



# Next-Generation Si Microwire Array Devices for Unassisted Photoelectrosynthesis

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## Background and Introduction

**Motivation:** A priority of the DOE–EERE H<sub>2</sub> Production subprogram is to demonstrate efficient and economically sustainable fuel-forming photoelectrosynthesis (PES), storing 0.6 – 0.8 V of potential as H<sub>2</sub> fuel.

**Proposal:** To realize unassisted H<sub>2</sub> evolution from hydrohalic acids using next-generation tandem Si-microwire-array-based, membrane-embedded PES devices incorporating earth-abundant nanoparticle electrocatalysts.

**Background and State of the Art:** In the 1980s, the Texas Instruments Corporation achieved ~9% solar-to-H<sub>2</sub> efficiency through HBr splitting using a tandem Si || Si device containing Pt–Ir alloy electrocatalysts. In 2007, the Lewis and Atwater laboratories at Caltech pioneered ordered arrays of crystalline Si microwires, fabricated by a chemical-vapor-deposition (CVD) process, for sunlight-to-electrical power conversion. Last year p-type Si microwire arrays, employing a thin n<sup>+</sup>-doped emitter layer (n<sup>+</sup>p-Si), achieved > 5% efficiency toward H<sub>2</sub> evolution from aqueous electrolytes when functionalized with nanoparticle Pt electrocatalysts (Fig. 1). In addition, less expensive alternatives to Pt, like Ni–Mo alloy, efficiently catalyze the H<sub>2</sub> evolution reaction on Si microwire arrays; and a Nafion<sup>®</sup> proton-exchange membrane supports free-standing Si microwire arrays.

The microwire-array geometry is advantageous for the proposed PES device:

### Device is scalable

- Tolerates less pure Si
- Mechanical removal of polymer-infilled array results in a free-standing device

### Rapid rate of fuel-formation

- Significant sunlight absorption occurs along microwire long dimension
- Microwire short, radial dimension affords rapid minority-carrier charge separation
- Nanoparticle electrocatalysts catalyze the two-charge-transfer reactions
- Ionomer membranes attenuate product crossover

### Large potentials stored in fuels (i.e. 0.4 – 0.8 V)

- Microwires support a space-charge region
- Micron-scale ionic drift results in negligible resistive potential losses

### Obstacles (Fig. 2)

- **Efficient n-type Si and p<sup>+</sup>n-Si microwire arrays**
- **Efficient molecular-halogen evolution through halide oxidation**
- **Protection of n-type Si from surface corrosion and passivation**
- **Interfaces with appropriate junction characteristics**

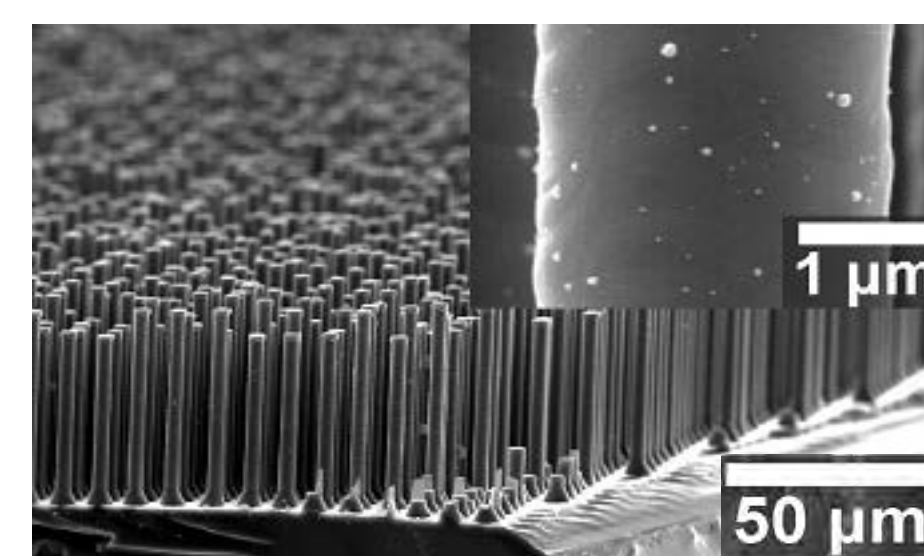


Figure 1. SEM of a Si microwire array with Pt catalysts

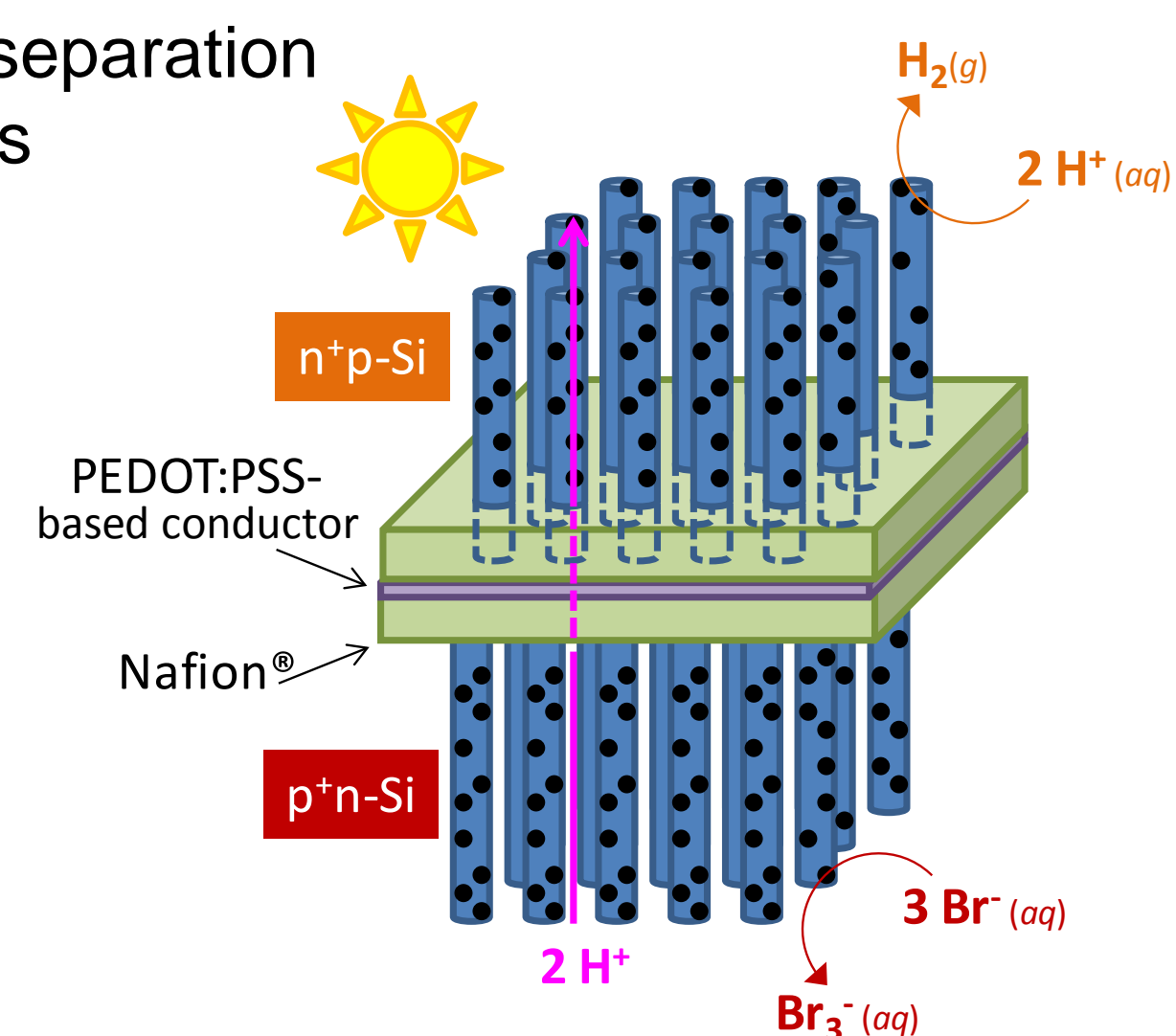


Figure 2. Proposed tandem Si || Si HBr splitting device

## Approach

### Efficient n-type Si and p<sup>+</sup>n-Si microwire arrays

- (1) Introduce PH<sub>3</sub> dopant gas in the SiCl<sub>4</sub>/H<sub>2</sub> stream during CVD growth (Lewis laboratories)
- (2) Fabricate p<sup>+</sup>-doped emitters using a boron–nitride solid dopant-diffusion source (Atwater laboratories)
- (3) Evaluate photoelectrode performance in a three-electrode, non-aqueous photoelectrochemical cell via *j*–*E* measurements (Lewis laboratories) (Fig. 3)

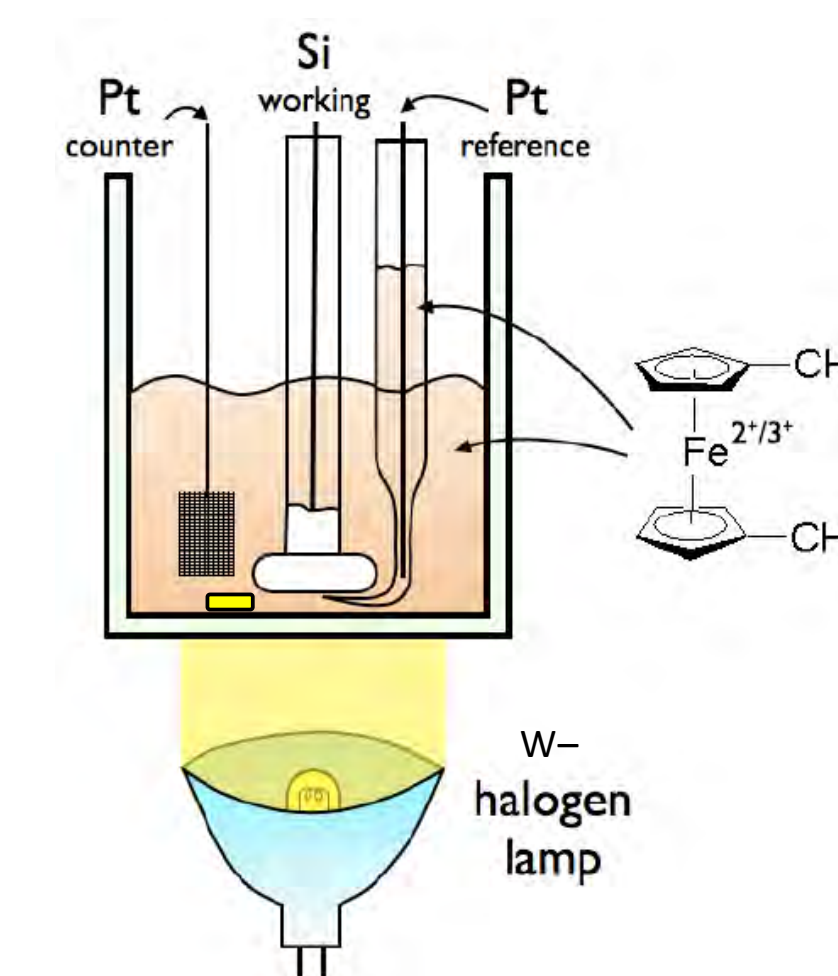


Figure 3. Three-electrode, non-aqueous photoelectrochemical cell

### Efficient molecular-halogen evolution through halide oxidation

- (1) Electrodeposit Pt or Ni–Mo alloy, and synthesize and drop-cast Mo/W(S,Se)<sub>2</sub> nanoparticle electrocatalysts on planar Si and Si microwire arrays (Lewis laboratories & JCAP)
- (2) Evaluate the nanoparticles for catalysis, long-term stability, and parasitic light absorption in a three-electrode aqueous photoelectrochemical cell via *j*–*E* measurements and spectral response (Lewis laboratories)

### Protection of n-type Si from surface corrosion and passivation

- (1) Methylate Si microwire atop sites via a two-step chlorination–alkylation procedure (Lewis laboratories) (Fig. 4)
- (2) Deposit heterojunctions (Co<sub>3</sub>O<sub>4</sub>, NiO, Cu<sub>2</sub>O) or tunnel barriers (MgO, TiO<sub>2</sub>, Mn<sub>x</sub>O<sub>y</sub>) on planar Si and Si microwire arrays via the following techniques:
  - Atomic layer deposition (Lewis laboratories)
  - Sputter deposition (Lewis laboratories)
  - Plasma-enhanced CVD (Kavli Nanoscience Institute at Caltech)
- (3) Evaluate electrode long-term stability in hydrohalic acids during the halide oxidation reaction via SEM, XPS, and AFM (Lewis laboratories, JCAP, and Molecular Materials Research Center at Caltech)

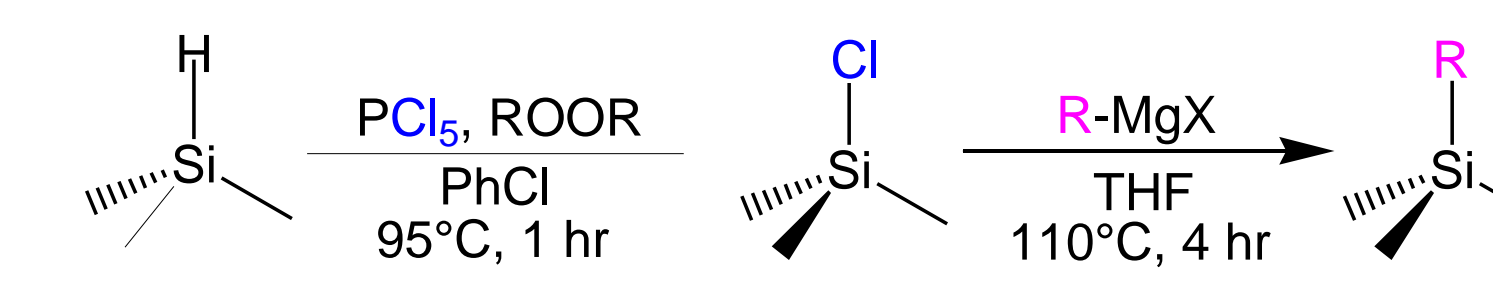


Figure 4. Two-step chlorination–alkylation procedure

### Interfaces with appropriate junction characteristics

- (1) Deposit catalysts electrochemically or by drop-casting (Lewis laboratories)
- (2) Generate back-surface fields in Si via dopant drive-in from the highly doped growth wafers (Lewis laboratories)
- (3) Deposit Al electrolessly on the backsides of Nafion<sup>®</sup>-embedded n-type Si microwire arrays (Lewis laboratories)

### Innovation Projects (Fig. 5)

- (1) Synthesize organic photovoltaics that also conduct protons to serve as a middle layer in a tandem device (Lewis laboratories & Walter group at the University of North Carolina, Charlotte)
- (2) Deposit an amorphous n<sup>+</sup>ip<sup>+</sup>-Si (a-Si) coating on the crystalline Si (c-Si) microwires as additional junctions (Deng group at the University of Toledo & Xunlight Corporation in Toledo, OH)

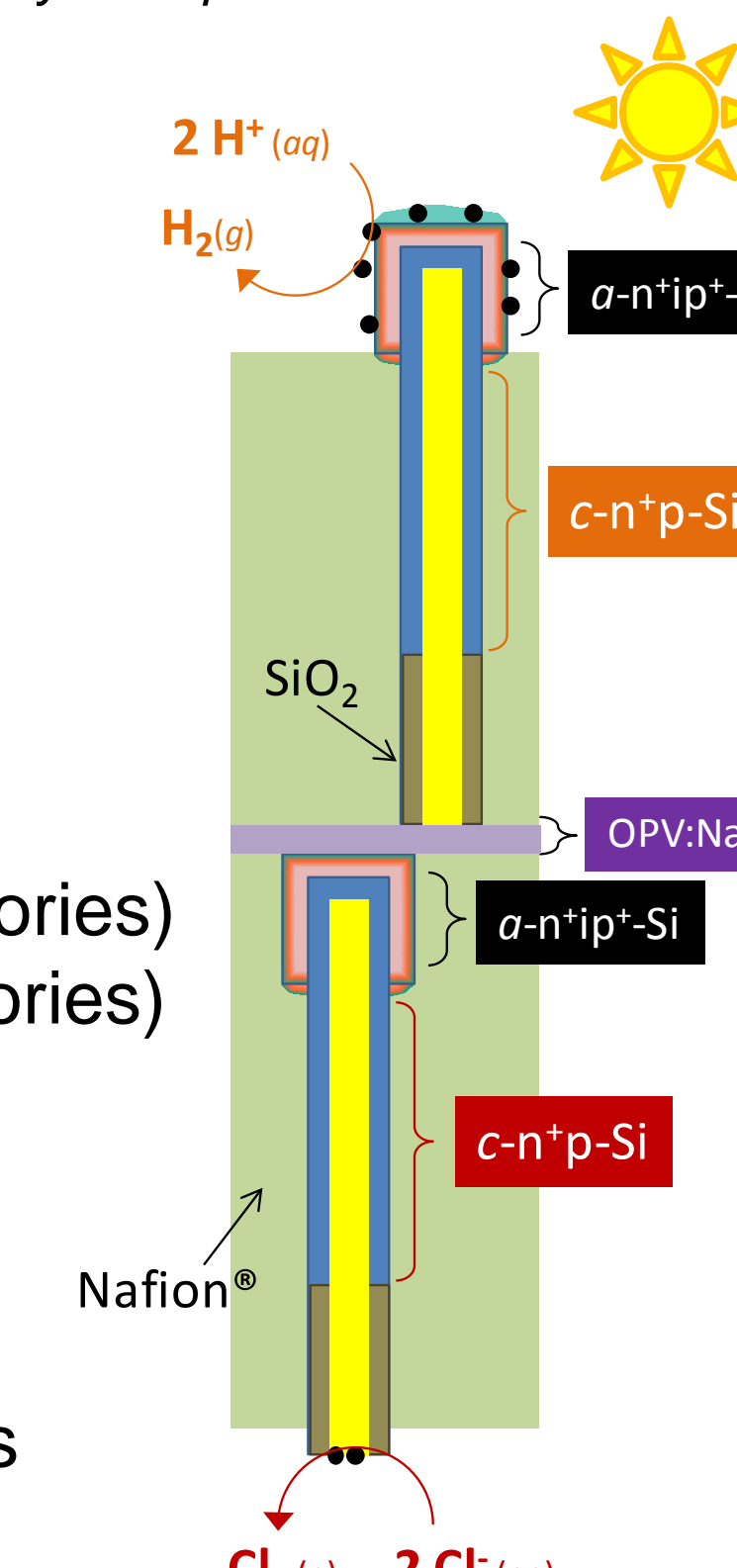


Figure 5. Quintuple-junction innovation project device

## Impact

Success of this project will result in an economically feasible technology for conversion of sunlight to H<sub>2</sub>. This technology is not only relevant to centralized solar fuel power plants but the chloralkali industry. The chloralkali process is extremely energy intensive, requiring > 1% of the world's electricity, yet is indispensable as it produces two of the top-ten worldwide commodity chemicals: NaOH and Cl<sub>2</sub>. Driving this electrochemical reaction with sunlight would alleviate the large electricity input and, because a byproduct of the reaction is H<sub>2</sub>, would also generate a large-potential, carbon-free fuel as H<sub>2</sub>/Cl<sub>2</sub>. Fuel cells based on H<sub>2</sub>/Cl<sub>2</sub> are more efficient than those based on H<sub>2</sub>/O<sub>2</sub>, thus further motivating hydrohalic acids as fuel precursors for H<sub>2</sub> fuel.

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**A recyclable fuel generated from the energy in sunlight using a single, economical assembly**