High Throughput Discovery and Optimization of Photo-Electrode Assemblies

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Abstract:

The development of efficient, stable photoelectrodes remain a primary materials challenge for solar fuels generation. The photoanode is needed to provide protons and electrons to the (photo)cathode, while development of a CO2RR-active photocathode provides opportunities to steer product selectivity, with both photoelectrodes providing energy gain for fuel formation. We demonstrate efficient high throughput evaluation of the performance of photoelectrode assemblies consisting of compositionally diverse metal oxide coatings on light absorbers, which reveals the critical role of effective surface passivation, and the inter-connected performance impacts of coating composition and loading, and electrolyte pH.

Introduction

Efficient and durable solar fuels devices require combining materials Materials historically discovered and optimized in isolation—then “integrated” Coatings and interfaces have multiple functions: Interface State Passivation—Catalyze Surface Reaction—Corrosion Protection—Enhance Charge Separation—Alter Band Bending and Band Edges—Light Trapping

Technological semiconductors require effective passivation.

Improved BiVO4 Photoanodes:

• Nanostructuring
• Doping and co-doping
• Hydrogen annealing process
• Carrier selective contacts
• Performance gains always require “catalyst” or multilayer coatings to reduce surface recombination

Outlook

Primary role of coatings on semiconductors is to passivate surface states. Catalysis is a secondary effect. Demonstrated efficacy of High Throughput methods for evaluation of integrated photoelectrode assemblies Future work:

• Coating on emerging semiconductors, such as CdTe and Cu3N.
• Evaluate addition of CO2RR catalyst layers

Learn more about the High Throughput Experimentation Teams.

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Results, Highlights, and Accomplishments

Integrated Photo-Anode Assembly Libraries

Ni-Fe-Co-CeOx OER CATALYST LIBRARIES ON BiVO4 AT pH 13

Automated data collection, processing, and performance visualization

SDC+UV-VIS +FIBER OPTIC LIGHT SOURCE

Integrated photoanode (BiVO4)

Current transients indicative of interfacial recombination occur over more coating compositions in pH 9 than pH 13.

Indicates the balance between role of surface passivation and catalysis shifts with pH.

Interface Passivation Important role of surface coatings on BiVO4

Optimal (Fe-Co-Ce)Ox Catalyst Composition and Loading at pH 13 and pH 9

• Theory and Experiment show CeO2 coating passivates BiVO4 surface.1-3
• An OER catalyst is also needed.

Sputtered (Ti-Cu)Ox Coating Composition and Loading on CuBi2Ox

Composition and performance mapping:

• Uncoated: radial Bi:Cu Ratio and performance
• Ti-CuOx coated: Ti and performance increases to top left

Photocurrent transients indicative of interfacial recombination occur over more coating compositions in pH 9 than pH 13.

Indicates the balance between role of surface passivation and catalysis shifts with pH.

Optimal Coating Depends upon Light Absorber Composition and Processing

Surface Passivation and Fermi Level Engineering

• Steady-state open-circuit potential (SOC): Cu2TiO4 coating passivates surface states.
• XPS valence band edge measurements indicate the Fermi level of Cu2TiO4 moves closer to the valence band with increasing Cu.
• Band edge offsets tuned relative to Cu2TiO4 for optimal charge separation.

SUMMARY

• Functional Solar Fuels Devices require simultaneous optimization of multiple materials and interfaces under operational conditions including variable pH.
• High Throughput Experiments enable this discovery and optimization.
• Demonstrated pipelines for evaluation of integrated photo-electrode assemblies.
• Best integrated photo-anode coating compositions very different from the best dark OER electrocatalyst compositions.
• Discoveries transferrable to other synthesis methods and device scales.
• Similar developments for coatings on CuBi2Ox photo-cathode assemblies.
• Reduced surface recombination through passivation of surface defect states and improved carrier extraction efficiency through Fermi level engineering.

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References: