



Global Climate & Energy Project
STANFORD UNIVERSITY

Artificial Photosynthesis: Membrane-Supported Assemblies that Use Sunlight to Split Water

Investigators

Nathan S. Lewis and Harry B. Gray, Department of Chemistry; Harry A. Atwater, Department of Applied Physics and Materials Science, California Institute of Technology

Objective

This research seeks to develop a photoconversion system that can produce hydrogen and oxygen directly from sunlight. The proposed device is composed of a conductive membrane that must both absorb the solar radiation and support the initial charge separation. Electrons and holes are directed to different sides of the membrane, where two specifically designed organic catalysts assist water reduction and oxidation.

Background

Direct conversion of solar energy into chemical fuels may solve one of the principal shortcomings of conventional solar technologies – the intermittent nature of solar energy – by providing a medium for energy storage and distribution. The use of sunlight to produce hydrogen from splitting water by mimicking natural photosynthetic processes is an ideal solution to this challenge. However, no water splitting system has yet been demonstrated that produces hydrogen cheaply enough to compete with fossil fuels. Electrolyzer systems that are currently used in combination with photovoltaic cells are too expensive and not scalable to the level needed to make them a significant component of global energy production.

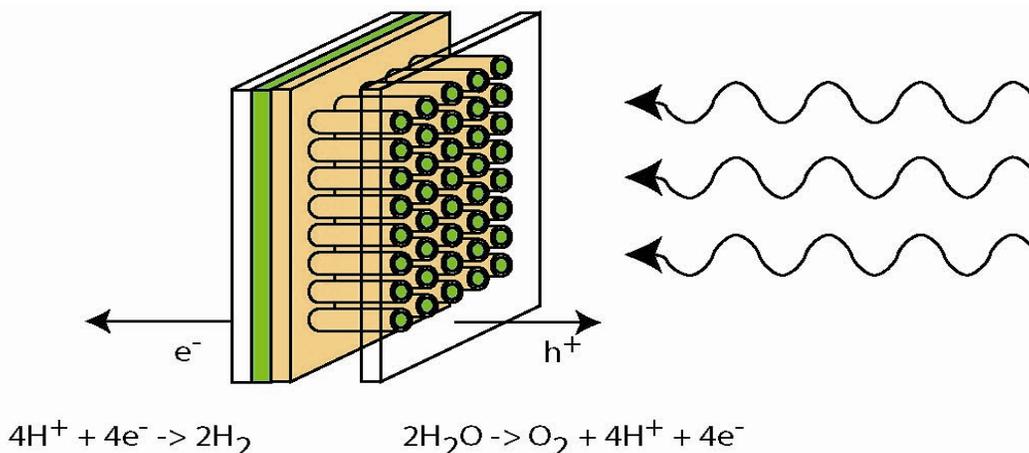


Figure 1: Schematic diagram of the rod/sleeve membrane structure

The concept underlying this project involves using sunlight directly to produce hydrogen and oxygen in a system that absorbs light and produces charges to drive separate water reduction and oxidation half-reactions. The system consists of a conductive photocatalytic membrane composed of two photoactive inorganic electrodes with bandgaps chosen to maximize sunlight absorption (1.1-1.4eV) and with energy levels generating an overall separation potential exceeding 1.23V to allow water splitting. The membrane has a rod/sleeve design (see Figure 1) that combines long absorption length (along the rods) and short charge collection distance (across the rods). This design relaxes the purity constraint on the absorber and allows the use of cheap polycrystalline semiconductors. Photoanode and photocathode stability properties are optimized for oxidizing and reducing environments respectively, since they are not exposed to both simultaneously. Specifically designed inorganic catalysts are adsorbed on the membrane surface to assist water redox reactions. This project focuses specifically on molecular catalysts because their activity can be tuned through molecular synthesis.

Approach

Combinatorial chemistry methods will be used to identify new metal oxide-based photoelectrode materials. For this purpose, a modified inkjet printer has been developed that allows fast screening of hundreds of metal oxide compounds against bandgap and stability in contact with aqueous electrolytes under illumination. Once the optimal photoelectrode materials have been selected, the photoanode valence band edge will be tuned by carbon and/or nitrogen doping and the photocathode conduction band optimized by exploring different transition metals. The nanorod structure of the membrane will be created either by using alumina templates or by vapor-liquid solid synthesis of self-supported semiconductor nanorods. Different combinations of semiconductors (such as Si/Si, Si/Ge_xSi_{1-x}, GaAs/Ge, In_xGa_{1-x}N/InN heterostructure templates on GaN nanorods) will be explored to investigate these fabrication methods.

The development of catalytic water-reduction and water-oxidation species is a major task of this project. Low-valent, redox-rich iron and cobalt platforms that can access various one- and two-electron redox couples will be examined as the bases for water-reduction catalysts. The same molecular design concepts will also be applied to other metal systems based on inexpensive materials such as nickel or copper. Particular attention will be given to functional catalyst systems that feature design elements exhibited by highly active enzymatic hydrogenases, such as FeFe hydrogenase systems. In the search for water-oxidation catalysts, this project aims to develop enhanced systems that address key deficiencies, such as poor stability, large overpotential, and slow turnover. Since O-O bonding is most likely the main barrier to water oxidation, compounds that catalyze the oxidation of water to either oxygen or hydrogen peroxide will be the principal targets of this investigation. Specifically, mononuclear metal complexes, such as metal dithiolene complexes and other polynuclear metal complexes, will be examined.

Once the individual components listed above have been fully investigated, the final task of this project will consist of building and testing a full demonstration system.