Solar Hydrogen Research in the US / Opportunities with Particle Suspension Reactors

Osterloh group at UC Davis

Research Corporation for Science Advancement

National Science Foundation CHE and CBET Programs
US Funding for Solar Hydrogen Research

National Science Foundation
Division of Chemical and Biological Transport CBET - Energy for Sustainability Program
Division of Chemistry (CHE)/ Catalysis Program
Division of Materials Science (DMR)

http://www.nsf.gov/awardsearch/

Department of Energy
Energy Efficiency and Renewable Energy (EERE) Program: Eric Miller

http://www.grants.gov/web/grants/search-grants.html

Department of Defense Research Corporation: Scialog on Solar Hydrogen

**CCI Solar Participants**

$20,164,946.00

**Principal Investigators**

- **Harry B. Gray**
  Caltech
  BILRC Website

- **Allen Bard**
  U Texas, Austin
  Group Webpage

- **R. David Britt**
  UC Davis
  Group webpage

- **Bruce S. Brunschwig**
  Caltech
  MMRC Website

- **Kyoung-Shin Choi**
  U. Wisconsin, Madison
  Group Website

- **Christopher C. Cummins**
  MIT
  Group Website

- **Giulia A. Galli**
  U. Chicago
  Group Website

- **Sharon Hammes-Schiffer**
  U Illinois, UC
  Group Website

**Completed Participants**

- **Paula T. Hammond**
  MIT

- **Thomas F. Jaramillo**
  Stanford

- **Daniel G. Nocera**
  Harvard

- **Bruce A. Parkinson**
  U. Wyoming

- **Jonas C. Peters**
  Caltech

- **Raymond E. Schaak**
  Penn State

- **Jennifer Schuttlefield Christus**
  U. Wisconsin, Oshkosh

- **Shannon S. Stahl**
  U. Wisconsin, Madison

- **Dino Villagran**
  U Texas, El Paso

- **Jay R. Winkler**
  Caltech

- **Jorge Colon**
  U. Puerto Rico

- **Michael Freund**
  Florida Institute of Technology
DOE: Solar Fuel Hub at Caltech/Berkeley: Joint Center for Artificial Photosynthesis
Harry Atwater (Director), Nathan Lewis (Scientific Director),
2010-2015: $122,000,000; renewed in 2015-: $75,000,000 under new leadership

Overview:
- **Mission**: Develop a solar-fuels generator to produce fuel from the sun 10x more efficiently than crop plants
- Launched in Sept. 2010; DOE announced renewal in April 2015
- Led by Caltech with LBNL as primary partner; additional partners are SLAC, UC San Diego and UC Irvine
- **First Funding Cycle**: Development of prototypes capable of efficiently producing hydrogen via photocatalytic water splitting
- **Second Funding Cycle**: Focus on CO₂ reduction discovery science

Research Accomplishments:
- Discovered method to protect light-absorbing semiconductors (e.g. Si, GaAs) from corrosion in basic aqueous solutions while still maintaining excellent electrical charge conduction
- Developed novel high throughput capabilities to prepare and screen light absorbers and electrocatalysts
- Established benchmarking capabilities that provide quantitative, objective evaluations of catalysts and light absorbers
- Designed, fabricated and tested integrated artificial photosynthetic prototypes with optimized properties
- Developed new multi-physics modeling tools for analysis of solar-fuels prototypes and processes
DOE: Energy Research Frontier Centers

32 EFRCs in 33 States + D.C.

http://science.energy.gov/bes/efrc/

Argonne-Northwestern Solar Energy Research Center (ANSER)
Michael Wasielewski, Northwestern University

Massachusetts
Solid-State Solar-Thermal Energy Conversion Center (S3TEC)
Gang Chen, Massachusetts Institute of Technology

Minnesota
Inorganometallic Catalyst Design Center (ICDC)
Laura Gagliardi, University of Minnesota

Missouri
Photosynthetic Antenna Research Center (PARC)
Robert Blankenship, Washington University in St. Louis

New Mexico
Center for Advanced Solar Photophysics (CASP)
Victor Klimov, Los Alamos National Laboratory

North Carolina
Center for Solar Fuels (UNC)
Thomas Meyer, University of North Carolina

Texas
Center for Frontiers of Subsurface Energy Security (CFSES)
Larry Lake, University of Texas at Austin

Washington
Center for Molecular Electrocatalysis (CME)
R. Morris Bullock, Pacific Northwest National Laboratory

California
Light-Material Interactions in Energy Conversion (LMI)
Ralph Nuzzo, California Institute of Technology

Delaware
Catalysis Center for Energy Innovation (CCEI)
Dionisios Vlachos, University of Delaware

Illinois
Center for Electrochemical Energy Science (CEES)
Paul Fenter, Argonne National Laboratory
Center for Bio-Inspired Energy Science (CBES)
Samuel Stupp, Northwestern University
DOE: Energy Research Frontier Centers  

http://science.energy.gov/bes/efrc/

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Particle Based Water Splitting Photocatalysts

Concept of Photochemical Diodes  

Single Absorber
12 examples

Dual Absorber  
(Tandem, z-Scheme)
8 examples

Solid state junction

Liquid junction  
(redox shuttle)
17 examples

Adapted from Maeda, K.; Domen, K. J. Phys. Chem. Lett. 2010, 1, 2655–2661
Solar Energy Conversion is Costly

Grid Parity in China

$ 0.10 / W

$ 0.20 / W ($0.007 / kWh)*

$ 0.5 / W ($0.02 / kWh)*

* 10 year lifetime and 8 h of sunshine / day

Ultimate thermodynamic limit from 1.0 sun

Grid Parity in India

$ 1.0 / W ($0.03 / kWh)*

Shockley-Queisser limit

Grid Parity in California

$ 3.50 / W ($0.12 / kWh)*

Adapted from DOE: Basic Energy Needs For Solar Energy Utilization, 2005

Photocatalysts

Future PV

Thin Film

Current PV

Suspended particles benefit from...........

**Improved Carrier Extraction**

**Improved Light Penetration**

**Electrolyte Effects**


**Quantum Size Effects**


Osterloh, F. E. *Chemical Society Reviews* 2013, 42 (6), 2294-2320.
but suffer from...........

Reduced Rectification

Lower Electric Fields – reduced charge separation

Slower Charge Transport

Surface Recombination

Osterloh, F. E. *Chemical Society Reviews* **2013**, *42* (6), 2294-2320.
Maximum reported quantum yields for visible-light-driven water splitting systems

Need Better Understanding of Nanoscale Charge Separation
Surface Photovoltage Spectroscopy
(Transistor, Brattain and Bardeen, 1940-50)


SPV spectrum: CPD change (photovoltage) as function of wavelength
Experimental Setup

Semi-transparent Gold Kelvin Probe

Light source: Xe arc lamp

25°C, 10^{-4} \text{ mbar}
Photovoltage in Nano-Rh: SrTiO$_3$/Pt photocatalyst


Hydrogen Evolution under visible light (> 400 nm, 112 mW/cm$^2$) with 50 mg catalyst in 50 mL of 20 vol% MeOH aqueous solution.

SPV spectra on gold substrate in vacuum
Effect of Pt / Ru Co-catalyst

TEM

Hydrogen Evolution

visible light (> 400 nm, 112 mW/cm²) with 50 mg catalyst in 50 mL of 20 vol% MeOH aqueous solution.
0.05 mL of 0.01 M methyl viologen dichloride, potassium ferricyanide, potassium iodide aqueous solution was added and dried under N₂. Methanol added as neat liquid.
Comparison with Thermodynamics of Redox system

Electrochemical Potential (V vs NHE) vs Vacuum Scale (eV)

- [MV]^2+ (-1.24 V*)
- H^+/H_2
- [Fe(CN)_6]^3- (-0.7 V)
- Au (-1.4 V)
- Pt (-1.1 V)
- Ti^{4+} 3d
- CH_3OH (+1.2 V)
- [Fe(CN)_6]^{4-} (+0.6 V)
- I_3^-/I^- (+0.4 V)
- Rh^{3+} 4d t_2g
- O^{2-} 2p

0.78 eV
Junction potentials controlled by....

1. built-in voltage \((E-E_{CB}; E_{VB}-E)\)
2. distance between donor and absorber
3. reversibility of redox couple
4. optical absorbance of film

J. Wang, J. Zhao and F. E. Osterloh, Energ. & Envi. Sci. 2015, 8, 2970-2976.
Built-in voltages at interfaces of
- metal oxides and cocatalysts
- tandem absorbers
- absorbers and redox couples

- molecular dyes and solids and redox couples

Mid Gap Defects
Polarons in P3HT and P3HT/PCBM bulk heterojunctions

download talk at https://sites.google.com/site/osterlohlab/