Gerischer
Electrochemistry
Today 2018

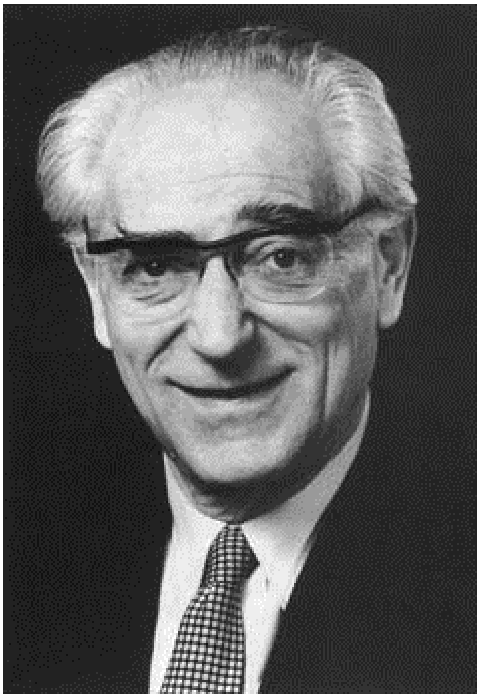
Gerischer Electrochemistry Today 2018 -
A Symposium

August 14-16, 2018

Sustainability, Energy
and Environment Community (SEEC)

University of Colorado

Boulder, CO



This Symposium features the scientific legacy of the research of the late Heinz Gerischer who pioneered the field of photoelectrochemistry, photoelectrochemical solar cells and the related interface science. The scope of the meeting will encompass the fundamental aspects of semiconductor electrochemistry, include combined fuel generating systems and address the surface science at these solid-liquid junctions.

Gerischer also studied a series of photoactive interfaces, providing another emphasis of the Symposium on the development of novel materials and new combinations for various energy conversion. His concept of decomposition potentials directly addresses a main challenge of energy conversion at a reactive interface: stability, which will be a topic of focus as well. Presentations will highlight present advances in surface- and interface science, including *in-situ* and *operando* techniques, which allow us new and deepened insight into semiconductors and catalytic processes, especially through the use of soft and tender x-rays at synchrotron.

Accordingly, the **Gerischer Today** meeting will address **the processes**, **the materials** and **the interfaces** in photoelectrochemical systems and is open to the interested community. The Renewable and Sustainable Energy Institute (RASEI) in Boulder, Colorado will host the Symposium . It is co-organized by the National Renewable Energy Laboratory (NREL) and the Fritz-Haber-Institute of the Max Planck Society (FHI) where Prof. Gerischer was affiliated.

Committee

Co-Chairs:
Joachim Lewerenz
Arthur J. Nozik
Mark T. Spitler

Organizing Committee:
Bruce Parkinson
Neal Armstrong
Laurie Peter
Daniel Esposito
Shane Ardo
Steve Maldonado
Ian Sharp
Gordana Dukovic
Kyoung-Shin Choi
Nathan Neale
Krishnan Rajeshwar
Nathan Lewis
Carl Koval
Katherine Ayers

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GERISCHER ELECTROCHEMISTRY TODAY 2018

August 14-16, 2018

Sustainability, Energy and Environment Community
University of Colorado East Campus
Boulder, Colorado

PROGRAM

<u>Tuesday Morning, August 14</u>

Tutorial Session

Arthur Nozik, Chair

9:00 a.m. A Tutorial on Fundamentals of Semiconductor Photoelectrochemistry
Nathan Lewis*, California Institute of Technology

9:50 a.m. Coffee Break

10:10 a.m. A Historical Walk through Important Problems in Gerischer Electrochemistry
Mark Spitler, Center for Photoconversion and Catalysis, University of Wyoming

11:00 a.m. Materials Developments in Solar Photoconversion
Bruce Parkinson*, University of Wyoming

***asterisk denotes invited speaker**

<u>Tuesday Afternoon, August 14</u>

Session I
New Techniques and Methods

Joachim Lewerenz, Chair

12:45 p.m Welcome – Arthur Nozik, Joachim Lewerenz and Mark Spitler

1:00 p.m. Excited States at Metal-Semiconductor Interfaces: Carrier Transport and Selective Photoelectrocatalysis
Harry A. Atwater*, Joint Center for Artificial Photosynthesis (JCAP)
California Institute of Technology

1:40 p.m. Utility of Semiconductor Ultramicroelectrodes
Stephen Maldonado*, University of Michigan, Ann Arbor

2:10 p.m. Emerging Tools for Imaging Nanoscale Structure-Activity in Electrocatalysis
Patrick R. Unwin*, University of Warwick, Coventry, UK

2:40 p.m. Using APXPS to Probe the Solid/Liquid Interface Under Operando Conditions
Ethan J. Crumlin*, Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley

3:10 p.m. Coffee Break

Mark Spitler, Chair

3:40 p.m. Intricacies of Electrochemical Interfaces from First Principles
Emily A. Carter*, Princeton University, Princeton

4:10 p.m. Energy materials and energy conversion devices explored by x-ray and electron spectroscopies
Marcus Baer*, Helmholtz-Zentrum Berlin für Materialien und Energie (HZB), Berlin, Germany

4:40 p.m. Towards simulations of complex electrochemical interfaces under realistic operating conditions
Brandon C. Wood*, Lawrence Livermore National Laboratory, Livermore

5:10 p.m. In situ Transient Reflectance Probe of Charge Carrier Dynamics at Semiconductor Photoelectrode/Liquid Interface
Tianquan (Tim) Lian*, Emory University, Atlanta

5:40 p.m. Light dinner

Tuesday Evening, August 14

Session II
Charge Transfer at Nanostructured Solids
Nathan Neale, Chair

6:30 p.m. Factors Controlling Band Edge Energetics and Charge Separation Efficiencies in Nanocrystalline Energy Conversion Materials
Nicholas Pavlopoulos, R. Clayton Shallcross, Jeffry Pyun, S. Scott Saavedra, **Neal R. Armstrong***, University of Arizona, Tucson

7:00 p.m. Semiconductor Quantum Dots as Photosensitizers
Prashant Kamat*, Radiation Laboratory, University of Notre Dame

7:30 p.m. Selected Modern Aspects of Photoelectrochemistry Based on Gerischer
Nathan Lewis*. California Institute of Technology, Pasadena

8:00 p.m. Elucidating how photoexcited semiconductor nanocrystals drive redox enzyme catalysis
Gordana Dukovic*, University of Colorado, Boulder

Wednesday Morning, August 15

Session III
Fundamental Advances

Ian Sharp, Chair

8:15 a.m.	Quasi-Fermi Levels, Hot Electrons, and Solar Photon Conversion in PEC cells **A.J. Nozik***, University of Colorado, Boulder
8:45 a.m.	Ultrafast Vibrational Spectroscopy of Heterogeneous Electron Transfer Reactions Baxter Abraham, Hao Fan, Elena Galoppini, and **Lars Gundlach*** Rutgers University-Newark and University of Delaware, Newark
9:15 a.m.	Molecular Host–Guest Complexes on Semiconductor Surfaces **Elena Galoppini**, Rutgers University-Newark
9:40 a.m.	Coupled transport-transformation phenomena in a dye-sensitized solar cell **Frances A. Houle**, Lawrence Berkeley National Laboratory, Berkeley
10:05 a.m.	Coffee Break

Gordana Dukovic, Chair

10:35 a.m	A normal and inverted look at charge transfer at polymer electrodes **Erin Ratcliff**, University of Arizona, Tucson
11:00 a.m	The Standard Chemical Potential for Creation of an Exciton using 2D Spectroscopy Jisu Ryu, Dmitry Baranov, Samuel D. Park, and **David M. Jonas** University of Colorado
11:25 a.m	Single-molecule, single-particle approaches to semiconductor photoelectrochemistry **Justin Sambur**, Colorado State University, Fort Collins
11:50 a.m	Lunch

Wednesday Afternoon, August 15

Session IV
Novel Solids

Nathan Lewis, Chair

1:00 p.m. Kinetic challenges for water oxidation on metal oxide photoelectrodes
James Durrant*, Imperial College, London

1:30 p.m. Building the Perfect Beast: The Role of Solid-State Chemistry in the Solar Fuels Conundrum
Krishnan Rajeshwar*, University of Texas at Arlington

2:00 p.m. Designing the Interface: Synthetic Control of Si(111) Photoelectrochemical Devices via Molecular Modification
Dylan G. Boucher and **Michael J. Rose**, University of Texas at Austin

2:25 p.m. Tuning Semiconductor Photoelectrode Energetics Through Surface Modification
Nathan R. Neale*, National Renewable Energy Laboratory, Golden

2:55 p.m. Electrochemical process to create nanostructured semiconductor bulk p/n homojunctions for solar energy conversion
Shalini Menezes and Anura Samantlike , InterPhases and Universidade de Minho, Braga, Portugal

3:20 p.m. Break

Neal Armstrong, Chair

3:45 p.m. Solar Fuels: The Past, Present and Future Prospects
Bruce Parkinson, University of Wyoming, Laramie

4:15 p.m. Opportunities Beyond Conventional Photoelectrodes: from 2D Transition Metal Chalcogenides to Lead Halide Perovskites
Csaba Janáky, University of Szeged, Hungary

4:40 p.m. Methods for connecting electronic structure and photocarrier loss mechanisms to guide photoabsorber discovery
Ian Sharp*, Walter Schottky Institute, Technical University of Munich, Germany

5:10 p.m. Oxide-Based Photoelectrodes for Use in Solar Water Splitting
Kyoung-Shin Choi*, University of Wisconsin-Madison, Madison

Wednesday Evening, August 15

5:45 p.m. **CONFERENCE BARBEQUE**

7:15 p.m. -9:00 p.m. **POSTER SESSION**

Thursday Morning, August 16

Session V
Advances in Photocatalysis
Kyoung-Shin Choi, Chair

8:15 a.m. Designing Materials for Optoelectronic Properties
William Tumas*, K. Persson, G. Ceder, M. Toney, D. Nocera, J. Tate, B. Gorman, V. Stevanovic, S. Lany, A. Zakutayev, and D. Ginley, National Renewable Energy Laboratory, Golden

8:45 a.m. Bridging Molecular and Heterogeneous Electrocatalysis Through Graphite Conjugation
Jackson, M. N.; Oh, S.; Kaminsky, C. J.; Chu, S. B.; **Surendranath, Y**.*
Massachusetts Institute of Technology

9:15 a.m. Cu_2O Assisted Facet-Dependent Photocatalysis for CO_2 Reduction
Yimin A. Wu, Ian McNulty, Kah Chun Lau, Larry A. Curtiss, Yuzi Liu**, Tijana Rajh**, Argonne National Laboratory

9:40 a.m. **Report from the Workshop Panel on the Photoelectrochemical Solar Production of Fuels**

Representative Panel Members

10:10 a.m. Coffee Break

Bruce Parkinson, Chair

10:30 a.m. Scrutinizing epitaxially prepared tandem device structures for efficient solar water splitting
T. Hannappel*, O. Supplie, M.M. May, H.-J. Lewerenz, W.-H. Cheng, M.H. Richter, H.A. Atwater, F. Dimroth, J. Ohlmann, Technical University Ilmenau, Helmholtz-Zentrum Berlin, Cambridge University, California Institute of Technology, and JCAP

11:00 a.m. Modelling, experimentation and scaling of photo-electrochemical fuel processing devices
Sophia Haussener, EPFL, Lausanne, Switzerland

11:25 a.m. Advancing Semiconductor-Electrocatalyst Systems: Application of Shadow Nanosphere Lithography for Efficient Solar Hydrogen Production
Katharina Brinkert, Matthias H. Richter, Ömer Akay, Michael Giersig, Katherine T. Fountaine, and Hans-Joachim Lewerenz, California Institute of Technology

11:50 a.m. Interrogating Photochemical and Photo-Iono-Chemical Charge-Transfer Processes in the Absence of Space-Charge Regions
Shane Ardo*, University of California, Irvine

12:20 p.m. Closing

Abstracts

of Oral Presentations

Session I

New Techniques and Methods

Excited States at Metal-Semiconductor Interfaces: Carrier Transport and Selective Photoelectrocatalysis

Harry A. Atwater
Joint Center for Artificial Photosynthesis (JCAP)
California Institute of Technology, Pasadena, CA

Harvesting non-equilibrium carriers at semiconductor-metal interfaces offers an opportunity to modify the rates and pathways for photochemical reactions at the nanoscale. The carrier generation, transport and interface dynamics can be addressed with a combination of first-principles theory for carrier excitation and relaxation, observation of carrier dynamics via hot-carrier photocurrent spectroscopy, ultrafast transient absorption spectroscopy, and photoelectrochemical measurements that assess current transport, product yield and selectivity. We use as an example the gold/n-type gallium nitride interface and compare results of theory to excited carrier transport measurements.

We also report the first known example of photoexcited hot hole injection at a metal-p-type wide bandgap semiconductor interface. Despite the presence of an interfacial Schottky barrier to hot-hole injection of more than 1 eV across the Au/p-GaN heterojunction, plasmonic Au/p-GaN photocathodes exhibit photoelectrochemical properties consistent with the injection of hot holes from Au nanoparticles into p-GaN upon plasmon excitation. The incident photon-electron conversion efficiency spectrum for the plasmonic photocathodes faithfully follows the surface plasmon resonance absorption spectrum of the Au nanoparticles, and a sustained photovoltage during plasmon excitation of plasmon-induced hot-hole capture and conversion, using a gold/p-type gallium nitride (Au/p-GaN) interface conditions tailored for studying photoelectrochemical CO_2 reduction.

Whereas the Au/p-GaN structure has an interfacial Schottky barrier to hot-hole injection of more than 1 eV, the Au/p-NiO has an approximately zero Schottky barrier height.. Taken together, our results offer experimental validation of photoexcited hot holes in high-barrier Au/p-GaN structures and also in low-barrier structures, such as Au/NiO.

These results, together with other recent advances, form an outlook for the use of photoexcited carriers as a tool for altering selectivity in photon-driven catalytic processes.

Utility of Semiconductor Ultramicroelectrodes

Stephen Maldonado
University of Michigan, Ann Arbor, MI

This presentation describes the preparation, characterization, and utility of semiconductor ultramicroelectrodes for the study of heterogeneous charge transfer reactions at semiconductor/electrolyte interfaces. Historical contexts will be provided regarding past precedents and opportunities for using electrodes with the capacity to measure high current densities. Ongoing efforts to push the smallest attainable length scales will be discussed and how they can enable fuller tests of existing charge transfer models.

Emerging Tools for Imaging Nanoscale Structure-Activity in Electrocatalysis

Patrick R. Unwin
University of Warwick, Coventry, UK

Electrochemical interfaces used for (photo)electrocatalysis and energy technologies are usually nanostructured to expose particular surface sites, but determining the intrinsic activity of these sites is often beyond current experimental capability. In our group, we have been developing electrochemical imaging probe techniques that can be deployed for direct electrochemical and topographical imaging of (photo)electrocatalytic materials at the nanoscale. Spatially-resolved topographical and electrochemical data are collected synchronously to create topographical images in which step-height features as small as 2 nm are easily resolved and potential-resolved electrochemical activity movies comprised of hundreds of images are obtained in a matter of minutes. Further, we expand these approaches such that highly resolved electrochemical data can be combined with information from other microscopy approaches in a correlative multi-microscopy strategy (1,2). We make use of nanopipettes (with dimensions down to a few 10s nm) as mobile electrode probes and electrochemical cells that can be moved quickly and intelligently near to surfaces to gather multiple electrochemical flux signals. The large data sets obtained can be presented as images, movies and pixel-resolved electrochemical plots (e.g. voltammograms, Tafel plots, choronamperograms)(3), and all can be analyzed and interpreted quantitatively using finite element method modelling. A further advantage is that nanopipette probes can be made in a matter of minutes, are easily characterized and low cost (disposable).

We shall describe the principles and applications of new electrochemical probe methods for mapping interfacial charge (4) and ion fluxes (5). These techniques have been used extensively to reveal the active sites on nanostructured electrode materials, and for patterning and printing in 2D and 3D at the nanoscale (6). We shall also highlight future trends in nanoscale electrochemical imaging, including multifunctional-multichannel probes and prospects for other types of electrochemical probe microscopes.

Dozens of talented PhD students, postdocs and colleagues have made outstanding contributions to our work on nanoscale electrochemical imaging and I am grateful to all of them.

References

1. Kang, M.; Momotenko, D.; Page, A.; Perry, D.; Unwin, P. R., Langmuir, 2016, 32, 7993-8008.
2. Bentley, C. L.; Kang, M.; Unwin, P. R., Curr. Opin. Electrochem. 2017, 6, 23-30.
3. Bentley, C. L.; Kang, M.; Unwin, P. R., J. Am. Chem. Soc. 2017, 139, 16813-16821.
4. Perry, D.; Paulose Nadappuram, B.; Momotenko, D.; Voyias, P. D.; Page, A.; Tripathi, G.; Frenguelli, B. G.; Unwin, P. R, J. Am. Chem. Soc., 2016, 138, 3152 -3160.
5. Kang, M.; Perry, D.; Bentley, C. L.; West, G.; Page, A.; Unwin, P. R., ACS Nano, 2017, 11, 9525-9535
6. Momotenko, D.; Page, A.; Adobes-Vidal, M.; Unwin, P. R., ACS Nano, 2016, 10, 8871-8878.

Using APXPS to Probe the Solid/Liquid Interface Under Operando Conditions

Ethan J. Crumlin
Advanced Light Source
Lawrence Berkeley National Laboratory, Berkeley, CA

Interfaces play an essential role in nearly all aspects of life and are critical for electrochemistry. Electrochemical systems ranging from high-temperature solid oxide fuel cells (SOFC) to batteries to capacitors have a wide range of important interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and/or converted. This talk will focus on our use of ambient pressure XPS (APXPS) to directly probe the solid/gas and solid/liquid electrochemical interface. APXPS is a photon-in/electron-out process that can provide both atomic concentration and chemical-specific information at pressures greater than 20 Torr. Using synchrotron X-rays at Lawrence Berkeley Nation Laboratory, the Advanced Light Source has several beamlines dedicated to APXPS endstations that are outfitted with various in situ/operando features such as heating to temperatures > 500 °C, pressures greater then 20 Torr to support solid/liquid experiments and electrical leads to support applying electrical potentials supports the ability to collect XPS data of actual electrochemical devices while its operating in near ambient pressures. This talk will introduce APXPS and provide several solid/liquid interface electrochemistry examples using operando APXPS including the probing of a Pt metal electrode undergoing water-splitting reaction to generate oxygen, semiconductor/liquid junction to directly observe band bending, and the ability to probe the electrochemical double layer (EDL). Gaining new insight to guide the design and control of future electrochemical interfaces.

Intricacies of Electrochemical Interfaces from First Principles

Emily A. Carter
Princeton University, Princeton, NJ

Electrochemically based water splitting to produce sustainable hydrogen remains impractical because of the dearth of inexpensive electrocatalysts that can efficiently carry out the more difficult half-reaction of water oxidation. Even more difficult is carbon dioxide reduction to useful products. This lecture will discuss structural and mechanistic characterization of (photo-)electrocatalysis at complex semiconductor electrodes, as derived from quantum mechanics calculations. High fidelity modeling of the water-semiconductor interface is crucial. Recent work identifying the most probable active crystal facets and key surface species involved in water oxidation at a Fe-doped NiOOH electrode, along with our latest findings related to photoelectroreduction of carbon dioxide at functionalized compound semiconductor electrodes, will be presented.

Energy Materials and Energy Conversion Devices Explored by X-ray and Electron Spectroscopies

Marcus Baer
Helmholtz-Zentrum Berlin für Materialien und Energie (HZB)
Berlin, Germany

The complexity of energy conversion devices, which are often comprised of a multitude of layers, interfaces, surfaces, elements, impurities, etc., make it both difficult and crucial to characterize and understand the chemical and electronic structure of each component and their interactions. It is demonstrated that the combination of different (soft and hard) x-ray and electron spectroscopies is an extraordinary method for illuminating the chemical and electronic material characteristics from many different perspectives, ultimately resulting in a comprehensive picture of these properties.

This presentation will first focus on our recent progress in the characterization of thin-film solar cell layer stacks. In detail, our results on the impact of different alkali fluoride post-deposition treatments (PDT) on the chemical and electronic surface structure of high-efficiency $Cu(In,Ga)Se_2$ (CIGSe) thin-film solar cell absorbers will be presented. The observed electronic structure changes are in agreement with the revealed chemical surface properties and can be linked to the recent breakthroughs in CIGSe device efficiencies.

The second part of the presentation will focus on the newly setup Energy Materials In-Situ Laboratory Berlin (EMIL) and its analytical and deposition capabilities. EMIL is a new multi-user large-scale research platform located at HZB's synchrotron radiation source BESSY II having access to x-rays ranging from 80 eV up to 10 keV. In order to bridge the pressure gap between UHV-based analytics and operational conditions, in particular in view of dye-sensitized solar cells, (photo)electrochemical water splitting, electrochemical energy storage, etc., a route to true operando studies under atmospheric conditions will also be presented.

Towards Simulations of Complex Electrochemical Interfaces under Realistic Operating Conditions

Brandon C. Wood
Lawrence Livermore National Laboratory, Livermore, CA

Interfaces between electrodes and electrolytes are crucial to the functioning of electrochemical energy storage and conversion devices, including photoelectrochemical cells for solar water splitting. Under operating conditions, these interfaces are often highly complex, introducing new chemical species and charge-induced interface polarization effects that can be difficult to unravel. I will discuss how first-principles methods can be applied to directly simulate electrochemical interfaces with minimal reliance on a priori assumptions, offering insights into device operation that can be used to engineer better materials. I will show examples of how such simulations have uncovered structure-property relationships and new interfacial mechanisms, highlighting instances where behaviors are dramatically altered by seemingly subtle changes in the interfacial structure and dynamics. Finally, I will review our recent efforts coupling ab initio molecular dynamics with in situ X-ray spectroscopy to better understand the complex interplay between chemical and electronic properties of semiconductor-water interfaces.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

In situ Transient Reflectance Probe of Charge Carrier Dynamics at Semiconductor Photoelectrode/Liquid Interface

Tianquan (Tim) Lian
Emory University, Atlanta, GA

Photoelectrochemical cells are a promising approach for converting solar energy to storable chemical energy in chemical fuels. The efficiency of these devices depends critically on efficient transfer of charge carrier across the electrode liquid interface to drive chemical transformation. Although transient absorption spectroscopy is a powerful tool for probing interfacial dynamics in high surface area electrodes, it is often not applicable on planar electrodes because the observed signal is often dominated by carrier dynamics in the bulk. In this paper, we report a study of carrier dynamics in planar photoelectrodes using transient reflection spectroscopy. Compared to transient absorption, this method is more sensitive to surface carrier density that can be more directly correlated to catalysis. We showed that transient reflectance change can be used to follow charge carrier dynamics and their amplitude can be directly correlated to IPCE for water reduction on GaP single crystals protected by TiO_2 ALD layer. Our finding suggests that IPCE is determined by the efficiency of initial ultrafast (< hundreds of ps) charge separation across the GaP/TiO_2 interface despite the much slower water reduction reaction. It is also observed that screening of the interfacial electrical field by high charge carrier density is a key loss mechanism in these devices.

Session II

Charge Transfer at Nanostructured Solids

Factors Controlling Band Edge Energetics and Charge Separation Efficiencies in Nanocrystalline Energy Conversion Materials

Nicholas Pavlopoulos, R. Clayton Shallcross, Jeffry Pyun, S. Scott Saavedra, Neal R. Armstrong
University of Arizona, Tucson, AZ

Heterostructured II-VI semiconductor nanocrystalline materials continue to be attractive platforms for study of those compositional, structural and energetic factors that control efficiencies of photo-induced charge separation and redox pathways that may lead to energy storage fuels like hydrogen. Regardless of length scale, the nanomaterial construct must be asymmetric, provide for vectoral separation and efficient flow of charge, and create band-edge energies at the reaction sites that maximize rates of the redox reactions, i.e. maximize the excess free energies which drive these electron transfer reactions. This talk will review our work on "tethered" CdSe and related quantum dots (QDs), and newer asymmetric CdSe@CdS nanorods (NRs) and unique CdSe@CdS tetrapods (TPs) where we increasingly demonstrate control over band edge energetics (e.g Type I versus quasi-Type II heterojunctions), and new approaches to characterization of defect states that steal energy efficiency through recombination, and their mitigation by surface passivation. Determination of band edge energies that are relevant to photoelectrochemical processes is extremely challenging, and we will discuss spectroelectrochemical, photoemission and transient absorbance approaches which provide complementary perspectives on these band edge energies.

Semiconductor Quantum Dots as Photosensitizers

Prashant Kamat
Radiation Laboratory
University Of Notre Dame, Notre Dame IN

Semiconductor nanoparticles are excellent building blocks for designing light harvesting assemblies. The first report on the size effect of photosensitization was published by Gerischer and Luebke.1 This seminal paper had a significant impact on the progress of quantum dot solar cells research in the following years.2 Of particular interest are the metal chalcogenide (CdS, CdSe) and metal halide perovskite (CsPBX3) quantum dots (QDs) which are very effective as photosensitizers. The ability to tune the optical and electronic properties by changing the size and composition remains an attractive feature of these semiconductor materials. We have now employed these semiconductor nanostructures to study electron transfer in mesoscopic TiO_2 films. The electron transfer from excited QDs to TiO_2 is an ultrafast process occurring with a rate constant of ~10^11 s-1. On the other hand the hole transfer to a redox couple or a hole transport material such as CuSCN is two to three orders of magnitude slower and remains a major limiting factor in dictating the overall efficiency in quantum dot solar cells. Photoelectrochemical and transient absorption studies that provide mechanistic and kinetic details of electron and hole transfer at the semiconductor interface will be discussed. Various interfacial charge transfer processes that limit the power conversion efficiency of these QDSC and strategies to overcome these limitations will be presented.

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1. Gerischer, H.; Luebke, M. A Particle Size Effect in the Sensitization of TiO2 Electrodes by a CdS Deposit. J. Electroanal. Chem. 1986, 204, 225-227.

2. Kamat, P. V. Quantum Dot Solar Cells. The Next Big Thing in Photovoltaics. J. Phys. Chem. Lett. 2013, 4, 908–918.

Selected Modern Aspects of Photoelectrochemistry Based on Gerischer

Nathan Lewis
California Institute of Technology, Pasadena, CA

This presentation will discuss recent work in our laboratories that elucidates some of the basic principles of photoelectrochemistry as developed and espoused by Gerischer. Specific recent work to be discussed will include use of scanning probe electrochemical methods on 2-D semiconductors and semimetals to understand interfacial charge-transfer rate constants within a Marcus-Gerischer framework; and measurements of photocorrosion of semiconductor photocathodes, including III-V materials, within the quasi-Fermi level framework developed by Gerischer.

Elucidating How Photoexcited Semiconductor Nanocrystals Drive Redox Enzyme Catalysis

Gordana Dukovic
University of Colorado, Boulder, CO 80309

This presentation will focus on the coupling of semiconductor nanocrystals as light absorbers with redox enzymes for multi-electron transfer reactions to drive solar photochemistry. Reactions of interest include hydrogen generation, carbon dioxide reduction, and nitrogen fixation. We have demonstrated that nanocrystal excited state behavior, charge transfer dynamics, and surface chemistry play a critical role in the overall photochemistry of nanocrystal-catalyst complexes. This presentation will describe our most recent findings on how the reactions of interest can be driven and controlled through manipulation of nanocrystal excited state dynamics. Emphasis will be placed on recent results on photochemical nitrogen fixation and carbon dioxide reduction.

Session III

Fundamental Advances

Quasi-Fermi Levels, Hot Electrons, and Solar Photon Conversion in PEC cells

A.J. Nozik
University of Colorado, Boulder, CO 80309

In the Gerischer model of the semiconductor-electrolyte junction under illumination, the distribution of electrons and holes within the space charge of the semiconductor is described by two separate Fermi levels, one for the electron population and the other for the hole population. These two Fermi levels are termed quasi-Fermi levels (QFLs) and the photovoltage developed in the junction is set equal to the separation between these two quasi-Fermi levels. The two quasi-Fermi levels merge into a single Fermi level deeper into the semiconductor beyond the space charge layer that is equal to the single Fermi level of the isolated semiconductor in the dark. For photo- electrosynthetic cells, the model also specifies that the splitting of the QFLs must be equal to the ΔG + overvoltage of the total cell redox reaction for a PEC cell with a single photoelectrode. For a two-photoelectrode cell the redox potential of the QFL for holes in the photoanode must be equal to the anodic half-reaction redox potential plus the anodic overvoltage and the redox potential of the QFL for electrons in the photocathode must be equal to the cathodic half-reaction redox potential plus the cathodic overvoltage. The validity of this aspect of the Gerischer model will be discussed when ultrafast charge transfer by ballistic electrons, and more generally hot carriers, occurs in PEC cells. Recent progress reported in 2018 regarding hot carrier effects in solar cells will also be discussed; this includes hot carrier extraction and multiple exciton generation in quantum dots.

Ultrafast Vibrational Spectroscopy of Heterogeneous Electron Transfer Reactions

Baxter Abraham, Hao Fan, Elena Galoppini, and Lars Gundlach*
Rutgers University and University of Delaware, Newark, DE

Interfacial electron transfer reactions constitute key physical phenomena central to a variety of energy related transport and conversion processes such as catalysis, photocatalysis, photovoltaics, energy storage, molecular electronics, etc. Heterogeneous material systems like organic/inorganic interfaces are of particular interest because they provide great potential to tailor properties according to application specific requirements. Electron transfer dynamics has been studied intensively in heterogeneous systems. The significance of electronic-vibrational coupling for heterogeneous electron transfer will be explored here.

The ultrafast nature of the process, the rapid intramolecular vibrational energy redistribution, and vibrational cooling complicates the study of vibronic coupling in HET. We present the application of a time domain vibrational spectroscopy - pump-degenerate four-wave mixing (pump-DFWM) - to dye-sensitized solid-state semiconductor films. Pump-DFWM can measure Raman-active vibrational modes that are triggered by excitation of the sample with an actinic pump pulse. The application of pump-DFWM to an anatase TiO_2 film sensitized by a Zn-porphyrin dye are discussed. We show an effective combination of experimental techniques to overcome typical challenges in measuring solid-state samples with laser spectroscopy and observe molecular vibrations following HET in a picosecond time window. The cation spectrum of the dye shows modes that can be assigned to the linker group and a mode that is localized on the Zn-phorphyrin chromophore and that is connected to photoexcitation.

Molecular Host–Guest Complexes on Semiconductor Surfaces

Elena Galoppini
Rutgers University-Newark, Newark NJ

A promising development in the field of nanostructured semiconductor sensitization is the use of molecular containers (cyclodextrins, cucurbiturils, Cram-type hosts) to bind encapsulated chromophores to the surface of wide bandgap metal oxide semiconductors. The host provides a binding method that is alternative to the covalent attachment through a linker-anchor group. Also, the molecular host shields the guest from the heterogeneous interface. The novel hybrid systems exhibited photophysical and electrochemical properties that differ from the properties of layers obtained by directly attaching the chromophore to the semiconductor through binding groups, including slower and homogeneous interfacial electron recombination dynamics, and diminished photodegradation.

Coupled Transport-Transformation Phenomena in a Dye-Sensitized Solar Cell

Frances A. Houle
Lawrence Berkeley National Laboratory, Berkeley, CA

Solar-driven generation of electricity in nanostructured systems such as dye-sensitized solar cells (DSSC) involves multiscale, multiphase couplings of excitation, charge flow and chemical reactions. These couplings, together with the properties of the components used, govern their efficiency. Numerous in-depth investigations have been invaluable for elucidating key physics and chemistry phenomena in dye-sensitized systems, and have inspired new materials concepts. What they have not yet done is explain at a molecular level how the dye, nanoparticles, electrolyte and reduction at the companion cathode work together to produce observed photocurrents and reaction products. Such knowledge would help identify system components that most strongly influence efficiency, and help develop a deeper understanding of how the kinetics connect across length and time scales in these systems. In this talk, I will describe a reaction-diffusion modeling framework that integrates the chemistry and physics of a DSSC from nano to micro/macro scale in space and time. Using literature data for cell geometry, reactant concentrations and rate constants, the stochastic simulations examine the time-resolved response of a TiO_2-dye-I-/I3- redox system to a range of light intensities and pore densities. Interfacial processes are captured with nanoscale resolution, while the electrolyte bulk is at micron scale. In addition to predicting current, the simulations reveal the corresponding spatial distributions of excitations, electrons, holes and electrolyte components inside the cell, enabling direct identification of how all these characteristics are associated with cell performance. The role of electrolyte chemistry throughout the system in controlling efficiency will be discussed.

A Normal and Inverted Look at Charge Transfer at Polymer Electrodes

Erin Ratcliff
University of Arizona, Tucson, AZ

Light-driven electrochemical reactions at photoelectrode surfaces continue to suffer from sluggish half reactions. One major challenge with inorganic semiconductors is predicting and controlling interfacial mid-gap states that undergo band bending when interfaced with the electrolyte. Alternatively, conductive polymer electrodes have offer the possibility to control both opto-electronic and redox properties through synthesis and processing, although the structure-property relationships in electrochemical systems are still few in number relative to the synthetic knowledge found in solid-state organic electronics. Importantly, these semiconductors demonstrate a hybrid electronic-ionic conduction mechanism, and thus, have unique electrochemical behaviors relative to classical inorganic semiconductor electrodes.

This talk will provide new insights into the mechanism of charge transfer at conductive polymer/redox probe interfaces. A mathematical framework will be demonstrated using a modified Marcus-Gerischer model that enables prediction of rate constants from simple film properties. Specifically, charge transfer is directly defined by the energetic overlap in the density of states (DOS) distributions in the polymer and electrolyte. Both normal and inverted regimes for rates of charge transfer can be observed as a function of potential. The inverted regime arises directly from the Gaussian distributions of electronic states characteristic of polymeric semiconductors and is not observed for inorganic semiconductor electrodes. Demonstration of the inverted regime offers a new paradigm towards controlling multi-redox couple or multi-electron transfer mechanism critical to photo-electrochemical processes.

Ref: Nature Communications 8, Article number: 1048 (2017) doi:10.1038/s41467-017-01264-2

The Standard Chemical Potential for Creation of an Exciton using 2D Spectroscopy

Jisu Ryu, Dmitry Baranov, Samuel D. Park, and David M. Jonas
University of Colorado, Boulder, CO

Generalized Einstein relations between absorption and emission allow the determination of the standard chemical potential for creation of excited electronic states under two conditions: one, the excited states must be fully equilibrated with respect to each other; two, the ensemble studied must be homogeneous. We have used 2D spectroscopy to remove inhomogeneity for an ensemble of colloidal PbS quantum dots in order to determine the standard chemical potential for creation of a 1S-1S exciton with an accuracy better than 10 meV. The standard chemical potential is important for transport measurements on quantum dot arrays, is simply related to the difference between conduction and valence band Fermi levels, and plays a role in determining the Shockley-Queisser limit for a given photovoltaic cell. The 2D method we have developed may be promising for characterizing photovoltaic quantities that have been considered "not easy to characterize" (see P. Wurfel and U Wurfel, "Physics of Solar Cells" Wiley, 2013).

Single-Molecule, Single-Particle Approaches to Semiconductor Photoelectrochemistry

Justin Sambur
Colorado State University, Fort Collins, CO

Nanostructured semiconducting materials typically exhibit lower photoelectrochemical energy conversion efficiencies than high quality single crystal materials. The poor performance stems from charge carrier recombination at material interfaces. For photoelectrochemical water splitting and photovoltaic systems, surface recombination can occur between charge carriers and photo generated surface intermediates. Here we discuss two recent studies on the role of photogenerated surface intermediates on the energy conversion properties of nanostructured materials. First, we discuss recent single-molecule reaction imaging results of model TiO_2 photoanodes, where we tracked the surface reaction intermediates and the photocurrent response when the TiO_2 nanorods transitioned from a dark equilibrium state to a light equilibrium state and back. Second, we discuss the role of surface structural motifs and photogenerated iodine on the energy conversion properties of $MoSe_2$ nanoflake electrodes in liquid junction photovoltaic cells.

Session IV

Novel Solids

Kinetic challenges for water oxidation on metal oxide photoelectrodes

James Durrant
Imperial College, London

There is increasing interest in the development of artificial photosynthetic systems for solar driven fuel synthesis. My talk will focus upon the role of charge carrier dynamics in determining the efficiency of such systems, including both photoelectrodes for water oxidation and reduction and hybrid molecular / inorganic systems for solar driven proton and CO_2 reduction. I will particularly focus on kinetics and catalysis of one of key reactions in artificial photosynthetic systems: water oxidation by four ‘holes’ or ‘oxidising equivalents’ to yield molecular oxygen. I will start by considering the relative timescales of the lifetimes of photogenerated charge carriers in typical photoelectrodes versus the timescales of water oxidation / reduction, and strategies to address this kinetic challenge. I will then go on to consider in more detail the kinetics of water oxidation on a range of relevant metal oxides, and how these kinetics depend upon electrical bias, charge density, temperature, light intensity and pH. Experimentally, these studies will be based around transient absorption spectroscopies on timescales from femtoseconds to seconds, conducted where appropriate under in operando conditions during (photo)electrochemical water oxidation.

Building the Perfect Beast: The Role of Solid-State Chemistry in the Solar Fuels Conundrum

Krishnan Rajeshwar
University of Texas at Arlington, Arlington, TX

Solid-state chemistry languished as an esoteric discipline till interest exploded on the so-called high-Tc 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. This perspective talk will examine how solid-state chemistry principles have contributed both to the design and synthesis of photoelectrode materials for PEC applications related to water splitting, CO_2 reduction, and environmental remediation. The design of new-generation oxide semiconductors with the correct optoelectronic and bulk/interfacial chemistry characteristics needed to efficiently drive the above reactions will be addressed. The list of material pre-requisites for efficient solar fuels generation or photocatalytic applications is daunting and it is hardly surprising that a “magic bullet” material has not emerged even after 4 decades of R&D effort. Synthetic challenges and solutions will be reviewed using recent examples of work in my laboratory and elsewhere.

Designing the Interface: Synthetic Control of Si(111) Photoelectrochemical Devices via Molecular Modification

Dylan G. Boucher and Michael J. Rose
University of Texas at Austin, Austin, TX

Silicon's small bandgap (1.1 eV) and large photocurrent density (~25 mA/cm^2 under 100 mW/cm^2 illumination) make it a nearly ideal photocathode material for photoelectrochemical hydrogen evolution (PEC-HER). However, silicon is prone to formation of an electrically insulating silicon oxide layer which limits device efficacy. Efforts towards stabilization of the Si(111) surface by alkylation have resulted in well-passivated, stable surfaces. However, the resulting interfacial dipole of the alkylated surface shifts the onset of HER to negative efficiencies, even on Pt decorated surfaces. To this end, our group has explored low-temperature, solution-based processing methods to significantly alter the interfacial properties of Si(111). Chemically derivatized surfaces (R: phenyl, para-nitrobephenyl, 9-anthracene, and 9-nitroanthracene) have been achieved using organolithium precursors. Mott-Schottky analysis revealed electrochemical potential shifts in the band-edge positions of the surfaces that were one to one with potential shifts in PEC-HER onset in pSi-R|TiO$_2$|Pt devices, indicating quantitative control of the photovoltage through molecular design. In addition, we found that the molecular identity of the modifier played a significant role in determining rates of surface recombination; we explore this relationship with two model systems: para-nitrophenyl (low surface recombination) and meta-dinitrophenyl (high surface recombination) and develop design principles for retaining high-quality surfaces with low rates of recombination. Finally, we extended these insights to a new class of fluorine containing molecular modifiers with a slim steric profile capable of achieving high surface coverages (~100% of atop Si sites occupied) whilst retaining high surface quality.

Tuning Semiconductor Photoelectrode Energetics Through Surface Modification

Nathan R. Neale
National Renewable Energy Laboratory, Golden, CO

Efficient water splitting using light as the only energy input requires stable semiconductor electrodes with favorable energetics for the water-oxidation and proton-reduction reactions.

In this presentation, we will discuss two strategies for tuning electrode energetics using covalent attachment of molecular dipoles to semiconductor surfaces. In the first approach, molecular dipoles based on fluorinated, aromatic molecules to p-GaAs(100) surfaces can be employed to tune the photocurrent onset potentials of p-GaAs(100) photocathodes and reduce the external energy required for hydrogen production. Results indicate that initial photocurrent onset potentials can be shifted by nearly 150 mV in pH –0.5 electrolyte under 1 sun illumination resulting from the covalently bound surface dipoles. In the second approach, we will discuss the effects of atomic layer deposition (ALD) coatings on top of molecular alkoxy-modified p-Si photoelectrodes. In this way, the ALD layer can serve to protect the underlying covalent molecular attachment.

We will additionally present a new impedance technique to quantify energetic shifts on dynamic photoelectrode surfaces. This technique, termed intensity-modulated high-frequency resistivity (IMHFR) spectroscopy, reveals the ultimate energy achievable by p-Si photocathodes for water splitting coated with a variety of ALD oxide and nanoparticle Pt catalyst layers. We use this IMHFR technique to show that purportedly “innocent” protective layers and catalysts instead transform the photocathodes into fundamentally new electrodes that have unique thermodynamics and kinetics responsible for performance in PEC water splitting and related electrochemical systems.

Electrochemical Process to Create Nanostructured Semiconductor Bulk p/n Homojunctions for Solar Energy Conversion

Shalini Menezes and Anura Samantlike
InterPhases Solar, Moorpark, and Universidade de Minho, Braga, Portugal

The semiconductor electrochemistry concepts, originated by Heinz Gerischer have evolved in diverse directions, ranging from solar fuels to nanostructured devices. The latter group includes bulk heterojunction (BHJ) devices; the BHJ configuration can circumvent cost, complexity, flexibility and scale-up challenges of conventional planar pn junctions. BHJ structures are currently produced by physically mixing organic polymers and/or inorganic colloidal particles. This approach invariably creates interface mismatch and low doping issues. We introduce a radically different, thermodynamically-driven single-step electrodeposition approach; it naturally creates self-stabilized bulk homojunctions, exemplified here by two copper-indium-selenide (CISe) compounds. The resulting film comprises an interconnected 3-D network of highly-ordered, sharp, abrupt truly-nanoscale pn BHJs; they exhibit unusual electro-optical properties, long lifetime and quantum confinement effects. Unlike colloidal nanocrystals the CISe nanocrystals are highly doped. Their ordered nanoscale morphology facilitates interpenetration for fast, efficient carrier separation and transport; minimizes recombination losses; and essentially performs the same functions as the high-end, crystalline planar pn junctions. This totality manifests as a significant advance in electrochemical processing of semiconductors; it discloses a generally accessible, very low-cost platform method to create high quality nanocrystalline pn BHJ absorbers with various chalcogenides. These inorganic BHJs can be directly used in devices. With addition of finely band-aligned contact electrodes, these BHJs can transition into high performance devices for solar energy harvesting or photoelectrodes for fuel generation. Furthermore, they can be roll-to-roll processed in simple flexible thin-film form factor for easy scale-up.

Methods for Connecting Electronic Structure and Photocarrier Loss Mechanisms to Guide Photoabsorber Discovery

Ian Sharp
Walter Schottky Institute, Technical University of Munich
Garching, Germany

One of the central challenges in the development of solar fuels generators is the lack of semiconductors that are efficient at converting solar photons into extractable charge and that are also chemically stable in active photoelectrochemical environments. In recent years, intensive research has yielded a remarkable array of new solid state light absorbers with moderate bandgaps and reasonably stable interfaces. However, nearly all of these materials exhibit energy conversion efficiencies that are far below their thermodynamic limits. Since the majority of these compounds comprise transition metal oxides that exhibit negligible room temperature photoluminescence, optical pump-optical probe transient absorption spectroscopy is often used to characterize photocarrier trapping and recombination processes. Here, we revisit fundamental aspects of this method for analysis of thin film transition metal oxides, present new interpretations for dominant spectral features, and discuss limitations associated with connecting ultrafast pump-probe transients to photoelectrochemcial performance characteristics. We then introduce a complimentary new method for combining optical modelling with external quantum efficiency measurements to determine the spatial collection profile in active photoelectrodes. This method allows operando determination of charge extraction lengths, quantification of bulk and surface losses, and analysis of the impacts of different optical transition types on overall photoconversion processes. Insights gained from these complimentary methods, as well as synchrotron X-ray absorption and emission spectroscopies, provides guidance on material properties and electronic structures of metal oxides that should be targeted, as well as those that should be avoided, in future discovery efforts.

Solar Fuels: The Past, Present and Future Prospects

Bruce Parkinson
University of Wyoming, Laramie, WY

The interest in the direct storage of solar energy as a chemical fuel in a semiconductor based photoelectrochemical system started with the demonstration of solar photoelectrolysis of water with large band gap oxide semiconductor electrodes in the late 1970s. In the last decade or so there has been both and increased interest and increased funding towards achieving a goal of efficiently producing cost effective fuels from solar energy with either water or carbon dioxide as a feedstock. This talk will review the progress towards this goal considering recent developments. One of these developments is that the cost of photovoltaic systems has been decreasing rapidly to where currently the cost of the solar panels is now exceeded by balance of systems cost. The cost of electrolyzers will be also decrease as they are improved and scaled. Connecting these two existing technologies has the advantage of producing hydrogen where and when it is needed and at pressure. These facts mean that the window for direct solar photoelectrolysis is rapidly closing. One possible breakthrough is that a new stable, efficient, inexpensive, defect-tolerant and scalable new materials are identified that can quickly improve the efficiency of photoelectrolysis much like the hybrid perovskites are have done for photovoltaic devices. This talk will review the progress in combinatorial approaches to discover new materials for photoelectrolysis with some examples including one from the Solar Hydrogen activity Research Kit (SHArK) Project, a distributed science project that provides undergraduates and high school students with the resources to produce and screen metal oxide semiconductors for photoelectrolysis activity. In addition the reasons for producing hydrogen from water rather than direct carbon dioxide reduction to produce fuels will be reviewed. A new system for storing solar energy directly as redox equivalents, a solar chargeable redox flow battery, will also be introduced and its advantages and disadvantages compared to solar hydrogen generation will be discussed.

Opportunities Beyond Conventional Photoelectrodes: from 2D Transition Metal Chalcogenides to Lead Halide Perovskites

Csaba Janáky
University of Szeged, Szeged, Hungary

The unique optoelectronic properties of lead halide perovskites as well as 2D transition metal dichalcogenides have triggered a new wave of excitement in materials chemistry during the past five years. Electrochemistry, spectroelectrochemistry, and photoelectrochemistry are viable tools both for analyzing the optoelectronic features of these materials as well as to utilize them in energy oriented application schemes. I will present two case studies using newly developed methodologies, which help to better understand the mechanistic details of the photoelectrochemical processes at the nanoscale.
First, I will demonstrate how we have succeeded in probing the influence of electrochemical bias on the charge carrier recombination process in CsPbBr3 and MAPbI3 films deposited on a mesoscopic TiO_2 film. The transient absorption spectroscopy experiments conducted at different applied potentials indicated a decrease in the charge carrier lifetimes as we increase the potential.

Subsequently, I will talk about the spatial and structural property-dependent (i.e., the basal/edge planes, the number of layers, and the defect density) reactivity of 2D semiconductors.

I will show our recently developed micro-scale photoelectrochemical setup, where we deposit small liquid droplets on the surface of the electrode, and measure photoelectrochemistry in the drop under illumination, also focused on the drop. Finally, I will present results on the effects of the structural properties of mechanically exfoliated flakes (i.e., $MoSe_2$ and WSe_2).

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Oxide-Based Photoelectrodes for Use in Solar Water Splitting

Kyoung-Shin Choi
University of Wisconsin-Madison, Madison. WI

Among various semiconductor electrodes (photoelectrodes) that have been investigated for solar fuel production, oxide-based photoelectrodes have the possibility of significantly lowering the materials processing costs while also being more stable in aqueous media. In the past decade, a significant effort has been made in investigating a variety of semiconductor oxides as photoelectrodes for a water splitting photoelectrochemical cell (PEC). In general, oxide-based photoelectrodes suffer from low carrier conductivity and their photon-to-current conversion efficiencies have been considerably lower than their theoretically expected efficiencies based on their bandgaps. Therefore, developing oxide-based photoelectrodes requires considerable optimizations of their compositions and morphologies to improve their charge transport properties. A continual significant improvement in the efficiency of oxide-based water splitting PECs also makes concurrent improvement of their photostabilities an important issue. In this presentation, we will review the progress made in oxide-based photoelectodes and discuss effective strategies to enhance charge transport properties and photostabilities of oxide-based photoelectrodes.

Session V

Advances in Photocatalysis

Designing Materials for Optoelectronic Properties

William Tumas,* K. Persson, G. Ceder, M. Toney, D. Nocera, J. Tate, B. Gorman,
V. Stevanovic, S. Lany, A. Zakutayev, and D. Ginley
National Renewable Energy Laboratory, Golden, CO

The discovery of new functional materials is critical for developing the needed disruptive technologies for energy conversion, delivery, storage, and use. Remarkable advances in theory as well as high-throughput materials synthesis and characterization are enabling a new approach to new materials discovery where theory can directly guide experimental materials development. We will provide an overview of materials discovery efforts for photoelectrochemical water splitting and also provide key results from the Next Generation for Materials by Design (CNGMD) Energy Frontier Research Center (cngmd-efrc.org) and other collaborative projects that tightly couple theory, experiment and characterization to discover and understand new inorganic semiconductor materials with optoelectronic functionality. Recent advances to incorporate functional metastable materials into materials by design will also be presented including understanding and establishing ranges for materials metastability as a function of the chemistry, energetics, and structure. Specific examples of three classes of metastable systems for metal oxides and nitrides will be presented: polymorphs, defects, and solid solutions (alloys). We are also working to develop a systematic theory-driven approach to guide the synthesis of new materials—including metastable systems—by coupling theory and state-of-the-art in-situ characterization to probe materials growth pathways.

Bridging Molecular and Heterogeneous Electrocatalysis Through Graphite Conjugation

Jackson, M. N.; Oh, S.; Kaminsky, C. J.; Chu, S. B.; Surendranath, Y. *
Massachusetts Institute of Technology;; Cambridge, MA

The efficient interconversion of electrical and chemical energy requires catalysts capable of accelerating complex multi-electron reactions at electrified interfaces. These reactions can be carried out at the metallic surface sites of heterogeneous electrocatalysts or via redox mediation at molecular electrocatalysts. Molecular catalysts yield readily to synthetic alteration of their redox properties and secondary coordination sphere, permitting systematic tuning of their activity and selectivity. Similar control is difficult to achieve with heterogeneous electrocatalysts because they typically exhibit a distribution of active site geometries and local electronic structures, which are recalcitrant to molecular-level synthetic modification. However, metallic heterogeneous electrocatalysts benefit from a continuum of electronic states which distribute the redox burden of a multi-electron transformation, enabling more efficient catalysis. We have developed a simple synthetic strategy for conjugating well-defined molecular catalyst active sites with the extended states of graphitic solids. Electrochemical and spectroscopic data indicate that these graphite-conjugated catalysts do not behave like their molecular analogs, but rather as metallic active sites with molecular definition, providing a unique bridge between the traditionally disparate fields of molecular and heterogeneous electrocatalysis.

Cu_2O Assisted Facet-Dependent Photocatalysis for CO_2 Reduction

Yimin A. Wu, Ian McNulty, Kah Chun Lau, Larry A. Curtiss, Yuzi Liu, Tijana Rajh*
Argonne National Laboratory, Argonne, IL

Copper compounds are very promising as photocatalysts with good multielectron transfer properties due to their loosely bonded d electrons. Cu_2O is an inexpensive material with near-ideal electronic properties for solar energy conversion into fuels. Importantly, Cu_2O shows intrinsic p-type conductivity due to the presence of negative-charged Cu vacancies with one of the lowest electron affinities, identifying Cu_2O as an optimal candidate for reduction of CO_2. However, as Gerischer showed in his early pioneering work,[1] crystalline Cu_2O is photocathodically unstable and therefore unsuitable for multielectron reductive photocatalysis, unless strong adsorption of the reactants that modifies active sites and kinetically enhances reduction reactions occurs. Herein, we report atomic level understanding of the active sites in Cu_2O that lead to the discovery of the facet specific adsorption and subsequent light induced reduction of CO_2 exclusively into liquid fuel – methanol. The activity of these sites was unraveled using operando multimodal correlated characterization of a single particle, and in situ activity measurements. By employing correlated scanning fluorescence x-ray microscopy and environmental transmission electron microscopy at atmospheric pressure, in operando, on a single particle level, we designed nanoparticles with highly active facet selective active sites and particles activity. A quantum yield for photocatalytic reduction of CO_2 to methanol using Cu_2O crystals was found to be ~ 72% , with ~ 25% solar-to-fuel efficiency. This high efficiency reflects significance of our directed growth of faceted selective Cu_2O photocatalysts.

1 H. R. Schoppel and H. Gerischer. Die kathodische Reduktion von Cu-I-Oxid-Elektroden als Beispiel fur den Mechanismus der Reduktion eines Halbleiter-Kristalls. Ber. Bunsen-Ges. Phys. Chem. 75, 1237-1239 (1971).

Report from the Workshop Panel on the Photoelectrochemical Solar Production of Fuels

Parkinson, Deutsch, T., Durrant, J., Esposito, D., Ginley,D., Hannappel, T., Haussener, S., Houle, F., MacIntyre, P., Maldonado, S., Modestino,M. Neale, N., Nocera, D. Parkinson, B., Sharp, I., and Xiang, C.

A report will be given on the output of a workshop held prior to this Symposium on August 13, 2018 that addressed the challenges in photoelectrochemical solar fuels production. The discussion in this workshop focused on systems where a semiconductor is in contact with solution and where hydrogen or other fuels are produced through exposure to light.

A series of discussion sessions were held in this workshop. One considered the need for an analytical facility for confirmation of cell efficiencies and the required measurements that should be made. Another dealt with the challenges in system prototyping. This was followed by discussions on the discovery of novel semiconductors as light absorbers with catalytic surfaces as well as the means for large area deposition of solids. A last topic focused on possible pathways to the design and assembly of a durable photocatalytic interface with the assumption that no catalytic interface is infinitely stable. With the analysis of these critical issues in this sequence, one can identify the critical research problems in the pathway towards practical application.

Scrutinizing Epitaxially Prepared Tandem Device Structures for Efficient Solar Water Splitting

T. Hannappel[1]*, O. Supplie[1], M.M. May[1,2,3], H.-J. Lewerenz[4], W.-H. Cheng[4], M.H. Richter[4], H.A. Atwater[4], F. Dimroth[5], J. Ohlmann[5]
1 TU Ilmenau, 2 HZB, 3 Cambridge University, 4 CalTech, JCAP, 5 FhG-ISE

Tandem device structures are capable to create sufficient chemical energy, i. e. a sufficient splitting of the Fermi levels, and in addition to explore the solar spectrum most efficiently [1,2] in the process of solar-driven direct water splitting. The scenario in such a photoelectrochemical cell can be divided into three different basic steps: (i) generation of electro-chemical potentials by light absorption a, (ii) transport of charges, and (iii) charge separation at the solid liquid interface. When utilizing tandem cells, STH efficiencies can be achieved clearly exceeding 20%. The difficulty arises to achieve a stable performance and to describe the microscopic processes at the challenging solid-liquid interface. Based on surface chemistry observed in model experiments, we firstly applied interfacial functionalization relevant for efficient III-V-semiconductor tandem absorbers, secondly studied in situ interfacial chemistry on the atomic scale, and thirdly prepared well-defined interfaces to explore different surface reconstructions on their initial interaction with water and oxygen [3]. Finally, in order to realize cost-competitive tandem devices structures, low-defect III-V semiconductor integration into the mature silicon technology needs to be accomplished. It is shown how to in situ control atomic scale preparation [4,5] and epitaxial growth of highly efficient device structures.

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[2] May et al., Nature Communications 6 (2015) 8256
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[4] Supplie et al., Advanced Materials Interfaces 4 (2017) 1601118
[5] Supplie et al., J. Phys. Chem. Lett. 6 (2015) 464.

Modelling, Experimentation and Scaling of Photo-Electrochemical Fuel Processing Devices

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The functionality of photo-driven electrochemical devices relies on complicated and coupled multi-physics processes, occurring at multiple temporal and spatial scales. Device modelling can actively and efficiently support the choice of the most promising – in terms of efficiency, cost, robustness, scalability, and practicability – conceptual design pathways, material choices, and operating approaches1. Modeling is usually accompanied by experimentation in order to provide missing properties, or morphological and performance indicators. Eventually, our research aims at the implementation and scaling of a practical device.

I focus on cost competitive photo-electrochemical (PEC) devices utilizing concentrated irradiation. Utilization of concentrated radiation requires implementation of the locally resolved energy conservation equation in order to determine if such devices are feasible and to understand how thermal management can be used to ensure high performance operation. The use of controlling strategies to ensure robust device operation is specifically discussed in the light of such devices exposed to non-predicable disturbances. I touch also on the importance of understanding and managing degradation. I then discuss experimental demonstration of a concentrated PEC device with high efficiency (17% solar-to-fuel, based on Gibbs energy) and unprecedented power and current density (27 W output power and 0.88 A/cm^2, respectively). Finally, I discuss ongoing scaling approaches by our lab for the design, implementation, and testing of these devices, in order to bridge the gap between research and practical application.

Advancing Semiconductor-Electrocatalyst Systems: Application of Shadow Nanosphere Lithography for Efficient Solar Hydrogen Production

Katharina Brinkert, Matthias H. Richter, Ömer Akay, Michael Giersig,
Katherine T. Fountaine, and Hans-Joachim Lewerenz
California Institute of Technology, Pasadena, CA

Efficient artificial photosynthesis systems follow the concept of the Z-scheme of natural photosynthesis. They are realized as catalyst- and surface-functionalized photovoltaic tandem devices enabling photoelectrochemical water oxidation while simultaneously recycling CO_2 and generating hydrogen as a solar fuel for storable renewable energy. The successful implementation of an efficient photoelectrochemical (PEC) water splitting cell is not only a highly desirable approach to solving the energy challenge on earth: an effective air revitalization system generating a constant flux of O_2 while simultaneously recycling CO_2 and providing a sustainable fuel supply is also essential for the International Space Station and long-term space missions, where a regular resupply from earth is not possible.

We demonstrate in a series of drop tower experiments that efficient direct hydrogen production can be realized photoelectrochemically in microgravity environment, providing an alternative route to existing life support technologies for space travel. The photoelectrochemical cell consists of an integrated catalyst-functionalized semiconductor system that generates hydrogen with current densities $>15\text{mAcm}^{-2}$ in the absence of buoyancy. Conditions are described adverting the resulting formation of ion transport blocking froth layers on the photoelectrodes. The current limiting factors were overcome by controlling the micro- and nanotopography of the electrocatalyst using shadow nanosphere lithography (SNL). We show that SNL can be used as a prosperous tool to obtain desired catalyst nanostructures of high fidelity on a light-absorbing semiconductor surface with tunable optical properties, also showing significant advantages for photoelectrochemical hydrogen production in terrestrial applications.

Interrogating Photochemical and Photo-Iono-Chemical Charge-Transfer Processes in the Absence of Space-Charge Regions

Shane Ardo
University of California, Irvine, CA USA

Most photoelectrochemical schemes depict semiconductors with electrostatic space-charge regions to provide the kinetic asymmetry needed to separate positive and negative mobile charge carriers and slow charge recombination. While in general this design has been shown to result in the most efficient conversion of solar power to chemical energy, it is not the only option. In my talk I will discuss recent work from my group on photochemical transformations that occur in the absence of significant space-charge regions. The centerpiece of this discussion will be experimental and numerical results obtained using photocatalyst particle suspensions for solar water splitting and photoacid-dye-sensitized ion-exchange membranes for light-driven ion pumping. Experimentally, each exhibits photovoltaic action in the presence of little-to-no space charge region. Numerical models provide substantial evidence that asymmetric charge transport can be designed by other means to provide the necessary conditions for effective charge separation and ultimately photochemical energy conversion. Using this as a backdrop, I will explain the basic science behind mechanisms and processes that result in effective photovoltaic action and photochemical transformations.

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Poster Abstracts

I. New Techniques and Methods

1. Combined Synchrotron Techniques for Probing Transient Electrochemical States During Water Oxidation

Robert Tang-Kong, Ryan Davis, Apurva Mehta, Christopher E.D. Chidsey, and Paul C. McIntyre, Stanford University

X-ray related characterization techniques are a powerful tool for structure identification of many materials. These techniques are commonly performed ex-situ, precluding the observation of some non-equilibrium states and behavior. Understanding of structural and chemical changes during electrochemistry is critical to the understanding and design of new, more efficient materials. Developing synchrotron techniques allows for in-operando examination of chemically active species and the observation of electrochemical changes far from equilibrium. A custom electrochemical cell was developed to allow for simultaneous diffraction and fluorescence measurements during operation.

As iridium is one of the most stable and efficient water oxidation catalysts, particularly at low pH, it is of vital importance to understand any changes that occur at the electrochemical interface, particularly those that compromise its catalytic activity. Using combined x-ray reflectivity (XRR), grazing incidence x-ray diffraction (GiXRD), and grazing incidence x-ray absorption (GiXAS) to probe the state of a 2 nm thin-film Ir/IrOx water oxidation catalyst, we observe transient changes in the catalyst state only present during electrochemistry. XAS measurements show approximately 49% of the iridium film is oxidized during chronoamperometry, and XRR data suggests the oxide is significantly rougher than the pristine iridium film. GiXRD and XRR demonstrate an immediate removal of this oxide upon return to open circuit potential, a phenomenon not observable with ex-situ techniques. These measurements suggest the partially reversible formation of an oxide layer under water oxidation conditions, correlated with a reduction in water oxidation activity of the iridium catalyst.

2. Soft X-ray Spectroscopy of the CdS/Cu(In,Ga)S_2 Interface for Photoelectrochemical Water Splitting

J. Carter, M. Blum, K. Horsley, A. Deangelis, W. Yang, D. Hauschild, L. Weinhardt, N. Gaillard, and C. Heske, University of Nevada, Las Vegas

In recent years, the efficiency of thin-film solar devices has significantly increased on both the laboratory and module scale. To further drive the optimization of efficient solar devices, a detailed understanding of the chemical and electronic structure of the pertinent surfaces and interfaces is required. Chalcopyrite-based compounds, such as Cu(In,Ga)(S,Se)$_2$ (CIGSSe), are regarded as one of the most promising material systems for use as an absorber in highly efficient solar devices. With regards to photoelectrochemical hydrogen generation (PEC), the band edges of these materials can be tailored and optimized to the solar spectrum and the water splitting potentials, respectively. This, in turn, makes CIGSSe a promising candidate for utilization in PEC devices.

In this contribution, the chemical and electronic structure of Cu(In,Ga)S_2 (CIGS) thin films and their interfaces to CdS buffer layers are investigated by different soft x-ray and electron spectroscopy techniques, both in the lab at UNLV and at the synchrotron (ALS, Berkeley Lab). The techniques include x-ray photoelectron (XPS) and soft x-ray emission (XES) spectroscopy to determine the surface and near-surface chemical environment, as well as complementary ultraviolet photoelectron (UPS) and inverse photoemission (IPES) spectroscopy for a derivation of the valence and conduction band edges, respectively. This combination allows for a full determination of the band alignment at the CdS/CIGS interface, which, in turn, helps to guide PEC research in developing promising materials candidates for cost-effective solar hydrogen production.

3. Measurement of Charge Transfer Kinetics at Semiconductor Ultramicroelectrodes

Mitchell Lancaster, Saurabh Acharya, and Stephen Maldonado, University of Michigan

Semiconductor ultramicroelectrodes (SUMEs) have been developed as a new tool to study charge transfer at semiconductor/electrolyte contacts. This presentation will highlight several aspects of voltammetry at unilluminated Group IV and III-V SUMEs. First, the SUME geometry will be described. The impact of the electrode recession on fitted kinetic parameters and observed capacitance will be highlighted. Second, the expected SUME voltammetric response will be detailed, specifically emphasizing the interplay between depletion layer formation at the semiconductor/solution interface and radial diffusion of acceptors in solution. Third, the nature of aqueous silicon interfaces will be described through voltammetric studies with n-Si SUMEs in contact with outer-sphere redox couples. Improved diode quality factors relative to macroscopic Si electrodes and stability over multiple measurements will be demonstrated. Finally, charge transfer measurements at microscopic n-GaP/fullerene contacts will be detailed. Rate constants and diode quality factors for each observed redox transition will be presented, including solvent dependence on the wave position and diode quality factor. The implications of these results to verification of fundamental charge transfer theories will be noted.

4. Fragment Basis Tight Binding method

Joshua S Brown, Dr. Bjoern Baumeier, Jens Wehner, Dr. Sean Shaheen, University of Colorado

Computational studies of charge transport in pi-conjugated polymer materials has largely been limited to Monte Carlo simulations such as the Gaussian Disorder Model originally develop by Bässler. Though effective at modeling the dependence of carrier mobility on electric field and temperature, these approaches often lack the topological insight that can be gained by considering the detailed conformations of the local molecular structure. However, the computational cost of Quantum Chemistry electronic structure calculations has remained a hurdle to more detailed investigations partly due to the N4 and N3 scaling of the Hartree fock and DFT based methods, respectively. Here we present a Fragment Basis Tight Binding method that shows near linear scaling with the number of fragments for ground state molecular orbital calculations for both Hartree Fock and DFT. Preliminary results using the approximation with small basis sets calculate the HOMO and LUMO energies within less than 1% error of the actual results for a 16-monomer strand of poly(3-hexylthiophene).

II. Charge Transfer at Nanostructured Solids

5. Activation Energies for Electron Transfer from TiO_2 to Interfacial Acceptors

Rachel E. Bangle, Ludo Troian-Gautier, Gerald J. Meyer, University of North Carolina, Chapel Hill

The population of electrons occupying trap states or the conduction band of mesoporous nanocrystalline TiO_2 have been altered by an electrochemical bias. The number of electrons in TiO_2 is known to enhance the rate of interfacial electron transfer (ET) to molecules on TiO_2 surfaces, but the dependence is not straightforward. (1) Specifically, the rate of interfacial ET to an oxidized, surface-bound molecule has been found to increase exponentially with forward bias (i.e. negative applied potentials) but, is insensitive to reverse bias. (2) Models of ET kinetics account for the forward bias dependence, but the lack of reverse bias dependence is seldom considered. (3)

In this presentation, we study ET processes from TiO_2 to surface-bound oxidized molecules and redox mediators dissolved in fluid solution. Temperature-dependent kinetic measurements at specific applied biases were performed to gain mechanistic understanding. Under forward bias, similarity of the activation energies for interfacial ET and electron transport would support a trapping/detrapping kinetic model. Differences in activation energies measured under reverse bias would imply that ET in this regime is governed by an alternative model. The origin(s) of the behavior will be discussed, and a model of interfacial ET from TiO_2 to interfacial electron acceptors will be proposed to give insights into deleterious reactions in dye-sensitized solar cells and dye-sensitized photoelectrochemical cells.

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6. Semiconductor-electrocatalyst interfaces: the behavior of Ni on n-Si photoanodes

Forrest Laskowski, Michael Nellist, Sebastian Oener, Shannon Boettcher, University of Oregon

Si is a desirable photoanode material for use in photoelectrochemical water splitting devices. However, Si self-passivates during the oxygen evolution half reaction and requires a protection layer to maintain high photoanodic efficiency. By using dual-working-electrode (DWE) photoelectrochemistry we find that thinner thermally evaporated Ni layers produce significantly higher photoanode efficiencies during in situ operation. This behavior is attributed to the development of spatial inhomogeneities which take advantage of the pinch-off effect. By patterning Si with successively smaller Ni nanocontacts we confirm this hypothesis. In general, atterning Si with smaller Ni islands produces more efficient photoanodes because pinch-off is enhanced.

7. Photoacid Assisted Water Dissociation: Direct Interrogation of the Förster cycle

Simon Luo, Joseph Cardon, Shane Ardo, University of California, Irvine

Ion-exchange membranes have similar characteristics to semiconductors in that when doped with fixed positive (or negative) charges they selectively conduct mobile negative (or positive) charges. Recently, we reported a new class of ion-exchange membranes that use photoacid molecules as co-dopants to sensitize traditional ion-exchange membranes to visible light. Photoacids are dye molecules whose pKa decreases in the excited state.1 Dye-sensitized ion-exchange membranes are theorized to undergo the Förster cycle and result in water dissociation. A plausible mechanism is that upon photoexcitation the photoacid releases a H+ that then charge separates. When the photoacid relaxes to its ground-state, it is reprotonated kinetically by either 55 M water (generating an OH–) or thermodynamically by H3O+, but details of this mechanism are not known. To interrogate the Förster cycle of photoacids in solution and in ion-exchange membranes, potentiometry and time-resolved laser spectroscopy were used. Electrochemically, a transparent reversible hydrogen electrode was used to probe the local proton activity at the electrode–dye interface. Spectroscopically, time-resolved microwave conductivity was used to probe transient generation of mobile charge carriers. This last technique is notable because the X-band microwave probe has a 1 mm penetration depth in water allowing contactless measurements of mobile carrier density and decay times in thin-film samples. Elucidation of this dye-sensitization mechanism will help in designing light-driven ion pumps that directly convert photons into ionic current for applications in desalination and energy storage.

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III Fundamental Advances

8. Controlling materials parameters to understand excited state proton transfer of photoacids on polymer scaffolds

Eric Schwartz, Leanna Schulte, William White, Shane Ardo, University of California, Irvine

Many electrochemical technologies use ion exchange membranes as passive systems to maintain pH gradients or pass ions selectively. These technologies can be improved, and new technologies could be developed if these membranes can actively transport charges. Recently, our group has developed a system which uses photoacidic molecules tethered to polymeric supports to induce ionic current and voltage via application of light [1]. To better understand how this system works, we are developing new polymeric scaffolds with fine control over layer thickness, hydrophilicity, and dye density. This will allow us to better understand the photocycle in these systems by probing effects of carrier collection length and conductivity on quantum yield.

[1] White, W., Sanborn, C. D., Fabian, D. M. & Ardo, S. Conversion of Visible Light into Ionic Power Using Photoacid-Dye-Sensitized Bipolar Ion-Exchange Membranes. Joule 2, 94–109 (2018).

9. Probing Defects of Zinc Oxide Nanoparticles Using Electronic Energy Transfer

Lacey M. Beck, Zach N. Nilsson, Duncan P. Ryan
Colorado State University, Fort Collins

Efficient charge transport though nanostructured devices is critical for optoelectronic and sensing applications. Charge carriers moving through a nanostructure or between nanostructures can become trapped at surface sites. Understanding the location and the chemical and electronic nature of defect sites in a nanoparticle could allow for more efficient nanostructured thin-film devices to be built. In this work, we show an ensemble-level method of probing defect sites on the surface of zinc oxide nanoparticles (NPs) with organic dyes that act as electronic energy transfer (EET) acceptors. We screened dyes with a wide range of spectral properties as well as different functional moieties to identify the best dye(s) for probing a specific type of defect. We then used super resolution fluorescence microscopy to determine the location of dye molecules on the surface of the NPs. Here we discuss the fraction of particles that have exposed surface defect sites.

10. Interpreting behavior from dye-sensitized-Nafion–liquid junction contacts using theories from Gerischer semiconductor–liquid junction

William White, Simon Luo, and Shane Ardo, University of California, Irvine

Many electrochemical technologies require ion-conducting polymer electrolytes to separate different electrolyte conditions and increase efficiency and lifespan of the entire device.[1] Traditionally ion-conducting polymeric electrolytes are passive in that electric bias across them drives ion migration in the thermodynamically favored direction.[2] Recently, I reported for the first time photovoltaic action from dye-sensitized ion-exchange membranes, where photoacids are covalently bound to a Nafion® support.3 Dyed membranes behave like protonic versions of p-type electronic semiconductors in that they predominantly conduct positive charge carriers and exhibit close to the expected thermodynamic electrostatic Donnan potential.[3] Moreover, the photocurrent depends nearly linearly on photon flux, the photovoltage is approximately logarithmic with photon flux, the spectral response is as expected, and the sign of the photovoltage is independent of the direction of illumination. Interestingly, the magnitude of the photoresponse is independent on the direction of illumination suggesting a collection length on the order of the thickness of the membrane (50µm). When configured in a pn-junction-like structure with a dyed p-type membrane annealed onto an n-type anion-exchange membrane, photovoltages increased by nearly two orders of magnitude greater than 100 mV. It is thought that this increased performance is in-part caused by the large internal electric field in the depletion layer located at the interface between the cation-exchange membrane and anion-exchange membrane.

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(2) Reiter et al. J. Electrochem. Soc. 2016, 163 (4), H3132–H3134.

(3) White et al. J. Am. Chem. Soc. 2017, 139 (34), 11726–11733.

11. New Approach to Study Driving Force Dependence of PCET Kinetics

Jenny Schneider, Rachel Bangel, and Gerald J. Meyer, Department of Chemistry, University of North Carolina at Chapel Hill

Despite the widespread attention to the Proton-Coupled Electron Transfer (PCET) reactions there are limited data on the driving force dependence of the PCET rate. For the first time, Hammarström et al.[1] has provided a rate/driving force dependence analysis with the qualitative estimation of the reorganization energy and the electronic coupling element for the PCET reactions of tyrosine and tryptophan in model complexes. The corresponding analysis of the PCET at the semiconductor/liquid interface has not been reported so far. In the present study we explored for the first time the photoinduced interfacial PCET between surface bound ruthenium polypyridyl water oxidation catalysts and the degenerately doped transparent conductive oxides (TCOs). The optical transparency of TCOs allowed the application of transient absorption spectroscopy to monitor the respective charge transfer kinetics, while their metallic character enabled the Fermi level tuning via the variation of the applied bias and thus to control the driving force for the interfacial charge transfer processes.[2] The decay kinetics for the back electron transfer from TCO to the oxidized catalyst was found to depend on the pH and on the applied bias. The driving force dependency of the interfacial electron transfer has been quantitatively described applying Marcus-Gerischer theory resulting in an experimental estimate for the total reorganization energy and the electronic coupling element. The application of TCOs for such studies is unique and has the potential to become a useful tool for the evaluation and quantification of PCET for a wide range of molecular assemblies.

References

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IV Novel Solids

12. Spatially resolved photo-electrochemical properties of monolayer and bilayer WSe_2/MoS_2 heterostructures

Li Wang, Justin B. Sambur, Colorado State University, Fort Collins

WSe_2/MoS_2 heterojunctions exhibit the largest conduction and valence band offsets among all the combinations of Mo and W transition metal ions and Se and S dichalcogenides. The large band edge offsets suggest that photoexcited charge carriers in the materials could be efficiently separated and utilized in energy conversion applications. However, the role of layer thickness and stacking orientation have not been studied in the context of photoelectrocatalysis. In this work, we studied the oxidative and reductive photoelectrocatalytic properties of ITO/MoS_2/WSe_2 and ITO/WSe_2/MoS_2 electrodes in H_2SO_4 and NaI electrolytes. We identified the optimum stacking configuration of oxidative photoelectrocatalysis. Furthermore, near diffraction-limited photocurrent microscopy revealed the role of layer thicknesses on the oxidative properties of the ITO/MoS_2/WSe_2 electrode, which can be linked to a driving force for electron transfer between the ultrathin semiconducting layers. We discuss the role of inter-layer coupling and heterogeneity in 2D materials heterojunctions.

13. Photoelectrochemical characterisation of p-GaP for solar water splitting

L. Eggert, M. Kurniawan, O. Supplie, R. Peipmann, T. Hannappel, A. Bund, Technische Universität Ilmenau, Germany

Hydrogen is an important energy carrier for renewable energies. It is mainly produced from hydrocarbons through chemical reforming processes. [1] The use of a semiconductor absorber as photoelectrode immersed in an electrolyte for direct solar water splitting is an attractive renewable alternative to produce hydrogen (photoelectrochemical water splitting (PEC)). [2] Gallium phosphide (GaP) is studied here as a reference material for GaP-based III-V top-absorbers, such as GaAsP or GaPNAs, to be used in tandem absorber PEC devices promising high conversion efficiencies.

The impact of the surface structure of p-type GaP was analysed with regard to the water splitting performance and stability. Regarding crystal orientation, we found that GaP(111) surfaces showed higher photostability than GaP(100) surfaces. Different atomic surface reconstructions on GaP(100) were prepared by metal-organic vapour epitaxy (MOVPE) and transferred in inert gas to the photoelectrochemical cell. Ga-rich and P-rich samples showed an increase of dark current after long time measurements in H_2SO_4 and exhibit low stability in comparison to pristine GaP(100). After the photoelectrochemical measurements, sulphur species were found on the surface by energy dispersive X-ray spectroscopy EDX. Such surface modifications involving elements of the electrolyte impact the water splitting performance. We found that a thin oxide layer can stabilise the performance of GaP(100). The in-situ formation of such oxide layers is particularly interesting to tune the semiconductor-liquid interface with regard to stability and electronic properties.

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[2] Electrochimica Acta, Volume 260, (2018), 861-871

14. The Role of Catalyst Adhesion in ALD-TiO_2 Protection of Water Splitting Silicon Anodes

Robert Tang-Kong, Roy Winter, Ryan Brock, Jared Tracy, Moshe Eizenberg, Reinhold H. Dauskardt, and **Paul C. McIntyre**, Stanford University

Atomic layer deposited titanium dioxide (ALD-TiO_2) has emerged as an effective protection layer for highly efficient semiconductor anodes which are normally unstable under the potential and pH conditions used to oxidize water in a photoelectrochemical cell.[1] Generally, failure of ALD protected photoanodes is attributed to chemical attack of the underlying substrate due to a failure of the protection layer to block oxidation, with few published works addressing other degradation pathways, but interactions at a catalyst – protection layer interface have not been studied in detail. The failure modes of silicon anodes coated with an Ir/IrOx oxygen evolution catalyst layer are investigated, and poor catalyst/substrate adhesion is found to be a key factor in failed anodes. Quantitative work of adhesion measurements yield a TiO_2/Ir interface debond energy of 6.02 ± 0.49 J/m^2, significantly greater than the debond energy of the Ir/IrO_x catalyst layer on SiO_2, i.e. in the absence of an ALD-TiO_2 protection layer. These results indicate the importance of catalyst adhesion to an interposed protection layer in promoting operational stability of high efficiency semiconducting anodes during solar-driven water splitting.

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15. Hybrid Molecular/Inorganic Passivation of Nanoporous Black Silicon

Ryan T. Pekarek, Steve S. Christensen, Jun Liu, Nathan R. Neale, National Renewable Energy Laboratory, Golden

Nanoporous 'black' silicon is an interesting photocathode due to its high current density and positive proton reduction onset potential (1). We passivate the porous substrate via covalently-bound organic monolayers buried under titania (grown by atomic layer deposition). Binding ferrocene to the monolayer reveals a 10-fold increase in surface coverage relative to the planar case. We use intensity-modulated high frequency resistivity (IMHFR) (2) to probe the effect of these layers on the band-edge position and find tuning of the molecular dipole yields a 300 mV improvement of the flatband potential. Pt nanoparticle catalysts are either a) etched into the bottom of the pores or b) deposited on top of the titania overlayer. As expected, when Pt is located within the pore, subsequent titania deposition decreases catalytic activity. Interestingly, activity is recovered after applying negative potentials. Samples with titania-bound Pt show a 300 mV improvement in the flatband potential after oxide deposition while their buried-Pt congeners do not demonstrate this enhancement. We determine neither architecture results in Fermi pinning to the Pt nanoparticle via pH-dependent IMHFR. These studies provide valuable insight into the energetics of photelelectrochemical electrodes.

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16. Photovoltaic Action from Anion- and Cation-Exchange Membranes Covalently Modified with a Double Photoacid

Margherita Taddei, Lawrence A. Renna, William White, Shane Ardo,
University of California, Irvine

Photoacids are a class of molecule whose protic bond disassociation constant decreases when photo-excited. In the Integrated Solar Photo-Dialysis system the Ardo Group is pioneering, photoacids are covalently bound to ion-exchange membranes that are engineered to generate ionic current rectification and show photovoltaic action when illuminated.1 All reports to-date have focused on cation-exchange materials and photoacid dyes working at low pH.2 My research seeks to investigate the photoelectrochemical performance of dyed anion-exchange membranes. The dye I used is an amino-pyrene based photoacid, 8-aminopyrene-1,3,6-trisulfonic acid, that I discovered has two accessible excited-state proton-transfer Förster photocycles, one for each of the two protons present in the amino group ($R\text{-}NH_2^+$). Through careful control of dye loading, I was able to change the net charge of the majority fixed ion in the membrane, which resulted in a change in membrane selectivity from anionic to cationic. This is important because the photoacid generates a minority carrier proton in the anion-exchange version and a majority carrier proton in the cation-exchange version. While both membrane types exhibited photovoltaic action, the magnitudes of the photo-activities varied greatly between the two types.

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17. Determination and optimization of material parameters of particle-based $LaTiO_2N$ photoelectrodes

Yannick Gaudy and **Sophia Haussener**
EPFL Lausanne, Switzerland

A validated numerical model capable of predicting the photocurrent-voltage characteristic and of identifying the critical parameters affecting the performance of oxide and oxynitride particle-based photoelectrodes was developed. Here, we used particle-based $LaTiO_2N$ photoelectrodes as the model system. Two different types of electrodes were studied: $LaTiO_2N$ photoelectrodes with TiO_2 inter-particle connections and the same photoelectrodes with NiOx/CoOx/$Co(OH)_2$ co-catalysts and a Ta_2O_5 passivation layer. The necessary material parameters, namely complex refractive index, permittivity, density of states of the conduction and valence bands, charge mobilities, flatband potential, doping concentration, recombination lifetimes and interfacial hole transfer velocity, were derived by density functional theory calculations, dedicated experiments, and fitting of the numerically determined photocurrent-voltage curves to the measured ones under back-side illumination. The model was validated by comparing its prediction to front-side illumination photocurrent-voltage measurements. A parametric study was then carried out to provide an extensive set of material design guidelines and key parameters for high-performing particle-based $LaTiO_2N$ photoelectrodes. The interfacial hole transfer velocity was identified as the most significant parameter for the performance of $LaTiO_2N$ photoelectrodes.

18. Designing the Interface: Synthetic Control of Si(111) Photoelectrochemical Devices via Molecular Modification

Dylan G. Boucher and Michael J. Rose
University of Texas at Austin

Silicon's small bandgap (1.1 eV) and large photocurrent density (~25 mA/cm2 under 100 mW/cm2 illumination) make it a nearly ideal photocathode material for photoelectrochemical hydrogen evolution (PEC-HER). However, silicon is prone to formation of an electrically insulating silicon oxide layer which limits device efficacy. Efforts towards stabilization of the Si(111) surface by alkylation have resulted in well-passivated, stable surfaces. However, the resulting interfacial dipole of the alkylated surface shifts the onset of HER to negative efficiencies, even on Pt decorated surfaces. To this end, our group has explored low-temperature, solution-based processing methods to significantly alter the interfacial properties of Si(111). Chemically derivatized surfaces (R: phenyl, para-nitrobephenyl, 9-anthracene, and 9-nitroanthracene) have been achieved using organolithium precursors. Mott-Schottky analysis revealed electrochemical potential shifts in the band-edge positions of the surfaces that were one to one with potential shifts in PEC-HER onset in pSi-R|TiO_2|Pt devices, indicating quantitative control of the photovoltage through molecular design. In addition, we found that the molecular identity of the modifier played a significant role in determining rates of surface recombination; we explore this relationship with two model systems: para-nitrophenyl (low surface recombination) and meta-dinitrophenyl (high surface recombination) and develop design principles for retaining high-quality surfaces with low rates of recombination. Finally, we extended these insights to a new class of fluorine containing molecular modifiers with a slim steric profile capable of achieving high surface coverages (~100% of atop Si sites occupied) whilst retaining high surface quality.

19. Single Particle Electrochromism

R. Colby Evans, Christy Cashen, Justin Sambur, University of Colorado

Tungsten trioxide (WO3) is a dynamic material that has been used in a wide variety of systems and applications, most notably electrochromic Smart Windows. Nanostructured WO3 electrochromic devices potentially offer shorter switching times than compact thin films because their high surface area provides shorter ion insertion path lengths during device operation. Nanostructured electrochromic devices are generally characterized with ensemble-averaged light absorption and electrochemical techniques that do not have single particle resolution. Here, we report first-of-their-kind single particle electrochromic measurements that report on optical and ion-insertion behavior of individual WO3 nanorods under working device conditions. In the future, TEM will be used to gain a better understanding of how lattice defects affect the electrochromic process.

20. Probing the Physical Properties of Molecular-based Surface Coatings for Applications in Electrocatalysis

Brian L. Wadsworth, Diana Khusnutdinova, Anna M. Beiler, and Gary F. Moore, Arizona State University, Tempe

Electrocatalysts powered by light-absorbing components provide an approach for achieving technologies that capture, convert, and store solar energy in the form of chemical bonds. Inspired by biological architectures, where amino acid residues provide coordination environments that control the physical properties of catalytic active sites, we have developed thin-film polymeric surface coatings as a strategy for interfacing human-engineered electrocatalysts onto semiconducting surfaces. [1-3] The resulting heterogenous-homogeneous assemblies are capable of generating hydrogen from aqueous solutions under solar illumination without use of sacrificial chemical reductants. This presentation describes efforts to export a polymer grafting chemistry we initially developed for applications on semiconductor surfaces, to include coatings on transparent conducting oxides (TCOs). [4] The chemically modified TCOs provide new opportunities, using optical and electrochemical techniques, to probe the physical properties of molecular electrocatalysts immobilized within the polymeric environments. Investigations using coatings containing cobalt-based redox catalysts provide information on the electronic and vibronic structure of the immobilized components and confirm the encapsulating polymer does not preclude formation of reduced metallic sites. The polymeric interfaces provide a bio-inspired strategy to controlling the redox properties and chemical stability of the hybrid materials.

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V Advances in Photocatalysis

21. Silicon Photoanodes with Iridium Oxide-Based OER Catalysts for PEC water-splitting

Micha Ben-Naim, Alaina Strickler, Dave Palm, Drew Higgins, Laurie King, Adam Nielander, Thomas Jaramillo, Stanford, University

Photoelectrochemical (PEC) water-splitting is a promising technology to split water into hydrogen and oxygen with sunlight, providing a storable and sustainable chemical fuel [1]. Silicon shows promise as a small bandgap absorber material (1.1 eV) to use in tandem PEC devices [1]. However, pairing catalysts with semiconductors has proven difficult due to poor energetic alignments and interfaces as well as stability concerns, which are especially limited in acid [2].

We developed a spin coating procedure to synthesize amorphous iridium oxide and biphasic strontium iridium oxide. The simple and low temperature processing make spin coating compatible with photoabsorber materials, unlike other deposition techniques. Material structure is probed by SEM, XPS, AES, and XRD, while electrochemical performance was measured under illumination and in the dark by cyclic voltammetry, chronoamperometry, and electrochemical impedence spectroscopy.

The addition of strontium to the catalyst gives 550 mV of photovoltage, a 100 mV improvement upon iridium oxide. Probing with a facile redox couple indicates that the strontium iridium catalyst forms a more beneficial electronic interface with silicon. A comparison of the as-prepared and post-test anodes via AES demonstrates that the predominant failure mechanism is film cracking and delamination, which originates from initial film heterogeneity.

(1) Seitz, L. C.; Chen, Z.; Forman, A. J.; Pinaud, B. A.; Benck, J. D.; Jaramillo, T. F. ChemSusChem 2014, 7, 1372.

(2) Bae, D.; Seger, B.; Vesborg, P. C. K.; Hansen, O.; Chorkendorff, I. Chem. Soc. Rev. 2017, 46, 1933.

22. Controlling the catalyst's local pH in bipolar junction anionic thin layer water electrolyzers

Sebastian Z. Oener, Dongyu Xu, Jingjing Qui, Shannon W. Boettcher, University of Oregon.

In proton exchange membrane electrolyzers high current densities, high differential pressure and elevated temperature operation are supported by the acidic polymer electrolytes used, e.g. Nafion. However, the oxygen evolution reaction in the acidic environment requires expensive precious metal catalysts. Here, we realize a compact bipolar junction thin anionic layer electrolyzer that utilizes a thin anion exchange ionomer layer to embed the oxygen evolution reaction catalyst in a basic local environment but that relies on conductive and stable Nafion for the product separation and mechanical robustness. Compared to regular bipolar membranes utilizing thick anion exchange membranes, the thin anion exchange ionomer layer ensures improved ionic conductance and improved water supply to the water-dissociating bipolar junction. The devices using such a geometry (1-2 μm FAA-3|50 μm Nafion) are able to support initially an electrolysis current density of 200 mA cm^{-2} at an applied voltage of ~2 V, while maintaining the catalyst material in an alkaline environment; a noteworthy performance, given that no additional water dissociation catalyst has been used. After the initial polarization curves, we observe a substantial improvement; current densities of 200 mA cm^{-2} at ~1.7 V are obtained. Possible mechanisms leading to the pronounced change are proposed. Bipolar junction anionic thin layer geometries are thus a promising route to integrate local alkaline catalyst environments into compact electrolyzer architectures. Compared to traditional bipolar membranes, they reduce ionic-conductivity constraints of the AEMs, improve water transport, and hence water dissociation, and thereby may enable higher supported current densities of BPM-type devices.

23. Multiscale Modeling of Photoelectrochemical Devices

Kara Kearney, Urbana, Illinois

The design of functionalized photocathodes for high-efficiency H_2 generation is a major interest in the field. However, there is a lack of theoretical research corroborating experimental analysis. In this talk, I present an integrated computational approach combining first-principles density functional theory calculations with solid-state drift/diffusion device modeling. This method is used to elucidate charge transport mechanisms across functionalized photoelectrodes and subsequently predict strategies for improving performance. The applicability of the model to organic monolayers and inorganic passivation layers will be discussed.

24. 100 cm² Dynamic Windows Based on Reversible Metal Electrodeposition with Sub-Minute Switching Speeds

Michael T Strand, Tyler S Hernandez, Daniel J Slotcavage, Christopher Barile, Michael D. McGehee, University of Colorado

While the demand for optically tunable windows is paramount in today's residential and industrial communities, traditional electrochromic windows have not yet been commercialized on a large scale. Dynamic windows based on reversible metal electrodeposition (RME) have emerged as an exciting, undeveloped class of electrochromic devices posed to overcome the challenges inherent to conventional technologies.[1] Metals are ideal light-modulators for dynamic windows because they can be color-neutral, inert, IR-reflective, and opaque at 20-50 nanometer thicknesses. Our team has demonstrated metal-based dynamic windows that boast cheap processing, fast switching, and stable performance over thousands of cycles on the 25 cm2 scale.[2,3]

Several technical challenges hinder further scalability of the technology. Common transparent electrode materials like indium tin oxide (ITO) have relatively high sheet resistance. By Ohm's Law, maintaining a uniform current density through resistive electrodes necessitates a voltage drop proportional to the electrode area. Large-scale dynamic windows must be engineered with a tolerance to the non-uniform potential distribution across the electrode surface in order to maintain optical uniformity during switching. Additionally, undesired side reactions like the hydrogen evolution reaction (HER) set strict limits on the potentials that may be applied in aqueous electrolytes. The ideal system will enable uniform nucleation and growth of metal films over the potential range set by side reactions inherent to aqueous electrolytes, and the voltage drop inherent to transparent conductors.

Prudent design of electrode structure enables uniform and reversible electrodeposition over large areas. Using a scalable process, we fabricate transparent electrodes coated with Pt nanoparticles for dynamic windows. The Pt nanoparticles serve as preferred nucleation sites for the electrodeposition reactions. By controlling the nanoparticle surface density, we have direct control over the active site density for nucleation, and thus the subsequent growth of the metallic film. This nucleation control enables transparent electrodes that exhibit uniform transmission versus time relationships over a large range of applied potentials.

Finally, we demonstrate 100 cm^2 dynamic windows based on reversible metal electrodeposition that switch uniformly despite the voltage drop across the working electrode. The devices switch reversibly from a clear state (60% transmission) to a color-neutral, opaque state (<5% transmission) in less than one minute.

[1] S. Araki, K. Nakamura, K. Kobayashi, A. Tsuboi, N. Kobayashi, Advanced Materials, 24, OP122 (2012).

[2] C. B. Barile, T. S. Hernandez, M. T. Strand, M. D. McGehee, et. al, Joule, 1, 133 (2017).

[3] T. S. Hernandez, C. B. Barile, M.T. Strand, M. D. McGehee, et. al, ACS Energy Letters, 3, 104 (2018).

25. Detailed studies on the photocatalytic properties of co-catalyst modified Rh-doped SrTiO3 for selective hydrogen evolution

William Gaieck, Sam Keene, Shane Ardo, University of California, Irvine

Solar photoelectrochemical and photocatalytic water splitting produce H_2, which can be used as a fuel or for seasonal energy storage. Efficient designs for this process include coupling separate photovoltaic and electrolyzer devices or an integrated wafer-based construct. Unfortunately, these designs are costly, relying on relatively large quantities of precious metal electrocatalysts and intensive fabrication/processing methods. In contrast to these designs is the particle slurry reactor where the hydrogen evolution reaction and the oxygen evolution reaction occur in different compartments, and the photocatalyst particles are connected ionically and electronically via a solution redox shuttle. This design is noteworthy because it has a credible pathway toward a technology that generates hydrogen that is cost-competitive with hydrogen produced from fossil fuels on an energy equivalent basis1. Herein, I report on my recent progress in component-level optimization of Rh-doped $SrTiO_3$ photocatalyst particles and $Fe^{3+/2+}$ aqueous redox shuttles. The unique aspects of this work are monitoring of the solar-to-hydrogen efficiency using in-line and operando mass spectrometry and gas chromatography, studies on the effects of changes in ambient atmosphere, particle size effects, and optical properties of slurry mixtures. Moreover, for the first time accurate internal quantum yields for these state-of-the-art materials are reported.

(1) B. D. James, G. N. Baum, J. Perez and K. N. Baum, Technoeconomic Analysis of Photoelectrochemical (PEC) Hydrogen Production, Directed Technologies Inc., (US DOE Contract no. GS-10F-009J), Arlington, VA, 2009.

26. Molecular species forming at the α-Fe_2O_3 and TiO_2 nanoparticle–aqueous solution interface

Robert Seidel, Hebatallah Ali, Marvin N. Pohl, and Bernd Winter, Helmholtz-Zentrum Berlin, Germany

With the recent vast experimental advances photoelectron spectroscopy has now become applicable even for the investigation of solid–liquid interfaces, enabling in situ photoemission characterization of electrochemical (aqueous) systems, and in particular allowing to study chemical reactions at electrode–electrolyte interfaces.

Among the most pressing questions with regard to the molecular-level understanding of electrolyte-electrode interfaces are how ions adsorb at the solid–solution interface, how interfacial ions are solvated, how the solvent molecules respond, and how all this affects charge-state and energy transfer across the interface. I will present recent liquid-jet measurements on metal oxide nanoparticle/aqueous interfaces, especially, α-Fe_2O_3 [1] and anatase phase TiO_2,[2] and I will demonstrate the usefulness of valence and (resonant) Auger spectroscopy to study the electronic structure and the solvation behavior of these systems. Most noteworthy, resonant photoelectron spectroscopy is shown to be sufficiently sensitive for the detection of adsorbed hydroxyl species, resulting from H_2O dissociation at the nanoparticle surface in aqueous solution. Additionally, from the experimental fraction of local versus non-local autoionization signals we then find a very fast, approximately 1 fs, charge transfer time from interfacial Fe3+ in hematite into the environment. Our experiments are complementary to ambient-pressure photoemission studies on solid–electrolyte systems, and also highlight the multiple aspects of photoemission that need to be explored for a full characterization of the transition-metal-oxide nanoparticle surface in aqueous phase.

[1] Chem. Sci., 2018, 9, 4511

[2] Rev. Sci. Instrum., 2017, 88, 073107

27. Using molecule-surface interactions to improve photoelectrochemical device performance

Ashwathi Iyer, Elif Ertekin, University of Illinois, Urbana

Recently, there has been renewed interest in using molecule/surface interactions to improve device performance. Focusing broadly on photoelectrochemical (PEC) water splitting cells, three density functional theory (DFT) studies are showcased on how these interactions can be used to design better photoelectrodes. In the first study, the overpotential of the oxygen evolution reaction (OER) on titanium dioxide (TiO_2) photoanodes is reduced by leveraging the interactions between adsorbates on the TiO_2 surface and the polarization of a ferroelectric support. In the second study, DFT is combined with device modeling to improve the efficiency of Si(111) hydrogen evolution photocathodes functionalized with organic molecules. The organic molecules act both as a passivating layer and improve charge separation by tuning the barrier height at the photocathode surface. Theoretical results are validated against experimental measurements of barrier heights. In the third study, molecule/surface interactions are used to model doped silicon slabs at experimental doping densities in a computationally tractable manner. Si(111) slabs are functionalized with organic donor or acceptor molecules, which dope the first few silicon monolayers n-type or p-type respectively. This model system is then used to validate experimental measurements of surface dipoles and the charge state of silicon dangling bonds. Even though this study focuses on Si(111) photocathodes, the approach presented can be used to computationally study doped slabs of any material and for any application. Our work points to the versatility and effectiveness of using molecule/surface interactions to tune and model a range of device properties for many different device applications.

28. Designing and characterizing photo-chloride dyes: the last major hurdle to realizing direct light-driven desalination

Rohit Bhide, Joseph Cardon, Shane Ardo, University of California, Irvine

Light-driven chloride pumps made from a photo-chloride dye bound to an ion-selective membrane could potentially be used for direct solar seawater desalination. A chloride pump drives chloride ions across an ion-selective membrane and is predicted to have better desalination efficiency as compared to a light-driven proton pump, in which part of photovoltage is wasted in transporting protons across the membrane. A photo-chloride dye shows no chloride ion binding in the ground state. However, in the MLCT excited state, such a dye can bind a chloride ion reversibly, or vice versa. This excited-state ion binding results in changes in the emission spectrum of the photo-chloride dye and can be monitored spectroscopically. Via steady-state absorption and photoluminescence titrations of these dyes at various chloride ion concentrations in aqueous medium, the ground-state and excited-state pKCl values were measured. No significant change in the absorption spectrum of the dye with varying chloride ion concentration was recorded. The steady-state photoluminescence, however, showed an increase in emission intensity with the increase in chloride ion concentration, which could be attributed to enhanced chloride ion binding in the excited-state. The emission intensity versus the pCl plot follows a sigmoidal curve and the excited state pKCl is calculated. Further investigations on mechanistic details are underway. It is unclear whether in the excited state, the chloride ions bind to the metal core or to the ligands present in the dye. Spectroscopic methods including H-NMR shifts and transient absorption and time-resolved photoluminescence spectroscopies are used to determine the thermodynamics of binding.

29. Mapping losses in photoelectrochemical cells for solar energy storage

Gideon Segev, Chang-Ming Jiang, Gregory Zaborski, Jason K. Cooper, Francesca M. Toma, Ian D. Sharp, Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Lab, Berkeley,

Detailed understanding of the opto-electronic properties of semiconductors and the driving forces and loss mechanisms that limit device performance is essential to the development of high efficiency solar photoelectrochemical storage systems. However, many new materials and systems are difficult to model and only few experimental methods are available for direct characterization of dominant loss processes under operating conditions. To this end, empirical extraction of the spatial collection efficiency (SCE) is an operando, analytical tool to study new materials, and devices. Defined as the fraction of charge carriers that are photogenerated at a given location that contribute to the measured current, the SCE provides a functional depth profile of the active regions in the device. By combining external quantum efficiency (EQE) measurements with optical modeling, we have extracted SCE cross-sectional profiles of emerging materials and photoelectrochemical cells. Analyzing the SCE at different operating potentials while performing different chemical reactions allows distinguishing between bulk and surface losses. Furthermore, by focusing on the SCE at the surface, we were able to discern between surface losses attributed to slow reaction kinetics and fast surface recombination processes through charged band states. In this contribution, we analyze the transport properties of four different phases of copper vanadate photoanodes with a wide range of copper vanadium ratios. The spatial collection efficiency analysis is used to extract the potential dependent surface reactivity and collection length thus shedding light on the role of copper in Fermi level pinning at the electrolyte interface and the photoanode dopant concentration.

30. A scanning photoelectrochemical microscopy screening study of doped $BiVO_4$ photocatalysts for efficient solar water splitting

Pravin S. Shinde, Xiaoniu Peng, Jue Wang, Yanxiao Ma, Louis E. McNamara, Nathan I. Hammer, Arunava Gupta and Shanlin Pan, University of Alabama

A scanning photoelectrochemical microscopy (SPECM) technique was used to investigate spatially resolved electrochemical/photoelectrochemical (PEC) properties of semiconductors. Herein, we present a SPECM study of cobalt-doped bismuth vanadate (Co-BiVO4) photocatalyst for efficient solar water splitting. For SPECM screening study, the arrays of Co-doped BiVO4 spots (400 µm) with varying Co (0 -15%) were synthesized on conducting substrates with appropriate volumetric proportions of Co, Bi and V precursors in pre-programmed fashion. The SPECM photocurrent imaging of arrays was performed using a 405 nm light through an optical fiber from 0.5 M Na_2SO_4 electrolyte. The optimal doping of Cobalt (6%) in BiVO4 showed ~200% photocurrent in the raster-scanned SPECM image. SPECM results were validated by preparing the pristine and 6% Cobalt-doped BiVO4 electrodes in thin film form by spin-coating the precursors of Co, Bi and V in a similar proportion. The PEC results of thin film electrodes showed similar photocurrent improvement with cathodic shift in water oxidation onset potential. Such Co-doped BiVO4 also improved the PEC performance when coupled with WO3 photoanode in a heterojunction. The enhanced water splitting performance by Co is attributed to largely due to enhancement in water oxidation kinetics via formation of cobalt oxide (Co3O4) on the surface of BiVO4, and partially due to enrichment in electronic conductivity of BiVO4 in the presence of Co. Finally, a Z-scheme solar water splitting system is demonstrated by combining an optimized Co-doped BiVO4/WO3 photoanode with a $CuO/CuBi_2O_4$ photocathode in a two-electrode configuration to generate hydrogen and oxygen at no external bias.

31. Atomic layer deposited coatings for durable (photo)electrochemical hydrogen evolution

David W Palm, Christopher Muzzillo, Nicolas Gaillard, Thomas F Jaramillo
Stanford University

A technologically relevant solar-driven water splitting device will require durability that translates to years of standalone operation. Since intrinsic stability has yet to be demonstrated for any efficient light-absorbing material, the field has investigated a number of conformal coatings to isolate these materials from direct contact with the aqueous electrolyte. In this work, we investigated the (photo)electrochemical durability of two canonical metal oxide and chalcogenide coatings derived from atomic layer deposition (ALD): titania (TiO_2) and molybdenum disulfide (MoS_2).

Both electrocatalytic experiments and photoelectrochemical experiments involving coated chalcopyrite (CuGaxSey) photocathodes were performed. Through x-ray photoelectron spectroscopic (XPS) interrogation of as-prepared samples and of those that had undergone electrochemical testing, some surprising results emerged. While ALD-deposited TiO_2 coatings have imparted good durability to photoanodes under oxygen-evolving potentials in basic conditions,[1,2] our analogously-prepared TiO_2 coatings completely degraded over a couple of hours of operation at hydrogen-evolving potentials in acidic conditions. Similarly, MoS_2 coatings prepared by the sulfidization of ALD-deposited molybdenum trioxide (MoO3) were shown to be dramatically less durable than previously reported Mo metal-derived MoS_2 coatings under hydrogen-evolving potentials in acidic conditions. High temperature anneals were shown to markedly improve the hydrogen-evolving durability of the ALD-deposited TiO_2 coatings, slowing the initial catalytic degradation rate by a factor of five. Additional next-generation oxide and chalcogenide coatings for hydrogen evolution were also examined and their results are presented herein.

[1] Chen, Y. W., et al. ($_2$011). Nature Materials, 10(7), 539–544.

[2] Hu, S., et al. (2014). Science, 344(6187), 1005–9.

32. Enabling Efficient, Replicable Electrocatalytic N_2 Reduction

Adam C. Nielander, Thomas F. Jaramillo, Stanford University

The activation of molecular nitrogen toward reduction is key to the efficient synthesis of valuable ammonia-based agricultural fertilizers. Utilizing an applied electric potential to overcome the kinetic barriers associated with N_2 transformation to NH3 in lieu of the high temperatures and pressures required for the thermal activation of N_2 via the Haber-Bosch process would promote both the coupling of ammonia production to renewable electricity sources (e.g. wind, solar) and the decentralization of ammonia production.

We have explored the electrocatalytic reduction of N_2 with a range of materials predicted to have measurable nitrogen reduction activity via DFT calculations. However, low selectivity toward non-H_2 products and contamination from ambient NH3 sources hampered analysis of N_2 reduction efficacy. Nonaqueous electrolytes were employed to attempt to reduce selectivity toward proton reduction, and the use of nonaqueous electrolytes required the development of analytical techniques capable of readily and accurately detecting NH3 in nonaqueous electrolyte while minimizing the possibility of further contamination and discriminating against NH3 contamination sources. A simple method for the efficient detection of ammonia in a variety nonaqueous electrolyte solutions via NMR was reported and quantified. Compatible solvents included ethanol, THF, DMSO, acetonitrile, propylene carbonate, diethyl either, and hexanes. The efficacy of the classic indophenol method in nonaqueous electrolyte solutions was also quantified.

33. Direct solar-to-hydrogen conversion with tandem III-V photoelectrodes

James L. Young, Myles A. Steiner, Henning Doesher, Ryan M. France, John A. Turner, Todd G. Deutsch, National Renewable Energy Laboratory, Golden

This poster presents our progress toward a 20% solar-to-hydrogen (STH) efficiency water splitting photocathode based on III-V semiconductors. We incorporated several key solid-state technological advances to achieve unprecedented efficiencies exceeding 16% STH. The first improvement was to increase the device current via a non-lattice-matched 1.2 eV InGaAs grown using the inverted metamorphic multijunction (IMM) technique developed by NREL. The second modification that led to device improvement was to add a thin n-$GaInP_2$ layer to p-$GaInP_2$ to generate a buried junction, which increased the photocurrent onset or Voc of the device by several hundred mV and enabled 14% STH efficiency. Finally, we increased the top junction photon conversion efficiency by adding an AlInP window layer, which is commonly used in solid-state PV devices to reduce surface recombination. Through the use of a collimating tube, we measured our devices outdoors under direct solar illumination and verified over 16% STH conversion efficiency. I will also briefly discuss common experimental pitfalls that can influence the accuracy of measured STH efficiencies of mulitjunction absorbers.

34. Photoelectrochemical Properties of Carbon Layer Modified Cu_2O Nanoneedles and TiO_{2-x} Nanorods and their use in a Tandem Cell

Nelly Kaneza, Pravin Shinde, Yanxiao Ma, and Shanlin Pan, University of Alabama

Nanoelectrodes have high surface area that can benefit catalytic reactions such as photoelectrochemical (PEC) reactions involved in solar water splitting and photodiodes. Most characterization methods of photoelectrodes involved in solar water splitting involve three electrode configurations without considering the overpotential required to fully complete water splitting with solar energy. Heterojunction structures or tandem cells in Z-scheme are needed to fully split water without external bias. Here we present a self-driven tandem cell for Z-scheme water-splitting system that consist of carbon-modified cuprous oxide (Cx / Cu_2O) nanoneedles and oxygen-deficient titanium dioxide (TiO_{2-x}) nanorods photoelectrodes. The synthesized photoelectrodes were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), Raman spectroscopy, and electrochemical impedance spectroscopy (EIS). The tandem cell performance was analyzed through the analysis of current-voltage responses in different photoelectrodes configurations. The PEC properties of the C10 / Cu_2O nanoneedles coupled with TiO_{2-x} nanorods in tandem configuration showed promising insights toward low cost-efficient unassisted solar water splitting.

35. Excited state processes that govern photochemical H_2 generation in CdS nanocrystal-hydrogenase complexes

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University of Colorado, Boulder, CO

A validated numerical model capable of predicting the photocurrent-voltage characteristic and of identifying the critical parameters affecting the performance of oxide and oxynitride particle-based photoelectrodes was developed. Here, we used particle-based $LaTiO_2N$ photoelectrodes as the model system. Two different types of electrodes were studied: $LaTiO_2N$ photoelectrodes with TiO_2 inter-particle connections and the same photoelectrodes with $NiO_x/CoO_x/Co(OH)_2$ co-catalysts and a Ta_2O_5 passivation layer. The necessary material parameters, namely complex refractive index, permittivity, density of states of the conduction and valence bands, charge mobilities, flatband potential, doping concentration, recombination lifetimes and interfacial hole transfer velocity, were derived by density functional theory calculations, dedicated experiments, and fitting of the numerically determined photocurrent-voltage curves to the measured ones under back-side illumination. The model was validated by comparing its prediction to front-side illumination photocurrent-voltage measurements. A parametric study was then carried out to provide an extensive set of material design guidelines and key parameters for high-performing particle-based $LaTiO_2N$ photoelectrodes. The interfacial hole transfer velocity was identified as the most significant parameter for the performance of $LaTiO_2N$ photoelectrodes.