Next-Generation Si Microwire Array Devices for Unassisted Photoelectrosynthesis

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May 15, 2013

Project ID # PD099

Overview

Project Timeline

- Start date: November, 2011
- End date: June, 2013
- Percent complete: 75%

Budget

- Total project funding
  - DOE share: $150,000
  - Contractor share: $0
- Funding by year
  - FY12: $75k
  - FY13: $50k (projected)

Barriers Addressed

- Photoelectrochemical Hydrogen Production – Photoelectrode System
- Materials Durability – Bulk and Interface
- Integrated Device Configurations

Partners / Collaborators

- University of Manitoba (Freund, Oliver, Thomson Groups): evaluation of single microwire–polymer junctions
- Technical University of Denmark (Chorkendorff Group): amorphous-MoS_x electrocatalyst synthesis
- École Polytechnique Fédérale de Lausanne (Ballif Group): amorphous-Si:H semiconductor deposition

Relevance

Objective: Fabricate a scalable Si microwire array-based device for sunlight to clean H_2 fuel production, through hydrohalic acid splitting

DOE Barriers and Targets	Project Goal
Photoelectrochemical Hydrogen Production – Photoelectrode System	• Fabricate polymer-embedded arrays of n-type and p-type crystalline Si microwires • Demonstrate stable sunlight-driven hydrohalic acid splitting • Identify stable and efficient non-noble-metal electrocatalysts
AF) Materials Durability – Bulk and Interface	• Stabilize Si from oxidation while passing anodic current in aqueous HI and HBr electrolytes
AG) Integrated Device Configurations	• Fabricate an organic photovoltaic that contains ionically conductive materials • Fabricate a tandem Si microwire array with an integrated amorphous-Si light absorber • Demonstrate sunlight-driven H_2 evolution through HBr splitting with a tandem device

Approaches / Milestones

May, 2012: 6-Month Report

Status & Description of Milestones	Results
A) 100% Complete; Stable n-type Si microwire array electrodes decorated with Pt electrocatalysts for sustained sunlight-driven iodide oxidation in HI*(aq)* with > 3% sunlight-to-electrical energy conversion efficiency and > 80% stability of the short-circuit photocurrent density, j_{sc} (200 hr operation)	**Substeps achieved:** Optimal CVD–VLS growth procedure for n-type Si microwire arrays, including: • Post-growth microwire processing and etching • Surface methylation of microwires for protection • Potentiostatic electrochemical deposition of Pt
B) 75% Complete; Peeled, flexible, radial buried-homojunction pn^+-doped Si microwire array devices decorated with Pt electrocatalysts and partially embedded in Nafion® for stable HI*(aq)* splitting with > 3% sunlight-to-hydrogen energy conversion efficiency **Remaining barrier: Devices leak through macroscopic pinholes in the Nafion® membrane, preventing useful efficiency measurements**	**Substeps achieved:** ● Pt electrocatalyst deposition on the backsides of peeled, polymer-embedded Si microwire arrays by electron-beam evaporation ● Methylation of the backsides of peeled, polymer-embedded Si microwire arrays for protection ● Fabrication of a measurement system, including: • A device holder (acrylic block and glass cuvettes) • A means of forced convection (inductive stirring) • An imaging system (borescope) • In situ reaction product detection capabilities to 1% j_{sc} (mass spectrometry and visible spectroscopy)

Approaches / Milestones

August and November, 2012: 9- and 12-Month Reports

Status & Description of Milestones	Results
C) 90% Complete; Radial, buried-homojunction np^+-doped Si microwire array electrodes with > 3% sunlight-to-electrical energy conversion efficiency in (non-)aqueous electrolyte *(Prerequisite: Milestone A)*	**Substep achieved:** Optimal boron emitter doping conditions from BN source wafers of 7 min at 950 °C **Remaining barrier: A 2.2% efficiency was observed in non-aqueous electrolyte, but a > 3% efficiency was attained for aqueous iodide photo-oxidation**
D) 50% Complete; Peeled, flexible, radial buried-homojunction $n(p^+)$-doped Si microwire array devices decorated with Pt electrocatalysts and partially embedded in Nafion® for stable HI*(aq)* splitting with > 3% sunlight-to-hydrogen energy conversion efficiency *(Prerequisites: Milestones B, C)*	**Substep achieved:** In situ growth of an n^+-doped region at the bottom of the microwires to form a low-resistance tunnel junction between the backsides of n-type Si microwires and Pt **Remaining barrier: Low-resistance contacts were not present after a required high-temperature oxidation step which gettered the dopants**
E) <u>No Go</u>; 10% Complete; Innovation Project: Ionically conductive organic photovoltaic with $V_{ion\text{-}drop}$ < 10 mV (at 10 mA/cm^2), V_{oc} > 600 mV, and j_{sc} > 10 mA/cm^2	**Remaining barrier: Efficient organic photovoltaics were fabricated by drop casting, but their water and air instability occluded measurements when Nafion® was introduced or when in contact with aqueous electrolyte**

Approaches / Milestones

May, 2013: 18-Month Report

Status & Description of Milestones	Results
F) 50% Complete; Stable p-type Si microwire array electrodes for sustained bromide oxidation in HBr*(aq)* in the dark with > 80% current stability (200 hr operation)	**Substep achieved:** PEDOT:PSS on surface-functionalized planar Si was stable for halide oxidation **Remaining barrier: Atomic layer deposition of TiO_x, AlO_x, or MnO_x on Si partially stabilized the Si but also significantly attenuated current flow**
G) <u>Go</u>; 50% Complete; Peeled, flexible, stable, tandem amorphous-Si on crystalline Si microwire array devices with Pt and partially embedded in Nafion® for stable HBr*(aq)* splitting with > 8% sunlight-to-hydrogen energy conversion efficiency *(Prerequisites: Milestones B or C, D, F)*	**Substep achieved:** Amorphous Si was deposited by PECVD on pn^+-doped Si microwire arrays, which exhibited $V_{oc\text{-}max}$ ≈ 960 mV in non-aqueous electrolyte, and $V_{oc\text{-}max}$ ≈ 780 mV for aqueous H_2 evolution **Remaining barrier: There is room for improvement because planar devices exhibited $V_{oc\text{-}max}$ ≈ 1.2–1.3 V**
H) 50% Complete; Peeled, flexible, stable, tandem p-Si || n-Si microwire array devices with Pt and partially embedded in Nafion® for stable HBr*(aq)* splitting with > 7% sunlight-to-hydrogen energy conversion efficiency *(Prerequisites: Milestones B, C, D, F)*	**Substep achieved:** A > 90% transparent electrically and ionically conductive membrane was fabricated **Remaining barrier: The optimal membrane formulation, containing Ag nanowires, PEDOT:PSS, and Nafion®, is not yet determined**

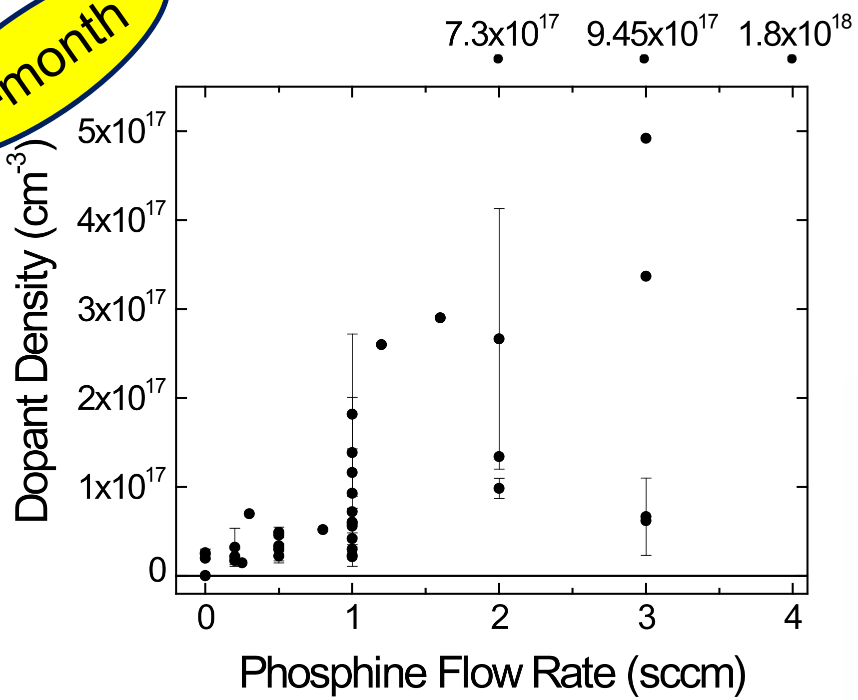
Approaches / Milestones

November, 2013: 24-Month Report

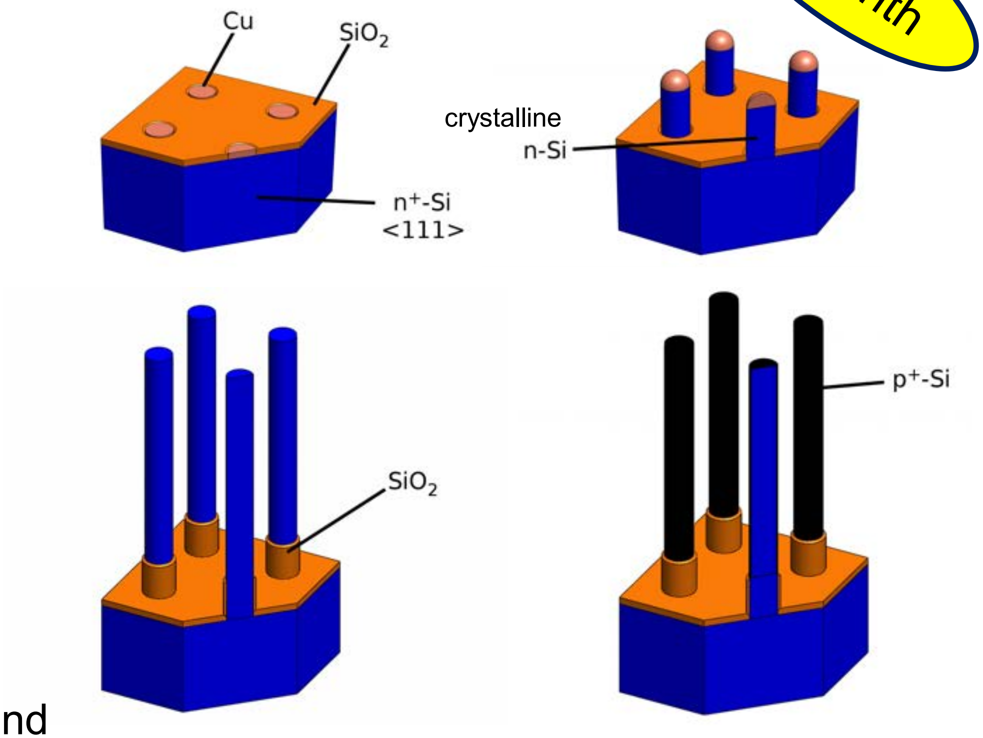
Status & Description of Milestones	Results
K) 50% Complete; Mo/W(S,Se)$_2$ nanometer-sized electrocatalysts for efficient halide oxidation and H_2 evolution in the dark with < 150 mV overpotential at 10 mA/cm^2	**Substep achieved:** PEDOT:PSS on surface-functionalized planar Si was stable and somewhat catalytic for halide oxidation **Remaining barrier: Amorphous MoS$_x$ on Si met this goal for H_2 evolution but MoS$_x$ is not stable during sustained halide oxidation**
L) 25% Complete; Peeled, flexible, stable, tandem p-Si || n-Si microwire array devices with Mo/W(S,Se)$_2$ electrocatalysts and partially embedded in Nafion® for stable HBr*(aq)* splitting with > 6% sunlight-to-hydrogen energy conversion efficiency *(Prerequisites: Milestones B, C, D, F, K)*	**Substeps achieved:** None
I, J, M) Removed these milestones, because my program timeline will be curtailed when I begin my independent faculty career this fall	**N/A**

Accomplishments / Progress

6-month



6-month

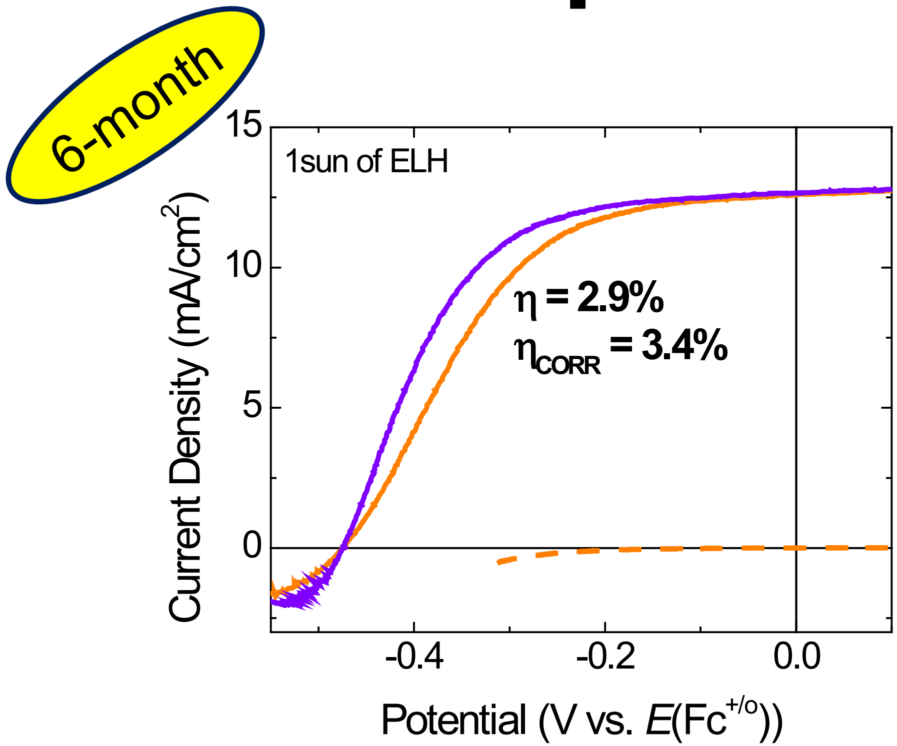


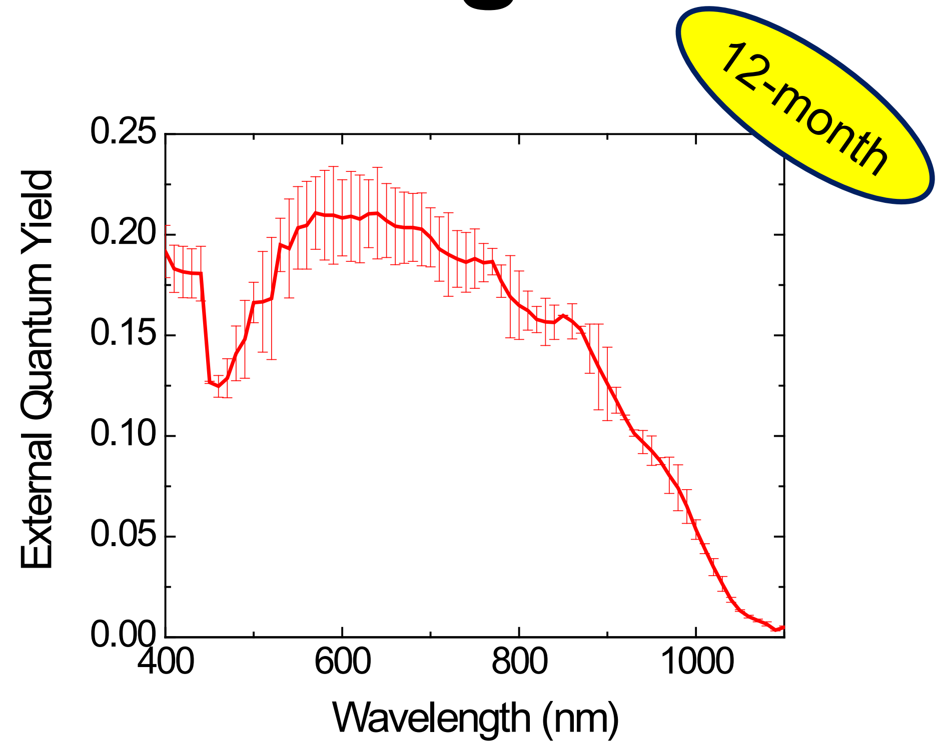
- Electrically active dopant density in individual n-type Si microwires before and after processing calculated from four-point-probe resistance measurements
- Dopant densities of ~1 x 10^{17} cm^{-3} resulted in the most efficient devices

- Four major steps in the CVD–VLS growth fabrication process of n-type Si microwire arrays, with optional radial n^+-type emitters

Fabrication protocol for n-type Si microwire arrays

Accomplishments / Progress





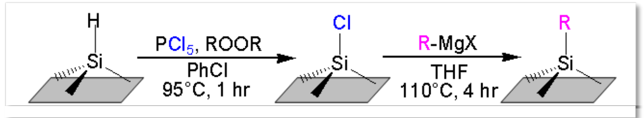
- Three-electrode *j–E* measurements in $Me_2Fc^{+/0}$–$LiClO_4$–CH_3OH demonstrate a state-of-the-art corrected η = 3.4%
- Electrode is an n-type Si microwire array after thermal oxidation processing

- Three-electrode spectral response measurements of the same electrode type in the same electrolyte demonstrate external quantum yields similar to those previously measured for p-type Si microwire arrays

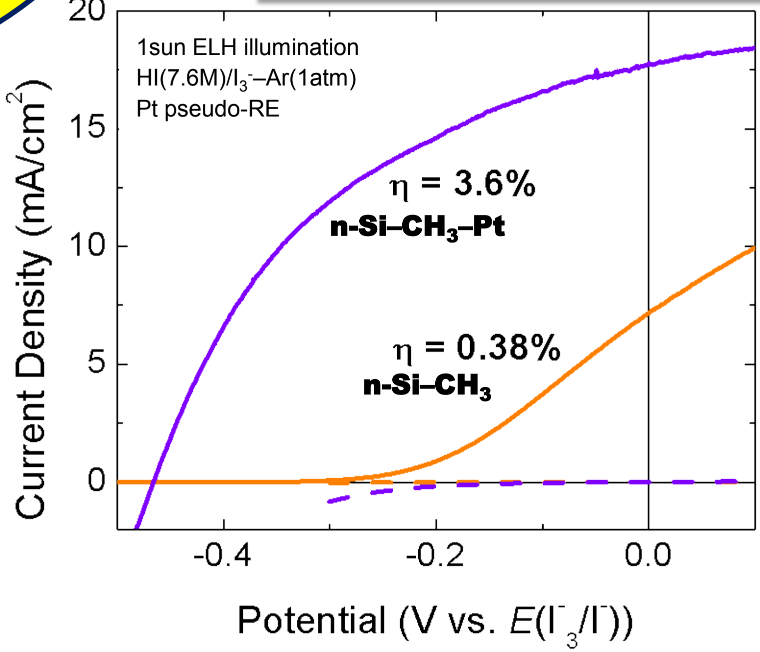
Efficient n-type Si microwires were realized

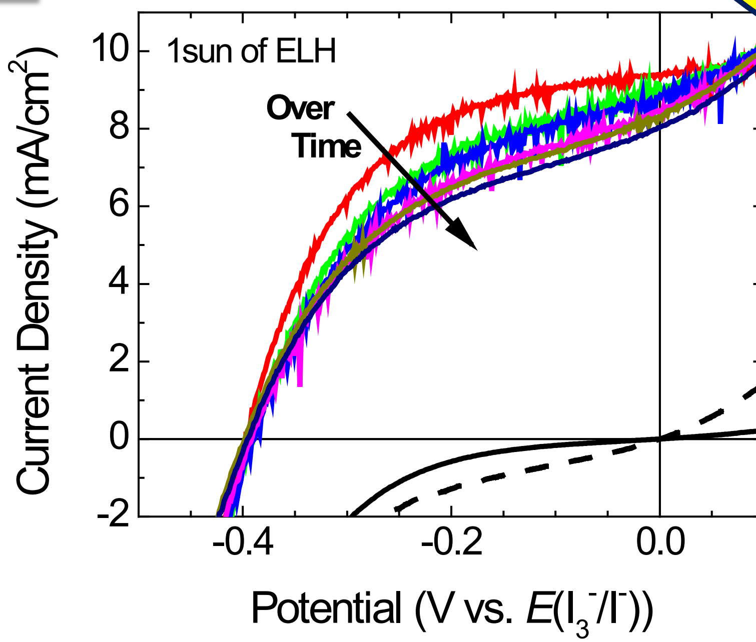
Accomplishments / Progress

6-month



6-month

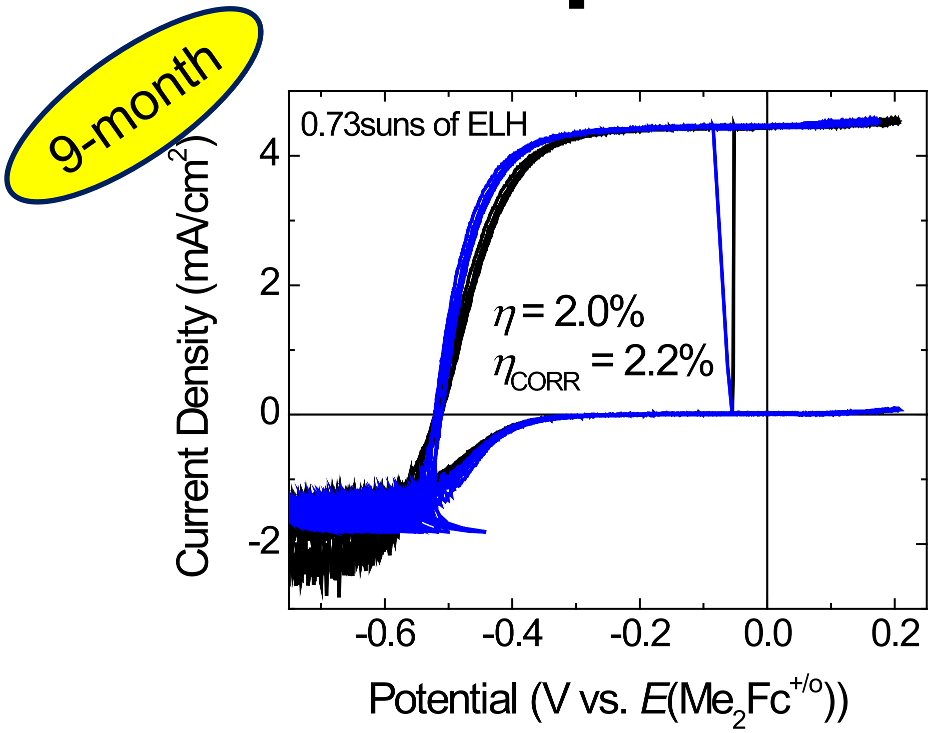


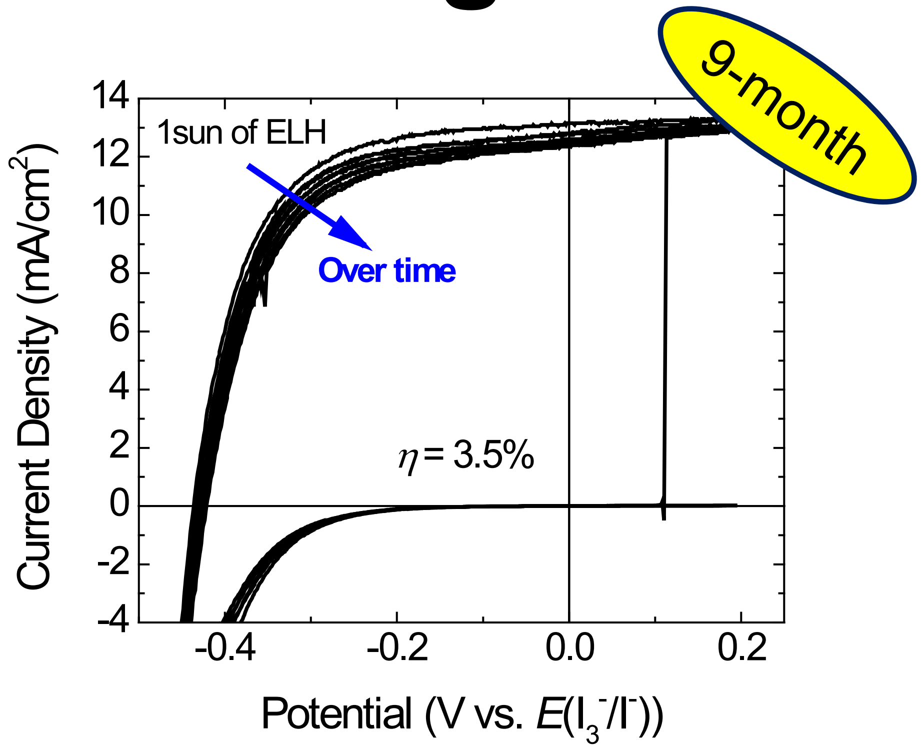


- Three-electrode *j*–*E* measurements in fuming aqueous HI demonstrate a state-of-the-art uncorrected $\eta = 3.6\%$
- Electrode is an n-type Si microwire array after thermal oxidation, surface methylation (scheme), and Pt catalyst deposition
- Three-electrode *j*–*E* measurements over 200 hours continued operation at short-circuit in fuming aqueous HI
- Stability was > 80 % of $j_{sc\text{-}initial}$ over 200 hours continued operation while continuously illuminated

Efficient and stable n-type Si microwires photo-oxidize iodide

Accomplishments / Progress





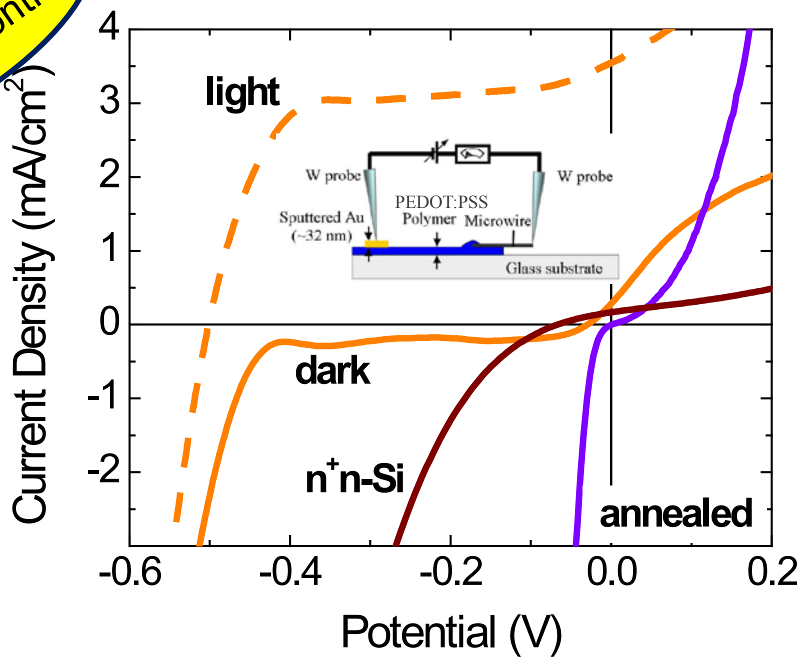
- Three-electrode *j–E* measurements in $Me_2Fc^{+/0}$–$LiClO_4$–CH_3OH demonstrate a corrected η = 2.2%
- Electrode is an undoped Si microwire array grown on an n^+-Si substrate after thermal oxidation and p^+ radial emitter doping

- Three-electrode *j–E* measurements in fuming aqueous HI demonstrate an uncorrected η = 3.5%
- Same electrode type but with Pt catalyst deposition (instability was due to lack of surface methylation)

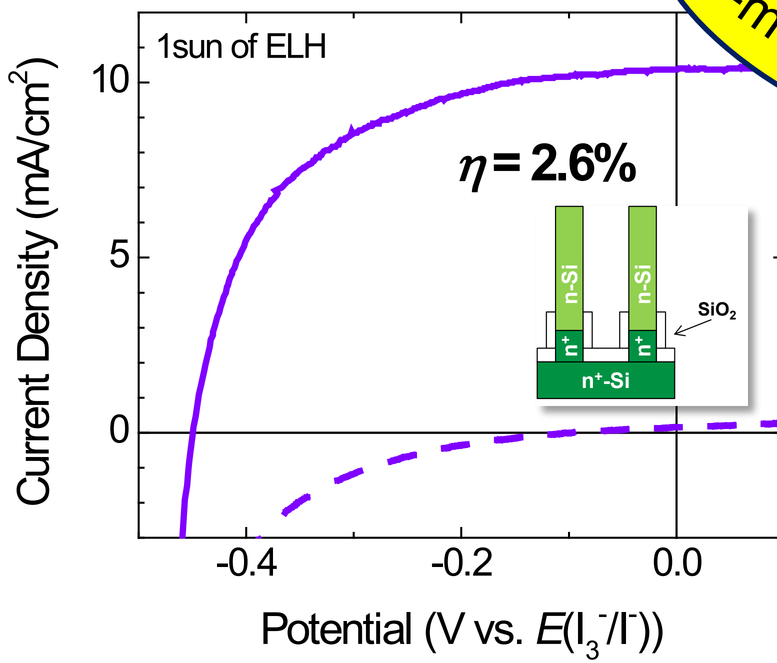
Efficient (n^+)ip^+-doped Si microwires were realized

Accomplishments / Progress

9/18-month



9-month

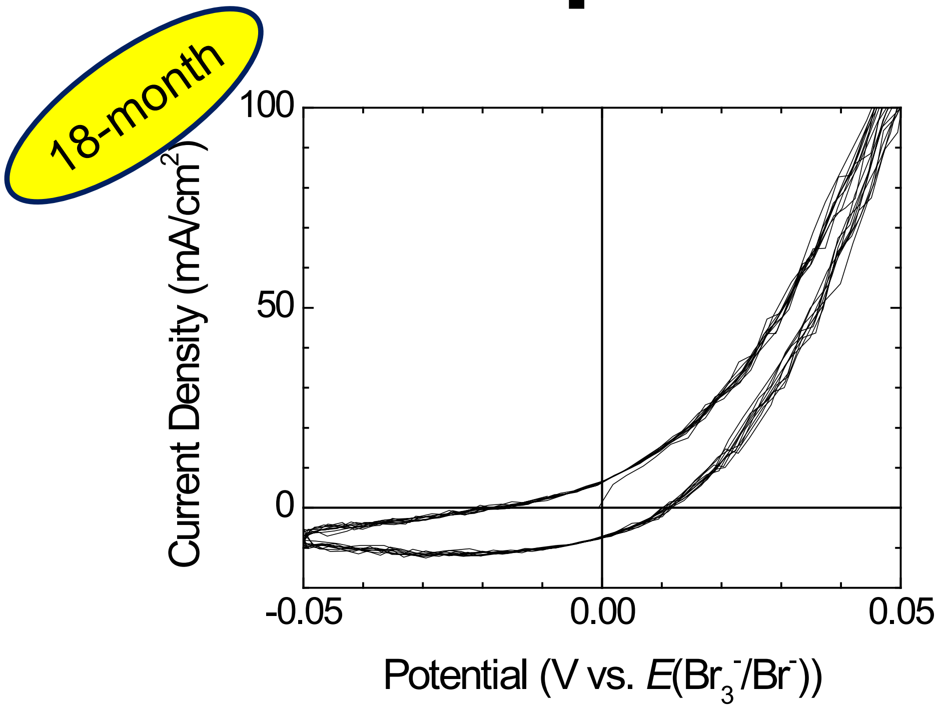


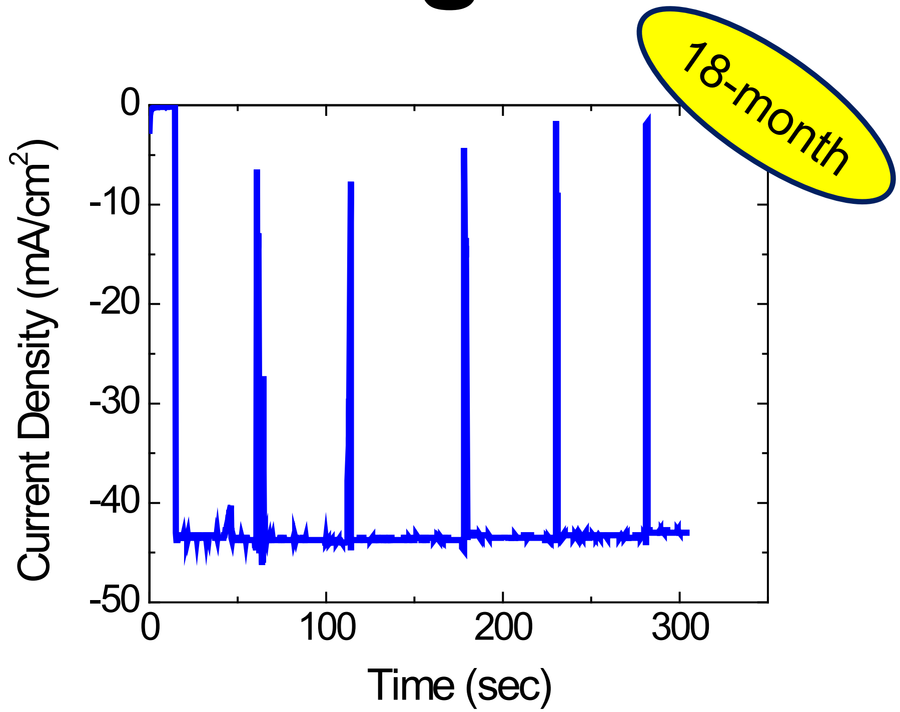
- Two-point-probe individual n-type Si-microwire–PEDOT:PSS *j–E* measurements (inset) evaluating the contact resistances: one that had been annealed 10 hr on an n^+(P)-Si substrate, and one that was grown as an axially doped n^+n-Si microwire and then went through the thermal oxidation process

- Three-electrode *j–E* measurements in fuming aqueous HI demonstrate an uncorrected η = 2.6%
- Electrode is an axially doped n^+n-Si microwire array grown after thermal oxidation, surface methylation, and Pt catalyst deposition (inset)

n^+n-doped Si microwires are efficient with little shunting, but are not degenerate after the thermal oxidation step

Accomplishments / Progress





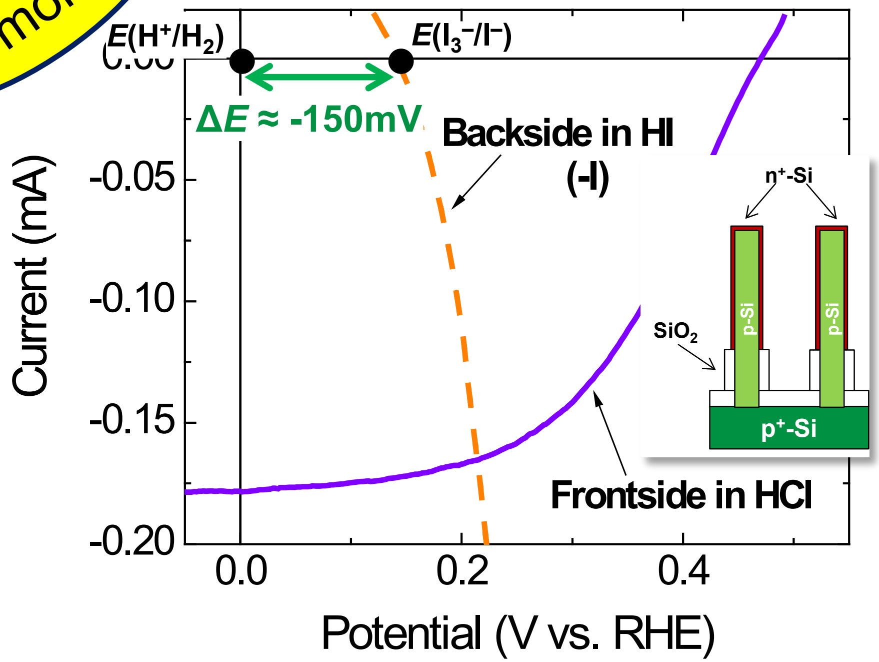
- Three-electrode *j*–*E* measurement in fuming aqueous HBr demonstrate very efficient and stable bromide oxidation catalysis in the dark
- Electrode is planar p-Si with mixed methyl/thienyl surface chemistry, and electropolymerized PEDOT:ClO_4

- Three-electrode chronoamperometry measurement in fuming aqueous HBr demonstrate very stable H_2 evolution catalysis in the dark
- Electrode is planar p-type Si with mixed methyl/thienyl surface chemistry, and electrodeposited amorphous MoS_x

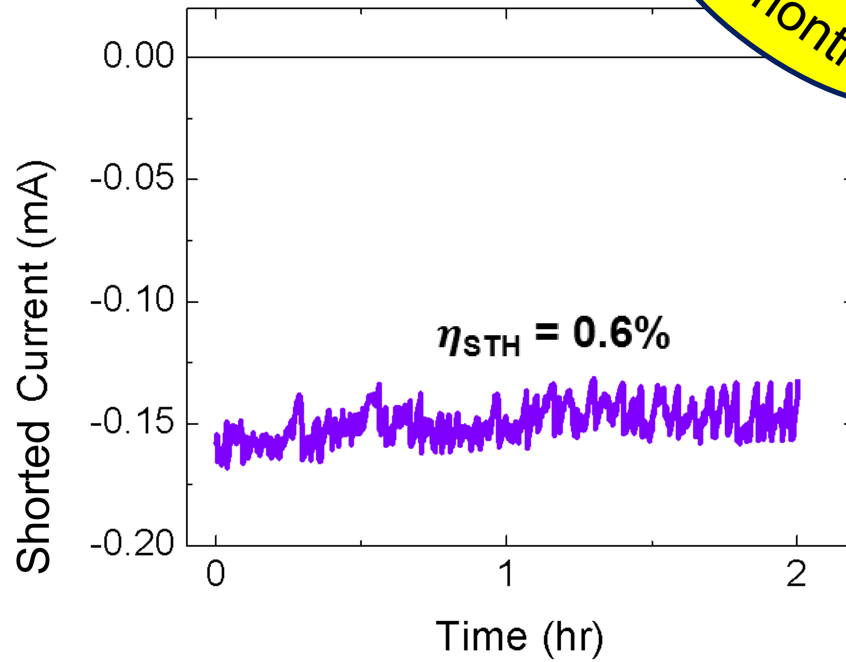
PEDOT:ClO_4 stabilizes Si from oxidation and efficiently catalyzes bromide oxidation, while *a*-MoS_x is stable during H_2 evolution catalysis in fuming HBr

Accomplishments / Progress

6-month



6-month



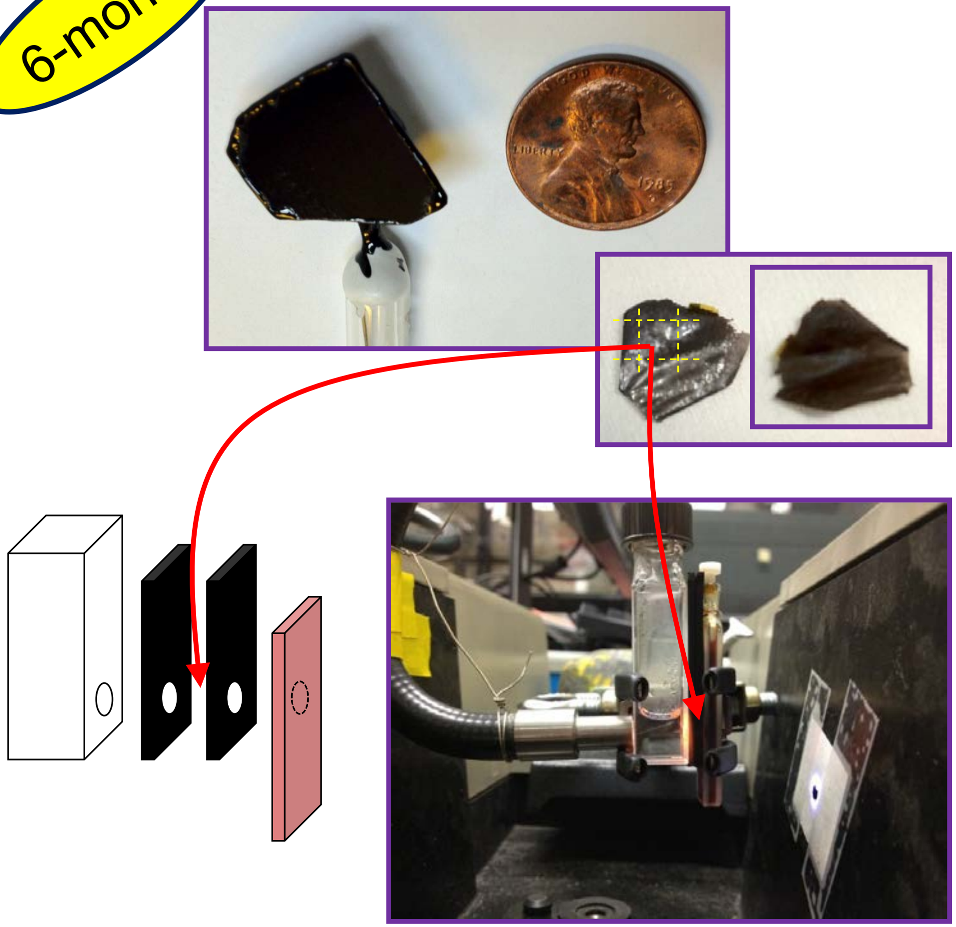
- Three-electrode *I*–*E* measurements in fuming aqueous HCl demonstrate an uncorrected η = 1.2% for H_2 evolution
- Electrode is a p-type Si microwire array after thermal oxidation, n^+ radial emitter doping, and Pt catalyst deposition (inset)

- Two-electrode, two-cell-compartment measurement with the pn^+-Si microwire array photocathode illuminated in fuming aqueous HCl separated from a backside electrode in fuming aqueous HI by a commercial Nafion® membrane, and shorted together via an external wire

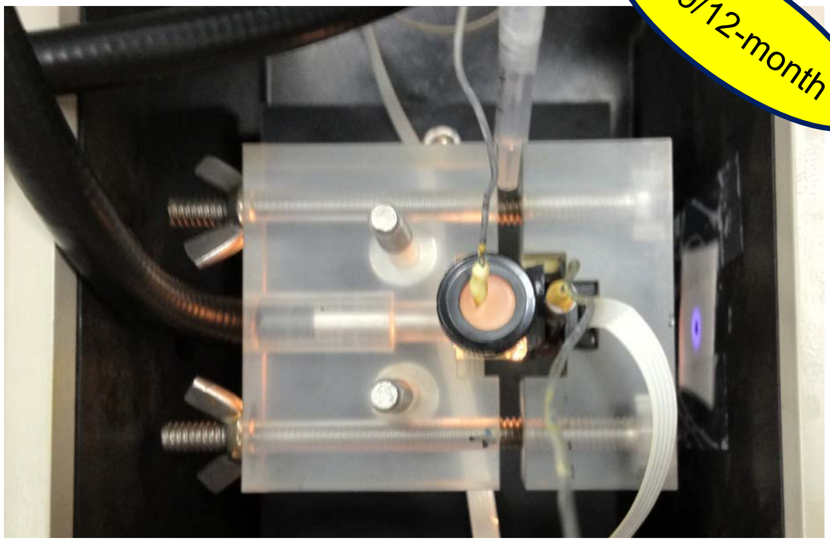
Unassisted HI splitting occurs via H_2 evolution at an illuminated pn^+-doped Si microwire photocathode while a backside electrode oxidizes iodide to triiodide

Accomplishments / Progress

6-month



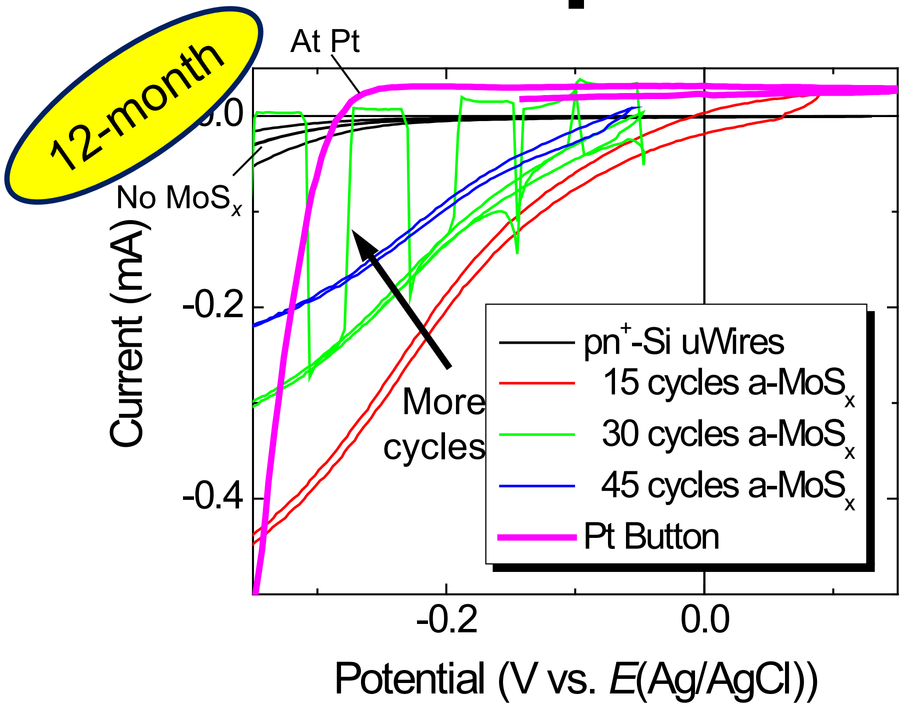
6/9/12-month

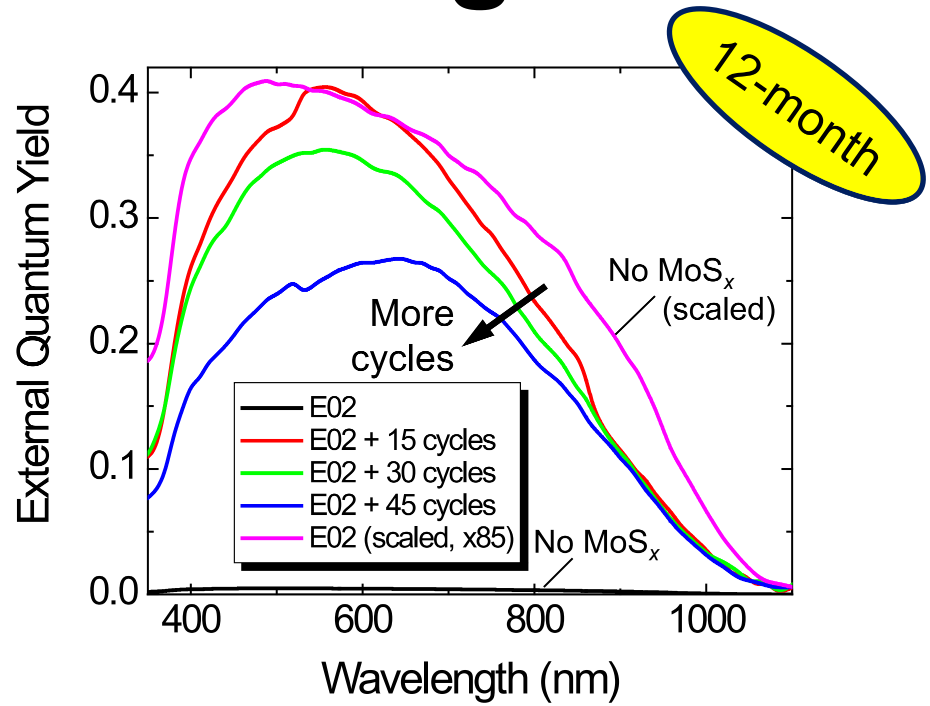


- Apparatus and conditions used to quantify I_3^- and H_2 products in situ using visible spectroscopy and mass spectrometry
- Fiber optic excitation source, inductive stirrers, gas-tight cathode compartment, and 2 mm pathlength anode compartment
- Products generated at (current) rates > 100 μA/cm² can be detected

Apparatus and measurement system for free-standing hydrohalic acid splitting from peeled, polymer-embedded microwire arrays was developed

Accomplishments / Progress





- Three-electrode *j–E* measurements in aqueous 0.5 M H_2SO_4 demonstrate photoelectrochemical H_2 evolution using amorphous MoS_x catalysts
- Electrode is a p-type Si microwire array after thermal oxidation, p^+ radial emitter doping, and *a*-MoS_x electrochemical deposition

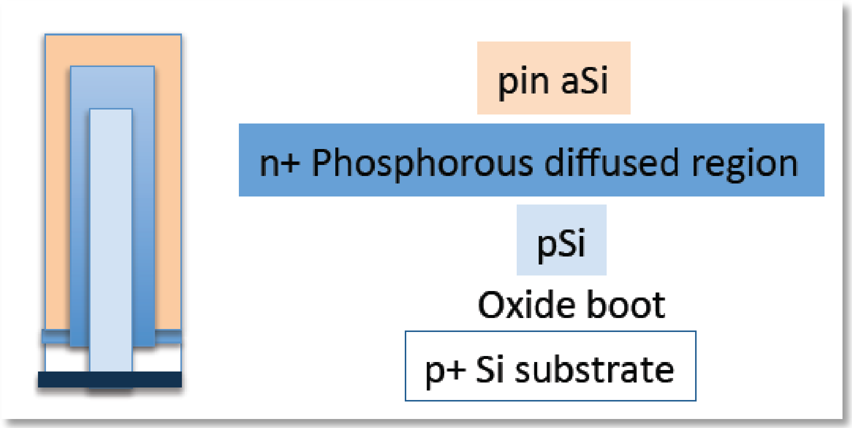
- Three-electrode spectral response measurements of the same electrode in the same electrolyte demonstrating the loss in absorbance above 850 nm with subsequent *a*-MoS_x deposition due to light absorption by the *a*-MoS_x semiconductor catalyst

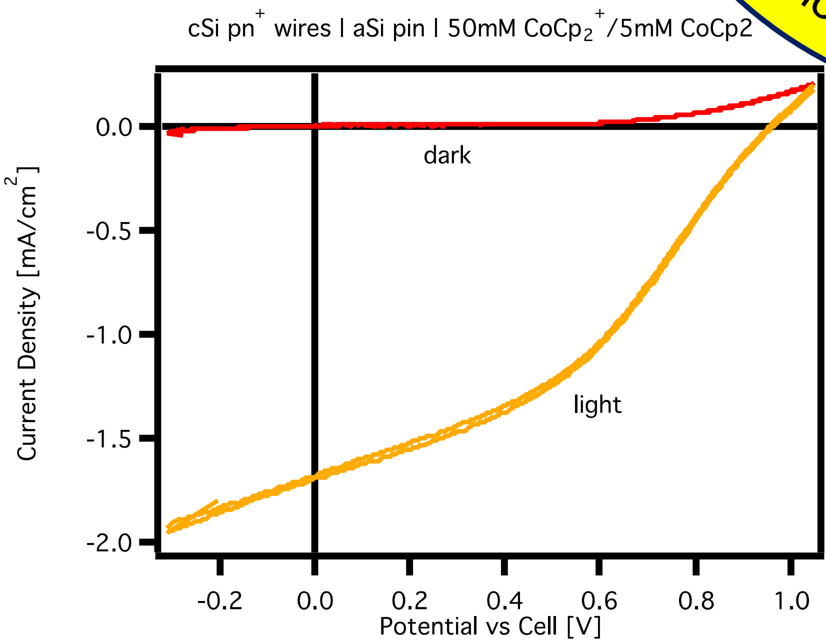
Amorphous MoS_x on pn^+-doped Si microwires catalyzes H_2 evolution in acidic electrolytes

Accomplishments / Progress

18-month

18-month





- Scheme depicting arrangement of materials in tandem amorphous-Si on crystalline Si microwire arrays

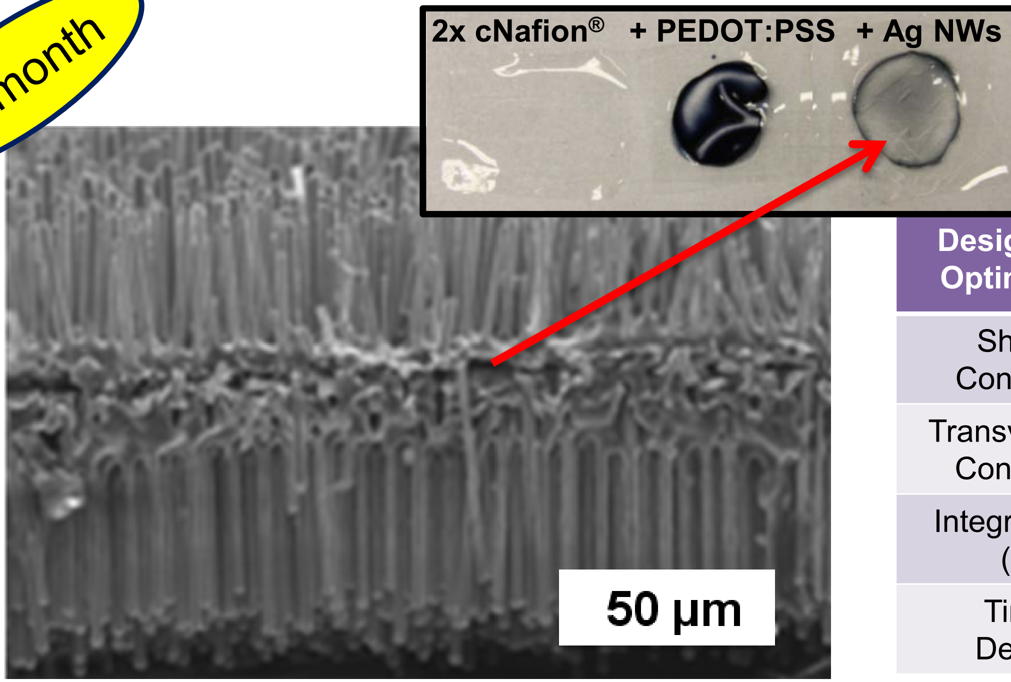
- Three-electrode *j*–*E* measurements in $CoCp_2$–$LiClO_4$–CH_3CN demonstrate a state-of-the-art uncorrected η = 0.65% with V_{oc} = 960 mV, and uncorrected η = 0.43% with V_{oc} = 780 mV in 0.5 M H_2SO_4 after Pt electrocatalyst deposition

Tandem amorphous-Si on crystalline-Si microwire arrays obtain larger photovoltages than Si microwire arrays alone

Accomplishments / Progress

12-month

12-month



Design of Experiments Optimized Component	Measured	Calculated
Sheet/Longitudinal Conductance (mS/sq)	69 ± 20	N/A
Transverse, Area-Specific Conductance (S cm^{-2})	26.9 ± 0.2	22.8
Integrated Transmittance (< 1100 nm; %)	89 ± 6	92
Time to Complete Delamination (min)	46 ± 19	37

- Two Si microwire arrays, each partially embedded in Nafion®, and held together with a composite membrane consisting of Nafion®, PEDOT:PSS and Ag nanowires in a 2.33 : 4.15 : 4.15 ratio (inset)

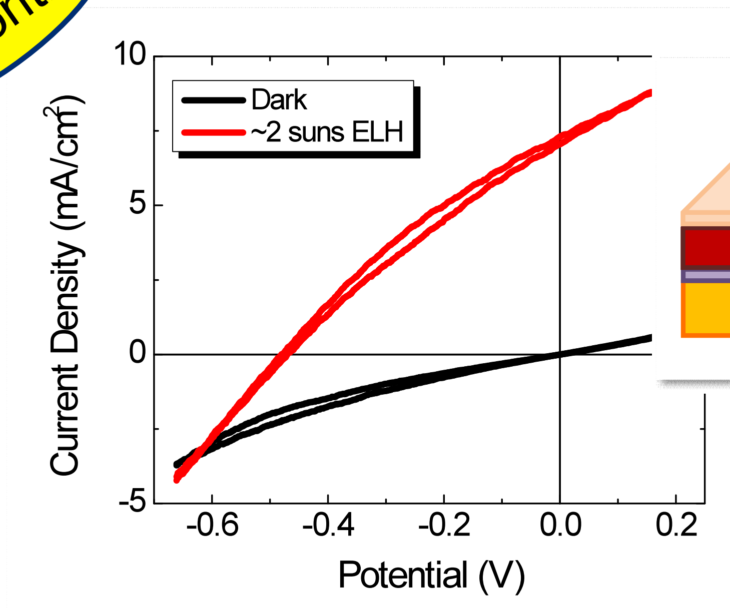
- Membrane performance parameters for the state-of-the-art membrane composition

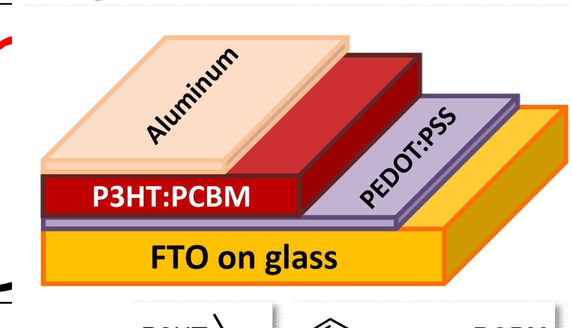
- This composition results in a negligible 0.4 mV potential drop at 10 mA/cm^2 and thus can be made less electrically conductive and more transparent and adhesive

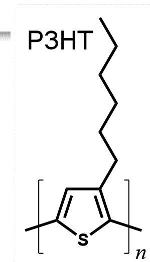
A transparent electrically and ionically conductive membrane was fabricated

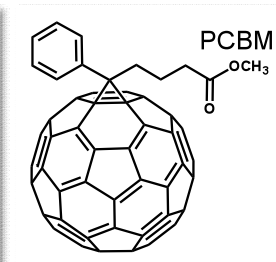
Accomplishments / Progress

9-month









- Solid-state two-electrode *j–E* measurements of a drop cast organic photovoltaic (scheme) to mimic a deposition condition that could be amenable to the backsides of peeled, polymer-embedded Si microwire arrays

This project is a no-go for making this OPV ionically conductive

Collaborations

- n-type Si microwire backside contacts
  - » Prof. Michael Freund, Prof. Derek Oliver, Prof. Douglas Thomson, Dr. Iman Yahyaie, Elahe Asgari at the University of Manitoba (individual microwire evaluation)
  - » Prof. Nathan Lewis, Noah Plymale at Caltech (metal contact characterization)
- Amorphous MoS_x electrocatalysts on Si microwire arrays
  - » Prof. Ib Chorkendorff, Dr. Brian Seger at the Technical University of Denmark (DTU) (catalyst synthesis techniques)
  - » Prof. Nathan Lewis, Chris Roske at Caltech (deposition and electrode evaluation)
- Amorphous-Si:H || crystalline-Si microwire tandem arrays
  - » Prof. Christophe Ballif, Dr. Corsin Battaglia, Mathieu Boccard at the École Polytechnique Fédérale de Lausanne (EPFL) (*a*-Si:H PECVD deposition)
  - » Prof. Nathan Lewis, Amanda Shing at Caltech (electrode evaluation)
- Electrically and ionically conductive membranes
  - » Prof. Nathan Lewis, Sang Hee Park, Rasmus Nørregård at Caltech (fabrication and characterization)
- Ionically conductive organic photovoltaics
  - » Prof. Nathan Lewis, Marino DiFranco at Caltech (fabrication and device evaluation)

Proposed Future Work

FY2013 (July, 2013: 20-Month Report)

Description of Work	Plan to Meet Milestones
B, D) Re-evaluate peeled, flexible, radial buried-homojunction Si microwire array devices with Pt electrocatalysts and partially embedded in Nafion® for stable HI*(aq)* splitting with > 3% sunlight-to-hydrogen energy conversion efficiency	Continue to perfect the infilling and peeling technique for microwire arrays partially embedded in Nafion®; alter formulation of Nafion® precursor solution to assist in more uniform, pinhole-free casting of membranes
H) Optimize formulation for electrically and ionically conductive membrane using Nafion®, PEDOT:PSS, and Ag nanowires	Define the essential parameters and evaluation techniques to quantify the membranes, and perform a design of experiments analysis to determine the optimal membrane composition
F, K) Continue to evaluate PEDOT:PSS and other candidate catalysts and protective layers to catalyze bromide oxidation and protect Si from oxidation in fuming HBr, respectively	Investigate nitride and carbide nanoparticle materials known to be efficient and stable halide oxidation catalysts in nitrile-based electrolytes
G) Continue to evaluate amorphous-Si on crystalline Si microwire array photoelectrodes for H_2 evolution	Alter the deposition protocol to increase the amorphous Si conformality and introduce a stable, conductive, transparent coating to attenuate *a*-Si oxidation

Project Summary

A scalable Si microwire array-based device for sunlight to clean H_2 fuel production, through hydroiodic acid splitting, was demonstrated

DOE Barriers and Targets	Key Take-Home Points
Photoelectrochemical Hydrogen Production – Photoelectrode System	• Peeled Nafion®-embedded arrays of n-type and p-type crystalline Si microwires were fabricated • Stable and efficient sunlight-driven hydroiodic acid splitting was demonstrated • Amorphous MoS_x catalyzes H_2 evolution in fuming HBr and is stable
AF) Materials Durability – Bulk and Interface	• PEDOT:ClO_4 stabilizes Si from oxidation while passing anodic current in aqueous HI and HBr electrolytes
AG) Integrated Device Configurations	• An efficient tandem Si microwire array, with an integrated amorphous-Si light absorber, was fabricated • A transparent electrically and ionically conductive membrane for a tandem device design was fabricated