II.K.7 Sunlight-Driven Hydrogen Formation by Membrane-Supported Photoelectrochemical Water Splitting

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Objectives

The goal of this work is to develop the components, and ultimately a demonstration in the laboratory for proof-of-principle, for a solar fuel generating system that is scalably manufacturable, uses earth-abundant elements, and is ten times more efficient at solar-to-chemical energy conversion than existing plants. This concurrent focus on system and electrode development represents a significant advance on previous water-splitting strategies. Specifically, we are developing an artificial photosynthetic system that will only utilize sunlight and water as the inputs and will produce hydrogen and oxygen as the outputs. The components of this water-splitting device will be synthesized and optimized separately. The modular nature allows the design to be incrementally improved with discovery and optimization of new photoelectrode materials.

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. By employing inorganic semiconductor rod arrays that allow radial charge-carrier collection, we can demonstrate good solar energy conversion efficiencies even with relatively low-cost, low-grade bulk materials. Importantly, we will show that the high aspect ratio photoelectrode architecture affords two additional substantial advantages that further amortize the total system cost. Rod arrays can be embedded in flexible, polymeric membrane materials, allowing the possibility of roll-to-roll system assembly. The form factor of the rod array photoelectrode lessens the activity requirements of the required heterogeneous catalytic materials.

Abstract

We are developing an artificial photosynthetic system that will only utilize sunlight and water as the inputs and will produce hydrogen and oxygen as the outputs. We are taking a modular, parallel development approach in which the three distinct primary components-the photoanode, the photocathode, and the product-separating but ion-conducting membrane-are fabricated and optimized separately before assembly into a complete water-splitting system. The design principles incorporate two separate, photosensitive semiconductor/liquid junctions that will collectively generate the 1.7-1.9 V at open circuit necessary to support both the oxidation of H_2O (or OH^-) and the reduction of H^+ (or H_2O). The photoanode and photocathode will consist of rod-like semiconductor components, with attached heterogeneous multi-electron transfer catalysts, which are needed to drive the oxidation or reduction reactions at low overpotentials. The high aspect-ratio semiconductor rod electrode architecture allows for the use of low cost, earth abundant materials without sacrificing energy conversion efficiency due to the orthogonalization of light absorption and charge-carrier collection. Additionally, the high surface-area design of the rod-based semiconductor array electrode inherently lowers the flux of charge carriers over the rod array surface relative to the projected geometric surface of the photoelectrode, thus lowering the photocurrent density at the solid/liquid junction and thereby relaxing the demands on the activity (and cost) of any electrocatalysts. A flexible composite polymer film will allow for electron and ion conduction between the photoanode and photocathode while simultaneously preventing mixing of the gaseous products. Separate polymeric materials will be used to make electrical contact between the anode and cathode, and also to provide structural support. Interspersed patches of an ion conducting polymer will maintain charge balance between the two half-cells. The modularity of the system design approach allows each piece to be independently modified, tested, and improved, as future advances in semiconductor, polymeric, and catalytic materials are made. Hence, this work will demonstrate a feasible and functional prototype and blueprint for an artificial photosynthetic system, composed of only inexpensive, earth-abundant materials, that is simultaneously efficient, durable, manufacturably scalable, and readily upgradeable.

Progress Report

We have made significant progress towards the goals listed under the hydrogen fuel initiative project grant (DE-FG02-05ER15754). The work performed to date has laid the foundation for the development of an efficient, scalable, semiconductor rod-based, photoelectrochemical water-splitting device. We have detailed the concept and specific merits of high aspect ratio photoelectrodes using macroporous n-Si and n-$CdSe_xTe_{1-x}$, quantitatively demonstrating that radial charge-carrier collection reduces the semiconductor purity constraint without sacrificing in principle the obtainable solar energy conversion efficiency. The use of macroporous n-Si exhibited minimal loss of open-circuit photovoltage relative to single crystal Si photoelectrodes, despite more than an order of magnitude increase in surface area due to the macropore formation. Photoanodes of n-$CdSe_xTe_{1-x}$ were shown to collect minority carriers more efficiently across the solar spectrum in rod array form as compared to planar form. Additionally, techniques for growth of large areas of Si rod arrays with high pattern fidelity have been developed. Photoelectrochemical cells based on such n-Si rod arrays have been prepared, exhibiting sizeable open-circuit photovoltages. Separately, we have made substantial advances in our combinatorial method for preparing and testing multi-component metal oxide materials. Our methodology allows for fast, comprehensive assessment of the chemical, electrochemical, and electrocatalytic properties of a large number of heretofore unexplored metal-oxide semiconductor materials, both as photocathodes and photoanodes, for use in water splitting applications.

Future Directions

The initial focus of this work is on known, common semiconductors as functional photoelectrodes in this solar fuel generation system design. Our preliminary focus will be on p-Si and n-WO_3 as photocathode and photoanode rod array materials, respectively. Both photoelectrode components will be fabricated individually, investigated systematically, and their materials, chemical, electrochemical, and photoelectrochemical properties will be understood and optimized before assembly into the complete system. The photoanode and photocathode components will be electrically, and ionically, interconnected through, but physically separated by, a flexible composite polymer film. In parallel with development of the photoanode and photocathode, multi-component membranes, composed of existing polymeric materials, that exhibit the mechanical pliability, electronic conductivity, and ion permeability properties necessary for a feasible water electrolysis system will be developed. Specifically, polypyrrole will be used to make electrical contact between the anode and cathode, while poly(dimethylsiloxane) (PDMS) will be used to provide structural support for the semiconductor rod arrays. For proton conduction in a cell operated under acidic conditions, Nafion will be employed, whereas vinylbenzyl chloride modified films of poly(ethylene-co-tetrafluoroethylene) (ETFE) will be used for hydroxide conduction in a cell operated under alkaline conditions. Importantly, not only will facile assembly of these three components into a solar-powered water photoelectrolysis system be demonstrated, the modularity of the system design approach allows each piece to be independently modified, tested, and improved, as future advances in semiconductor, polymeric, and catalytic materials are made.

DOE Sponsored Publications (2005-2007)

1. Brendan M. Kayes, Christine E. Richardson, Nathan S. Lewis, and Harry A. Atwater, "Radial PN Junction Nanorod Solar Cells: Device Physics Principles and Routes to Fabrication in Si", *Proc IEEE,* **2005**, *1*, 55-58.

2. Brendan M. Kayes, Harry A. Atwater, and Nathan S. Lewis, "Comparison of the device physics principles of planar and radial p-n junction nanorodsolar cells," *J. Appl. Phys.* **2005,** *97 (11)*, 114302.

3. Nathan S. Lewis, Ph.D., and George Crabtree, Ph.D., "Scientists Chart New Horizons Researchers look to cutting-edge advances for the solar technologies of tomorrow", Solar Today ,**2006**, Jan/Feb, 16–19.

4. Nathan S. Lewis and Daniel G. Nocera, "Powering the Planet: Chemical Challenges in Solar Energy Utilization", *Proc. Natl. Acad. Sci., USA*, **2006**, *103 (43)*, 15729-15735.

5. George W. Crabtree and Nathan S. Lewis, "Solar Energy Conversion", *Phys. Today*, **2007**, *60 (3)*, 37-42.

6. Nathan S. Lewis, "Toward Cost-Effective Solar Energy Use", *Science,* **2007**, *315 (5813)*, 798-801.

7. Brendan M. Kayes, Christine E. Richardson, Nathan S. Lewis, Harry A. Atwater, "Radial PN Junction Nanorod Solar Cells: Device Physics Principles and Routes to Fabrication in Si", *Proc. IEEE*, **2005**, 55-58.

8. James R. Maiolo III, Brendan M. Kayes, Michael A. Filler, Morgan C. Putnam, Michael D. Kelzenberg, Harry A. Atwater, Nathan S. Lewis, "High Aspect Ratio Si Rod Array Photoelectrochemical Cells", *J. Am. Chem. Soc.*, **2007**, *129 (41)*, 12346-12347.

9. Nathan S. Lewis "The World Energy Book (contributed chapter)*",* **2007**.

10. Brendan M. Kayes, Joshua M. Spurgeon, Thomas C. Sadler, Nathan S. Lewis, Harry A. Atwater, "Synthesis and Characterization of Si Nanorod Arrays for Solar Cell Applications", *Proc. IEEE*, **2006**, 221-224.

11. Stephen Maldonado, Anthony G. Fitch, and Nathan S. Lewis, "Semiconductor/Liquid Junctions in Photoelectrochemical Cells", *Vol.III of Photoconversion of Solar Energy,* **2007**, *in press*.

12. Nathan S. Lewis, "Legal and Policy Issues Related to a Global Carbon Emissions-Control Regime", *Stanford Law and Policy Review*, **2007**, *submitted for publication*.

13. Brendan M. Kayes, Michael A. Filler, Morgan C. Putnam, Michael D. Kelzenberg, Nathan S. Lewis, and Harry A. Atwater, "Growth of Vertically Aligned Si Rod Arrays Over Large Areas (>1 cm^2) with Au and Cu Catalysts" *Appl. Phys. Lett.*, **2007**, *91*, 103110.

14. 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,* **2007**, *accepted.*

15. Nathan S. Lewis, "Powering the Planet", *MRS Bulletin*, **2007**, *32*, 808-820.

16. 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-nanorod Si Solar Cells, *Nano. Lett*, **2007**, *in press*.

17. James R. Maiolo III, Harry A. Atwater, and Nathan S. Lewis, "Macroporous Si as a Model for Si Rod Array Solar Cells, *J. Phys. Chem. C,* **2007**, *accepted.*