High-Aspect Ratio Structures in Light-Absorbers and Electrocatalysts for Solar Fuels Devices

Thesis by

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ABSTRACT

Solar fuels devices produce hydrogen fuel from water and sunlight and address a critical societal need for inexpensive, long-duration energy storage. Such devices are prepared from combinations of light-absorbing semiconductors and catalysts to sunlight to drive thermodynamically uphill reactions. This dissertation puts forth strategies for controlling the three-dimensional structure of semiconductors, electrocatalysts, and the film of gas bubbles evolved on the top and bottom of a solar fuels device. High-aspect ratio features led to unexpected effects in semiconductor/electrocatalyst assemblies. Optical losses were decoupled from the mass-loading of cobalt phosphide and copper electrocatalysts integrated onto silicon microwire photocathodes for the photoelectrochemical generation of hydrogen and hydrocarbons, respectively. Anti-reflective silicon microcone arrays were patterned with continuous films of Pt or CoP particles with minimal reflection losses due to the catalyst films. Transparent metal films were prepared from nanostructured metal phosphides, a class of earth-abundant hydrogen evolution catalysts. Silicon microwire array (photo)electrode surfaces were used to force bubbles away from electrocatalyst surfaces, even when oriented against gravity, leading to sustained operation in the absence of external convection.

PUBLISHED CONTENT AND CONTRIBUTIONS

1. **Kempler, P. A.**, Gonzalez, M. A., Papadantonakis, K. M., & Lewis, N. S. (2018). Hydrogen evolution with minimal parasitic light absorption by dense Co–P catalyst films on structured p-Si photocathodes. *ACS Energy Letters*, 3(3), 612-617. https://doi.org/10.1021/acsenergylett.8b00034

   P.A.K. prepared the samples, collected and analyzed the data, and assisted in the writing and the editing of the manuscript.

2. **Kempler, P. A.,** Ricther, M. H., Cheng, W.H., Brunschwig, B.S., & Lewis, N.S. (2020). Si Microwire-Array Photocathodes Decorated with Cu Allow CO_2 Reduction with Minimal Parasitic Absorption of Sunlight. *ACS Energy Letters, 5(8),* 2528-2534. https://doi.org/10.1021/acsenergylett.0c01334

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3. Yalamanchili, S.,* **Kempler, P. A.**,* Papadantonakis, K. M., Atwater, H. A., & Lewis, N. S. (2019). Integration of electrocatalysts with silicon microcone arrays for minimization of optical and overpotential losses during sunlight-driven hydrogen evolution. *Sustainable Energy & Fuels*, 3(9), 2227-2236. https://doi.org/10.1039/C9SE00294D

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4. **Kempler, P. A.**, Fu, H. J., Ifkovits, Z. P., Papadantonakis, K. M., & Lewis, N. S. (2020). Spontaneous Formation of> 90% Optically Transmissive, Electrochemically Active CoP Films for Photoelectrochemical Hydrogen Evolution. *The Journal of Physical Chemistry Letters.* 11(1), 14-20. https://doi.org/10.1021/acs.jpclett.9b02926

   P.A.K. prepared the samples, collected the photoelectrochemical data, collected the data for the optical characterization of the films, developed the film model for spectroscopic ellipsometry, and assisted in the writing and the editing of the manuscript.

5. **Kempler, P.A.**, Coridan, R.H., Lewis N.S. (2020). Effects of Bubbles on the Electrochemical Behavior of Hydrogen-Evolving Si Microwire Arrays Oriented Against Gravity. *Energy & Environmental Science, 13,* 1808-1817. https://doi.org/10.1039/D0EE00356E

   P.A.K. prepared the samples, collected and analyzed the data, and assisted in the writing and the editing of the manuscript.

6. **Kempler, P. A.**, Ifkovits, Z.P., Yu. W., Carim, A.I., & Lewis, N.S. (2020). Optical and electrochemical effects of H_2 and O_2 bubbles at upward-facing Si photoelectrodes. *In preparation*

   P.A.K. prepared the samples, collected and analyzed the data, and assisted in the writing and the editing of the manuscript.

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