

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

Thesis by  
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the degree of  
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The logo for the California Institute of Technology (Caltech), featuring the word "Caltech" in a bold, orange, sans-serif font.

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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

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