

DFG SPP 1613 Summer School

September 25-28, 2016

Hotel Teikyo, Berlin-Schmoeckwitz

Book of Abstracts

DFG SPP 1613 Summer School, September 25-28, 2016, Hotel Teikyo Berlin-Schmoeckwitz - Program

Sunday, 25th September

18:00–19:30	Arrival, welcome
19:30–20:30	Dinner

Monday, 26th September

07:30-08:30	Breakfast	
General Introduction		
08:30-09:00	Prof. Dr. Wolfgang Jaegermann	Introduction into the scientific questions of the SPP 1613
09:00-10:00	Prof. Krishnan Rajeshwar	In a Solid-State Materials Wonderland: A 40-Year Odyssey
Fundamentals of Photoelectrochemical Junctions		
10:00-11:00	Prof. Laurence Peter	An Introduction to Semiconductor Photoelectrochemistry
11:00-11:30	Coffee Break	
11:30-12:30	Prof. Hans Joachim Lewerenz	Photoelectrochemical Water Splitting: From Concepts to Solar Fuel Generating Devices
12:30-13:30	Prof. Anders Nilsson	Operando X-ray Studies of Photo- and Electrocatalysis
13:30-14:30	Lunch	
Novel Photoabsorbers		
14:30-15:30	Prof. Dr. Michael Graetzel	Mesoscopic Photosystems for the Generation of Fuels from Sunlight
15:30-16:30	Prof. Bruce Parkinson	Solar Fuels: Progress and Prospects
16:30-17:00	Coffee Break	
17:00-18:00	Prof. Frank Osterloh	Solar Water Splitting with Particle Photocatalysts
18:00-18:30	Prof. Dr. Fatthakova	Nanostructuring concepts in the design of electrodes for photo/electrochemical water splitting
18:30-19:30	Dinner	
Industrial Perspectives		
19:30-20:30	Dr. Gilles Dennler	Accelerated discovery of new energy materials by high throughput ab-initio computations and experimental validation
20:30-21:30	Dr. Guenter Schmid	Single Step Direct Electrocatalytic Reduction of CO ₂ Towards CO and Hydrocarbons

Tuesday, 27th September

07:30-08:30	Breakfast	
Advanced Electrocatalysts		
08:30-09:30	Prof. Dr. Marc Koper	Multiple proton-coupled electron transfer for electrochemical generation of fuels
09:30-10:00	Prof. Dr. Dau	Investigating mechanisms in (electro)catalysis of water oxidation
10:00-11:00	Prof. Dr. Beatriz Roldan Cuenya	Size, shape and chemical state effects in the electroreduction of CO ₂ over nanostructured Cu and Ag catalysts
11:00-11:30	Coffee break	
Device Development I		
11:30-12:00	Dr. Finger/Prof. Dr. Fiechter	Integrated photovoltaic-electrochemical water splitting modules as a tool for optimization of catalyst materials, upscaling and module geometries
12:00-13:00	Prof. Ib Chorkendorff	Water splitting and the making of renewable chemicals
13:00-14:00	Lunch	
14:30-19:00	Excursion: Boat trip	
19:00-20:15	Dinner	
20:15-	Open discussion/Poster session	

Wednesday, 28th September

07:30- 08:30	Breakfast	
Device Development II		
08:30- 09:30	Dr. John Turner	Semiconductor Systems and Catalysis for Photoelectrochemical Water Splitting
09:30-10:30	Prof. Kevin Sivula	Emerging materials for the photocathode/photoanode tandem cell
10:30-11:00	Coffee break	
11:00-12:00	Prof. Jae Sung Lee	Materials and Systems for stand-alone Solar Fuel Production
12:00-13:00	Lunch	
Theory and Modeling		
13:00-14:00	Prof. Geoffroy Hautier	Finding the Needle in a Haystack: A High-Throughput Computational Approach to Materials Discovery
14:00-15:00	Prof. Dr. Alexander Auer	Bridging heterogenous and homogenous catalysis - <i>in theory</i> similarities and differences from surfaces to molecule
15:00	Coffee/Departure	

In a Solid-State Materials Wonderland: A 40-Year Odyssey

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Solid-state chemistry languished as an esoteric discipline till interest exploded on the so-called high-T_c superconductor materials; oxides were discovered to have unique properties in this regard. Paralleling this was the gradual realization that solid-state chemistry principles underpinned many technologically-important areas such as batteries, supercapacitors, and even solar cells. The culmination of this trend was in the application of solid-state chemistry to the preparation and characterization of electrode materials in photoelectrochemical (PEC) cells.

The talk will focus on work in the author's laboratory on the use of carbon and oxide semiconductor nanocomposites for driving multi-electron processes of interest (such as CO₂ reduction) both in the dark and under solar irradiation. Of the myriad electrode materials that have been used for the electrochemical (EC) and photoelectrochemical (PEC) reduction of carbon dioxide in aqueous media, copper oxide/copper interfaces have shown a remarkable range of hydrocarbon and oxygenated products including acids, aldehydes, ketones, and alcohols.

This perspective talk will highlight experimental evidence for the fact that both EC and PEC reduction scenarios have similar chemical and morphological underpinnings in the in situ formation of copper nanocubes on the (photo)cathode surface. Recent rapid developments in our fundamental understanding of these interfaces and areas requiring further studies are discussed in the light of recent studies in the authors' laboratories and elsewhere.

An Introduction to Semiconductor Photoelectrochemistry

Laurie Peter

University of Bath

This lecture will look at some fundamental aspects of photoelectrochemical reactions at semiconductor electrodes. The topics are subdivided under the following headings

- Key concepts of solid state physics. Band energies, doping, Fermi levels.
- The ideal semiconductor/electrolyte junction: band alignments, flatband potentials.
- Thermodynamics and kinetics of minority carrier reactions: quasi Fermi levels.
- Surface states, non-ideal behaviour and Fermi level pinning.
- Loss mechanisms: competition between electron transfer and surface recombination.
- Multistep photoelectrochemical reactions. Intermediates and rate-determining steps.
- Photoelectrochemistry of nanostructured systems: advantages and disadvantages of nanostructuring.

Chapters suitable for background reading

1. *Kinetics and Mechanisms of Light-Driven Reactions at Semiconductor Electrodes: Principles and Techniques*. Laurence Peter in *Photoelectrochemical Water Splitting: Materials, Processes and Architectures*. pp. 19-51. Editors Hans-Joachim Lewerenz and Laurie Peter. RSC Publishing, 2013.
2. *Photoelectrochemistry: From Basic Principles to Photocatalysis*. Laurence Peter in *Photocatalysis: Fundamentals and Perspectives*. pp 1-28. Editors Jenny Schneider, Detlef Bahnemann, Jinhua Ye, Gianluca Li Puma, Dionysios D Dionysiou. RSC Publishing, 2016.
3. *Semiconductor Electrochemistry*. Laurence Peter in *Photoelectrochemical Solar Fuel Production. From Basic Principles to Advanced Devices*. pp. 3-40. Editors: Sixto Giménez and Juan Bisquert. Springer, 2016.

Photoelectrochemical Water Splitting: From Concepts to Solar Fuel Generating Devices

H.J. Lewerenz

Division of Engineering and Applied Science

Joint Center for Artificial Photosynthesis

California Institute of Technology, Pasadena, California, USA

Abstract

Fundamental aspects of light-induced water splitting that encompass the background on semiconductor-Schottky and -electrolyte junctions are outlined. Photoprocesses in advanced semiconductor structures and at the electrolyte junction are reviewed. The theoretical limits of water photolysis in the Shockley-Queisser limit and for realistic conditions are derived providing guidelines for experimentalists. Physical properties of tandem structures will be presented and their use for high-efficiency water splitting is commented. The recent development of efficient water splitting using an *in-situ* photoelectrochemical surface modification procedure is treated. It will be shown that the interplay of conditioning and surface analyses enabled the optimization of the structure. Further surface analysis of the semiconductor-electrolyte interface using tender X-ray photoelectron spectroscopy shows that the data experimentally validate Gerischer's concept of this junction.

Operando X-ray Studies of Photo- and Electrocatalysis

Anders Nilsson

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I will demonstrate how electron and x-ray spectroscopy can be used to address fundamental questions regarding the reaction mechanism and active sites of the Oxygen Evolution Reaction (OER), Hydrogen Evolution Reaction (HER) and CO₂ reduction reaction (CO₂RR). We have developed in-situ X-ray Photoelectron Spectroscopy (XPS) capabilities using a membrane assembly where either the anode or cathode side is exposed to a differential pumped environments where direct measurements of the changes in the catalyst and various reaction intermediates can be probed during OER on IrO₂ and HER conditions for MoS₂. We have also recently conducted high-energy resolution fluorescence detection (HERFD) in X-ray Absorption Spectroscopy (XAS) studies of the Fe and Ni K-edges under OER conditions in the highly active Ni-Fe oxyhydroxides to determine the nature of the active sites. In particular we observe that Fe encounter an extremely strained local geometry when Ni undergoes a transformation from the 2+ to 3+ state. We have followed the change of Cu catalyst after oxidative activation and then reduction into the metallic state using XAS and ambient pressure XPS to elucidate the nature of the enhanced selectivity towards ethylene in CO₂RR.

Mesoscopic Photosystems for the Generation of Fuels from Sunlight

Michael Graetzel

Laboratory of Photonics and Interfaces (LPI)

Institute of Chemical Science and Engineering Faculty of Basic Science

Ecole Polytechnique Federale de Lausanne, Switzerland

Abstract

I shall discuss mesoscopic photosystems that produce fuels from sunlight, water and CO₂ mimicking the life sustaining process of natural photosynthesis. Synthesizing these energy carriers using the power directly from the sun paves a way for the storage of solar energy and towards closing the anthropogenic carbon cycle at the same time. I shall demonstrate two approaches for solar H₂ production and CO₂ reduction, one being driven by photovoltaics, whereas the other uses photoelectrochemical tandem cells.

Solar Fuels: Progress and Prospects

*Bruce Parkinson**

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** Presenting author. E-mail: bparkin1@uwyo.edu*

This talk will first evaluate the present state of photoelectrochemical energy conversion including the efficacy of producing hydrogen from water as opposed to reducing carbon dioxide to liquid fuels. Producing hydrogen from sunlight and water, to enable a sustainable hydrogen economy, is the preferred goal if it can be accomplished both efficiently and cheaply. However we are very far from achieving this goal and there is not much time to develop systems given the time necessary to optimize them, test them and scale them up to the point where they can have a real influence on climate. The field of solar water splitting has recently bifurcated into either using conventional materials with stabilization layers or developing new materials that are themselves stable in electrolyte solutions under illumination. Since no such stable semiconductors are currently known, the current efforts to discover and develop these new materials are key to reaching this goal. An undergraduate student participating in the Solar Hydrogen Activity research Kit (SHArK) project, a distributed combinatorial outreach materials discovery program [1,2], discovered a low band gap p-type semiconducting iron chromium aluminum oxide that was verified in our lab to have a surprisingly high photovoltage for hydrogen evolution [3]. Several research groups in Germany also produced this material with different fabrication methods and verified its photoactivity. This provides an example of how to “fail quickly” if the research community can be mobilized to rapidly evaluate the many potential materials that will result from combinatorial efforts at the various research centers devoted to photoelectrochemical water splitting.

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[2] B. A. Parkinson, “Distributed Research: A New Paradigm for Undergraduate Research and Global Problem Solving”, *Energy & Environmental Science*, 3, 509-511, (2010)

[3] John G. Rowley, Thanh D. Do, David A. Cleary and B. A. Parkinson, “Combinatorial Discovery Through a Distributed Outreach Program: Investigation of the Photoelectrolysis Activity of p-type Fe, Cr, Al Oxides”, *ACS Appl. Mater. Interfaces*, Article ASAP, DOI: 10.1021/am406045j

Solar Water Splitting with Particle Photocatalysts

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The identification of an artificial photosynthesis method to turn solar energy into globally usable amounts of fuel is considered one of the most important challenges today. Photochemical water splitting with particle-based systems has the greatest potential to achieve this goal. Because of the total integration of components for light absorption and water electrolysis, particle-based photocatalysts (see Figure below) can be over one order of magnitude cheaper than photoelectrochemical or photovoltaic cells. For example, a photocatalyst reactor operating at 10% Solar-to-Hydrogen (STH) efficiency would produce H_2 at a cost of \$1.63 per Kg. Currently, the development of such systems is limited by intrinsic materials issues and by an incomplete understanding of the reactions of photochemical charge carriers at irregular interfaces. This talk will discuss these obstacles and present ways to overcome them using recent examples from the literature and from the author's own laboratory.

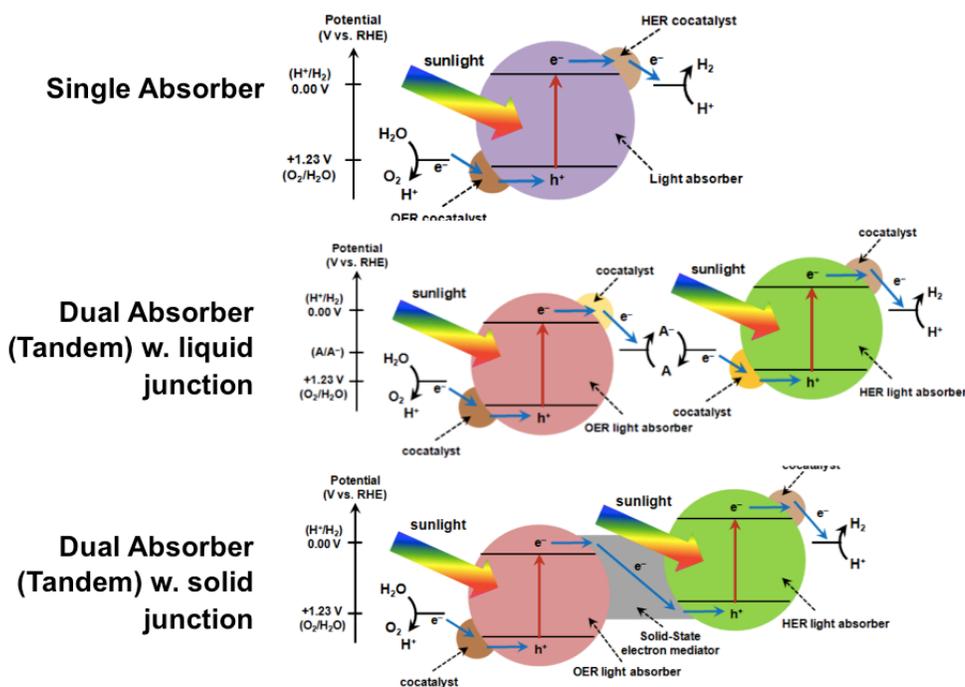


Figure adapted from Fabian et al., *Energ. & Envi. Sci.* 2015, 8, 2825-2850.
<http://dx.doi.org/DOI:10.1039/C5EE01434D>.

Accelerated discovery of new energy materials by high throughput ab-initio computations and experimental validation

G. Dennler,

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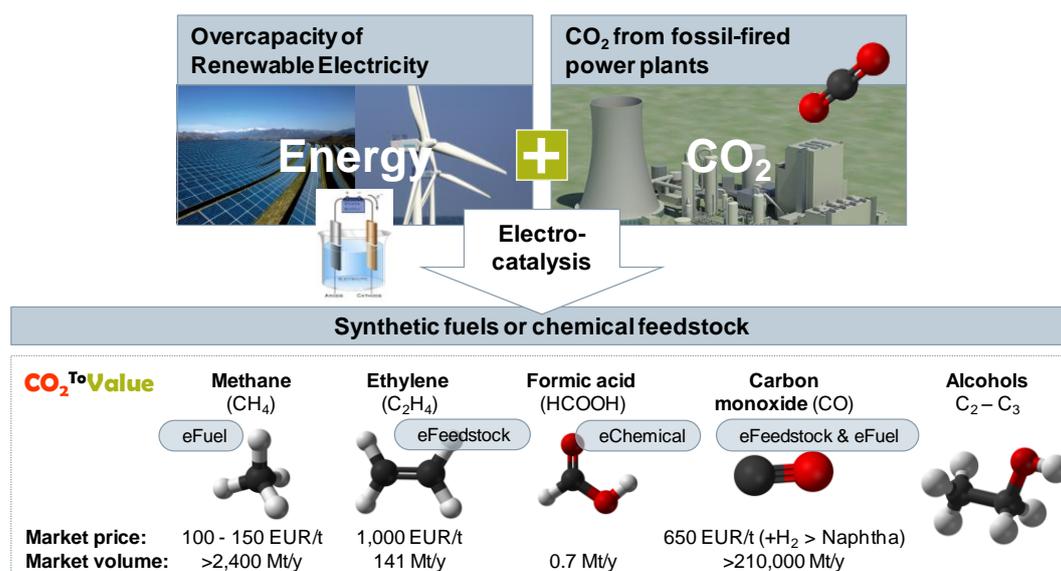
Large market penetration and social acceptance of renewable energy devices require the identification and development of new materials based on non-toxic and non-critical elements. This criticality of raw materials, as defined by the European Commission and its Directorate General for Internal Market, Industry, Entrepreneurship and SMEs (DG-GROWTH), has become through the H2020 program, an unavoidable parameter to account for while searching for new performing compounds. Furthermore, in order to increase industrial competitiveness and to fulfil the demand of the current energy market pull, accelerating the discovery of such new materials appears crucial.

During the presentation, we will discuss the definition of criticality of raw materials, and describe the various parameters taken into account. Furthermore, we will illustrate how, within our industrial environment, we employ an integrated computational and experimental approach to identify and optimize new energy materials conforming to the boundary conditions of non-criticality and non-dangerousness. We will give several examples of Density Functional Theory (DFT) guided development of novel materials for solar cells, solid oxide fuel cells, thermoelectric generators, and water splitting.

Single Step Direct Electrocatalytic Reduction of CO₂ Towards CO and Hydrocarbons

Dr. Günter Schmid, Dr. Christian Reller, Dr. Ralf Krause, Bernhard Schmid, Sebastian Neubauer, Prof. Dr. Max Fleischer; Siemens AG, Erlangen, Munich

Switching from fossil based to renewable power generation requires the installation of large overcapacities of wind and solar due to their intermittency. Storage or conversion possibilities are essential due to the volatility of electricity. Economic feasibility is difficult when considering the low fossil energy carrier prices and the physical efficiency limitations of the processes. Therefore, we choose to focus on high volume chemical feedstock such as Ethylene or CO, where the chemical value exceeds by far its pure heating value.



Electrocatalysts facilitate the conversion of CO₂ to valuable base chemical feedstocks – for selectivity improvements substantial advances in electrode design are required. Depending on the electro catalytic system, CO₂ can be electrochemically reduced to carbon monoxide (CO), methane (CH₄), ethylene (C₂H₄) and various other hydrocarbons even in aqueous media. CO could be obtained with faradic efficiencies over 90% at current densities exceeding the industrial necessary level of 100 mA/cm² with a total energy efficiency approaching 50%. Ethylene is more challenging due to the highly complex reduction process involving 12 electrons and 8 protons. Faradic efficiencies up to 57% for ethylene at current densities above 150 mA/cm² could be obtained using *in-situ*-deposited nano-structured copper based electrocatalysts. In many experiments we observed a large gap in the sum of the current efficiencies of gaseous products to 100% FE. It is well known, that the electro-reduction of CO₂ also yields liquid products. This gap could be fully closed by detailed analysis of the electrolyte revealing a strongly pronounced formation of ethanol (> 20% FE) accompanied by wide range of C₁-C₃ alcohols, carboxylates and ketones in yields up to ~ 5%. To the best of our knowledge, the here reported faradaic efficiencies for ethanol above 20% in a current density regime above 150mA/cm² have been unrepresentative in the literature so far. In addition time resolved parallel analysis of the gaseous and liquid product distribution revealed striking relationships between different species *i.e.* the parallel formation of ethylene and ethanol.

Multiple proton-coupled electron transfer for electrochemical generation of fuels

Marc T.M. Koper

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This talk will outline a simple but general theoretical analysis for multiple proton-electron transfer reactions, based on the microscopic theory of proton-coupled electron transfer reactions, recent developments in the thermodynamic theory of multi-step electron transfer reactions, and the experimental realization that many multiple proton-coupled electron transfer reactions feature decoupled proton-electron steps in their mechanism. It is shown that decoupling of proton and electron transfer leads to a strong pH dependence of the overall catalytic reaction, implying an optimal pH for high catalytic turnover, and an associated optimal catalyst at the optimal pH. When more than one catalytic intermediate is involved, scaling relationships between intermediates may dictate the optimal catalyst and limit the extent of reversibility that may be achievable for a multiple proton-electron-transfer reaction. These scaling relationships follow from a valence-bond-type binding of intermediates to the catalyst surface. The theory is discussed in relation to the experimental results for a number of redox reactions that are of importance for sustainable energy conversion, including the electrocatalytic reduction of CO₂, focusing on their pH dependence and structure sensitivity.

Investigating mechanisms in (electro)catalysis of water oxidation

Prof. Dr. Holger Dau

Freie Universität Berlin, FB Physik

Abstract

Water oxidation typically involves metal-oxide materials that act as catalysts. In biological photosynthesis, water is efficiently oxidized by a protein-bound Mn_4Ca -oxide cluster. NiFe oxides currently may be the best catalyst material for heterogeneous water oxidation at alkaline pH, but also other often non-crystalline (amorphous) oxides are of high interest. Atomistic insight in structure-function relations, basic and specific functional principles, and catalytic mechanism can support the development of improved catalyst materials. We combine electrochemical methods with X-ray absorption spectroscopy at metal *K*-edges, complemented by UV/vis and vibrational spectroscopy. It is discussed how these in-operando experiments can address crucial mechanistic questions.

Size, shape and chemical state effects in the electroreduction of CO₂ over nanostructured Cu and Ag catalysts

Beatriz Roldan Cuenya

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The electrocatalytic reduction of CO₂ to industrial chemicals and fuels is a promising pathway to sustainable electrical energy storage and to an artificial carbon cycle, but is currently hindered by the low energy efficiency and low activity displayed by traditional electrode materials.

Using colloidal synthesis, nanoparticles (NPs) with well-defined size and interparticle distance were prepared and tested as catalysts for CO₂ electroreduction. Cu and CuAu NP catalysts displayed a drastic increase in activity and selectivity for H₂ and CO with decreasing NP. Hydrocarbon (methane and ethylene) selectivity was increasingly suppressed with decreasing NP size. For Au NPs, a drastic increase in current density was observed with decreasing NP size, along with a decrease in faradaic selectivity towards CO. The H₂/CO product ratio could be tailored by tuning the NP size. For CuAu catalysts, the selectivity trends observed could be assigned to reaction-induced segregation of gold atoms to the particle surface. In addition, interparticle distance is also a critical parameter for controlling reactivity. For largely spaced NPs, selectivity to CO is enhanced. On the contrary, for closely spaced NPs we find that hydrocarbon selectivity is enhanced, since the re-adsorption of reaction intermediates on neighboring NPs can facilitate the multi-step pathway required for hydrocarbon production.

Another critical parameter for selectivity control in nanostructured electrocatalysts is the chemical state. We will discuss new oxide-derived (plasma-treated) metal catalysts (Cu and Ag-based) that can reduce CO₂ with lowered overpotential and improved ethylene (Cu) and CO (Ag) selectivity. Insights into the catalyst reaction mechanism which were unraveled using structural and chemical information obtained under *operando* conditions via X-ray absorption fine-structure spectroscopy will be presented.

Finally, the role of the NP shape, in particular, the presence of (100) facets in Cu nanocubes and the evolution of the NP structure and dispersion under reaction conditions will be discussed based on *operando* electrochemical AFM data and chromatography. The relative contribution to catalytic selectivity of a given NP structure versus its chemical state or the stabilization of certain ions on the NP surface will be discussed.

Integrated photovoltaic-electrochemical water splitting modules as a tool for optimization of catalyst materials, upscaling and module geometries

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The generation of fuels from sunlight and water is considered as a task of paramount importance for a sustainable energy supply in the future. Decomposition of water by a photoelectrochemical process is a possibility to harvest solar energy in the form of hydrogen in a large scale. For this purpose, a device can be used which, when immersed in an aqueous electrolyte and illuminated by sunlight, will be able to split water into hydrogen and oxygen.

We will show different approaches that have been pursued in our labs to realize artificial leaf type structures:

- Multijunction thin film a-Si/ μ c-Si solar cells in superstrate geometry with integrated catalysts [1-3]
- Tandem junction solar cells combined with novel metal oxide semiconducting photoanodes [4]

In the first approach a stand-alone integrated solar water splitting module with an area of up to 10x10 cm² will be presented consisting of a multijunction thin film silicon solar cells as photocathode, a sheet metal which forms both the rear contact of the solar cell and the substrate for the hydrogen evolving catalyst, a membrane and an appropriate counter electrode for the oxygen evolving catalyst. All components are encased in a compact metal/plastic frame with feedthroughs for electrolyte and gas in- and outputs, respectively. The sheet metal ensures long term stability of the module by protecting the semiconductor solar cell from the electrolyte and the modular set-up allows to vary and optimize the device components (solar cell, low series resistance loss front contacts, catalysts, electrolyte) individually in this convenient toolbox.

One of the main bottlenecks in the second approach is the performance of the metal oxide photoelectrode in combination with a Si solar cell [4]. Our current efforts are aimed at developing and optimizing CuBi₂O₄ and BiVO₄, but also other oxides and oxynitrides are under investigation [5]. Compared to conventional semiconductors, metal oxides show good chemical stability and are relatively easy to process with e.g. wet-chemical techniques. However, their semiconducting properties are usually poor. We discuss several approaches that can be used to address these intrinsic material limitations.

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Water splitting and the making of renewable chemicals.

I. Chorkendorff

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Hydrogen is the simplest solar fuel to produce and in this presentation we shall give a short overview of the pros and cons of various devices [1,2,3] for hydrogen production. Since most relevant semiconductors are very prone to corrosion the advantage of using buried junctions and using protection layers offering shall be discussed [4-6]. In particular we shall show how doped TiO₂ is a very generic protection layer for both the anode and the cathode [7]. Next we shall discuss the availability of various catalysts for being coupled to these protection layers or simply used in electrolyzers and how their stability and amount needed may be evaluated [8]. Notably NiO_x promoted by iron is a material that is transparent, providing protection, and is a good catalyst for O₂ evolution [9]. We shall show how mass selected nanoparticles can be used to elucidate the effectiveness of the various catalysts both for HER [10] and for OER [11, 12]. Finally, we shall also discuss the possibility of making high energy density fuels by hydrogenation of CO₂ or CO instead of hydrogen evolution [13]. We shall here show how we can investigate the recent ethanol synthesis on oxygen derived Cu found by Kanan et al. and show how acetaldehyde seems to be an important intermediate [14]. New methods for detecting volatile products using a “Sniffer” setup will also be discussed [15].

References

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Semiconductor Systems and Catalysis for Photoelectrochemical Water Splitting

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Abstract

Forty years after the first reported photoelectrochemical (PEC) water splitting experiment, commercial hydrogen production from PEC is still a dream. Literally 100's of millions of dollars and thousands of papers later and still no semiconductor system has been identified that has the potential for economical hydrogen production from PEC water splitting.

Recent technoeconomic analysis studies indicate that a >15% solar-to-hydrogen PEC conversion efficiency is necessary for a commercially viable system. Additional requirements of lifetime (years), and cells costs (<\$400/m²) make a working device extremely challenging.

To achieve such high efficiencies, semiconductors with superior electronic properties are required as well as highly active catalysts. Clearly then one must decide whether to use an existing PV-based semiconductor or search for a new semiconductor with the necessary electronic properties. The majority of the research has been directed at metal oxides due to their expected low costs, ease of synthesis and stability, but their poor electronic structure prevents them from reaching the high efficiencies necessary for a working device.

The III-V-based solar cells show the highest solar PV efficiency and thus are excellent candidates for a PEC system, but cell costs are high and lifetime is limited.

Incorporation of proper electrocatalysts onto the illuminated SC surface is necessary to both stabilize the PEC interface and increase catalysis, thus enhancing the overall device performance. Noble metals, particularly platinum, are mostly commonly applied as they are the most active for the water redox reactions. The branching ratio between catalysis and corrosion must be extremely high (>10⁶) in order for the system to have the necessary lifetime, thus the catalysts must have a very high turnover frequency (TOF) and turnover number (TON). Noble metals are neither earth abundant nor low-cost, so identifying catalytic systems that can match the activity and stability of platinum but are based on earth abundant materials are clearly a high-priority area of research. Such materials for SC surface modification are particularly beneficial if they are potentially low-cost and scalable, transparent and conductive while also highly catalytically active and stable. Work on hydrogen evolution catalysts has been a very active area of research where numerous molecular, nanomaterial, and bulk catalysts have been developed.

This presentation will discuss some of the challenges and opportunities facing PEC community in our search for a workable PEC solar water-splitting system that could lead to a commercial device. The discussion will include tandem cells for PEC water splitting and the importance of surface treatments for band edge control and the advantage of a visible-light transparent hydrogen evolution catalyst.

Emerging materials for the photocathode/photoanode tandem cell

Kevin Sivula

Institute of Chemical Sciences and Engineering

École Polytechnique Fédérale de Lausanne

Abstract:

High-efficiency direct solar-to-fuel energy conversion can be achieved using a photoelectrochemical (PEC) device consisting of an n-type photoanode in tandem with a p-type photocathode. However, the development of robust and inexpensive photoelectrodes are needed to make PEC devices economically viable. In this presentation the optoelectronic and electrochemical electrode requirements as well as device architecture will be presented. Recent efforts to apply new materials for economically-prepared, robust, and high performance overall PEC water splitting tandem cells for H₂ production will be discussed.

Materials and Systems for stand-alone Solar Fuel Production

Jae Sung Lee

School of Energy and Chemical Engineering, Ulsan National Institute of Science & Technology

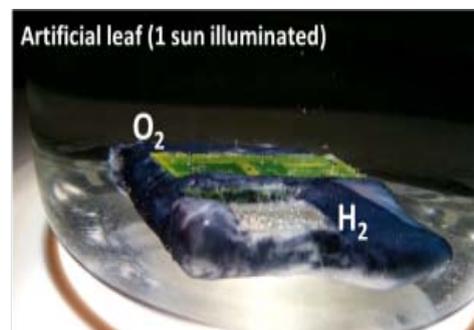
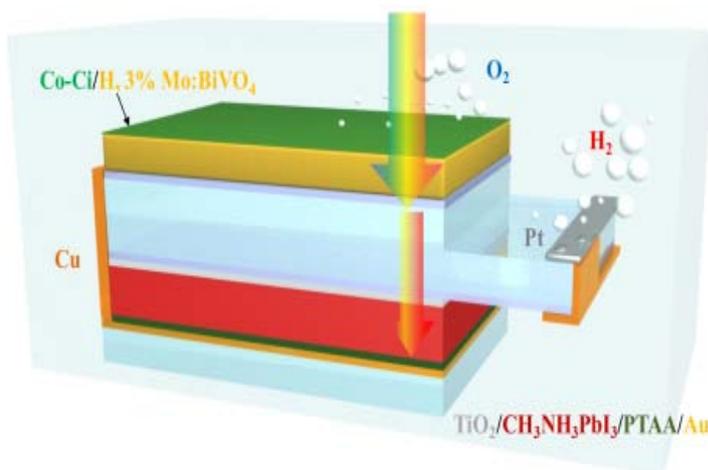
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About 400 semiconductor solids are known to have photocatalytic activity for water splitting. Yet there is no single material that could satisfy all the requirements for desired photocatalysts: i) suitable band gap energy ($1.7 \text{ eV} < E_g < 2.3 \text{ eV}$) for high efficiency, ii) proper band position for reduction and/or oxidation of water, iii) long-term stability in aqueous solutions, iv) low cost, v) high crystallinity, and vi) high conductivity. Hence, in the selection of photocatalytic materials, we better start from intrinsically stable materials made of earth-abundant elements. The band gap energy is also the primary consideration to absorb ample amount of solar energy of wide wavelength spectrum. It sets the limit of theoretically maximum efficiency and it could also be extended by band engineering techniques.

Upon selection of the candidate materials, we can also modify the materials for full utilization their potentials. The main path of efficiency loss in PEC water splitting process is recombination of photoelectrons and holes. We discuss the material designs including i) p-n heterojunction photoanodes for effective electron-hole separation, ii) electron highway to facilitate interparticle electron transfer, iii) metal or anion doping to improve conductivity of the semiconductor and to extend the range of light absorption, iv) one-dimensional nanomaterials to secure a short hole diffusion distance and vectorial electron transfer, and v) loading co-catalysts for facile charge separation.

Finally, we need to construct a stand-alone solar fuel production system by combining with a solar cell in tandem, which provides bias voltage needed for the photolytic reactions making possible the fuel production only with solar energy without any external energy supply.



Finding the Needle in a Haystack: A High-Throughput Computational Approach to Materials Discovery

Geoffroy Hautier

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Abstract

Ab initio methods (i.e., computations solving the approximations to the Schrodinger equation) can now routinely be used to compute essential materials properties. When combined with the rising computational power, this predictive power provides the opportunity for large-scale computational searches for new materials. Thousands of materials can be screened by their computed properties even before they are investigated experimentally, accelerating tremendously the identification of the most promising candidates.

In this talk, I will present the challenges as well as the opportunities in the materials discovery from high-throughput computing. I will illustrate this new paradigm with examples in transparent conducting oxides and thermoelectrics. Beyond the identification of new compounds, I will demonstrate how large computational databases can be data mined to detect trends and relationships between chemistries, structures and properties. Finally, I will present the Materials Project (<http://www.materialproject.org>): a collaborative effort aiming at disseminating high-throughput generated data through a free and open database and website.

Bridging heterogenous and homogenous catalysis - *in theory* **similarities and differences from surfaces to molecule**

Alexander Auer

Theoretical Methods and Heterogeneous Reactions

Molekulare Theorie und Spektroskopie

MPI für chemische Energiekonversion, Mülheim, Germany

Abstract

In principle, photovoltaics + electrocatalysis in energy conversion addresses the same task like proteins in green leaves - they convert accessible sources of energy and store it in available form.

The details of these systems, however, could not be more different conceptually. Inorganic materials, semiconductors and noble metals on the one hand, organic compounds, enzymes and monoatomic active sites on the other hand. While at first sight, we appreciate the differences and observe that only few aspects are transferable, for example from biosystems to industrial processes, there are unifying concepts but also fundamental differences.

In this presentation I will give an outline of the methodologies of electronic structure theory to treat catalytic processes and discuss some of the details what theory is able to do and how to interpret results of electronic structure theory.

I will then focus on conceptual similarities and differences in heterogenous catalysis and homogenous- and biocatalysis. This includes the discussion of the underlying physics and chemistry and how one can identify common phenomena and understand the differences in approaches to treat the different regimes of catalysis.

Program of the SPP 1613 Annual Project Meeting, Teikyo Hotel Berlin, 29-30 September 2016

28th September 2016:

Arrival

19:30

Dinner

29th September 2016:

ID	Time	Principal Investigators	Topic
	07:30 – 09:00		Breakfast
	09:00 – 09:10	Jaegermann, Darmstadt	Welcome / Introduction
1	09:10 – 09:35 3 projects	Bahnemann, Hannover Bredow, Bonn Wark, Oldenburg	Ferrites for photoelectrochemical water splitting
2	09:35 – 10:05 4 projects	Bein, München Fattakhova-R., München Pentcheva, Duisburg Scheu, Düsseldorf	Metal oxide nanostructures for electrochemical and photoelectrochemical water splitting
3	10:05 – 10:35 4 projects	Behrens, Essen Fischer, Freiburg Lerch, Berlin Schedel-Niedrig, Berlin	Novel thin film composites and co-catalysts for visible light-induced water splitting
4	10:35 – 11:00 3 projects	Beránek, Bochum Devi, Bochum Eichberger, Berlin	Development of optimum bandgap photoanodes for tandem water-splitting cells based on doped complex metal oxides and III-V semiconductors coupled to water oxidation electrocatalysts
	11:00 - 11:30		Coffee break
5	11:30 – 11:55 3 projects	Dau, Berlin Fiechter, Berlin Kurz, Freiburg	Development of catalysts, namely manganese oxides and molybdenum sulphides, for implementation in a light-driven water-splitting device using a multi-junction solar cell
6	11:55 – 12:20 3 projects	Fiechter, Berlin Ludwig, Bochum Schuhmann, Bochum	High-throughput characterization of multinary transition metal oxide and oxynitride libraries. New materials for solar water splitting with improved properties
7	12:20 – 12:45 3 projects	Finger, Jülich Jaegermann, Darmstadt Kaiser, Darmstadt Schäfer, Darmstadt	Photoelectrochemical water splitting using adapted silicon based semiconductor multi-junction cell structures
8	12:45 – 13:00 1 project	Jooß, Göttingen	In-situ environmental TEM studies of electro- and photoelectrochemical systems for water splitting
	13:00 – 14:15		Lunch

ID	Time	Principal Investigators	Topic
9	14:15 – 14:30 1 project	Klüner, Oldenburg	Quantum chemical and quantum dynamical studies of the photocatalytic water splitting on titanium dioxide surfaces
10	14:30 – 14:45 1 project	Mathur, Köln	PhotoElectroChemical applicAtion of Uranium oxides for enhanced Light Absorption (PECULIAR)
11	14:45 – 15:00 1 project	Marschall, Gießen	Sustainable solar energy conversion with defined ferrite nanostructures
12	15:00 – 15:20 2 projects	Muhler, Bochum Winterer, Duisburg	Zn-doped Gallium Oxynitride Nanoparticles as Efficient Photocatalyst for Water Splitting
13	15:20 – 15:35 1 project	Schmuki, Erlangen	Ta3N5 nanotubes and -rods: doping, band-gap engineering and stabilization (co-catalysis)
	15:35 - 16:05		Coffee break
14	16:05 – 16:25 2 projects	Strasser, Berlin Teschner, Berlin	Nanostructured mixed metal oxides for the electrocatalytic oxidation of water
15	16:25 – 16:40 1 project	Toimil-Molares, Darmstadt	Investigation and optimization of the physical processes in light induced water splitting with 3D nanowire model systems
16	16:40 – 16:55 1 project	Weidenkaff, Stuttgart	Photocatalytic anion substituted perovskite phases PAP
	16:55 – 18:30		Poster session & cooperation discussions I
	18:30 - 20:00		Dinner
	20:00 – 21:15		Poster session & cooperation discussions II

30th September 2016:

	07:30 – 08:30		Breakfast
	08:30 – 09:30		Organizational topics: future meetings, organization of cooperation, time table and organization of SPP
	09:30 – 10:30		Discussion of cooperation within the main three project areas: Novel Photoabsorbers, Advanced Electrocatalysts, Device Development
	10:30 - 11:00		Coffee break
	11:00 – 12:00		Discussion of cooperation beyond the main project areas
	12:00 – 13:00		Lunch

13:00 Departure