

Photoelectrosynthetic Hydrogen Evolution from Free-Standing Silicon Microwire Arrays

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Introduction

Our sun provides the largest source of renewable energy available to humankind. Sunlight can be harvested and transduced into useful energy using semiconductor–liquid junction solar cells, which generate power through the transfer of electronic energy to molecules dissolved in fluid solution. If two such interfacial electron-transfer events are coupled at an efficient catalyst, chemical bonds can be formed, an important step to powering our planet with fuels derived from renewable energy. Toward this, periodic arrays of crystalline silicon microwires were used to photogenerate H₂ from aqueous HI solutions, as described further below.

Experimental

Fabrication of Si Microwire Arrays. Si microwire arrays were grown by a chemical-vapor-deposition vapor–liquid–solid (VLS) growth process on degenerately doped planar Si wafer substrates, of (111) orientation: p-type ($\rho < 0.001 \Omega \text{ cm}$; B-doped), n-type ($\rho \leq 0.004 \Omega \text{ cm}$; As-doped), and n-type ($\rho < 0.004 \Omega \text{ cm}$; P-doped). A hexagonal pattern of Cu-filled, HF-etched holes in a thermal oxide on the top of the planar Si wafers served as the VLS growth catalysts.¹ It was patterned by photolithography using S1813 and Cu was deposited by thermal evaporation followed by liftoff. Precursor gases were introduced at elevated temperatures under a reducing atmosphere as SiCl₄, BCl₃, and/or PH₃.

Si Microwire Array Post-Processing. Industry standard cleaning protocols were utilized to remove the Cu VLS growth catalysts from the tops of the Si microwires, followed by a KOH etch.² Oxide boots on the microwires were introduced through thermal oxidation followed by an HF etch, employing a polydimethylsiloxane mask at the microwire bases.² Degenerately doped emitters were introduced by diffusion doping from solid sources (Saint-Gobain Advanced Ceramics).^{2,3} Si microwire surface sites were functionalized with methyl groups by a two-step chlorination–alkylation procedure.⁴ Pt electrocatalysts were deposited by electron-beam evaporation or potentiostatic deposition from aqueous K₂Pt(II)Cl₄/LiClO₄ solutions. Free-standing wire arrays embedded in Nafion[®] cation-exchange membrane were fabricated by spin coating followed by mechanical removal.⁵

Instrumentation and Measurements. Microscopy images were obtained on an Olympus optical microscope and a ZEISS field-emission scanning electron microscope. A Surface Science Instruments M-Probe x-ray photoelectron spectrometer was used to characterize the redox states of near-surface atoms. The doping density of Si microwires was determined by electrical four-point probe measurements.¹ Ionic conductivity of the membranes was measured by a solution four-point probe measurement employing Luggin capillaries.⁵ Three-electrode photoelectrochemical measurements characterized the behavior of the electrodes immersed in deaerated electrolytes containing non-aqueous 1,1'-dimethylferrocene⁺⁰ (Me₂Fc⁺⁰), aqueous methyl viologen^{2+/+} (MV^{2+/+}), or aqueous acidic I₃⁻/I⁻, under AM1.5G sunlight-simulated illumination. Two-electrode measurements, ultraviolet–visible spectroscopy, and gas chromatography with thermal conductivity detection were used to quantify reaction products as H₂ and I₃⁻.

Results and Discussion

Open-circuit photovoltages measured for each type of wire array were 400 – 500 mV, with n⁺p-Si in MV^{2+/+} and HI/H₂, and n-Si in Me₂Fc⁺⁰ and acidic I₃⁻/I⁻. Electrodes evaluated in aqueous HI utilized nanoparticulate Pt electrocatalysts. Methylation of the Si atop sites of n-type Si was required to attenuate corrosion; sustained light-driven iodide oxidation was maintained for ~3 days with < 10% loss in activity. Short-circuit current densities were within error of those measured previously (~10 mA/cm²).^{1,2} Light-scattering elements were not employed,² even though the projected areal filling fraction of the Si microwires was < 10%. Light-to-electrical and solar-to-hydrogen conversion efficiencies of ~3% were realized. Faradaic yields for H₂ and I₃⁻ generation were near unity.

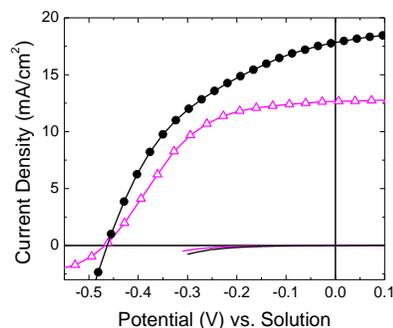


Figure 1. Current density as a function of applied potential for champion n-type Si microwire arrays in Me₂Fc⁺⁰ methanol electrolyte (magenta, open triangles) and I₃⁻/I⁻ acidic aqueous electrolyte (black, filled circles) under simulated sunlight conditions (symbols + lines) and in the dark (lines only).

Conclusions

Crystalline silicon microwire arrays were used to photogenerate H₂ from aqueous HI solutions. Si microwire arrays represent an inexpensive alternative to traditional planar Si photovoltaics. Orthogonalization of the directions of light absorption and minority-carrier charge separation allows for less pure materials to be used. Less than 10% of the Si in a planar photovoltaic is required and light manipulation techniques can be employed to harvest the maximum amount of sunlight. These systems are sustainable because the HI fuel precursor is inorganic, thus not generating CO₂, and HI can be regenerated in a fuel cell as H₂ + I₂.

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