II.G.3 Oxidatively Stable Nanoporous Silicon Photocathodes for Photoelectrochemical Hydrogen Evolution

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Objectives

Within our BES Solar Photochemistry program, we are developing improved understanding of the interactions at the liquid-solid interface during catalyzed photoelectrochemistry using nanostructured photoelectrodes. To understand basic issues critical to increasing the photocarrier-driven fuel-producing chemical reaction rates and their selectivity over parasitic reactions, we apply catalysts to photocathodes of well-understood, near-ideal semiconductors into which we can build random or controlled nanostructures through novel metal-assisted chemistries. The application of well-understood single-crystal semiconductors like silicon allows us to separate out and study the important new photoelectrochemical (PEC) science introduced by nanostructuring and the interactions of catalysts with the nanostructured surface.

Technical Barriers

- Understand how to control fundamental interactions such as light absorption in molecules and solids, charge transport and recombination, interfacial electron transfer, and coupled transfer of multiple electrons and protons through a catalyst.
- Based on this knowledge, develop efficient semiconductor photoelectrodes stable to both photo-assisted and dark corrosion processes.

Abstract

Stable and high-performance nanoporous "black silicon" photoelectrodes with electrolessly deposited Pt nanoparticle (NP) catalysts are made with two metal-assisted etching steps. Doubly etched samples exhibit >20 mA/cm^2 photocurrent density at +0.2 V vs. reversible hydrogen electrode (RHE) for photoelectrochemical hydrogen evolution under 1 sun illumination.

We find that the photocurrent onset voltage of black Si photocathodes prepared from single-crystal planar Si wafers increases in oxidative environments (e.g., aqueous electrolyte) owing to a positive flat-band potential shift caused by surface oxidation. However, this beneficial oxide layer becomes a kinetic barrier to proton reduction that inhibits hydrogen production after just 24 h. To mitigate this problem, we developed a novel second Pt-assisted etch process that buries the Pt NPs deeper into the nanoporous Si surface. This second etch shifts the onset voltage positively, from +0.25 V to +0.4 V vs. RHE, and reduces the charge-transfer resistance with no performance decrease seen for at least two months.

Progress Report

Recently, nanostructured Si photocathodes have been developed for hydrogen production due to their advantages of low reflectivity and a higher surface area compared to bulk planar Si, which improves charge collection, exchange current density, and hydrogen gas surface-desorption. Our group and others have focused on the metal-assisted solution etching of planar Si to prepare nanostructured Si—also called "black Si"—a process that is suitable for large-scale manufacture and has been applied to make high-efficiency Si solar cells.

But the performance of Si electrodes used in any aqueous PEC system normally deteriorates from surface oxidation, an effect that appears to be unavoidable because of the high reactivity of Si with O_2, especially in the presence of water. In a deployed PEC hydrogen production system, surface oxidation might be expected during the night and at other times when photoelectrons are not providing cathodic protection against surface oxidation. Although the deposition of a surface-adsorbed catalyst such as Pt can help reduce the kinetic barrier for proton reduction, the PEC properties of Pt-deposited Si photoelectrodes are also found to degrade significantly upon surface oxidation.

Here we find that our black Si photoelectrodes with electrolessly deposited Pt NP catalysts (Pt/b-Si) exhibit improved PEC hydrogen production performance relative

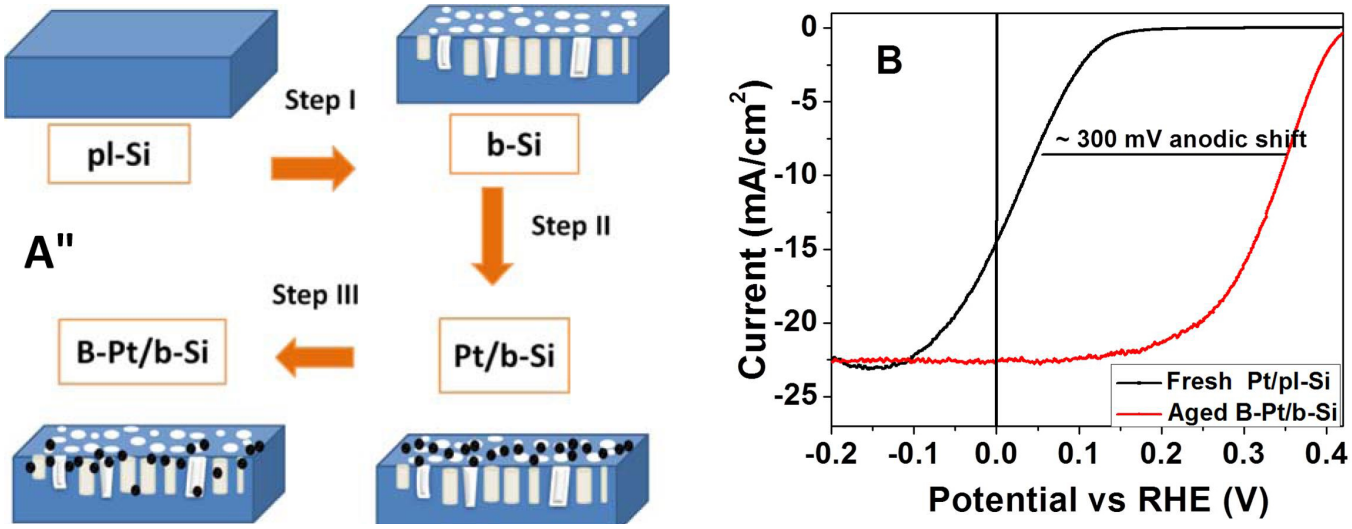

FIGURE 1. (A) Schematic of the preparation process for air-stable high-performance nanoporous B-Pt/b-Si photocathodes. (B) Comparison of J–V curves for the photoelectrochemical production of hydrogen at 0.5 M H2SO4 and 100 mW/cm2 irradiation for a fresh Pt/plSi photocathode (black curve) and a B-Pt/b-Si photocathode aged for 1 month in air (red curve).

to planar Si (pl-Si) electrodes. In particular, the deleterious effect of air exposure for more than 1 h on pl-Si or catalyst-free black Si (b-Si) electrodes are not observed in Pt/b-Si at aging times greater than 24 h. Instead, the nanoporous Pt/b-Si electrode exhibits a positive onset potential shift (by ~200 mV) upon aging for 24 h that improves its PEC performance. To explore the mechanism for the positive onset potential shift of nanoporous b-Si after exposure to air, Mott-Schottky (MS) plots of the pl-Si, b-Si, and Pt/b-Si electrodes were measured in 0.5 M H_2SO_4 after different aging times. The MS data confirm that oxide growth results in a positive flat-band potential shift for the Si photocathodes, which initially improves PEC performance but eventually degrades it with further oxide growth.

To address this issue, we have developed a novel re-etching process as described in Fig. 1A. This process results in high PEC performance despite the presence of surface oxide. These black Si photoelectrodes with buried Pt NP catalysts (B-Pt/b-Si) exhibit an ~300 mV positive shift for hydrogen evolution compared to a Pt-modified planar Si photoelectrode and are stable even after months of air exposure (Fig. 1B). Electrochemical impedance studies reveal that the second etch leads to a considerably smaller interfacial charge-transfer resistance than samples without the additional etch, suggesting that burying the Pt NPs improves the interfacial contact between the black Si surface and the Pt catalysts.

Future Directions

We plan fundamental experiments to probe the nature of the interface between Pt and b-Si using high-resolution transmission electron microscopy, scanning tunneling microscopy, x-ray absorption spectroscopy, and related techniques. Utilizing this secondary etching treatment with buried p-n junction photocathodes may reduce the overpotential for hydrogen evolution and make possible tandem overall water splitting devices using this photocathode and an appropriately matched photoanode such as bismuth vanadate.

Selected Publications

1. Anti-Reflective Nanoporous Silicon For Efficient Hydrogen Production, US Patent No. US 2012/0103825 A1, Jihun Oh, Howard Branz

2. Oh, J.; Deutsch, T.G.; Yuan, H.-C.; Branz, H.M., Nanoporous Black Silicon Photocathode for H_2 Production by Photoelectrochemical Water Splitting. *Energy Environ. Sci.* **2011**, *4* (5), 1690-1694.

3. Seabold, J.A.; Zhu, K.; Neale, N.R., Efficient Solar Photoelectrolysis by Nanoporous Mo:$BiVO_4$ Through Controlled Electron Transport. *Phys. Chem. Chem. Phys.* **2014**, *16* (3), 1121-1131.

4. Zhao, Y.; Neale, N.R.; Zhu, K.; Oh, J.; van de Lagemaat, J.; Yuan, H.-C.; Branz, H.M., Oxidatively Stable Nanoporous Silicon Photocathodes with Enhanced Onset Voltage for Photoelectrochemical Hydrogen Evolution. *Submitted* **2014**.