Artificial Photosynthesis: Membrane Supported Assemblies That Use Sunlight to Split Water

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Abstract

This project is focused on developing a photoelectrochemical system that uses sunlight to drive the splitting of water into H_2 and O_2. The device will consist of a photoanode, a photocathode, and a flexible membrane that will separate products and provide electrical contact between two absorber layers. Each absorber layer is optimized separately prior to assembly into a complete water-splitting system, and in this way, allows for the replacement of individual components by more efficient ones as parallel research progresses. The two photosensitive semiconductor/liquid junctions collectively need to generate 1.7-1.9 V at open circuit, the voltage necessary to support both the oxidation of H_2O (or OH^-) and the reduction of H^+ (or H_2O).

The membrane will consist of two semiconductor rod array structures connected back-to-back with ohmic contacts. Taken together the semiconductor (SC) arrays will straddle the hydrogen (p-type SC) and the oxygen (n-type SC) evolution potentials. The development of highly ordered arrays of micron or nano-sized crystalline Si rods grown using inexpensive starting materials has provided new platforms for studying the hydrogen evolving reaction at the photocathode. The motivation for studying microrod geometries is the orthogonalization of the directions of light absorption and charge carrier collection. This lowers the material purity requirements and increases the surface area for water reduction. Investigations of Si arrays as the photocathode in a photoelectrochemical cell configuration have been conducted. The band-edge potential of p-type silicon photocathodes is sufficiently negative to reduce water/protons to dihydrogen; however kinetic limitations necessitate deposition of catalysts, historically metals such as Pt, for efficient hydrogen production with silicon. Our goal of a photoelectrochemical water splitting system has also directed our research efforts toward the advancement of new semiconducting materials as photoabsorbers, fabrication of arrays microstructured radial junction semiconductors, catalyst attachment, and the development of methods to electrically connect two photoelectrodes to the desired membrane assembly.

In the past year we made significant progress towards our solar-driven water splitting scheme. We have conducted a comparative study of hydrogen evolution reaction (HER) catalyst materials coupled to Si microwire arrays, and investigated how the introduction of a radial n^+-emitter affects the band energetics and energy conversion properties of our Si microwire arrays in an aqueous environment. We have investigated the electron transfer and catalysis of the HER in nature and applied those concepts to synthetic HER catalysts. Foresight has led our investigations toward the study of bubble formation, a factor that can have a large effect in a complete device.

1. Development of Efficient Hydrogen Evolving Photocathodes

Introduction

The goal of this research has been the development of a water-splitting photoconversion system that can produce hydrogen fuel from sunlight and water. We have focused on the development of VLS-grown silicon photocathode materials, as they are the most versatile semiconductor absorber we have developed to date. We previously demonstrated the ability to peel our single crystalline wire arrays in a flexible polymer. Additionally, we have characterized the light absorption and electrical properties of these arrays after they have been removed from the substrate. We have also made a great deal of progress in adding proton reduction catalysts to the surface of our wire arrays and measuring their performance for the hydrogen production half of the water-splitting reaction.   In the past year, we have focused on some of the final steps toward demonstrating functional, high efficiency hydrogen evolving photocathodes employing exclusively earth-abundant, scalable materials.

Background

Our prior theoretical work suggested that a semiconductor device consisting of arrays of radial p-n junction nanorods would enable a decoupling of the requirements for light absorption and carrier extraction into orthogonal spatial directions. Each individual p-n junction nanorod in the cell could be long in the direction of incident light, allowing for optimal light absorption, but thin in another dimension, thereby allowing for effective carrier collection. The focus of this project has been on the photocathode, but work is underway to apply similar principles to photoanode materials. Our ability to peel these arrays is working toward an efficient, functional water splitting system employing two semiconductors bound on opposite sides of a membrane. Our experimental results have been exciting because they demonstrate that it is possible to grow low cost semiconductor materials with controlled properties, and that those semiconductors are near the point at which they may be leveraged into a scalable device architecture.

Results

pH Dependence of Si Radial Junction Microwire array Band Edges

Our prior results on H_2 conversion from radial junction Si microwire arrays were carried out in strongly acidic conditions, where Pt is stable, but most other potential catalyst materials are not. In order to couple earth-abundant catalysts to our n^+p wire arrays, we first investigated the pH dependence of the band edges of p-Si and n^+p Si in a regenerative electrochemical system. Unfortunately, bare silicon has band positions that are strongly influenced by pH, which limits the attainable photovoltage from p-Si/aqueous systems. Introduction of an n^+-doped emitter layer, to create a "buried junction," should decouple the band banding, and thus the photovoltage, of the photoelectrode from the energetics of the semiconductor/liquid contact. The ability to decouple the photovoltage of a Si photocathode from the pH of the contacting aqueous solution should increase the versatility of these materials for use in photoelectrochemical fuel-forming systems.

The effects of introducing a doped emitter layer have been evaluated for both planar Si photoelectrodes and for radial junction Si microwire-array photoelectrodes (Figure 1). In contact with the pH-independent, one-electron, outer-sphere, methyl viologen redox system ($MV^{2+/+}$), the pH dependence of the band-edge positions of Si in contact with aqueous electrolytes yielded open-circuit voltages, V_{oc}, for both planar and wire array Si photoelectrodes that varied as the pH of the solution was changed. Increases in the pH of the electrolyte produced a decrease in V_{oc} by approximately -44 mV/pH unit for both planar electrodes and Si microwire array electrodes. In contrast, introduction of a highly doped, n^+ emitter layer produced $V_{oc} = 0.56$ V for planar Si electrodes and $V_{oc} = 0.52$ V for Si microwire array electrodes, with the photoelectrode properties in each system being essentially independent of pH over six pH units (3<9). Hence, formation of an n^+
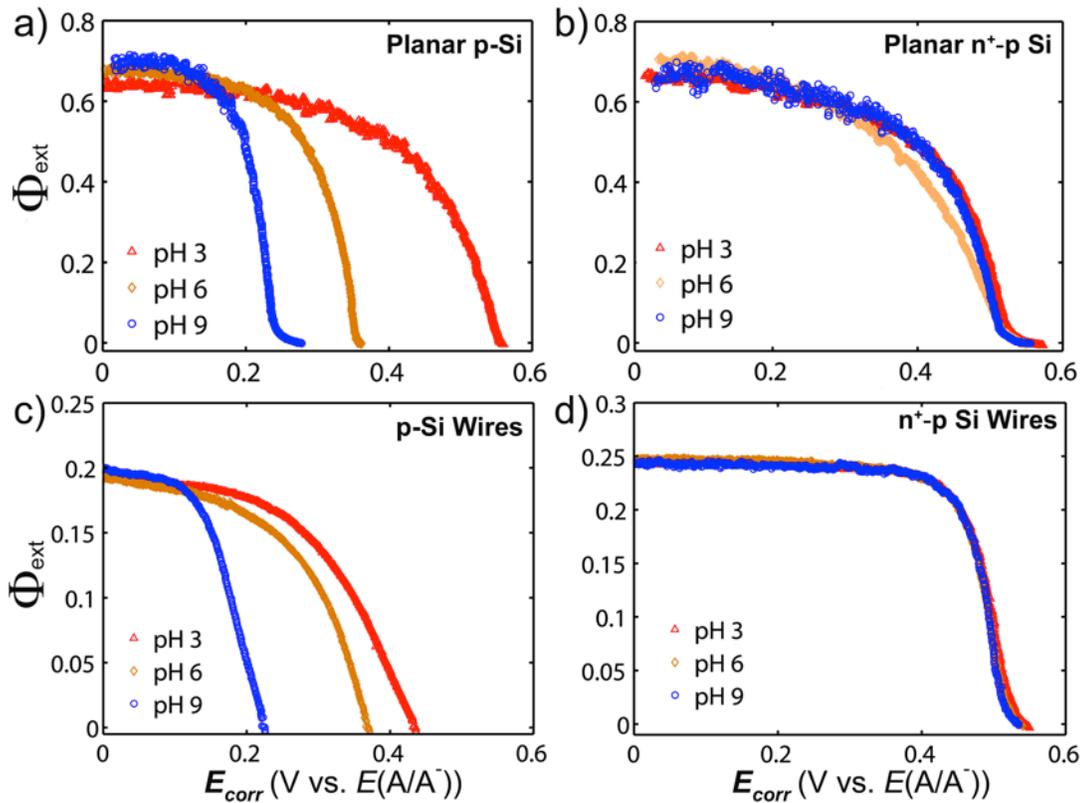

Figure 1: Representative external quantum yield (Φ_{ext}) vs. potential data as a function of pH for a) planar p-Si, b) planar n^+p-Si, c) p-Si wire arrays, d) and n^+-p radial junction wire arrays. Red triangles correspond to pH = 2.9, yellow diamonds to pH 5.9, and blue circles to pH 8.9. All electrodes were measured under 60 mW cm^{-2} of 808 nm illumination in aqueous solution with 50 mM $MV^{2+/+}$. Data are corrected for the solution effects, including uncompensated cell resistance (~20 Ω) and concentration over-potentials, to obtain photoelectrode performance parameters inherent to the Si electrodes. Data were referenced to the solution potential, which was maintained between -0.60 and -0.59 V vs. SCE by bulk electrolysis of MV^{2+} to MV^+. For samples without a diffused junction, V_{oc} decreased with increasing pH, whereas n^+p-Si samples displayed essentially no change in Φ_{ext}-E behavior, or in V_{oc}, across six pH units.

emitter layer not only improved the photovoltages for planar and Si microwire array photoelectrodes, but decoupled the band energetics of the semiconductor (and hence the obtainable photovoltage) from the value of the redox potential of the solution.

We are currently investigating the performance of H_2 evolution from radial junction wire arrays with different catalysts in aqueous solutions with varying pH. Our initial results indicate that our open circuit voltages are unaffected, but the "fill factor" (the ratio of the maximum power point to the product of the open circuit voltage and short circuit current) of our Pt devices decreases at higher pH, likely due to the different catalytic mechanisms for H^+ and H_2O reduction.

Heterogeneous catalysts for aqueous $H_2(g)$ evolution

Previously, we reported that Pt metal can be interfaced to Si semiconductor photocathodes in order to efficiently drive the photoelectrochemical conversion of protons into $H_2(g)$. We showed that Pt-deposited n^+p radial junction Si microwire arrays were able to produce 6% overall, thermodynamically based $H_2(g)$ conversion efficiency. Pt metal, however, is not a desirable material for use in a scalable solar water splitting scheme, due to its low elemental abundance and concomitant high cost. As a result, in our last report we noted that we had begun working on Ni-Mo alloy as a non-noble alternative to Pt for efficiently catalyzing the hydrogen evolution reaction (HER) on Si semiconductor photoelectrodes. We have since completed a thorough study of Ni-Mo on Si, and this catalyst remains a promising candidate for use in an integrated overall water splitting system.

We have determined that Ni-Mo alloy can be easily electrodeposited onto both degenerately doped (p^+) and p-type Si planar and microwire electrodes from a mildly acidic plating bath. These conditions avoid problems associated with rapid oxidation of the Si surface under basic conditions. On p^+-Si electrodes (Figure 2), the "dark" electrocatalytic activity of the electrodeposited Ni-Mo alloy was determined to fall between that of pure Ni, the most active non-noble pure metal HER catalyst, and Pt. When deposited onto p^+-Si microwire arrays, however, the activity of Ni-Mo actually approaches that of Pt, as the activities of both catalysts approach the limits imposed by physical characteristics of the testing cell (e.g. pH, buffer capacity, solution resistance, etc.). Thus Ni-Mo has demonstrated itself to be an attractive non-noble HER catalyst when Si microwire arrays are used as the substrate.

Furthermore, we have deposited Ni-Mo alloy onto p-type Si photoelectrodes in both planar and microwire geometries (Figure 3). The overall, thermodynamically based, energy conversion efficiencies if planar p-Si electrodes under 100 mW cm^{-2} ELH illumination is only approximately 0.2-0.4%. This is very similar to efficiencies of p-Si photoelectrodes deposited with Ni catalyst, and somewhat lower than those deposited
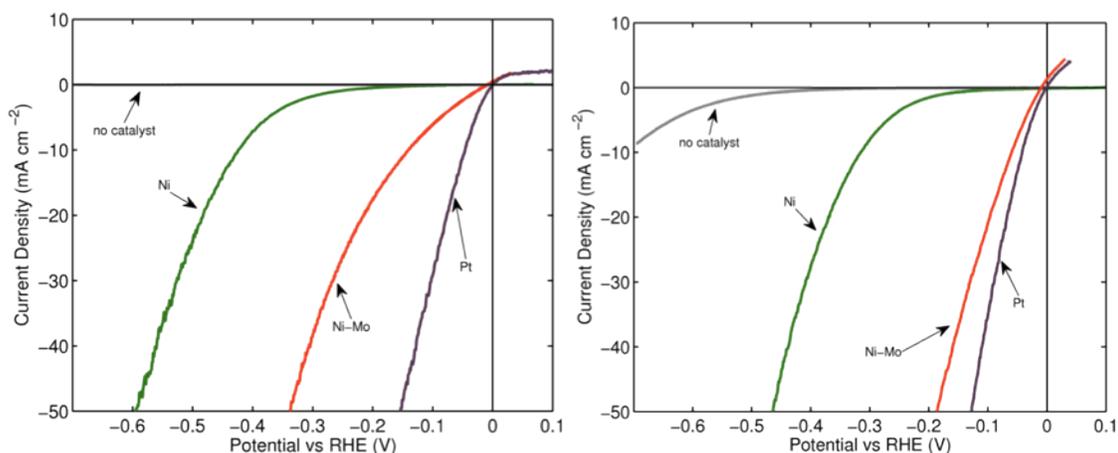
Figure 2: Representative current density-potential curves for "dark" electrocatalysis of Ni, Ni-Mo alloy, and Pt on p^+-Si planar (left) and microwire array (right) electrodes. Data were collected in aqueous solution using 0.5 M K_2SO_4 supporting electrolyte and buffered to pH 4.5 with 0.2 M potassium hydrogen phthalate. Potentials are references to the reversible hydrogen electrode (RHE) potential in the same electrolyte, which was measured explicitly using a platinized Pt wire immediately before electrode testing.

with Pt from an electroless deposition bath (~1%). Photoelectrodes deposited with Ni-Mo alloy actually attain these similar overall efficiencies to Ni in spite of significantly lower photovoltages, precisely because they exhibit better HER catalysis. Additionally, p-Si microwire array photoelectrodes also produce similar overall thermodynamic energy conversion efficiencies in spite of significantly diminished photocurrents relatively to their planar counterparts. This similarity is again attributable to more efficient catalysis in the microwire case. Thus, it is clear that the major limitation of these photoelectrodes is the relatively small photovoltage that can be generated from mildly acidic aqueous solution in the absence of an n^+p junction. As such, we are currently pursuing several routes to increasing the photovoltages available from p-type Si photoelectrodes in aqueous solution, including the use of n^+p homojunctions.
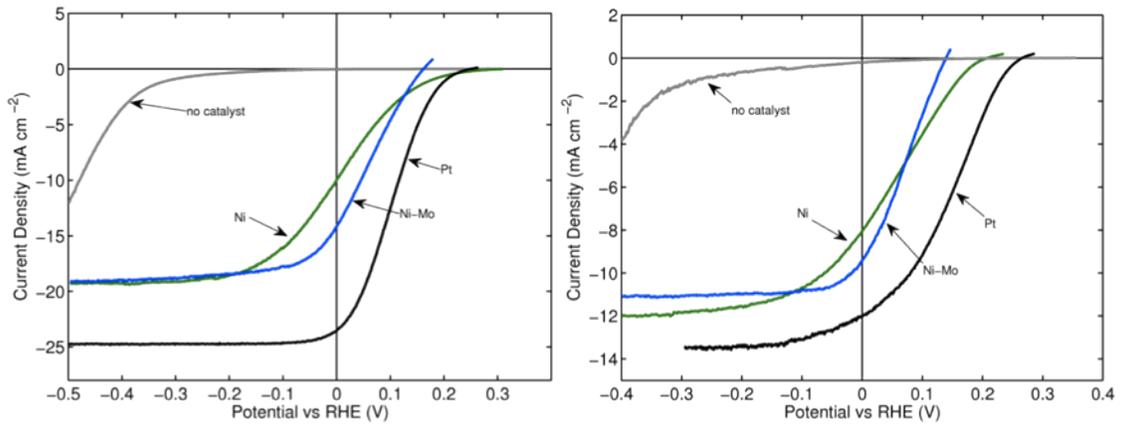
Figure 3: Representative current density-potential curves for photoelectrocatalysis of Ni, Ni-Mo alloy, and Pt on p-Si planar (left) and microwire array (right) photoelectrodes. Data were collected under the same conditions as noted in Figure 2.

## 2. Molecular Electrocatalysts for Aqueous H₂ Evolution

Introduction

Nature has developed the machinery to carry out the two most important chemical reactions on our planet: photosynthesis, the solar powered oxidation of water, and respiration, the reduction of oxygen to water. We have investigated long-range electron transfer phenomena that govern these vital processes in proteins and models, providing valuable insights into biological and bioinspired processes essential to the generation of clean fuels. Our GCEP funded projects have explored many topics ranging from site-directed mutagenesis of enzyme active sites that markedly alter redox properties to building photosystems for long range electron transfer across membrane proteins to drive reactions that generate fuels. We also have developed several promising new molecular catalysts for solar-driven water splitting.

Background

Previously, we have used electrochemical and photochemical methods to probe the catalytic pathway(s) of H₂ evolution of a set of cobalt-containing macrocycles, shown in Scheme 1. Our efforts in this area have contributed to an increased understanding of the mechanisms underlying transition metal mediated multi-electron transfer, and increased interest in the area of homogeneous electrocatalysis for hydrogen evolution.

Our investigations of new water and carbon dioxide reduction catalysts have continued to explore the catalytic behavior and reaction mechanisms of known complexes as a means towards new complexes with tunable ligands tailored for water tolerance and stabilization of multiple metal oxidation states. We have previously studied tetraazamacrocycle- and porphyrin-supported complexes of nickel and cobalt via photochemical and electrochemical methods. Our recent photochemical work intended to demonstrate homogeneous water reduction mediated by $[Co(TMPyP)]^{4+}$ in the presence of a sacrificial electron donor and $[Ru(diimine)_3]^{2+}$ has shown that these catalysts decompose within minutes under standard aqueous reaction conditions, likely via
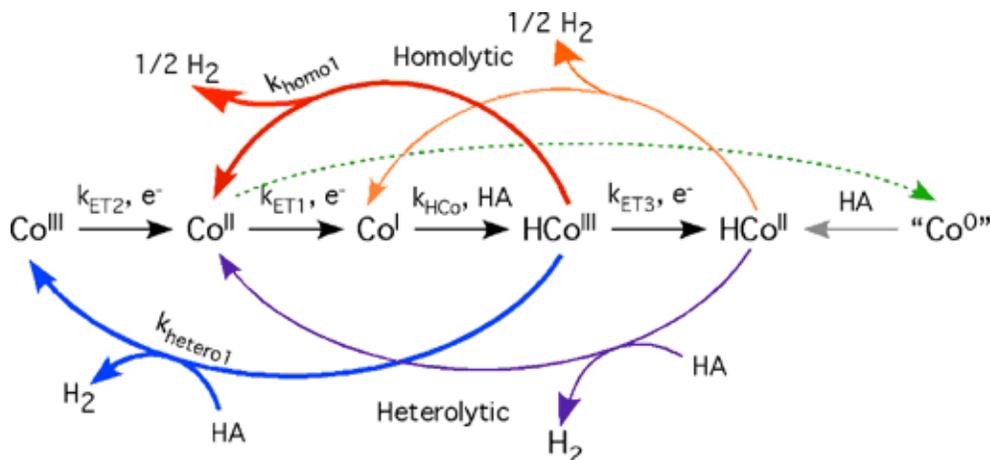
Scheme 1: Plausible reaction pathways for H₂ evolution via H_3O^+/H_2O reduction.

reduction of the photochemically reduced porphyrin ring, preventing sufficient water reduction to H_2 to perform detailed mechanistic studies. As a result, our remaining interest in these complexes lies in evaluation of their electrocatalytic properties, building on initial studies with related complexes.

Results

In the realm of molecular catalyst discovery, first generation cobalt electrocatalysts bearing readily accessible bis(iminopyridine) ligands operate at modest overpotentials and rapidly evolve H_2 under a broad range of homogeneous aqueous conditions (pH 2 to pH >7). Faradaic yields as high as 90% have been measured by GC analysis of controlled potential electrolyses, and apparent second-order rate constants $k_{app} = 10^6–10^8$ M^{-1} s^{-1} (10^2-10^3 × literature precedent) have been measured by cyclic voltammetry for the protonation of monovalent cobalt generated at the electrode.
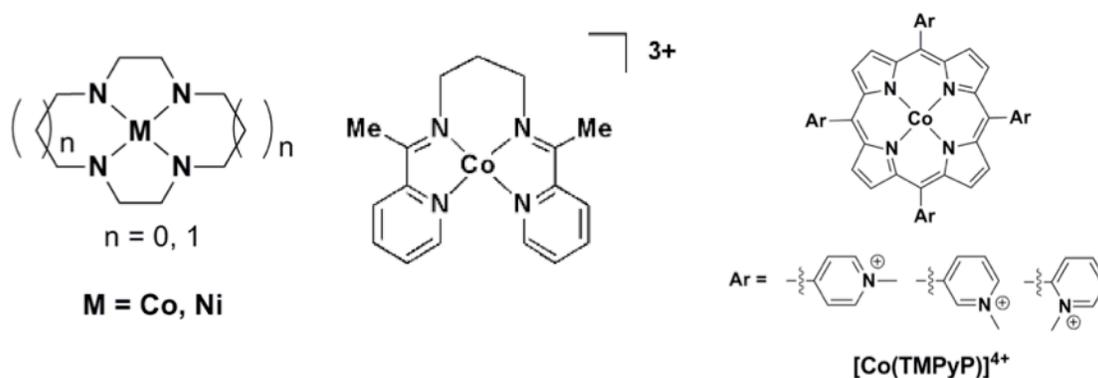

Figure 3: Molecular motifs of interest for novel aqueous molecular water reduction catalysts.

Interestingly, in addition to the catalytic wave normally observed near the $Co^{2+/1+}$ redox couple of tetraiminocobalt electrocatalysts, a second, catalytically more active reduction wave is observed within ca. 0.2 V of the initial reduction. While this could be reduction of the putative Co^{3+}–H to the analogous Co^{2+}–H species, it is more likely attributable to a ring reduction corresponding to Co^{3+}–H(L_4)/Co^{3+}–H($L_4^{·-}$).Similar ligands in support of first row transition metals have been shown to be exhibit noninnocent behavior, and we will seek to exploit this enhanced reactivity in rationally improving ligand design. Moreover, scan rate dependences of electrocatalytic waves in the present complexes suggest that catalytic water reduction occurs in a homogeneous fashion, without adsorption to mercury electrodes.

Preliminary photochemical studies using $[Ru(bpy)_3]^{2+}$ as photosensitizer and ascorbate as both sacrificial reductant and pH 4 buffer further indicate homogeneous catalysis, evolving H_2 powered by visible light (TON = 245, N_t = 10 h^{-1} vs. $[Co^{3+}]_0$). This homogeneous behavior has allowed detailed study of catalytic behavior in purely aqueous media and will direct future ligand modification toward improved catalysts that retain high activity and operate at considerably less negative potentials. First generation cobalt bis(iminopyridine) complexes are prepared in high yield via a templated condensation

reaction, and given the synthetic availability of substituted pyridine precursors, we are now generating CF_3- and NO_2-substituted ligands that should operate at less negative potentials and move us closer to molecular H_2 evolution catalysts powered entirely by the sun.

3. Optical Microscopy of Water Photoelectrolysis

Introduction and Background

Traditional measurements of gas evolution during water photoelectrolysis rely either on measurement of the overall electrochemical current or capturing macroscopic quantities of gas. However, the current may not fully reflect the photoelectrolysis rate due to parasitic corrosion reactions or chemical reactions in the electrolyte other than water splitting, and neither technique measures the *local* reaction rate on the surface in a spatially resolved manner. We have undertaken experiments to monitor optically the nucleation rate and growth rate of gas bubbles at different areas on the semiconductor surface, we hoped to obtain insight into the active catalytic sites, and important surface features, can be obtained.

Results

Semiconductor photoelectrodes for water splitting are most efficient with unique surface features such as high-surface-area morphologies or heterogeneous catalysts. As a method to compare the local reaction rate at different areas of a sample, we recorded the oxygen bubble growth on a n-SrTiO3 single-crystal photoanode in basic electrolyte under illumination with focused above-bandgap radiation. We analyzed the bubble growth rate by performing image analysis on the recorded video (Figure 4).
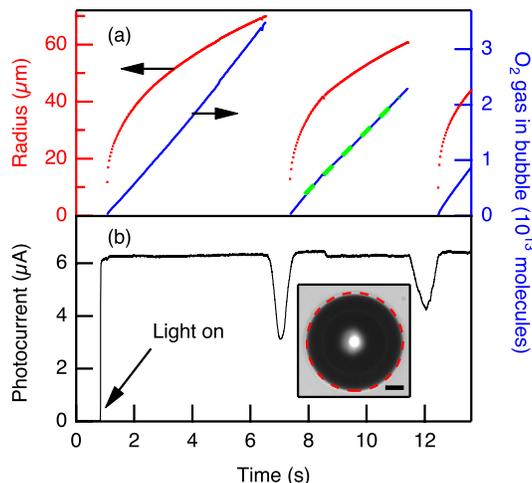

Figure 4: (a) Measured bubble radius and calculated gas present, and (b) photocurrent as a function of time at an irradiance of 1.8×10^5 W/m^2. The dotted line in (a) is the fit whose slope gives the reaction rate. Inset: Example of an analyzed video frame with the bubble perimeter shown as a dotted line (10 µm scale bar).

The reaction rate measurement was very similar to the rate measured via the photocurrent (Figure 5), indicating that careful observation of the bubbles can yield a satisfactory measurement of the gas-evolving reaction rate. Though the presence of a bubble blocks some area of the surface from the electrolyte, it also scatters light away
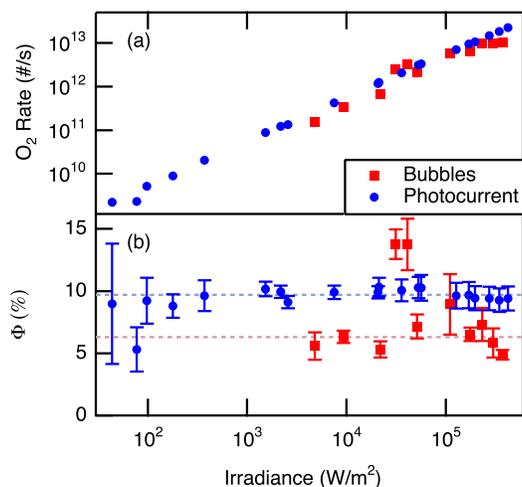
Figure 5: (a) Oxygen production rate and (b) quantum yield as a function of laser irradiance measured by the current (squares) and by the bubble growth rate (circles). The laser spot radius was 20 µm. The dotted lines indicate the approximate quantum yields measured by the two methods.

from its base, reducing its detrimental effect as compared to on a dark electrode. However, the high local gas supersaturation necessary to nucleate a bubble on a smooth surface required high levels of illumination, so artificial bubble nucleation sites would be necessary to use this characterization method in general. Spatially confined catalyst particles could serve as such nucleation sites, and thus more efforts are certainly warranted to understand the relationship between optical and electrochemical phenomena involved in bubble nucleation on functional semiconductor water splitting devices.

4. Summary and Conclusions

Our GCEP-funded research has been predicated on the notion that a near complete conversion to renewable energy sources is required for the mitigation of greenhouse gas emissions and climate protection, and that, based on scale, solar energy will certainly be required as a major component of any future renewable energy infrastructure. Importantly, solar energy cannot be utilized when and where the sun is not readily available; thus, methods are required for the robust and efficient storage of energy in the form of chemical fuels such as H_2.

Our GCEP proposal involved undertaking several fundamental research projects required for the development of an efficient, scalable system for splitting water into H_2 and O_2 using sunlight as the sole energy input. Our efforts in these areas have been tremendously successful. In the span of a few years, we have succeeded in the understanding, development, and demonstration a number of key insights, including:

(1) Si microwire arrays can be fabricated using inexpensive Si feedstocks.

(2) Microwire arrays can be doped p-type, and in aqueous electrolyte give large photovoltages to drive electrochemical reductions.

(3) Microwire arrays can be embedded in an optically transparent membrane material and within this membrane; microwire arrays can be used to successfully drive photoelectrochemistry.

(4) Microwire arrays, embedded in a transparent membrane, give rise to optical concentration effects allowing a much smaller mass of absorber material to be used relative to conventional single crystal Si devices.

(5) Heterogeneous electrocatalysts, including those derived from earth abundant, non-noble metals, can be used to drive the net conversion of incoming light to $H_2(g)$ in aqueous solution on p-type Si microwire arrays.

(6) Homogeneous electrocatalysts can be made to operate near the thermodynamic potential for hydrogen evolution in nonaqueous solution, and their catalytic mechanisms were probed using a combination of electrochemistry and transient spectroscopy so as to enable rational design of still better molecular catalysts.

(7) Bubble nucleation and generation result in a complex set of optical and electrochemical phenomena at semiconductor-catalyst-electrolyte interfaces that are warrant further study.

Insights generated by GCEP-funded research have already been successfully leveraged into continuing efforts in the Gray, Lewis, and Atwater groups to develop systems and insights necessary for the cheap, efficient storage of solar energy in chemical bonds. Notably, our work on molecular and heterogeneous catalysts has been used as a branching-off point for extensive research projects in the NSF-sponsored CCI Solar project, based at Caltech. Additionally, our work on Si microwire arrays, membranes, device fabrication, heterogeneous catalysts, and bubble studies, is currently being used to

initiate much more extensive work in the DOE-funded Joint Center for Artificial Photosynthesis, based at Caltech and the Lawrence Berkeley National Lab. Thus, the initial financial support put forward by GCEP has and continues to be multiplied many times over in continued efforts in fundamental and applied research in chemistry, physics, and engineering, all focused on developing key technologies for massively reducing greenhouse gas emissions.

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