Fundamental Optical, Electrical, and Photoelectrochemical Properties of Catalyst-Bound Silicon Microwire Array Photocathodes for Sunlight-Driven Hydrogen Production

Prof. Nathan S. Lewis (Principal Investigator), Prof. Harry A. Atwater, Dr. Bruce S. Brunschwig, Prof. Shannon W. Boettcher, Emily L. Warren, Dr. Morgan C. Putnam, Elizabeth A. Santori, Daniel Turner-Evans, Dr. Michael D. Kelzenberg, Dr. Michael G. Walter, James R. McKone, Dr. Joshua M. Spurgeon, Dr. Shane Ardo,* Dr. Chengxiang Xiang, Sang Hee Park, Dr. Qixi Mi, Dr. Karla R. Reyes-Gil
California Institute of Technology
Division of Chemistry and Chemical Engineering
Beckman Institute, Kavli Nanoscience Institute, and Joint Center for Artificial Photosynthesis
m/c 127-72, 210 Noyes Laboratory
1200 E. California Blvd.
Pasadena, CA 91125
Phone: (626) 395-6335; Fax: (626) 395-8867
E-mail: nslewis@its.caltech.edu

DOE Program Manager: Dr. Mark T. Spitler
Phone: (301) 903-4568
E-mail: Mark.Spitler@science.doe.gov

Objectives

The goal of this work is to develop a fundamental understanding of the properties and photoelectrochemical performance of Si wire-array based photocathodes for H2 evolution. This work has three general scientific objectives: to develop a fundamental understanding of Si microwire arrays, H2 evolving catalysts, and solution-based mass transport and bubble phenomena associated with H2 production. We will systematically vary the geometric, electronic, and compositional characteristics of the Si microwire arrays, to understand, and thus gain control over, the photoelectrochemical behavior of such systems. Experiments using the combined microwire array–catalyst material will be performed in order to determine active H2 catalysts based on alternatives to Pt, e.g. Ni–Mo alloy and MoS_2, and ideal catalyst loading, for optimization of the Si microwire array photoelectrochemical performance and catalytic turnover. Computational modeling, in conjunction with experimental measurements on Si microwire arrays under operating conditions, will be used to obtain a fundamental understanding of the energy penalty associated with mass-transport limitations, and complications due to production of H2 bubbles, for various photoelectrode geometries.

Technical Barriers

Current photovoltaic and photoelectrochemical technologies employ a planar-junction design, requiring the use of expensive, high-purity semiconducting materials for efficient and stable operation. Si microwire arrays afford rapid radial charge separation while using a fraction of the material and with relaxed purity requirements, while the micron-scale interwire spacing can present interesting, not-yet-elucidated issues involving mass transport of reactants and products under operating conditions. In addition, the formation of bubbles due to efficient H2 evolution at Si microwire array electrodes can reduce the overall photoelectrode performance. Realization of efficient technologies for photoelectrochemical H2 evolution using Si microwire arrays requires that the geometry and photophysical properties of the microwire arrays, light scattering elements, and electrocatalysts be optimized. Also, because noble metal materials, like Pt, are too expensive to serve as feasible components in a globally scalable H2-evolving photoelectrode, other potential catalysts must be identified.

Abstract

We have investigated and made significant progress on key components of a solar-driven water splitting scheme: Si microwire photocathodes, and metal oxide photoanodes. Radial p–n^+ (n^+p) junction Si microwire arrays functionalized with Pt or Ni nanoparticulate metallic electrocatalysts functioned as efficient photocathodes for H2 evolution. Further exploration of geometric parameters that influence the photoelectrochemical response of the Si microwire arrays is proposed. In addition, experimental measurements and computational modeling will be employed to investigate how catalysis is affected by mass-transport limitations, H_2 bubble formation, and the use of alternative electrocatalysts. The photoresponse of WO3 photoanodes was improved by implementation of a porous film geometry.

Progress Report

We have made very significant progress toward the goals listed under the DOE hydrogen fuel initiative project grant (DE-FG02-05ER15754) for p-Si microwire photocathodes and porous WO3 photoanodes. We have demonstrated a high level of control over the material and light absorption properties of p-Si microwire array photocathodes. We have tested the performance of p-Si microwire arrays embedded in a flexible, processable set of polymeric membranes and have further demonstrated the ability to reuse the planar Si(111) growth substrate after the Si wire arrays were removed from the growth substrate. We have introduced a radial n^+p junction to improve the photoconversion efficiency of these electrodes in both regenerative and fuel-forming photoelectrochemical configurations. We have developed techniques to deposit Pt and Ni electrocatalyst particles onto the wire arrays, and have investigated their stability and performance for the hydrogen evolution reaction. Toward the development of a photoanode, we have synthesized a porous film morphology that improves the photoresponse of WO3 toward the oxygen evolution reaction. We have also developed a method to reduce the bandgap of WO3 from 2.6 eV to 1.8 eV by calcining ammonium para- or meta-tungstate in O2 at 420°C.

Future Directions

We are investigating the fundamental photoelectrochemical properties of Si wire-array based photocathodes for H2 evolution. The proposed research will focus on Si microwire arrays, H2 evolving catalysts, and solution-based mass transport and bubble phenomena associated with H2 production. Our recent demonstration of solar-driven H2 evolution from water at an n^+p-Si microwire array photocathode will be the starting point for the studies. The proposed work will elucidate the fundamental effects of interfacial structure on the chemistry and physics of such photocathodes. We will systematically vary structural variables, including the wire diameter, height, spacing, and pattern, as well as functional variables, including the doping density and junction area, of the Si microwire arrays, to comprehend, and thus gain control over, the photophysical and photoelectrochemical behavior of such systems. The fundamental properties of electrocatalysts on Si wire-array electrodes are also not yet understood. An effective catalyst, such as Pt, will be used to explore how the deposition and coverage affect the catalytic function on both planar Si and on Si microwire arrays. After gaining insight into those variables, other potential catalysts, such as Ni–Mo alloy and MoS2, will be investigated. The enhanced physical surface area of wire arrays affords increased rates of catalytic H2 evolution (per projected area) relative to planar Si. However, the aforementioned alternative microwire geometries, junction locations, and placement of electrocatalysts can result in issues involving mass transport of reactants and products and electrical and optical complications due to production of H2 bubbles. Computational modeling, in conjunction with experimental measurements on Si microwire arrays under operating conditions, will be used to obtain a fundamental understanding of these problems. The proposed fundamental science will aid in the development of systems not exclusively derived from Si microwire arrays. General guidelines for the design and implementation of successful systems that utilize interfacial reactions driven by light absorption at the photocathodes will be realized. Thus, the fields of photoelectrochemistry and photoinduced heterogeneous catalysis will both benefit from the results garnered by the proposed studies.

Publication list (including patents) acknowledging the DOE grant or contract

1. George W. Crabtree and **Nathan S. Lewis**, "Solar Energy Conversion" *AIP Conf. Proc. (Physics of Sustainable Energy)*, **2008**, *1044*, 309-321.

2. Brendan M. Kayes, Michael A. Filler, M. David Henry, James R. Maiolo III, Michael D. Kelzenberg, Morgan C. Putnam, Joshua M. Spurgeon, Katherine E. Plass, Axel Scherer, **Nathan S. Lewis**, and Harry A. Atwater, "Radial pn Junction, Wire Array Solar Cells", *Conference Record of the Thirty-third IEEE Photovoltaic Specialists Conference*, **2008**.

3. Michael D. Kelzenberg, Daniel B. Turner-Evans, Brendan M. Kayes, Michael A. Filler, Morgan C. Putnam, **Nathan S. Lewis**, and Harry A. Atwater, "Single-Nanowire Si Solar Cells", *Conference Record of the Thirty-third IEEE Photovoltaic Specialists Conference*, **2008**.

4. Michael D. Kelzenberg, Daniel B. Turner-Evans, Brendan M. Kayes, Michael A. Filler, Morgan C. Putnam, **Nathan S. Lewis**, and Harry A. Atwater, "Photovoltaic Measurements in Single-Nanowire Silicon Solar Cells", *Nano Lett.*, **2008**, *8(2),* 710-714.

5. **Nathan S. Lewis**, "Powering the Planet: Where in the World Will Our Energy Come From?", *Energeia*, **2008**, *19(4)*, 1.

6. James R. Maiolo III, Harry A. Atwater, and **Nathan S. Lewis**, "Macroporous Silicon as a Model for Silicon Wire Array Solar Cells", *J. Phys. Chem. C*, **2008,** *112(15)*, 6194-6201.

7. Stephen Maldonado, Anthony G. Fitch, and **Nathan S. Lewis**, "Semiconductor/Liquid Junction Photoelectric Chemical Solar Cells", in *Series on Photoconversion of Solar Energy Volume III - Nanostructured and Photoelectric Chemical Systems for Solar Photon Conversion*, Mary D. Archer and Arthur J. Nozik (Eds.), Imperial College Press: London, **2008**, 537.

8. Joshua M. Spurgeon, Harry A. Atwater, and **Nathan S. Lewis**, "A Comparison between the Behavior of Nanorod and Planar Cd(Se, Te) Photoelectrodes", *J. Phys. Chem. C*, **2008**, *112(15)*, 6186-6193.

9. Joshua M. Spurgeon, Katherine E. Plass, Brendan M. Kayes, Bruce S. Brunschwig, Harry A. Atwater, and **Nathan S. Lewis**, "Repeated Epitaxial Growth and Transfer of Arrays of Patterned, Vertically Aligned, Crystalline Si Wires from a Single Si(111) Substrate", *Appl. Phys. Lett.*, **2008**, *93*, 032112.

10. **Nathan S. Lewis**, "A Perspective on Forward Research and Development Paths for Cost-Effective Solar Energy Utilization", *ChemSusChem*, **2009**, *2(5)*, 383-386.

11. Katherine E. Plass, Michael A. Filler, Joshua M. Spurgeon, Brendan M. Kayes, Stephen Maldonado, Bruce S. Brunschwig, Harry A. Atwater, and **Nathan S. Lewis**, "Flexible Polymer-Embedded Si Wire Arrays", *Adv. Mater.*, **2009**, *21(3)*, 325-328.

12. Morgan C. Putnam, Daniel B. Turner-Evans, Michael D. Kelzenberg, Shannon W. Boettcher, **Nathan S. Lewis**, and Harry A. Atwater, "10 µm Minority-Carrier Diffusion Lengths in Si Wires Synthesized by Cu-Catalyzed Vapor-Liquid-Solid Growth", *App. Phys. Lett.*, **2009**, *95,* 163116.

13. Karla R. Reyes-Gil, Joshua M. Spurgeon, and **Nathan S. Lewis**, "Silicon and tungsten oxide nanostructures for water splitting", *Proc. SPIE*, **2009**, *7408*, 74080S.

14. Shannon W. Boettcher, Joshua M. Spurgeon, Morgan C. Putnam, Emily L. Warren, Daniel B. Turner-Evans, Michael D. Kelzenberg, James R. Maiolo, Harry A. Atwater, and **Nathan S. Lewis,** "Energy Conversion Properties of Silicon Wire-Array Photocathodes", *Science*, **2010**, *327(5962)*, 185-187.

15. Michael D. Kelzenberg, Shannon W. Boettcher, Jan A. Petykiewicz, Daniel B. Turner-Evans, Morgan C. Putnam, Emily L. Warren, Joshua M. Spurgeon, Ryan M. Briggs, **Nathan S. Lewis**, and Harry A. Atwater, "Enhanced absorption and carrier collection in Si wire arrays for photovoltaic applications", *Nature Mater.,* **2010**, 9(3), 239-244.

16. Joshua M. Spurgeon, Shannon W. Boettcher, Michael D. Kelzenberg, Bruce S. Brunschwig, Harry A. Atwater, and **Nathan S. Lewis,** "Flexible, polymer-supported, Si wire array photoelectrodes", *Adv. Mater.*, **2010**, *22(30)*, 3277-3281.

17. Emily L. Warren, Shannon W. Boettcher, James R. McKone, and **Nathan S. Lewis**, "Photoelectrochemical water splitting: silicon photocathodes for hydrogen evolution", *Proc. SPIE*, **2010**, *7770*, 77701F.

18. Shannon W. Boettcher, Emily L. Warren, Morgan C. Putnam, Elizabeth A. Santori, Daniel Turner-Evans, Michael D. Kelzenberg, Michael G. Walter, James R. McKone, Bruce S. Brunschwig, Harry A. Atwater, and **Nathan S. Lewis**, "Photoelectrochemical hydrogen evolution using Si microwire arrays", *J. Am. Chem. Soc.*, **2011**, *133(5)*, 1216–1219.

19. Michael D. Kelzenberg, Daniel B. Turner-Evans, Morgan C. Putnam, Shannon W. Boettcher, Ryan M. Briggs, Jae Yeon Baek, **Nathan S. Lewis**, and Harry A. Atwater, "High-performance Si microwire photovoltaics", *Energy Environ. Sci.*, **2011**, *4*, 866–871.

20. Emily L. Warren, Shannon W. Boettcher, Michael G. Walter, Harry A. Atwater, and **Nathan S. Lewis**, "pH-independent, 520 mV open-circuit voltages of Si/methyl viologen$^{2+/+}$ contacts through use of radial n$^+$p-Si junction microwire array photoelectrodes", *J. Phys. Chem. C*, **2011**, *115(2)*, 594–598.