

HL 68: Focus Session: Semiconductor Materials and Nanostructure for Photocatalysis

Time: Thursday 9:30–12:30

Location: POT 51

Invited Talk

HL 68.1 Thu 9:30 POT 51

Solar-driven photoelectrochemical water splitting and carbon dioxide reduction — ●JOEL AGER — Joint Center for Artificial Photosynthesis, Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA USA — Department of Materials Science and Engineering, UC Berkeley

Solar to fuel conversion, if it could be performed in a sustainable manner, could provide an alternative to mankind's currently unsustainable use of fossil fuels. Solar fuel generation by photoelectrochemical (PEC) methods is a potentially promising approach to address this fundamental and important challenge.

While there are number of laboratory-scale solar to hydrogen (STH) conversion devices whose efficiencies exceed 10%, there are very few reports of long term operational stability. In this context, the long term stability of protective coatings for water oxidation photoanodes will be discussed, with an emphasis on the experimental procedures required to predict the operational lifetime.

Electrochemical carbon dioxide reduction is comparatively less mature as a technology and hence the challenges are more basic. Indeed, there are very few reports of systems which produce usable fuel products with high selectivity. Recently, building on work performed with Cu nanocubes, we have designed Cu nanostructures which achieve up to 70% conversion of carbon dioxide to C₂⁺ products. When coupled with high efficiency solar cells, overall energy conversion efficiencies exceeding that of natural photosynthesis can be achieved.

HL 68.2 Thu 10:00 POT 51

Tuning the electronic structure of Nb₃O₇(OH) by titanium doping for enhanced light-induced water splitting — WILAYAT KHAN¹, ●S. BETZLER², O. SIPR³, CH. SCHEU⁴, and J. MINAR⁵ — ¹New Technologies-Research Center, University of West Bohemia, Univerzita 8, 306 14 Plzen, Czech Republic — ²Department of Chemistry and Center for NanoScience, LMU Munich, Butenandtstraße 11, 81377 Munich, Germany — ³NTC, University of West Bohemia, Plzen, Czech Republic — ⁴Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Straße 1, Du^{*}sseldorf, Germany — ⁵NTC, University of West Bohemia, Plzen, Czech Republic

Water photolysis is a clean and renewable source for hydrogen fuel and is therefore considered as a potentially important part of the solution of the energy crises. An extensive work has been performed on transition metal oxides semiconductors like TiO₂, WO₂ and Fe₂O₃, which can be used as electrode materials. Recently, Nb₃O₇(OH) has been proposed as a promising material for this propose due to its stability and suitable band gap [1]. Here we report on the modification of the structure and electronic properties of Nb₃O₇(OH) due to the Ti doping. Our theoretical study is based on the density functional theory using FP-LAPW method. The Ti-doped Nb₃O₇(OH) showed a direct band gap at the G point in the calculated band structures. In addition, Ti doping modifies the optical properties of the host material in a desirable way. Theoretical study is accompanied by a corresponding detailed experimental EELS study. [1] W. Khan et. al., J. Phys. Chem. C, 2016, 120 (41), 23329-23338

HL 68.3 Thu 10:15 POT 51

Semiconductor surface stabilization under photoelectrochemical conditions — ●WAQAS SADDIQUE, KLAUS STALLBERG, GERHARD LILIENKAMP, and WINFRIED DAUM — Institute of Energy Research and Physical Technologies, TU Clausthal, Leibnizstr. 4, 38678 Clausthal-Zellerfeld, Germany

The production of hydrogen by solar energy via water splitting in photoelectrochemical (PEC) cells is a field of current research and challenges in materials research. III-V semiconductors with suitable band gaps are candidates for water splitting but frequently subjected to corrosion during the water splitting process and suffer from corrosion-related decrease in efficiency. GaP has an indirect band gap of 2.26 eV which covers both the hydrogen and oxygen evolution potentials. So GaP can in principle be used as photocathode and photoanode, respectively. We have studied structural and chemical properties and modifications of an n-GaP(100) photoanode after extended photoelectrochemical activity. A 4 nm thin oxide film was produced at the surface of an n-GaP(100) photoanode via oxidizing the surface at specific PEC conditions and subsequently hydrogenating the surface to

passivate defects in the oxide film. This specific process results in the formation of a stable Ga surface oxide, which inhibits corrosion while allowing the light and the charge carriers to pass through the thin oxide for the completion of the PEC process. No other prior surface treatments or catalysts were required for this process. An open-circuit potential Voc of 1.2 V vs the reversible hydrogen electrode (RHE) was also determined.

Invited Talk

HL 68.4 Thu 10:30 POT 51

Quantum confined colloidal semiconductor nanocrystals for solar fuels — ●FRANK JÄCKEL — Stephenson Institute for Renewable Energy and Department of Physics, University of Liverpool, UK

Co-catalyst decorated colloidal semiconductor nanocrystals are currently receiving increasing interest as a potentially cheap and scalable means for the photocatalytic generation of solar fuels such as solar hydrogen. [1,2] At the same time, colloidal semiconductor nanocrystals offer size-tuneable optical and electronic properties which allow the realisation of material properties beyond the bulk. In this talk, I will address how quantum confinement can be used to optimise quantum efficiencies and the use of the solar spectrum for photocatalytic hydrogen generation.[3] I will also present new approaches towards solving the stability-efficiency-dilemma frequently encountered in these systems. [4]

[1] M. Berr, A. Vaneski, A. S. Susha, J. Rodriguez-Fernandez, M. Döblinger, F. Jäckel, A. L. Rogach, and J. Feldmann, Appl. Phys. Lett. 97 093108 (2010).

[2] T. Simon, N. Bouchonville, M. J. Berr, A. Vaneski, A. Adrovic, D. Volbers, R. Wyrwich, M. Döblinger, A. S. Susha, A. L. Rogach, F. Jäckel, J. K. Stolarczyk, J. Feldmann, Nature Materials 13 1013 (2014).

[3] W. Li, G. O'Dowd, T. J. Whittles, D. Hesp, Y. Gründer, V. R. Dhanak, F. Jäckel Nanoscale 7 16606 (2015).

[4] W. Li, J. Lee, F. Jäckel ACS Appl. Mater. & Interf. 8 29434 (2016).

Coffee Break

HL 68.5 Thu 11:30 POT 51

Photo-catalytic carbon dioxide reduction with InGaN photoelectrodes — ●VIKTORIA KUNZELMANN, ANDREAS ZEIDLER, ANDREA WINNERL, and MARTIN STUTZMANN — Walter Schottky Institut, Technische Universität München, Garching, Deutschland

Carbon dioxide (CO₂) has reached a critical level in atmosphere and counts as one of the reasons for global warming. Reducing this greenhouse gas to hydrocarbon fuels would help solving environmental issues and simultaneously address challenges such as energy storage and resource shortage. Using a photo-catalytic reaction to convert CO₂ into fuels is one way to address this issue. Due to the chemical inertness of CO₂ and the instability of suitable catalysts, efficient CO₂ reduction is still challenging. Using gallium nitride (GaN) as a photo-electrode is promising, since GaN is relatively stable under operating conditions and provides electrons with sufficient energy. Tuning the band gap by alloying GaN with indium might additionally enhance desired reduction processes. The current work concerns charge transfer processes on the interface of p- and n-type GaN or indium gallium nitride (InGaN), grown by molecular beam epitaxy, and an electrolyte. The characterization of the photo-electrode material is done by: atomic force and scanning electron microscopy for topography analysis, Kelvin probe force microscopy to analyze the surface potential landscape of the samples, surface photo-voltage measurements to evaluate the change of the electronic band structure due to illumination and Hall effect measurements to clarify the charge carrier density. Additionally, first results of photoelectrochemical measurements will be presented.

HL 68.6 Thu 11:45 POT 51

Omnidirectional Photoelectrochemical Activity of Ultrathin CdS film on Periodic Three-Dimensional Composite Pillar/Truncated-Pyramid Au arrays — ●RUI XU, LIAOYONG WEN, HUAPING ZHAO, SHIPU XU, MAX SOMMERFELD, YANG XU, YAN MI, YAOGUO FANG, and YONG LEI — Institute of Physics & Institute of Micro- and Nanotechnologies (ZIK MacroNano), Ilmenau University of Technology, 98693 Ilmenau, Germany

Photonic mode and surface plasmon resonance show prominent promise in improving light utilization of solar energy-related devices. In order to incorporate both features simultaneously, we designed and manufactured ordered array of three-dimensional metal pillar/truncated-pyramid (PTP) nanostructures. The experiments along with simulation indicate that the Au PTP arrays demonstrate multiple SPR and PM originated from the two structural elements leading to superior and broadband anti-reflection performance. To take these advantages, a conformal 90-nm-thick CdS film was coated on the PTP nanostructures and the resultant photoanode reaches a respectable light absorption over 90% in the overall optical operation regime. More importantly, the efficient light-trapping is omnidirectional and the calculated average absorptivity keeps almost the same in at least 50 degree range. The PTP photoanode demonstrated a dispersive light absorption, which worked in concert with CdS surface extension and strong light absorption to achieve a tremendous current promotion by a factor of 2.8 from the flat counterpart at -0.2 V (vs. Ag/AgCl).

Invited Talk

HL 68.7 Thu 12:00 POT 51

Photo-electrochemistry modelling beyond idealised surfaces and the computational hydrogen electrode — ●HARALD OBERHOFER — Technical University Munich Garching, Germany

The role computer modelling plays today in understanding and optimising catalysts for photo-electrochemical reactions is undisputed. Yet, state of the art simulation approaches tend to rely on a number of assumptions and simplifications which—according to newest results—may not be fully justified. For example, simulation of the all-important electro-catalytic water oxidation reaction is mainly based on idealised surfaces and the computational hydrogen electrode (CHE) approach, which evaluates the thermodynamic feasibility of a catalyst looking at pathway where each hydrogen abstraction is coupled to the removal of one electron (PCET). The precise reactive site of the catalyst is thereby viewed as irrelevant, based on the premise of idealised surfaces. Yet, especially on semi-conducting catalysts both the assumption of PCET and of pristine, defect-free catalyst surfaces are not necessarily fulfilled.

The great success of the CHE approach is in part due to its low computational cost allowing a computational screening of suitable catalyst materials. Any other scheme going beyond PCET and pristine surfaces should therefore match this advantage, ideally avoiding costly numerical sampling of solvent degrees of freedom. Yet, recent developments in thermodynamic modelling as well as embedding techniques, both liquid and solid-state, especially considering the interface between catalyst and solvent, point the way towards photo-electrochemistry modelling beyond the computational hydrogen electrode.