Optical plasmonic nano-structures for enhanced photochemistry

Main Proposer: Prof. Edwin C. Constable (University of Basel, Department of Chemistry)
Co-Proposer: Dr. Sören Fricke (CSEM Muttenz); Prof. Catherine E. Housecroft (University of Basel, Department of Chemistry)

Aim of this PhD project is to combine the experience and know-how of the Constable-Housecroft Group in materials photochemistry and photophysics with the expertise of CSEM Muttenz in simulation, large-area manufacturing, and characterization of optical plasmonic nano-structures, in order to study and demonstrate the potential of these innovative nano-optical surfaces for the production of solar-fuels.

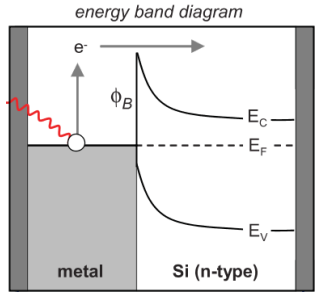
Solar-fuels is a collective term for chemical energy sources created by harnessing solar-energy. Solar-fuels can be used to store the energy in a chemical form and regain it by a chemical process, such as oxidation, as in classical combustion processes. The concept of solar-fuels is quite intuitive in approaching the question on energy storage from the energy density point of view. The highest known energy mass densities can be found in nuclear fission and nuclear decay followed by chemical energy, which exhibits a 10-100 times higher energy mass density then electrochemical energy sources, such as batteries. In nature, photosynthesis is one of the key photochemical reactions for life, although the overall efficiency is low. Since 2007, solar-fuels have raised increasing interest in the scientific community, thus resulting in a tremendous increase of publications, with a particular emphasis on artificial photosynthetic systems.

Main focus of this PhD project will be water splitting to create H_2 from water as a solar-fuel: this process yields the maximum energy density for a chemical fuel. In particular, it requires two electrons, while for other solar-fuels like methane or ethanol, multiple electrons per mole of target are required, thus significantly reducing the efficiency of the photo-synthesis process. It is therefore reasonable to focus on the water-splitting approach. In the Constable-Housecroft Group, significant know-how has been developed on the synthesis of catalysts for water-splitting [1]. This PhD project will build on the existing background and aim to develop functional demonstrator devices to prove and assess the overall concept. For the two electron process, it is important to have an overlap in time of two excited electrons that can contribute to the reaction. Recent publications have been based on proton-coupled electron transfer [2,3]. The PhD student will study this latter approach on the efficiency increase that can be achieved using optical plasmonic nano-structures.

Several limitations to the efficiency of the water-splitting are known [4]. One is a low absorption of many semiconductors due to a large and/or not overlapping bandgaps. Others are reflection due to a high refractive index of the semiconductor material and recombination due to a short minority carrier distance. The challenges are similar to those observed in organic (OPV) and Si (Si-PV) photovoltaics, two fields, where CSEM is particularly active through its PV Center. Plasmonic enhancement of the conversion efficiency have been studied for both PV systems. Water-splitting can benefit from this existing know-how: plasmonic structures and/or nanoparticles may lead to a significant enhancement of the conversion efficiency. Plasmonic nanoparticles are already reported in literature as giving significant enhancement to the conversion efficiency. Very similar to the enhancement mechanism in OPV, the nanoparticles act like antennas receiving the light and transferring the plasmon energy to a nearby absorber.

Plasmonic nano-structures in the range of approx. 100 – 200 nm can address similarly the known limitations by injecting hot electrons and holes into the semiconductor [4,5]. Furthermore, nano-structures can be used to increase the effective optical path of photons propagating through photochemical active materials in order to increase the probability of absorption, and thus the overall efficiency. In contrast to the enhancement obtained using plasmonic nanoparticles [6], to the best of our knowledge, both the theoretical and the experimental proof-of-concept of large scale optical plasmonic nano-structures for enhanced water splitting have to not been investigated so far. Plasmonic nano-structures yield the potential for cost effective

and high reproducibility production of large areas, which will be a key for competitiveness of the described technology.

a) 

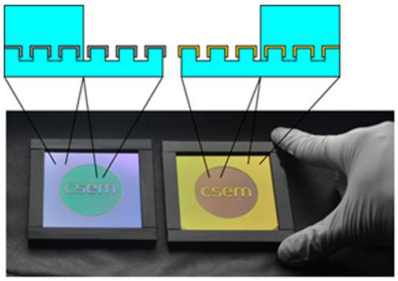
b) 

Figure 1: a) Band diagram for plasmonically driven hot electron injection over a Schottky barrier (φ_B). Source: M.W. Knight [5]. b) Large area plasmonic structures developed and manufactured at CSEM.

CSEM Muttenz has a strong background in both refractive and diffractive micro- and nanooptics, as well as in optical plasmonic nano-structures. Design and simulation tools and large-area manufacturing processes are available in-house, which can be used to create well-controlled plasmonic nano-structures and to replicate them on large surfaces. Due to its activities in OPV, CSEM Muttenz is fully equipped with solar simulators and has a strong background in light-management for photovoltaics. The PhD student can therefore rely on proven experimental setups for characterization of the conversion efficiency.

In this PhD project, the student will perform theoretical and experimental studies on the efficiency of light to solar-fuel conversion. The PhD student will focus on the design and the manufacturing of optical plasmonic nano-structures in order to improve the efficiency of the photochemical water-splitting. The target is to combine an optimized electronic structure of the photo-catalyst with a supporting plasmonic and light-management structure to increase the overall efficiency. As a final result demonstrator devices for conversion of pH 7 water to H_2 by sunlight will be realized.

The PhD student will spend most of his/her time working in the lab facilities of CSEM Muttenz in the Rosental-Area. For this reason, in order to comply with legal and insurance rules, he/she will be an employee of CSEM. Note that at the end of 2017, the Constable/Housecroft research group will move to the building 1096 in the Rosental-Area, which is within a few minutes walk from the CSEM Muttenz facilities, thus allowing easy and efficient communications between the research teams.

[1] H. Lv, J. a Rudd, P. F. Zhuk, J. Y. Lee, E. C. Constable, C. E. Housecroft, C. L. Hill, D. G. Musaev, Y. V. Geletii, *RSC Adv.* **2013**, *3*, 20647.

[2] A. Yamaguchi, R. Inuzuka, T. Takashima, T. Hayashi, K. Hashimoto, R. Nakamura, *Nat. Commun.* **2014**, *5*, 4256.

[3] C. J. Gagliardi, A. K. Vannucci, J. J. Concepcion, Z. Chen, T. J. Meyer, *Energy Environ. Sci.* **2012**, *5*, 7704.

[4] S. C. Warren, E. Thimsen, *Energy Environ. Sci.* **2012**, *5*, 5133.

[5] M. W. Knight, H. Sobhani, P. Nordlander, N. J. Halas, *Science* **2011**, *332*, 702.

[6] Z. Liu, W. Hou, P. Pavaskar, M. Aykol, S. B. Cronin, *Nano Lett.* **2011**, *11*, 1111.

Edwin Charles CONSTABLE

Department of Chemistry, The University of Basel, Spitalstrasse 51, Basel CH4056,
Phone: +41 (0)61 267 1001 E-Mail: edwin.constable@unibas.ch
Date of Birth: 11th August 1955, Edinburgh, Scotland
Nationality: British
Marital Status: Married to Professor Catherine E. Housecroft, no children
Qualifications: B.A. (Oxon.), M.A. (Oxon.), D. Phil. (Oxon.), Ph.D. (Cantab.)
Education
St Catherine's College Oxford, 1974-1978: BA (Hons First class) Chemistry.
Linacre College, Oxford, D. Phil Chemistry 1978-2000: D. Phil Chemistry.
Employment:
S.E.R.C. Post-Doctoral Research Fellow, University of Cambridge 1980-1982
University Demonstrator, University of Cambridge 1983-1987
University Lecturer, University of Cambridge 1987-1993
Ordinarius for Inorganic Chemistry, University of Basel. 1993-2000
Professor of Inorganic Chemistry, University of Birmingham 2000-2001
Head of School of Chemistry, University of Birmingham 2001-2002
Ordinarius for Chemistry, University of Basel 2002-
Research Dean, Natural Sciences Faculty, University of Basel. 2008-2011
Vice Rector for Research and Talent Promotion, University of Basel 2011 -
Summary
Professor Edwin Constable has been involved in supramolecular chemistry since its inception and has published over 500 research papers and many books. He studied chemistry in Oxford, and then moved to Cambridge where he held an 1851 Research Fellowship, a University Demonstratorship and finally a Lectureship and was a Fellow of Darwin and Robinson Colleges. In 1993 he accepted a call to the Chair of Inorganic Chemistry in Basel where he remained until 2000 when he returned to the United Kingdom to a Chair of Chemistry in Birmingham. In 2002 he returned to Basel where he currently holds a Chair of Chemistry. He was Research Dean of the Faculty and is currently Vice-Rector for Research. His scientific interests and expertise lie in metallosupramolecular and materials chemistry, especially in the use of metal ions for the assembly of novel architectures incorporating specific electronic or photophysical properties. He is a highly cited researcher and is actively involved in industrial collaborations, national and EU funded programs relating to interfacial and heterogeneous chemistry and their application to nanoscale electronic, catalytic and electrocatalytic devices. Interest centres upon the development of new dyes for the dye-sensitized nano crystalline solar cell and new materials for OLEDs and related lighting technologies.
He received an ERC Advanced Grant (2011-2016) for his project LiLo (Light-In, Light- Out) relating to sustainable materials chemistry and is actively involved in the Swiss Nanoscience Institute. He has a strong record of funding in pure and applied science projects and a long-standing interest in the use of homogeneous and heterogeneous systems for solar energy conversion and for water activation chemistry. He runs the research group jointly with his wife, Professor Catherine Housecroft.
He has a vision for higher education in which social responsibility is combined with cutting edge training and research in all disciplines. His philosophy is based in aninterdisciplinary approach in which traditional areas coexist in symbiosis and learn from one another. He is a keen advocate of the public awareness of science and of the need for scientists to better communicate with the wider public and to interact with the social sciences and humanities to understand and engineer the social consequences of technological change. His academic vision is one in which core competencies are coupled with the ability to respond to new challenges and opportunities.

Catherine Elizabeth Constable-HOUSECROFT

Department of Chemistry, The University of Basel, Spitalstrasse 51, Basel CH4056,
Phone: +41 (0)61 267 1008 E-Mail: catherine.housecroft@unibas.ch
Date of Birth: 23 February 1955, Bradford, West Yorkshire
Nationality: British
Marital Status: Married to Professor Edwin C. Constable; no children
Qualifications: B.Sc. (Durham), M.A. (Cantab.), PhD (Durham), Umhabilitatiert (Basel)
Employment:
Postdoctoral Associate, Department of Chemistry , University of Notre Dame, USA
Assistant Professor, Department of Chemistry, University of New Hampshire, USA
College Lecturer in Chemistry, Newnham College, Cambridge, UK
Royal Society Research Fellow, University of Cambridge, UK
Lecturer in Inorganic Chemistry, University of Cambridge, UK
Privat Dozentin, Department of Chemisrty, University of Basel
Titular Professor, Department of Chemistry, University of Basel
Catherine Housecroft is Titular Professor of Chemistry at the University of Basel. She is co-director of a highly active and productive research group with Edwin Constable, and has a broad range of interests spanning organometallic and coordination chemistries. She is also a work-package leader and PI within the NCCR Molecular Systems Engineering. Current research is focused towards the application of coordination chemistry to sustainable energy and functional coordination polymers. She has published ~400 research papers and 60 review articles in peer reviewed journals, in addition to a number of chapters in edited books and reference works. She has written or coauthored 12 undergraduate textbooks and is an internationally recognized author; *Chemistry* (coauthored with her husband Edwin Constable) and *Inorganic Chemistry* (with the late Alan Sharpe) are both in their fourth editions – *Inorganic Chemistry* has been translated into French, German, Spanish, Portuguese, Czech, Greek and Japanese.

Sören FRICKE

Section Head for Manufacturing Technologies in the Division Thin Film Optics, Centre Suisse d'Electronique et de Microtechnique SA, Tramstrasse 99, CH 4132 Muttenz

Phone: +41-61-690-6018 **E-Mail:** snf@csem.ch

Date of Birth: 30.08.1977, Seeheim, Germany

Marital Status: unmarried, no children

Qualifications: Dipl. Phys. ETHZ, Dr. Ing. (Saarland University)

Employment:

2003 – 2004	Internship at Sony „Fusion Domain Laboratory", Tokyo
2005 – 2008	PhD Student in the Corporate Research Center of EADS (Airbus), Munich
2008 – 2010	Engineer for Semiconductors and MEMS Assembly and Packaging at Bosch Automotive Electronics, Stuttgart
2011	Project Manager for Semiconductors and MEMS Assembly and Packaging at Bosch Automotive Electronics, Stuttgart
2012 – 2013	Team Manager for Semiconductors and MEMS Assembly and Packaging at Bosch Automotive Electronics, Stuttgart
2013 – 2015	Project Manager for industrial and ESA projects at CSEM, Muttenz
2015 – now	Section Head for Manufacturing Technologies at CSEM, Muttenz

Dr. Sören Fricke received his Diploma degree in Physics from the Swiss Federal Institute of Technology (ETHZ), Zurich, Switzerland in 2004. He joined Sonys Fusion Domain Laboratory in Tokyo, Japan, where he prepared his Diploma Thesis. In 2005, he continued his research on micro-sensors at the Corporate Research Centre of EADS in Ottobrunn, Germany and received his PhD degree from Saarland University, Germany in 2010. In 2008 he joined Robert Bosch GmbH and worked in the field of semiconductor and MEMS packaging in the business unit Automotive Electronics. From 2012 to 2013, he was team manager of an international engineering team, responsible for the volume production of automotive pressure sensors. End of 2013, he joined CSEM Muttenz in the position of a Project Manager, and since beginning of 2015 he is Section Head for Manufacturing Technologies. Sören Fricke was involved in several national and international projects including ESA projects and two recent EU projects Medilight and Smartonics. He published several peer-reviewed articles and holds 3 patents. As a member of the program committee he actively contributed to the SPIE conference "Smart Sensors, Actuators and MEMS" since 2011.