# High Throughput Discovery and Optimization of Photo-Electrode Assemblies

Joel A. Haber, Aniketa Shinde, Zemin Zhang, Lan Zhou, Dan Guevarra, Kevin Kan, Guiji Liu, Jeffery B. Neaton, Jason K. Cooper, Francesca M. Toma, John M. Gregoire

JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

## 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.

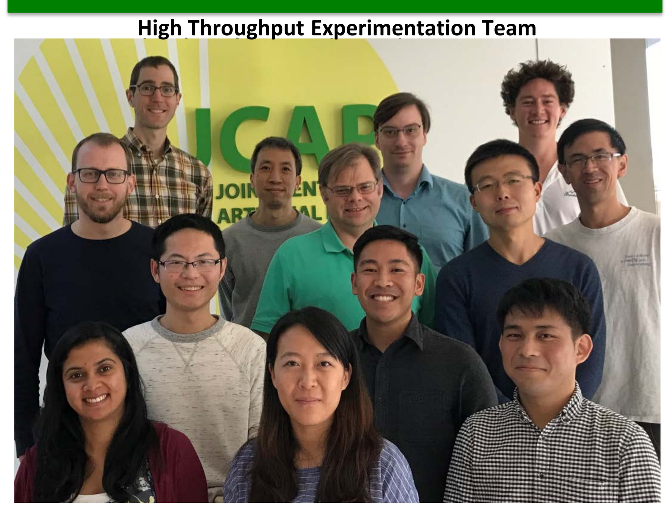
**Improved $BiVO_4$ Photoanodes:**

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

1. Zhong, Choi, Gamelin *J. Am. Chem. Soc.* **2011**, *133*, 18370
2. Kim and Choi *Science* **2014**, *343*, 990.
3. Abdi, Firet, van de Krol *ChemCatChem* **2013**, *5*, 490
4. Zachaus, Abdi, Peter, van de Krol *Chem. Sci.*, **2017**, *8*, 3712

## Team

High Throughput Experimentation Team



Directed Integration & Scale-up


## 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

## Acknowledgments

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## Results, Highlights, and Accomplishments

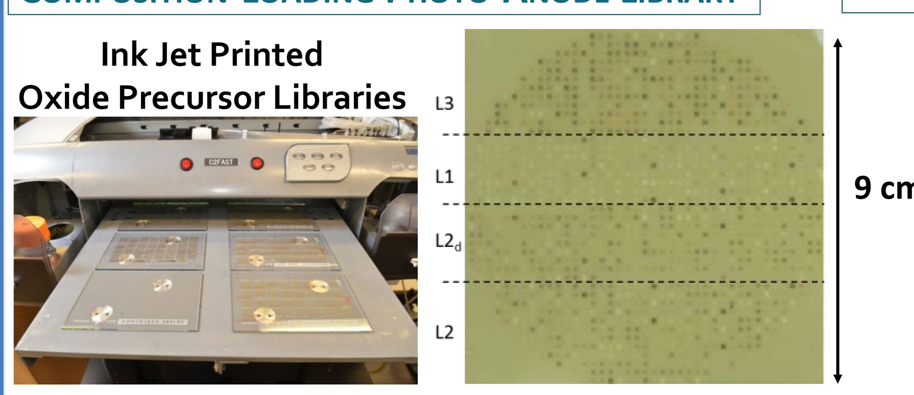
### Integrated Photo-Anode Assembly Libraries

#### $(Ni\text{-}Fe\text{-}Co\text{-}Ce)O_x$ OER catalyst libraries on $BiVO_4$ at pH 13

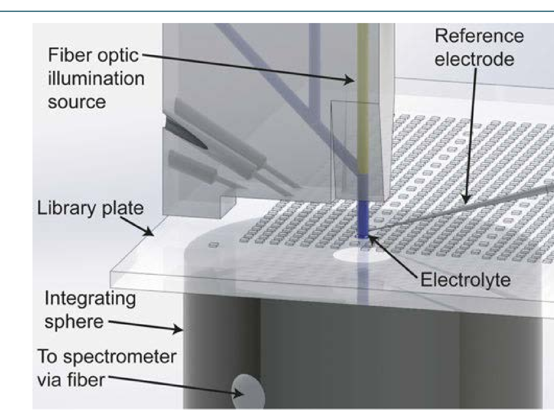
**Automated data collection, processing, and performance visualization**

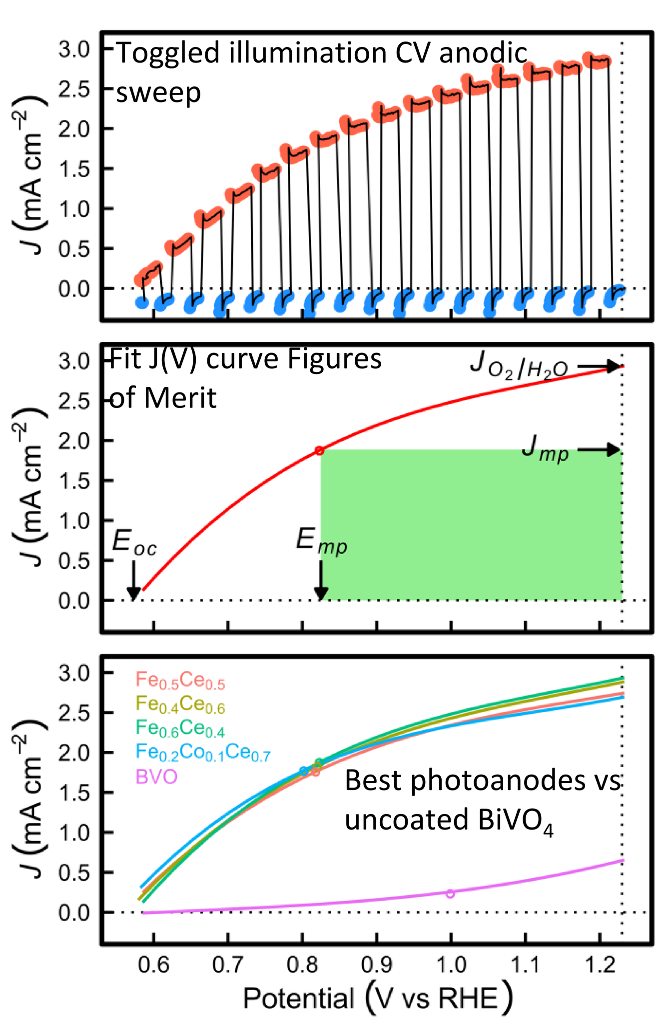
Composition-Loading Photo-Anode Library

Ink Jet Printed Oxide Precursor Libraries

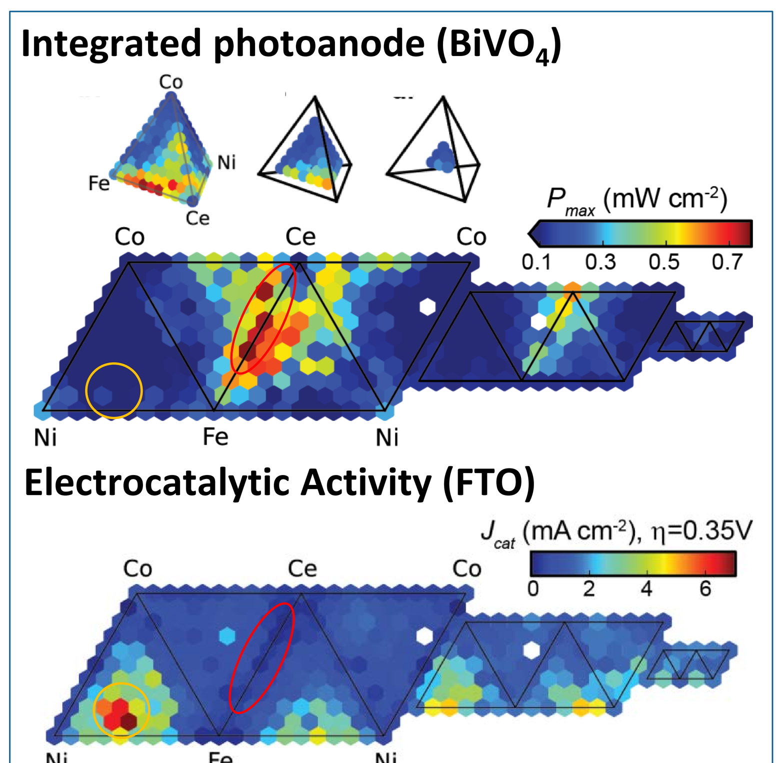



SDC+UV-VIS +Fiber Optic Light Source




Integrated photoanode ($BiVO_4$)




**Best photoanodes from poor catalysts**

**Poor photoanodes from best catalysts**

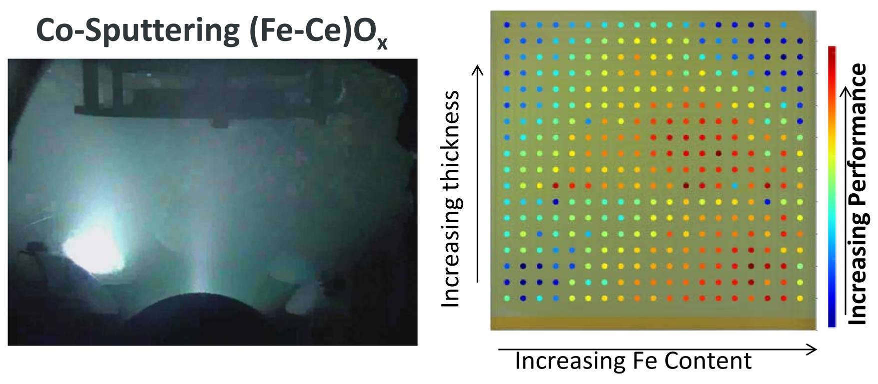
Best coating compositions are on the $(Fe\text{-}Ce)O_x$ pseudo-binary line

Interface Passivation important role of surface coatings on $BiVO_4$

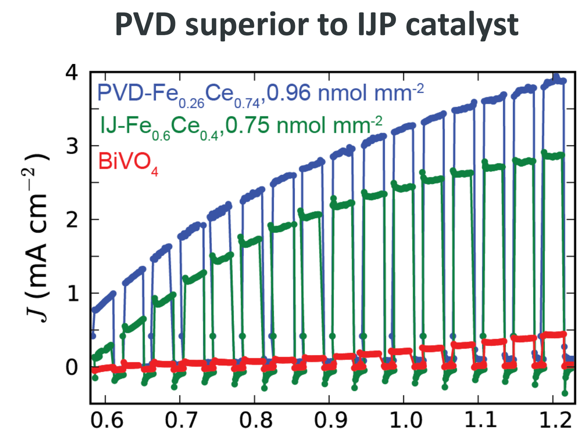
1. A. Shinde, D. Guevarra, G. Liu, I.D. Sharp, F.M. Toma, J.M. Gregoire, J.A. Haber *ACS Appl. Mater. Interfaces* **2016**, *8*, 23696.
2. D. Guevarra, A. Shinde, S.K. Suram, I.D. Sharp, F.M. Toma, J.A. Haber, J.M. Gregoire, *Energy Environ. Sci.* **2016**, *9*, 565.

#### Optimal $(Fe\text{-}Ce)O_x$ catalyst compositon and loading at pH 13 and pH 9

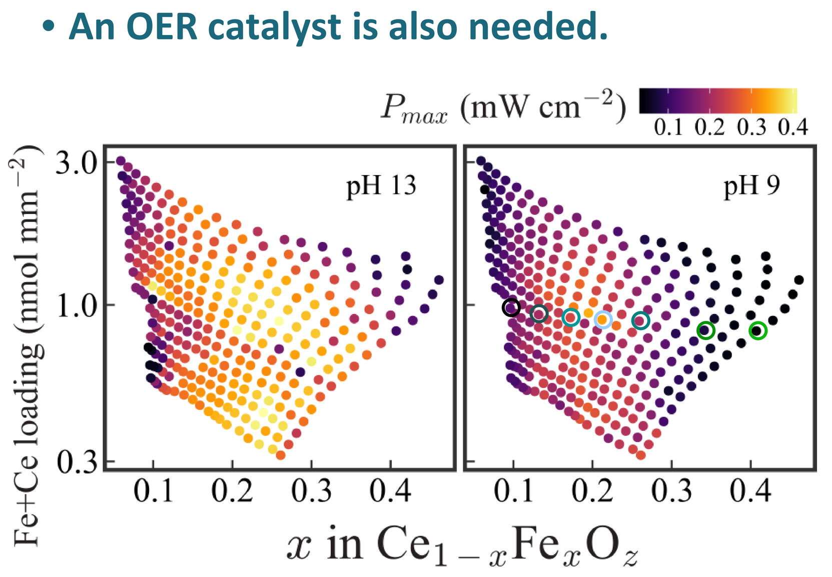
Co-Sputtering $(Fe\text{-}Ce)O_x$

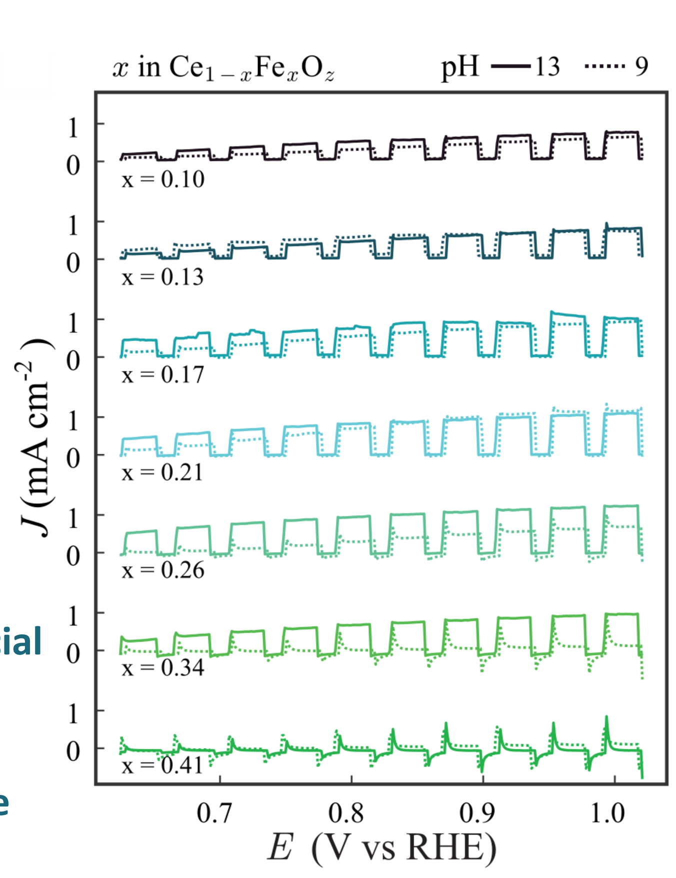



PVD superior to IJP catalyst




- **Theory and Experiment show $CeO_2$ coating passivates $BiVO_4$ surface.[1-3]**
- **An OER catalyst is also needed.**




- **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.**

1. Shinde, Li, Zhou, Guevarra, Suram, Toma, Haber, Neaton, Gregoire *J. Mater. Chem. A*, **2016**, *4*, 14356
2. Zhou, Shinde, Guevarra, Toma, Stein, Gregoire , J.A. Haber *ACS Appl. Energy Mater.*, **2018**, *1*, 5766
3. Liu, Eichhorn, Jiang, Scott, Hess, Gregoire, Haber, Sharp, Toma, *Sustainable Energy Fuels*, **2019**, *3*, 127-135

### Integrated Photo-Cathode Assembly Libraries

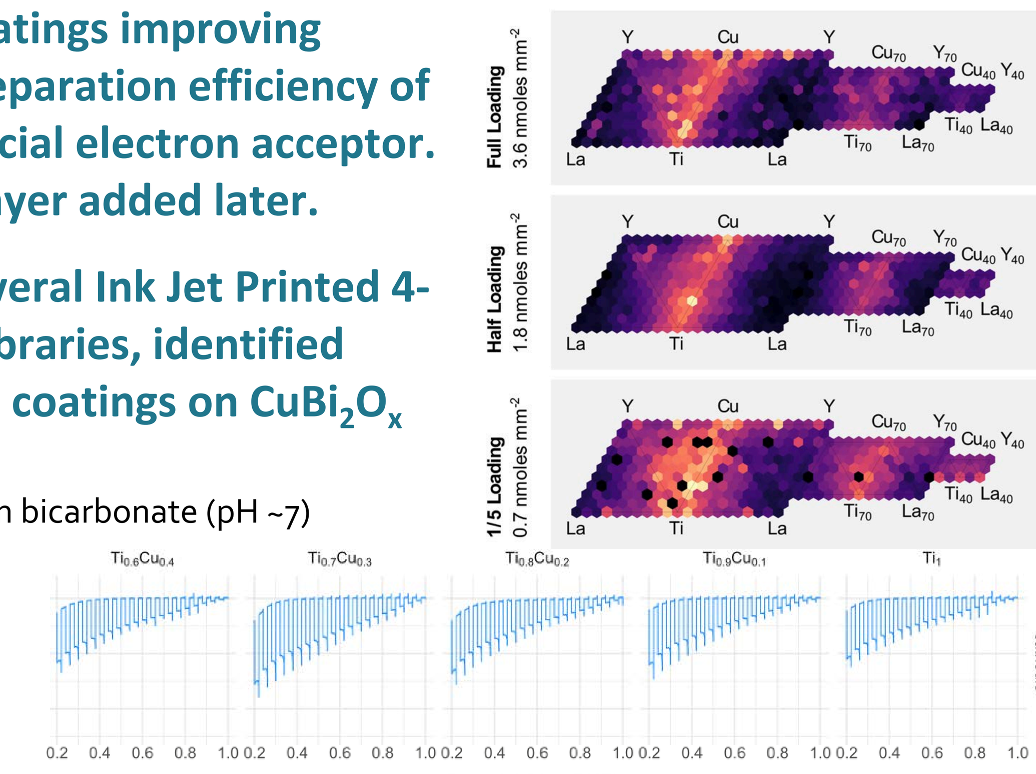
#### $(La\text{-}Y\text{-}Ti\text{-}Cu)O_x$ coating libraries on $CuBi_2O_4$ in pH 7 with electron acceptor

**Objective: Identify coatings improving stability and charge separation efficiency of $CuBi_2O_4$ using a sacrificial electron acceptor. A $CO_2$RR co-catalyst layer added later.**

**Rapid screening of several Ink Jet Printed 4-metal oxide coating libraries, identified $(Ti\text{-}Cu)O_x$ as beneficial coatings on $CuBi_2O_4$**

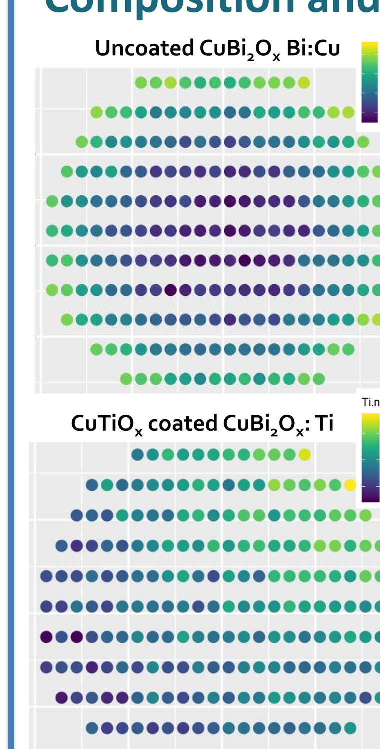
**Measurement details:**

CO2-bubbled 0.1 M potassium bicarbonate (pH ~7)
+ **0.1 M sodium persulfate**
+ 0.25 M sodium sulfate
One CV cycle at 40mV/s from +1.2 to +0.4 V vs RHE
455 nm LED with 1 s illumination period



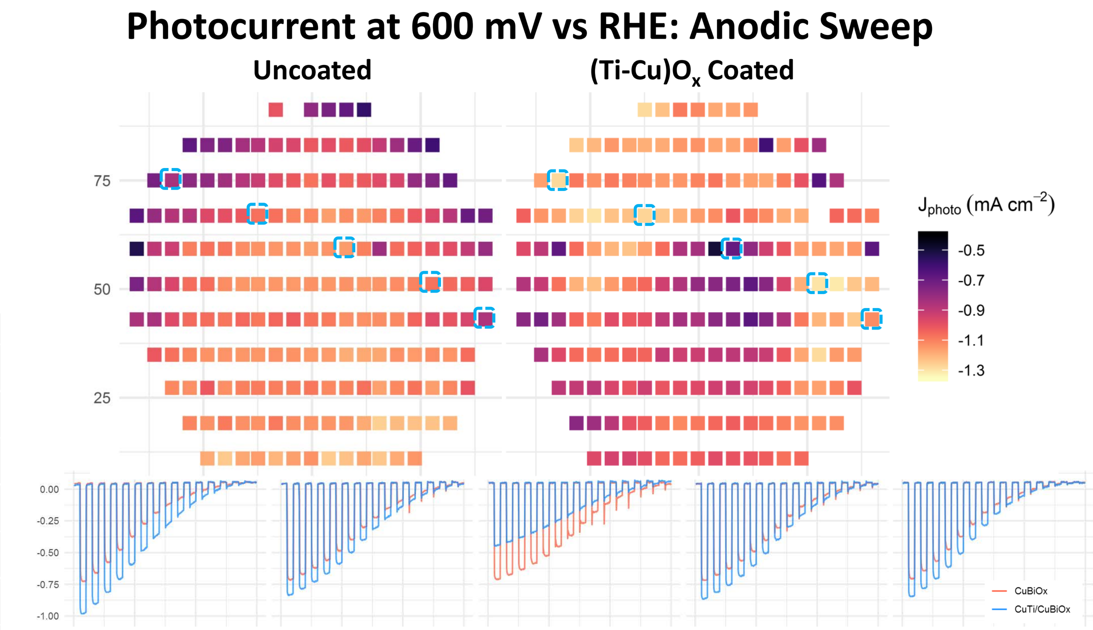

#### Sputtered $(Ti\text{-}Cu)O_x$ coating compositon and loading on $CuBi_2O_x$

**Composition and performance mapping:**



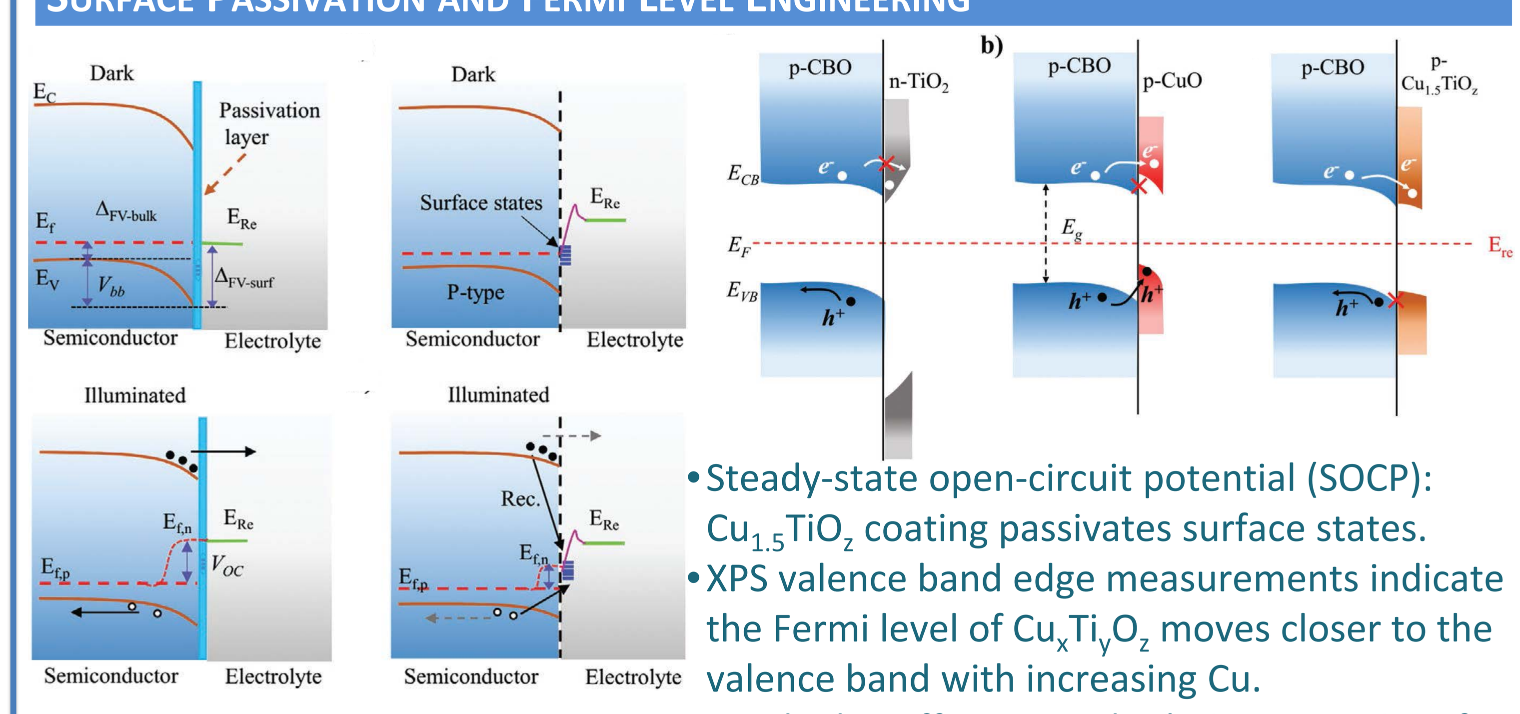

- Uncoated: radial Bi:Cu Ratio and performance
- $(Ti\text{-}Cu)O_x$ coated: Ti and performance increases to top left

**Photocurrent at 600 mV vs RHE: Anodic Sweep**




Optimal coating depends upon light absorber composition and processing

#### Surface Passivation and Fermi Level Engineering




- Steady-state open-circuit potential (SOCP): $Cu_{1.5}TiO_z$ coating passivates surface states.
- XPS valence band edge measurements indicate the Fermi level of $Cu_xTi_yO_z$ moves closer to the valence band with increasing Cu.
- Band edge offsets tuned relative to $CuBi_2O_4$ for optimal charge separation.

Zhang, Lindley, Guevarra, Kan, Shinde, Gregoire, Han, Xie, Haber, Cooper *Adv. Funct. Mater.* 2020, 2000948.

### 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 electocatalyst compositions.
- Discoveries transferable to other synthesis methods and device scales.
- Similar developments for coatings on $CuBi_2O_x$ photo-cathode assemblies.
- Reduced surface recombination through passivation of surface defect states and improved carrier extraction efficiency through Fermi level engineering.

Simultaneous Discovery of Improved Materials & Interfaces