Telluride Workshop

Solar Solutions to Energy and Environmental Problems

Aug. 3-7, 2015
Telluride Elementary School @ 447 W Columbia Ave, Telluride CO
Co-Organizers: Jao van de Lagemaat and Ksenija Glusac
TSRC Host: Mark Kozak, 970-708-4426

Sunday, August 2

6:30 – 8:30 pm Reception at the Arroyo Wine Bar. Badges can be collected from TSRC representatives in the Sheridan bar across the street 6-9 pm.

Monday, August 3

8:00 – 8:30 Breakfast at the TSRC meeting site for participants only
8:30 Welcome and Introductory remarks - Jao van de Lagemaat and Ksenija Glusac

Singlet Fission and Other Molecular Multiexciton Processes

9:00 – 9:45 *Structural Design Rules for Singlet Fission Materials*
Josef Michl, CU Boulder

9:45 – 10:05 *Singlet-Based Cooperative Energy Pooling for Photon Upconversion*
Daniel Weingarten, CU Boulder

10:05 – 10:50 *Theory of Singlet Fission in Carotenoid and Acene Crystals, and in Low Band Gap Donor-Acceptor Polymers*
Sumit Mazumdar, U of Arizona

10:50 – 11:35 *Singlet Fission & Solar Energy Conversion Beyond the Limit*
Xiaoyang Zhu, Columbia

11:35 – 1:00 Catered Lunch Provided at the TSRC Meeting Site

1:00 – 2:00 Discussion: *Inexpensive ways of exceeding the Shockley-Queisser limit (singlet fission, MEG, hot carriers, photon pooling).*

Molecular Catalysis

2:00 – 2:45 *Thermodynamic Considerations in the Design of Molecular Electrocatalysts for Efficient H^+ and CO_2 Reduction*

Jenny Yang, UC Irvine

2:45 – 3:30 *New Systems for the Conversion of* CO_2 *to Fuels using Sunlight*
Joel Rosenthal, U of Delaware

3:30 – 4:30 Discussion: *(a) How to capture* CO_2 *that is already dispersed in air? (b) Stability of molecular catalysts.*

Tuesday, August 4

8:00 – 8:30 Breakfast at the TSRC meeting site for participants only

Dye Sensitization and Photoelectrodes

8:30 – 9:15 *Dye-Sensitized Solar Fuels and Solar Batteries*
Yiying Wu, OSU

9:15 – 10:00 *Merging Dye Sensitization and Catalysis: Photochemical Fuel Forming Reactions Using p-GaP Photoelectrode and Biomimetic* NAD^+*/NADH Analogs*
Ksenija Glusac, BGSU

10:00 – 10:45 *Designing Chemically Robust Solar-Responsive Oxide Materials for Photoelectrochemical Oxidation Reactions*
Bart Bartlett, U of Michigan

10:45– 11:45 Discussion: *Benchmarks for assessing solar energy-to-chemical energy conversion*

11:45– 1:00 Catered Lunch Provided at the TSRC Meeting Site

1:00 – 1:45 *Dye-Sensitized Photoelectrosynthesis Cells*
Gerald J. Meyer, Chapel Hill

1:45 – 2:30 *Semiconductor Systems and Catalysis for Photoelectrochemical Water Splitting*
John Turner, NREL

2:30 – 3:15 *Hybrid Materials for Solar Fuel Production*
Gary Moore, ASU

3:15 – 4:00 *Protons: The Other Charge Carrier in Solar Fuels Reactions*
Shane Ardo, UC Irvine

4:00 – 5:00 Discussion*: 1) Transparent electrodes; 2) Economic, environmental impact, and competitiveness of future generation PV and solar fuels compared to Si and other present day technologies; 3) pH effects in solar water splitting.*

6:00 - 7:15 TSRC town talk: Forest Rohwer, Professor of Biology, San Diego State University: *Personalized Medicine for Coral Reefs*, Telluride Conference Center in Mountain Village

Wednesday, August 5

8:00 - 8:30 am breakfast at the TSRC meeting site for participants only

8 am – 3 pm Via Ferrata/Free time

12:00– 1:00 Catered Lunch Provided at the TSRC Meeting Site

Metal-Organic Frameworks and Proton Transport

4:00 – 4:45 *AIM-ing for Catalyst Discovery*
Joseph Hupp, Northwestern

4:45 – 5:30 *Exploring Metal Organic Frameworks for Use as Integrated Artificial Photosynthetic Assemblies*
Amanda Morris, Virginia Tech

5:30 – 6:00 Discussio*n: Ideal architectures for photoelectrochemical devices (wireless vs. wired devices)*

6:00 – 9:00 TSRC picnic: Telluride Elementary School at 447 W Columbia Ave (under the tent - family welcome)

Thursday, August 6

Perovskites

8:00 – 8:30 Breakfast at the TSRC meeting site for participants only

8:30 – 9:15 *Perovskite Solar Cells: Materials, Devices and R&D Opportunities*
Kai Zhu, NREL

9:15 – 10:00 *Interfacial Energetics and Ultrafast Dynamics of Excitons and Charge Carriers in Perovskites*

Jao van de Lagemaat, NREL

10:00 – 10:45 *Prospects for Future Generation Solar Photon Conversion to PV and Fuels: Multiple Exciton Generation in Quantum Dot Solar Cells, Organic PV and Singlet Fission, and Perovskites*
Arthur Nozik, CU Boulder

10:45 – 11:45 Discussion: *Perovskites (their effect on dye-sensitized cells and organic photovoltaics; what makes the charge separation in perovskites so efficient)*

11:45 – 1:00 Catered Lunch Provided at the TSRC Meeting Site

Organic PVs

1:00 – 1:45 *Redox Potentials Without Electrolyte and Charge Transport Along Conjugated Chains*
John Miller, Brookhaven

1:45 – 2:30 *The Prospects of Using Spectrum Splitting as a Feasible Route to Exceeding the Shockley Queisser Limit*
Sean Shaheen, CU Boulder

2:30 – 2:50 *CELIV Measurements of Charge Transport Properties and Their Dependence on Polymer Packing in Organic Photovoltaics*
Alexander Dixon, CU Boulder

2:50 – 3:50 Discussion: *1. Charge Transport in Defect Systems; 2. What are the necessary steps towards a commercial solar water splitting device?*

6:00 – 8:00 Closing dinner, location TBD

Friday, August 7

7:30 - 8:00 am breakfast at the TSRC meeting site for participants only

PROTONS: The other charge carrier in solar fuels reactions

Shane Ardo, Department of Chemistry, University of California, Irvine, CA 92697-2025, USA, E-mail: ardo@uci.edu

Generation of fuels from sunlight requires the concerted movement of electrons and protons. For example, in order to make and break chemical bonds during solar water splitting, four protons and four electrons must be removed from water to generate O_2, and two protons and two electrons must be joined to form H_2. Sunlight indirectly drives these reactions by transferring the energy in solar photons to the electrons; the electrons then drive both the electrochemical reactions and proton transport. The main question I will pose and discuss relates to the converse scenario: *Can solar photons energize protons which then drive both the reactions and electron transport*? To begin to answer this question I will present a literature overview and then share my group's recent research results using ionically conductive organic photovoltaics, where light drives *ion* transport instead of electron transport, using dye-sensitized Nafion membranes and track-etched conical nanopores in poly(ethylene terephthalate) (PET) plastic sheets. Time-permitting, related work consisting of numerical device physics simulations of an integrated solar desalination device that contains an interdigitated back-contact crystalline silicon wafer and a laboratory-scale prototype that performs electrodialysis will be presented.

A second topic that is of great interest and debate in the solar fuels community is electrolyte pH. It is rather well-known that the initial demonstration of solar water splitting by Fujishima and Honda in the early 1970s used rutile TiO_2, which required that the catholyte was more acidic than the anolyte. Inherently this was not problematic, but in this specific demonstration it was because a salt bridge was used to join the electrolytes and thus the pH gradient likely dissipated over the course of days. The main question I will pose and discuss is: *What are the benefits and drawbacks of using various pH conditions, either alone or simultaneously, in solar fuels devices*? To start the conversation I will present a literature overview and, time-permitting, I will share my group's recent research results on local pH changes during water electrolysis, interpretation of electrochemical data when two different pH electrolytes are used simultaneously, and proton-selective membranes.

Designing Chemically Robust Solar-Responsive Oxide Materials for Photoelectrochemical Oxidation Reactions

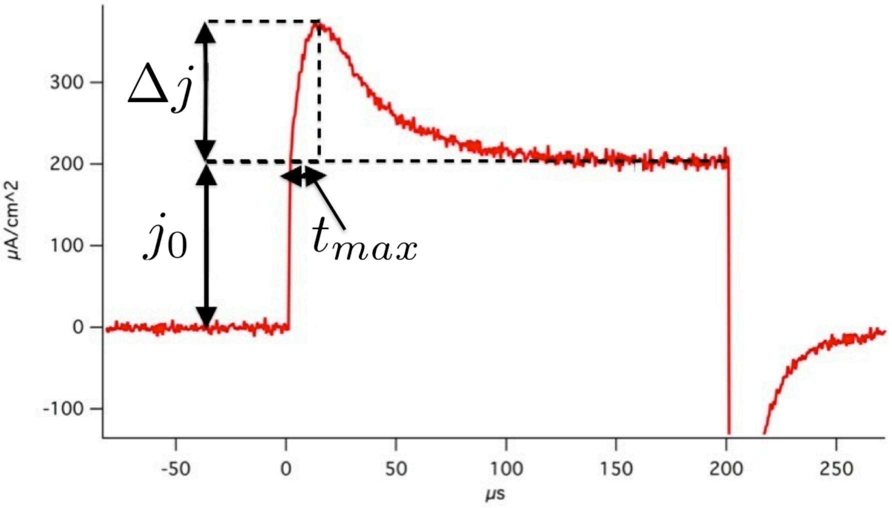
Bart M. Bartlett, *University of Michigan*, *Department of Chemistry*, *930 N. University Avenue*, *Ann Arbor, MI 48109-1055*, *Tele: (734) 615-9279*, *E-mail: bartmb@umich.edu*

Solar driven water splitting for large-scale hydrogen fuel production from semiconductor photoelectrodes has the potential to provide energy on large scale from renewable, sustainable sources. My group's research focuses on generating ternary oxide thin film photoelectrodes prepared by low-temperature, solution-based processes for the kinetically more demanding oxygen-evolution reaction. The workhorse material in our group is $CuWO_4$, which we have synthesized by several routes: electrochemical deposition, sol-gel processing, and spray pyrolysis. These methods afford highly reproducible, chemically pure, and robust electrodes on transparent conducting substrates. $CuWO_4$ is an *n*-type semiconductor with a band-gap energy of ~2.4 eV. Thin films of $CuWO_4$ photooxidize water with simulated solar radiation with a nearly quantitative Faradaic efficiency for O_2 evolution in borate-buffered saline solution. Most important, they are chemically stable against photocorrosion when illuminated with visible light at neutral pH, and they are selective for water oxidation in the presence of the Cl^- or HSO_4^-, common anions in aqueous electrolytes. These characteristics are a significant improvement to the more commonly studied binary phase, WO_3. Moreover, we can deposit amorphous FeOOH on WO_3 or anchor derivatives of known molecular water oxidation catalysts such as $Fe(tebppmcn)Cl_2$ (tebppmcn is the κ^4-nitrogen donor, tetraethyl *N,N'*-bis(2-methylpyridyl-4-phosphonate)-*N,N'*-dimethyl-cyclohexyl-diamine) toWO_3 to improve its efficiency for selective photoelectrochemical water oxidation. Finally, current efforts focus on extending the reaction scope beyond water oxidation to include chemoselective oxidative amine coupling reactions on $CuWO_4$.

CELIV Measurements of Charge Transport Properties and Their Dependence on Polymer Packing in Organic Photovoltaics

Alex G. Dixon' Department of Physics, University of Denver, Denver, CO 80208, USA

Charge Extraction by Linearly Increasing Voltage (CELIV) is a powerful technique for performing measurements of charge carrier mobility and recombination of semiconductor materials in functioning solar cell devices. In this work, we have used variations on this technique to investigate the charge transport properties in poly(3-hexylthiophene) (P3HT) and how they are impacted by changes to the polymer molecular weight, and thus polymer microstructure. We found that the carrier mobility peaks at a mid-range molecular weight (~47 kDa), where the polymer forms a semicrystalline structure, but the degree of recombination continues to decrease with increasing molecular weight. We also examined how the small molecular differences between the polymers PTB-7 and PCE-10 (PBDTT-FTTE) can affect their packing and thus the mobilities in the polymer. Using Metal-Insulator-Semiconductor CELIV (MIS-CELIV) measurements, we have found that the substitution of thiophene rings for oxygen in the side chains of PCE-10 causes a roughly 3x increase in hole mobility over PTB7 in bulk heterojunction blends.



MERGING DYE SENSITIZATION AND CATALYSIS: PHOTOCHEMICAL FUEL FORMING REACTIONS USING P-GAP PHOTOELECTRODE AND BIOMIMETIC NAD$^+$/NADH ANALOGS

Ksenija D. Glusac, Department of Chemistry, Center for Photochemical Sciences, BGSU, Bowling Green, Ohio, 43403.

Recent scientific efforts aim to blend dye-sensitized solar cell motifs with the fuel forming water-splitting catalysis as a novel method to store the energy captured from the Sun. Our group investigates an approach towards dye-sensitized photoelectrochemical cell (DS-PEC) that consists of a dual light-harvesting system composed of a blue-absorber (p-type GaP photocathode, $\lambda_{ABS}<550$ nm) and a red absorber (dyes constructed from NAD$^+$-analogs, $\lambda_{ABS}>550$ nm). This dual absorber system increases the possible theoretical efficiency of the cell (Figure 1a). The organic molecular framework serves both as a dye sensitizer (NAD$^+$ analog) and as the H_2-evolving catalyst (NADH analog, Figure 1b), thus reducing the complexity of the solar cell.

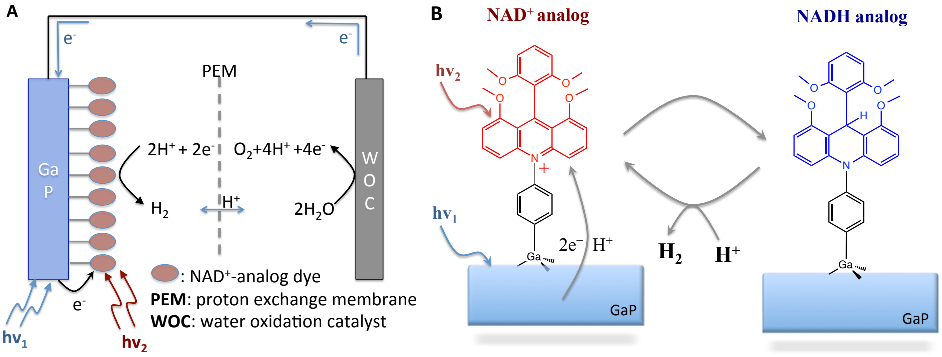


Figure 1: A) Schematic representation of the proposed DS-PEC with dual light-harvesting system consisting of p-GaP photocathode and NAD$^+$ analog dyes; B) Evolution of hydrogen in the proposed DS-PEC: upon dye sensitization, NAD$^+$ analog is converted into NADH analog, which then serves to reduce protons to molecular hydrogen.

In the present study, we investigated the GaP sensitization by a series of of cationic dyes made of flavin, acridine and triarylmethane-based frameworks. Based on the UV/Vis absorption spectra and cyclic voltammetry of the model compounds, we find that all six dyes exhibit favorable thermodynamics for the photoinduced hole injection into GaP. However, the sensitization experiments revealed that only two of the six dyes sensitized GaP at wavelengths above 550 nm. The explanation for such behavior was obtained from ultrafast pump-probe experiments, which showed that the four inefficient dyes exhibit very fast excited-state deactivation to the ground state (few picoseconds). These results provide valuable insights into the design of future, more efficient photosensitizers for GaP.

AIM-ing for Catalyst Discovery

Joseph Hupp, Northwestern

We know that for reactions relevant to solar fuels production, Nature uses catalysts featuring small, polypeptide-embedded metal-oxygen or metal-sulfur clusters. We also know that at least some catlysts (e.g. hydrogenases) are remarkably effective on a "per active site" basis. With these primitive notions as inspiration we have been focusing on ways of making atomically well defined clusters of transition metal ions and oxygen or sulfur anions, and exploring their promise as catalysts for water oxidation, water reduction, carbon fixation, and other processes. Some desirable features for candidate catalytic clusters are open metal (or sulfide) sites, immunity to aggregation, accessibility to reactants (water, protons, hydroxide, carbon dioxide, electrons, holes, and so on), and, if configured as a material, a high spatial density of active sites. Our approach to making clusters is centered on "AIM" and related methods. AIM is a meta-acronym: **A**LD **I**n **M**OFs where ALD is atomic-layer-deposition and MOFs are metal-organic frameworks. I will described some unpublished results that point to cluster-size-dependent variations in rate-determining catalytic steps, and to optimal performance by mixed-metal clusters having compositions that are forbidden based on bulk phase diagrams, but are readily accessed on the cluster scale.

DYE-SENSITIZED PHOTOELECTROSYNTHESIS CELLS

Gerald J. Meyer, Department of Chemistry, University of North Carolina at Chapel Hill
Chapel Hill, NC 27510

Solar cells based upon mesoporous thin films of nanocrystalline (anatase) TiO_2 sensitized to visible light with inorganic coordination compounds that serve as dyes continue to be of practical interest in photovoltaics. Under simulated sunlight conditions, solar-to-electrical power conversion efficiencies in excess of 11.4 % have been confirmed at certified laboratories. The sensitized materials have an enormous surface area, a long effective pathlength, and a high photoconductivity that enables fundamental spectroscopic and electrochemical study of light driven interfacial charge transfer processes. In an attempt to increase solar conversion efficiencies, we have extended this chemistry to bromide photo-oxidation. Very recent studies provide direct evidence that MLCT excited states oxidize Br^- to the Br atom on a 40 ns time scale with $-DG^o = 230$ meV. The Br atoms subsequently react with Br- to form a Br-Br chemical bond. Charge recombination to regenerate ground state reactants, $Ru^+ + Br_2^{-\bullet}$ à $Ru^{II} + 2Br^-$, was thermodynamically downhill ($-DG^o = 1.63$ eV) and occurred near the diffusional limit. The preliminary data in hand indicates that bromide oxidation can be fast and competitive with charge recombination and hence may be of use for electrical power generation. As part of the University of North Carolina at Chapel Hill Energy Frontier Research Center (UNC-EFRC) on Solar Fuels we have extended this chemistry to water oxidation and to the development of Dye-Sensitized Photoelectrosynthesis Cells (DSPECs) through molecular level studies of light driven interfacial electron transfer catalysis. We have found that single photon absorption events can be coupled to multi-electron transfer water oxidation catalysis at a sensitized mesoporous thin film materials with a core-shell structure. The DSPEC design enables solar light to be efficiently harvested and stored in the form of chemical bonds. The state-of-the-art DSPECs will be presented and the possibilities for practical applications will be discussed.

Redox Potentials Without Electrolyte and Charge Transport Along Conjugated Chains

John R. Miller, Brookhaven National Laboratory

We are attempting to determine redox potentials in the absence of electrolytes. While redox potentials measured using voltammetry and related techniques are of great and almost universal value, they remain somewhat blunt instruments for understanding the energetics of charge transfer processes in low polarity media. Charge separation in photosynthesis or in organic photovoltaics takes place in environments of low polarity that are nearly free of electrolyte. We will seek measurement of thermodynamic potentials based on a scheme involving observation of chemical equilibria without electrolytes and in the presence of electrolytes at varied concentrations. We anticipate that these measurements will be straightforward in highly polar liquids, will become more challenging in liquids of moderate dielectric constants ε of 6-10, and will be difficult for $\varepsilon < 6$. The experiments make use of capabilities of pulse radiolysis to create free ions in polar and nonpolar media. I hope workshop members will examine and discuss assumptions inherent in our methods. The method relies on determinations of ion pairing in low-polarity media and experimental methods including our new transient infrared detection with pulse radiolysis provide new insights into this old phenomenon.

I'd also discuss a continuing quest to learn the potential to understand charge and exciton transport in long conjugated molecules, which are candidates to act as "molecular wires." Charges and excitons in these polymers are typically "pretty delocalized" over a few nm, rather than highly delocalized as in some inorganic semiconductors. While this partial delocalization appears to help transport, we like to understand what limits both delocalization and transport.

Hybrid Materials for Solar Fuel Production

Gary F. Moore, *Department of Chemistry and Biochemistry, Arizona State University,*
Tempe, AZ 85287-1604, Email: gfmoore@asu.edu

Solar energy offers a desirable approach to fulfilling global human energy demands with minimal environmental impact provided efficient, low-cost systems can be developed for its capture, conversion and storage.[1-2] In biology, enzymes catalyze a myriad of technologically relevant chemical reactions by providing discrete three-dimensional environments for binding substrate, releasing product, and lowering transition-state energies along a reaction coordinate. Thus, in accordance with the Sabatier principle, they can have exceptionally high activities and, perhaps more importantly, selectivity for specific chemical transformations.

A method for facile connection of biomimetic fuel production catalysts to semiconductor photocathodes will be presented.[3-5] Successful attachment is characterized by grazing angle attenuated total reflection Fourier transform infrared spectroscopy (GATR-FTIR) as well as X-ray photoelectron spectroscopy (XPS). Photoelectrochemical experiments analyzing the energetics and efficiency of these constructs will also be discussed. These results give insights to designing improved photocathodes with additional performance gains and illustrate the potential to directly couple human-engineered catalysts for fuel production with light capture and conversion materials. This approach could allow catalysts made from earth-abundant elements to replace the use of precious metals currently implemented in many solar-fuel generator prototypes as well as other technologies capable of reducing net carbon dioxide emissions.

[1] Najafpour, M. M.; Shen, J-R.; Barber, J.; Moore, G. F.; Govindjee, **Running on Sun**. *Chemistry World,* **2012**, November, 43.

[2] Faunce, T. A.; Lubitz, W.; Rutherford, A. W.; MacFarlane D.; Moore, G. F.; Yang, P.; Nocera, D. G.; Moore, T. A.; Gregory, D. H.; Fukuzumi, S.; Yoon, K. B.; Armstrong, F. A.; Wasielewski, M. R. **Energy and Environment Policy Case for a Global Project on Artificial Photosynthesis**. *Energy Environ. Sci.* **2013**, *6***,** 695-698.

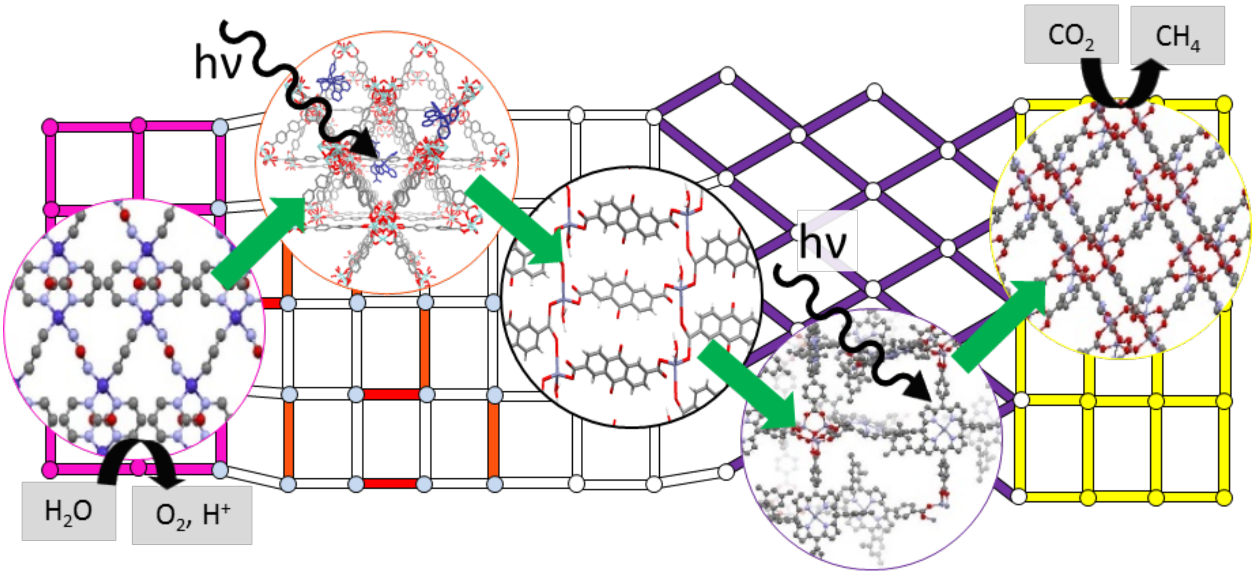
[3] Cedeno, D.; Krawicz, A.; Moore, G. F. **Hybrid Photocathodes for Solar Fuel Production: Coupling Molecular Fuel-Production Catalysts with Solid-State Light Harvesting and Conversion Technologies**. *Interface Focus* **2015**, *5*, 20140085.

[4] Krawicz, A.; Yang, J.; Anzenberg, E. Yano, J. Sharp, I. D.; Moore, G. F**.** **Photofunctional Construct That Interfaces Molecular Cobalt-Based Catalysts for H_2 Production to a Visible-Light-Absorbing Semiconductor**. *J. Am. Chem. Soc.* **2013**, *135*, 11861-11868.

[5] Cedeno, D.; Krawicz, A.; Doak, P.; Yu, M.; Neaton, J. B.; Moore, G. F. **Using Molecular Design to Control the Performance of Hydrogen-Producing Polymer-Brush-Modified Photocathodes**. *J. Phys. Chem. Lett.* **2014**, *5*, 3222-3226.

Exploring Metal Organic Frameworks for Use as Integrated Artificial Photosynthetic Assemblies

Amanda J. Morris, Assistant Professor, Department of Chemistry, Virginia Tech



Two of the remaining challenges that limit the utilization of solar energy are the development of cheap and efficient solar harvesting materials and advances in energy storage technology to overcome the intermittent nature of the sun. In the talk, the research projects to be discussed focus on the development of an integrated artificial photosynthetic array for solar energy storage. Photosynthetic systems consist of light harvesting arrays and redox mediators that can funnel the electrochemical potential stored in a molecular excited states to catalytic centers to drive the oxidation of water and the reduction of CO_2 to sugars. Many artificial approaches to this chemistry have been reported. In the Morris group, we investigate porous coordination networks (PCNs) as both light harvesters and high surface area catalysts as photosynthetic mimics. PCNs combine the synthetic diversity possible with molecular catalysts and the ease of recovery of heterogeneous catalysis. Theoretically, the high surface area of PCNs can be exploited to produce a higher catalytic rate per geometric area than those realized by other approaches. Additionally, the incorporation of molecular chromophores into networks has been show to lead to enhanced luminescence quenching. Our studies span the scope of artificial photosynthetic chemistry and include mechanistic investigations of homo-resonance energy transfer, electron transport, and catalysis within PCNs.

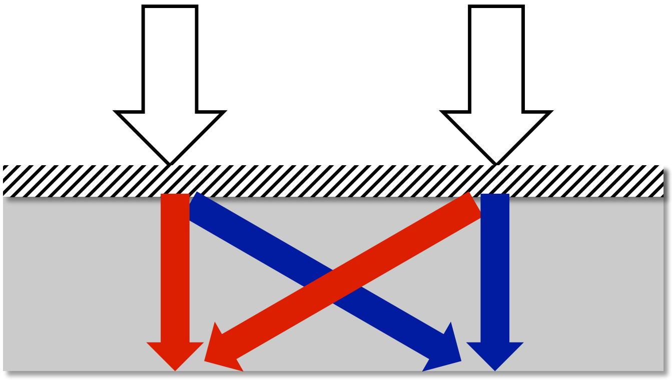
Prospects for Future Generation Solar Photon Conversion to PV and Fuels: Multiple Exciton Generation in Quantum Dot Solar Cells, Organic PV and Singlet Fission, and Perovskites

A. J. Nozik, Department of Chemistry and Biochemistry, University of Colorado, Boulder 80309 and National Renewable Energy Laboratory, Golden, CO 80401

In quantum dots (QDs), quantum rods (QRs) and unique molecular chromophores that undergo singlet fission (SF) the relaxation pathways of photoexcited states can be modified to produce efficient multiple exciton generation (MEG) from single photons. Efficient MEG has been observed in PbSe, PbS, PbTe, and Si QDs and efficient SF in molecules that satisfy specific requirements for their excited state energy levels. MEG has been reported in close-packed QD arrays where the QDs are electronically coupled in the films and thus exhibit good transport while still maintaining quantization and MEG. Relatively simple, all-inorganic QD solar cells that produce large short-circuit photocurrents and respectable power conversion efficiencies have been reported both for nanocrystalline Schottky junctions and nanocrystalline p-n or p-i-n junctions. These solar cells also show for the first time external quantum yields (QYs) for photocurrent that exceed 100% in the photon energy regions of the solar spectrum where MEG is possible (i.e.,energy conservation is satisfied); the photocurrent internal QYs from MEG as a function of photon energy match those determined via time-resolved spectroscopy and settles controversy concerning MEG. Efficient SF in thin films of molecular crystals of 1,3 diphenylisobenzofuran, tetracene, and pentacene at nearly the optimum threshold of 2Eg (Eg ≡ T_1-$S_{0 \text{ transition energy}}$) has been reported, reflecting the creation of two excited triplet states from the first excited singlet state. Various possible configurations for novel solar cells based on MEG in QDs and SF in molecules that could produce high conversion efficiencies will be presented, along with progress in developing such new types of solar cells. Recent analyses of the dramatic effects of solar concentration combined with MEG or SF on the conversion efficiency of solar cells will also be discussed. Regarding production of solar fuels, all viable systems must have the following features: (1) two photosystems arranged either in a Z-scheme analogous to biological photosynthesis, or two tandem *p-n* junctions connected in series where sufficient photopotential (1.23 V + overvoltage for H_2O splitting) is generated to drive the redox reactions; (2) strong absorption of solar photons; (3) efficient separation of the photogenerated e-h pairs, (4) efficient transport to and collection of the separated carriers at electrocatalytic surfaces; (5) low overvoltages; (6) appropriate alignment of the redox potentials in the photoelectrodes with those of the fuel-producing reactions; and (7) resistance to dark-and photo-corrosion achieving long-term photostability. Cells with buried junctions in a tandem p-n configuration or a Z-scheme can achieve these requirements, and assuming an overvoltage of 0.4V the optimal bandgaps are 0.8 eV and 1.5 eV, and the maximum PCE is 33%. The prognosis for the large scale implementation of these future generation approaches to PV and solar fuels will be discussed.

The Prospects of Using Spectrum Splitting as a Feasible Route to Exceeding the Shockley Queisser Limit

Sean E. Shaheen, *ECEE Department, Department of Physics, Renewable and Sustainable Energy Institute University of Colorado Boulder, Boulder, Colorado, 80309*



The spatial separation of the solar spectrum through optical engineering, known as spectrum splitting, allows for the fabrication of multijunction photovoltaic devices in geometries other than the vertically-stacked architectures commonly used. This allows for simplification of some of the design constraints and potential cost reductions while maintaining the fundamental efficiency enhancements enabled by the multiple light absorbing junctions. I will discuss fundamental and practical efficiency gains possible with the technique and show preliminary data from a tandem OPV spectrum splitting system. This system utilizes a holographic spectrum splitting optical element integrated with two OPV devices with optical band gaps of 1.6 eV and 1.9 eV. The resulting power conversion efficiency of the system shows a 12% relative increase over either of the individual junctions [1]. I will conclude with a few, broad comments of the feasibility of the technique, and of PV in general, to addressing the global energy crises.

[1] Shelby D. Vorndran, Silvana Ayala, Yuechen Wu, Juan M. Russo, Raymond K. Kostuk, Jacob Friedlein, Sean E. Shaheen, "Holographic Spectral Beamsplitting for Increased Organic Photovoltaic Conversion Efficiency", *Proc. SPIE 9184, Organic Photovoltaics XV,* 918423 (6 October 2014).

Semiconductor systems and Catalysis for Photoelectrochemical Water Splitting

John A. Turner, Research Fellow, National Renewable Energy Laboratory Golden, CO 80401, John.Turner@nrel.gov

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

Recent technoeconomic analysis studies indicate that a 20% solar-to-hydrogen PEC conversion efficiency is necessary for a commercially viable system. Additional requirements of lifetime (years), and cells costs (<\$400/m^2) make a working device extremely challenging.

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

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

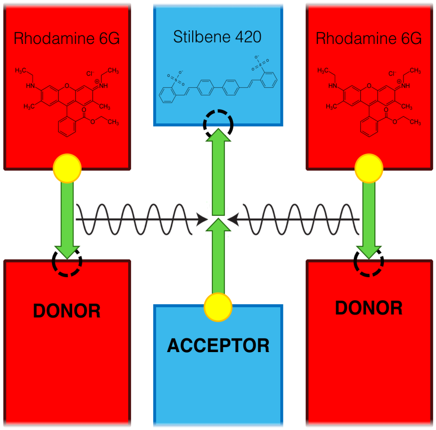
Incorporation of proper electrocatalysts onto the illuminated SC surface is necessary to both stabilize the PEC interface and increase catalysis, thus enhancing the overall device performance. Noble metals, particularly platinum, are mostly commonly applied as they are the most active for the water redox reactions. The branching ratio between catalysis and corrosion must be extremely high ($>10^6$) in order for the system to have the necessary lifetime, thus the catalysts must have a very high turnover frequency (TOF) and turnover number (TON). Nobel metals are neither earth abundant nor low-cost, so identifying catalytic systems that can match the activity and stability of platinum but are based on earth abundant materials are clearly a high-priority area of research. Such materials for SC surface modification are particularly beneficial if they are potentially low-cost and scalable, transparent and conductive while also highly catalytically active and stable. Work on hydrogen evolution catalysts has been a very active area of research where numerous molecular, nanomaterial, and bulk catalysts have been developed.

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

Cooperative Energy Pooling: Singlet-Based Upconversion in Organic Thin Films

Daniel H. Weingarten

Department of Physics, Renewable and Sustainable Energy Institute University of Colorado Boulder,
Boulder, Colorado, 80309



Solid-state photon upconversion has many potential applications, from nonlinear photonics and biophotonics to expanding the spectrum available for solar energy harvest. Here we demonstrate a novel upconversion pathway in an organic thin film utilizing two-photon absorption (2PA) properties to improve upconversion efficiency via a process called Cooperative Energy Pooling (CEP). By using a blend geometry of sensitizer and upconverter chromophores, the energy of low-energy photons absorbed by the sensitizers is temporarily localized near the upconverting chromophores, effectively increasing the excitation energy available to the upconverter chromophores at any given moment in time and relaxing the excitation intensity dependence of the 2PA mechanism. In blend films of Stilbene-420 (upconverter) and Rhodamine 6G (sensitizer) we observe a tenfold increase in up-converted fluorescence compared to the fluorescence yield of 2PA in pristine stilbene films. While 2PA typically has quadratic dependence on excitation intensity, these blend films exhibit sub-quadratic intensity dependence, which dramatically improves upconversion efficiency at lower excitation intensities. While upconversion has been repeatedly demonstrated in lanthanide nanoparticle and triplet-triplet annihilation systems, these mechanisms involve rare elements or multiple inherent intersystem crossing energy-loss steps, respectively. Time-resolved photoluminescence decay measurements reveal that all excited states involved in the CEP mechanism are singlets, indicating the potential for reduced energy losses when compared to TTA while maintaining the materials-abundance advantages of using an all-organic system. Many incidental loss pathways are identified in this system, indicating a potential for dramatically higher upconversion efficiencies and pointing the way towards design guidelines for improved CEP systems.

Thermodynamic Considerations in the Design of Molecular Electrocatalysts for Efficient H+ and CO2 Reduction

Jenny Yang, UC Irvine

Thermodynamic mesaurements of the ionicity of the M-H bond, or hydride donor ability, can provide a framework for designing new catalysts. In these studies, we are measuring the hydride donor ability of a series of transition metal complexes in organic solvents and water. This information is being used to rationalize reactivity and develop new catalysts for H_2O reduction to H_2 and CO_2 reduction to $HCO2^-$. Electrocatalysts for fuel forming reactions using CO_2 are important for energy storage applications. Selectivity for CO2 reduction in the presence of H+ still remains a challenge, as competitive H2 formation can be a major contribution. The relationship between CO2 activation, reduction potential, and basicity will be discussed for a series of molecular cobalt complexes. Strategies and progess in catalyst design to improve the selectivity toward CO_2 reduction using thermodynamic considerations will be discussed.

Singlet Fission & Solar Energy Conversion Beyond the Limit

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The absorption of one photon by a semiconductor material usually creates one electron-hole pair, but this general rule breaks down in a few organic semiconductors, where one photon absorption may result in two electron-hole pairs in a process called singlet exciton. Singlet fission may be used to increase the efficiency of solar energy conversion. Recent measurements in my group by time-resolved two-photon photoemission (TR-2PPE) spectroscopy in crystalline tetracene, pentacene, and hexacene provided spectroscopic signatures in singlet fission of a critical intermediate known as the multiexciton state. These measurements provide an experimental foundation for a quantum coherent mechanism in which the electronic coupling creates a quantum superposition of the singlet and the multiexciton state by optical excitation. We demonstrate the feasibility of harvesting the multiexciton state for multiple charge carriers or the triplets. We outline a set of design principles for molecular materials with high singlet fission yield and for the implementation of singlet fission in solar cells with power conversion efficiency beyond the Shockley-Queisser limit.

[1] W.-L. Chan, M. Ligges, A. Jailaubekov, L. Kaake, L. Miaja-Avila, X.-Y. Zhu, "Observing the Multi-Exciton State in Singlet Fission and Ensuing Ultrafast Multi-Electron Transfer," *Science* 334 (2011) 1541-1545.

[2] W.-L. Chan, M. Ligges, X.-Y. Zhu, "The energy barrier in singlet fission can be overcome through coherent coupling and entropic gain," *Nature Chem.* 4 (2012) 840-845.

[3] W.-L. Chan, J. R. Tritsch, X.-Y. Zhu, "Harvesting singlet fission for solar energy conversion: one versus two electron transfer from the quantum mechanical superposition," *J. Am. Chem. Soc.* 134 (2012) 18295–18302.

[4] W.-L. Chan et al. "The quantum coherent mechanism for singlet fission: experiment and theory," *Acct. Chem. Res.* 46 (2013) 1321-1329.

[5] J. R. Tritsch, W.-L. Chan, X. Wu, N. R. Monahan, X.-Y. Zhu, "Harvesting singlet fission for solar energy conversion via triplet energy transfer," *Nature Commun.* 4 (2013) 2679.

[6] N. R. Monohan, X.-Y. Zhu, "Charge Transfer-Mediated Singlet Fission" *Annu. Rev. Phys. Chem.* **2015**, *66*, 601-618.

[7] M. Tuan Trinh, Yu Zhong, Theanne Schiros, Qishui Chen, Steffen Jockusch, Matthew Y. Sfeir, Michael Steigerwald, Colin Nuckolls, X.-Y. Zhu, "Intra- to Inter-Molecular Singlet Fission," *J. Phys. Chem. C* **2015**, *119*, 1312-1319.

[8] Erik Busby, Jianlong Xia, Qin Wu, Jonathan Z. Low, Rui Song, John R. Miller, X-Y. Zhu, Luis M. Campos, Matthew Y. Sfeir, A design strategy for intramolecular singlet fission mediated by charge-transfer states in donor-acceptor systems. *Nature Mater*. **2015**, *14*, 426-433.

Perovskite Solar Cells: Materials, Devices, and R&D Opportunities

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Organic-inorganic hybrid halide perovskites have rapidly become a focal point of the photovoltaic (PV) community as a promising next-generation PV technology [1,2]. Various perovskite absorbers (e.g., $CH_3NH_3PbI_3$, $CH_3NH_3PbI_{3-x}Cl_x$, and $CH_3NH_3PbBr_3$) and device architectures (e.g., mesoporous, planar, and mesoporous-planar hybrid cell configurations) have been examined with promising results by using either solution processing or thermal evaporation [3,4]. The certified efficiency of a single-junction perovskite solar cell (PSC) has reached 20.1% after only a few years of active research. In addition to solar cell application, the fascinating optical and electronic properties of these perovskite systems have enabled their usage for various electronic devices including light emitting diodes, photodetectors, and transistors. Despite these remarkable progresses associated with perovskites, there are still many fundamental questions to be addressed at both material and device levels. Further improvements are required to advance our understanding on the material effects on the fundamental physical and chemical processes that are important to device operations. In this presentation, I will first give a general overview of recent development of material synthesis, device development, and basic characterization of perovskite solar cells. I will then discuss some of our recent investigations on the material growth, charge transport, recombination, and device characteristics of perovskite solar cells. The impact of device composition and fabrication conditions on the solar cell characteristics will be discussed. Finally, I will discuss the R&D opportunities to make perovskite solar cells a viable photovoltaic technology in the future.

References

[1] Park, N. G. *J. Phys. Chem. Lett.* **2013**, *4*, 2423.
[2] Snaith, H. J. *J. Phys. Chem. Lett.* **2013**, 3623.
[3] Liu, M.; Johnston, M. B.; Snaith, H. J. *Nature* **2013**, *501*, 395.
[4] Burschka, J.; Pellet, N.; Moon, S. J.; Humphry-Baker, R.; Gao, P.; Nazeeruddin, M. K.; Grätzel, M. *Nature* **2013**, *499*, 316.