. Luber, Colloquium of the Wilhelm Ostwald Institute, Leipzig, Germany, January 2019: “Advanced computational methods for spectroscopy and catalysis” (talk)
- S. Luber, Katalytikertagung Weimar, Germany, April 2019: “Zooming on artificial water splitting by advanced ab initio methods” (talk)
- S. Luber, Dozententagung, Klobenz, Germany, April 2019: “Innovative Methoden fuer die Modellierung in der Spektroskopie und Katalyse” (talk)
- J. Mattiat, 10th Triennial Congress of the International Society for Theoretical Chemical Physics. Tromso, Norway, July 2019: “Recent development in dynamic spectroscopy methods for the gas and condensed phase” (talk)
- S. Luber, CPMD meeting, Lausanne, Switzerland, July 2019: “Recent developments of spectroscopic methods using ab initio molecular dynamics” (talk cancelled to maternity leave)
- M. Schilling, 19th International Conference on Biological Inorganic Chemistry, Interlaken, Switzerland, August 2019: “Computational studies and design in the field of bio-inspired solar light-driven water splitting” (talk)
- S. Luber, 705. WE-Heraeus-Seminar on “Frontiers in Size Selected Cluster research: Bridging the Gap”, Bad Honnef, Germany, September 2019: “Recent advances in computational vibrational spectroscopy (talk cancelled due to maternity leave)
- S. Luber, 19th Time Resolved Vibrational Spectroscopy Conference, Auckland, New Zealand, September 2019: “Dynamic ab initio methods for spectroscopy” (talk cancelled due to maternity leave)