

## SUNLIGHT-DRIVEN HYDROGEN FORMATION BY MEMBRANE-SUPPORTED PHOTOELECTROCHEMICAL WATER SPLITTING

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### OVERVIEW

During the project, we made significant advances in the development of the polymer-supported photoelectrochemical water-splitting system that was proposed under DOE grant number **DE-FG02-05ER15754**. We developed Si microwire-array photoelectrodes, demonstrated control over the material and light-absorption properties of the microwire-array photoelectrodes, developed inexpensive processes for synthesizing the arrays, and doped the arrays p-type for use as photocathodes. We also developed techniques for depositing metal-nanoparticle catalysts of the hydrogen-evolution reaction (HER) on the wire arrays, investigated the stability and catalytic performance of the nanoparticles, and demonstrated that Ni-Mo alloys are promising earth-abundant catalysts of the HER. We also developed methods that allow reuse of the single-crystalline Si substrates used for microwire growth and methods of embedding the microwire photocathodes in plastic to enable large-scale processing and deployment of the technology. Furthermore we developed techniques for controlling the structure of WO<sub>3</sub> films, and demonstrated that structural control can improve the quantum yield of photoanodes. Thus, by the conclusion of this project, we demonstrated significant advances in the development of all components of a sunlight-driven membrane-supported photoelectrochemical water-splitting system.

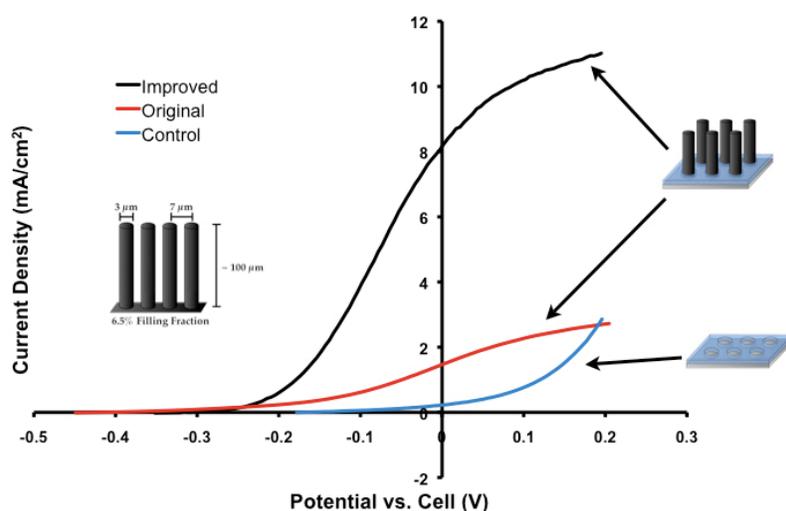
This final report provides descriptions of some of the scientific accomplishments that were achieved under the support of this project and also provides references to the peer-reviewed publications that resulted from this effort.

### GROWTH OF STRUCTURED SEMICONDUCTORS FOR SOLAR ENERGY CONVERSION

The planar geometry typically used for Si photoelectrodes requires high purity single-crystalline materials to convert sunlight to collected charge carriers at high efficiencies because there is a mismatch between the optical absorption depth and the minority-carrier diffusion lengths in impure materials. Semiconductor microwire-array structures allow for increased solar energy-

conversion efficiencies from impure, and hence potentially inexpensive, materials by allowing the charge-carrier collection distance to be varied independently of the material thickness.

We developed methods to grow vertically oriented n-type silicon wire arrays using chemical-vapor deposition (CVD) and metal vapor-liquid-solid (VLS) catalysts (Figure 1). In order to understand the properties of the wire arrays for solar energy capture and conversion, we immersed them in a liquid electrolyte that functions as a conformal contact. These wire arrays gave photovoltages in excess of 400 mV and significant photocurrents. Surface etching produced dramatic improvements in the solar energy conversion performance of the samples, and all samples showed much higher performance than the control samples. Given the filling fraction of the microwires, as viewed from above, the current densities measured in the best samples were 2–3 times the expected maximum current density, indicating significant light trapping by the wire array.



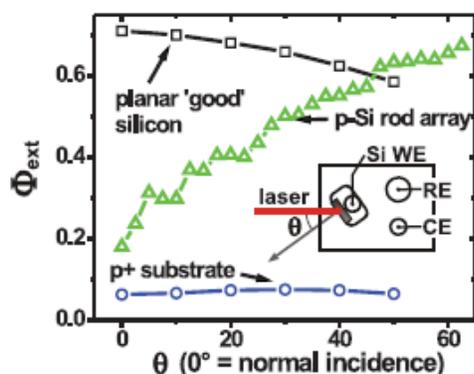
**Figure 1. Photoelectrochemical solar cells from VLS-grown n-type silicon microwire arrays.** The etched wire-array samples (black curve at top) give significant photocurrents and photovoltages. The control sample (blue), consisting of the base wafer upon which the wires were grown, had no significant photoresponse.

This better-than-expected performance suggested that the microwire arrays not only allow for reduced-purity (i.e. cheaper) materials to be used than in planar cells, but that less material can also be used since the light is more efficiently absorbed. These early results demonstrated significant progress toward low-cost silicon solar energy-conversion devices.

## DEVELOPMENT OF SI MICROWIRE-ARRAY PHOTOCATHODES

We developed a method for controlled p-type doping of the Si microwire arrays by introducing  $\text{BCl}_3$  gas during the CVD growth process and by using Cu (instead of Au) as the VLS growth catalyst. The p-type doping allows the microwire arrays to be used as hydrogen-evolving photocathodes. Measurements of single microwires that were removed from the arrays showed that the dopant density can be controlled by varying the flow rate of  $\text{BCl}_3$ . The use of Cu as the VLS-growth catalyst was critical to the ability to grow microwires with high inherent energy-conversion performance because, unlike Au, Cu does not diffuse deeply into the Si bulk where the metal atoms would act as trap states, but rather collects on surfaces where it can be removed by chemical etching.

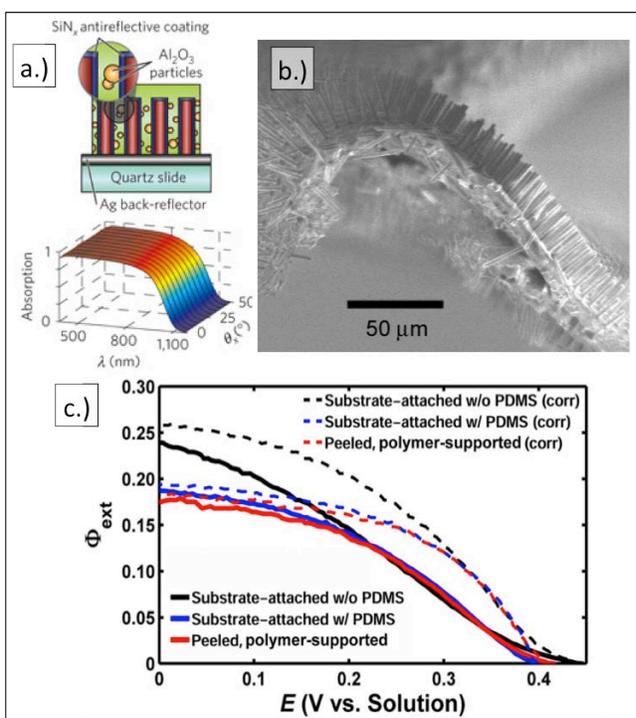
The electronic properties of the p-type Si microwire arrays were studied in an aqueous electrochemical cell using the methyl viologen<sup>2+/+</sup> redox couple. Good voltages ( $\sim 0.410$  V) and high fill factors ( $\sim 0.5$ ) were measured for the cells and energy-conversion efficiencies of  $\sim 3\%$  were observed for monochromatic 808-nm light at fluxes comparable to solar illumination. The internal quantum yields at short circuit were at least 0.7, but the external quantum yields were only  $\sim 0.2$ . Figure 2 shows the results of angle-resolved photocurrent measurements, which indicated that the external quantum yields measured for the microwire photocathodes were light-absorption limited, and thus the quantum yields for the microwire arrays could be made to approach the quantum yields of high-purity planar electrodes by increasing the length or filling fraction of the microwire arrays in order to allow them to absorb all of the incident radiation.



**Figure 2. Angle-resolved photocurrent measurements of Si microwire array photocathodes.** The measurements were performed with a 633-nm He-Ne laser (2.6 mW). The inset shows a schematic of the cell.

## POLYMER-EMBEDDED MICROWIRE ARRAYS

We developed techniques for embedding Si microwire photocathodes in flexible polymer layers and for removing the embedded microwires from the growth substrate. Specifically, arrays of Si rods were embedded in polydimethylsiloxane (PDMS), an inexpensive material that is transparent to visible light. The PDMS-embedded microwire arrays were removed from the rigid crystalline Si growth substrate, resulting in a composite material that merged the benefits of single-crystalline silicon with the flexibility of a polymer. With this technique, inorganic solar-cell light-absorber materials with the potential to achieve high energy-conversion efficiencies can be prepared by high-temperature processing and transformed into a flexible form. Addition of a silicone monomer with a low boiling point to the PDMS mix enabled the production of polymer-embedded Si microwire arrays where the majority of the length of each microwire protruded from the polymer.



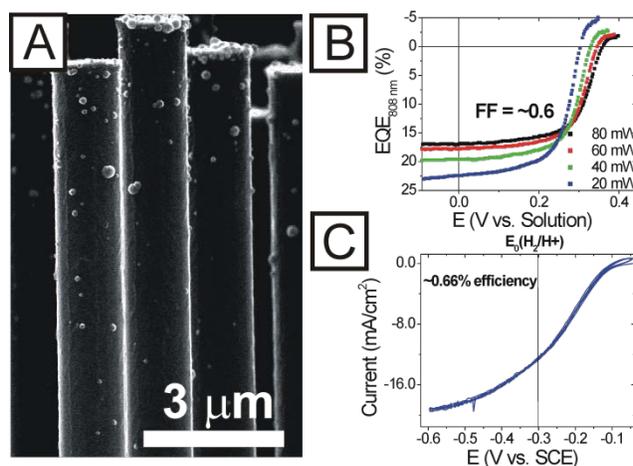
We characterized the photoelectrochemical performance of polymer-embedded microwire arrays that were peeled off of the growth substrate and extended the peeling technique to polymers that can serve as both structural supports and selectively permeable membranes.

Furthermore, to reduce the expense of the single-crystal Si wafer required to grow well-defined, highly uniform wire arrays, we developed a technique that allows the wafer to be reused as a

template for growth of additional microwire arrays after an array is peeled off of the substrate in PDMS. The combination of the polymer-embedment and wire-regrowth techniques provides a processing scheme in which inorganic semiconductor microwire arrays can be economically fabricated and incorporated into durable organic layers comparable to the ion-transport membranes needed for a water-splitting device.

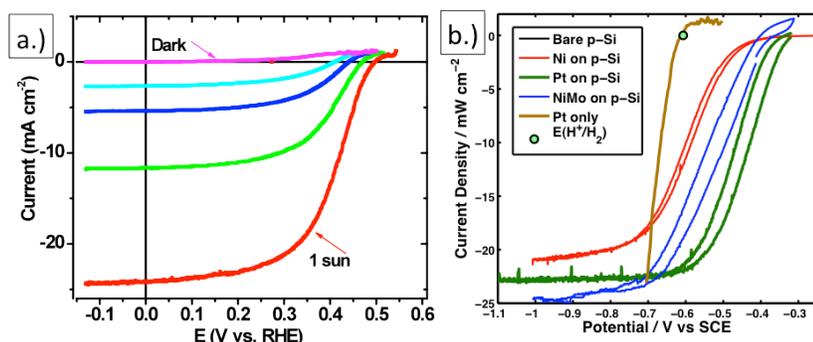
## INTEGRATION OF HYDROGEN-EVOLUTION CATALYSTS ONTO STRUCTURED PHOTOCATHODES

We successfully deposited nanoparticulate catalysts of the HER on the p-type Si microwire arrays using a galvanic displacement reaction from metal salts in dilute HF solutions (Figure 4A). Pt-modified silicon rod arrays with an open-circuit voltage ( $V_{OC}$ ) of  $\sim 250$  mV generated hydrogen under solar illumination with efficiencies approaching 1% (Figure 4C).



**Figure 4. p-Si microwire arrays with nanoparticulate Pt HER catalysts.** (A) Pt functionalized microwires, (B) photoelectrochemical performance in contact with a reversible redox couple (C) hydrogen generation with an efficiency approaching 1 %.

Since platinum is an expensive and scarce catalyst material, we then investigated earth-abundant HER catalysts such as Ni and Ni-Mo alloys. We showed that Ni-Mo has comparable performance to Pt as a dark catalyst, investigated the catalytic performance of Ni-Mo on p-Si photocathodes (Figure 5b), and incorporated Ni-Mo catalysts into polymer-embedded n<sup>+</sup>p-Si microwire-array photocathodes. Under nominally the same conditions, the efficiency of the Ni-Mo-coated system



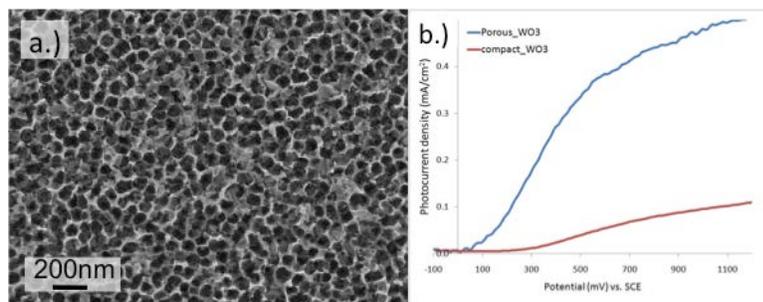
**Figure 5.** a.) H<sub>2</sub> production from n<sup>+</sup>/p radial junction wires coated with a Pt catalyst in a pH = 1 electrolyte; b.) comparison of the activities of Ni, Pt, and Ni-Mo for catalysis of the HER on planar p-Si photocathodes in a buffered pH 6.5 solution under 100 mW cm<sup>-2</sup> illumination.

was comparable to that of Pt-coated n<sup>+</sup>p-Si microwire-array photocathodes, demonstrating that earth-abundant electrocatalysts can provide performance comparable to noble-metal catalysts for photoelectrochemical hydrogen evolution.

## TUNGSTEN OXIDE PHOTOANODES FOR WATER OXIDATION

Wide band-gap metal oxides are stable, non-toxic, inexpensive, and possess some catalytic activity, and are thus candidates for photoanodes to drive the oxygen-evolution half-reaction for water splitting. However, many metal oxides have band gaps that are too high to allow the material to capture light efficiently, and the morphology of the materials is often impractical for solar applications. For this project, we investigated whether the band gap of WO<sub>3</sub> photoanodes can be reduced by doping the material, or whether structuring WO<sub>3</sub> will enable charge-carriers to efficiently reach the water oxidation interface.

Nanoporous WO<sub>3</sub> layers were fabricated by potentiostatic anodization of tungsten foil in fluoride electrolytes. We investigated the influence of voltage, reaction duration, and electrolyte on the morphology of the porous layers. Results indicated that porous WO<sub>3</sub> electrodes are stable under aqueous conditions, and produce open circuit voltages over 800 mV and significantly higher photocurrent densities and external quantum yields than compact WO<sub>3</sub> electrodes (Figure 6b).



**Figure 6. Porous WO<sub>3</sub>** a.) SEM image of porous WO<sub>3</sub>. b.) Comparison of compact and porous WO<sub>3</sub> photoanodes in pH 4 buffered solution under 100 mW cm<sup>-2</sup> illumination.

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