Functional Semiconductors and Interfaces for Artificial Photosynthesis: State of the Art and Perspectives

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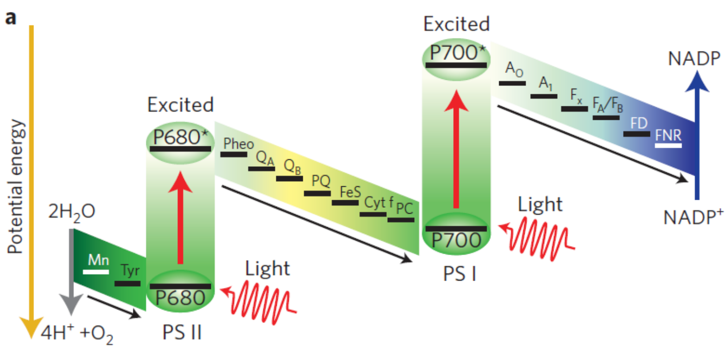
April 20th, 2018

Renewable Fuel Generation by Artificial Photosynthesis

- 120,000 TW solar incident
- >400 GW installed globally (total PV)
- The problem: Intermittent power

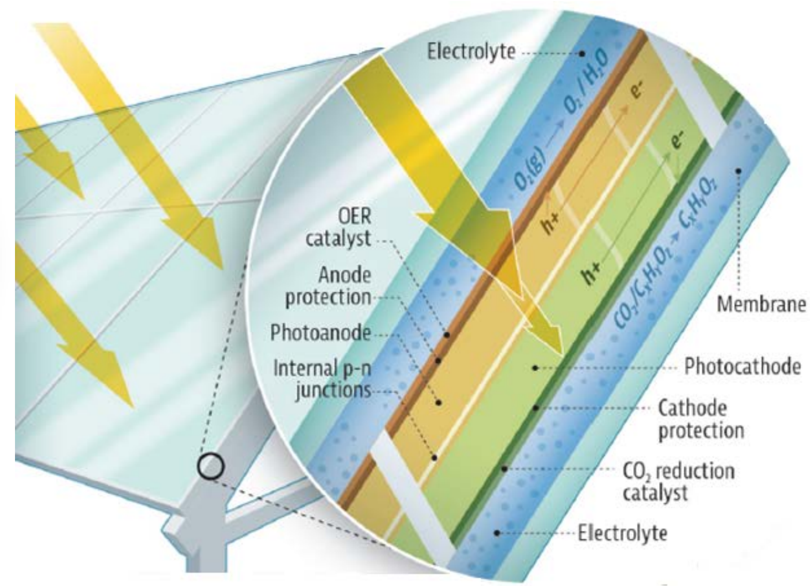
Scalable energy storage is critical for a sustainable future

Natural Photosynthesis: Storing Solar Energy in Chemical Bonds



Durrant *et al.*, Nature Photonics 6, 511 (2012)

Artificial Photosynthesis



Solar-driven Water Splitting at Work

$$H_2O + h\upsilon \rightarrow H_2 + O_2$$

Walczak *et al*. Adv. Energy Mater. **7**, 1602791 (2017)

Solar-driven Water Splitting at Work

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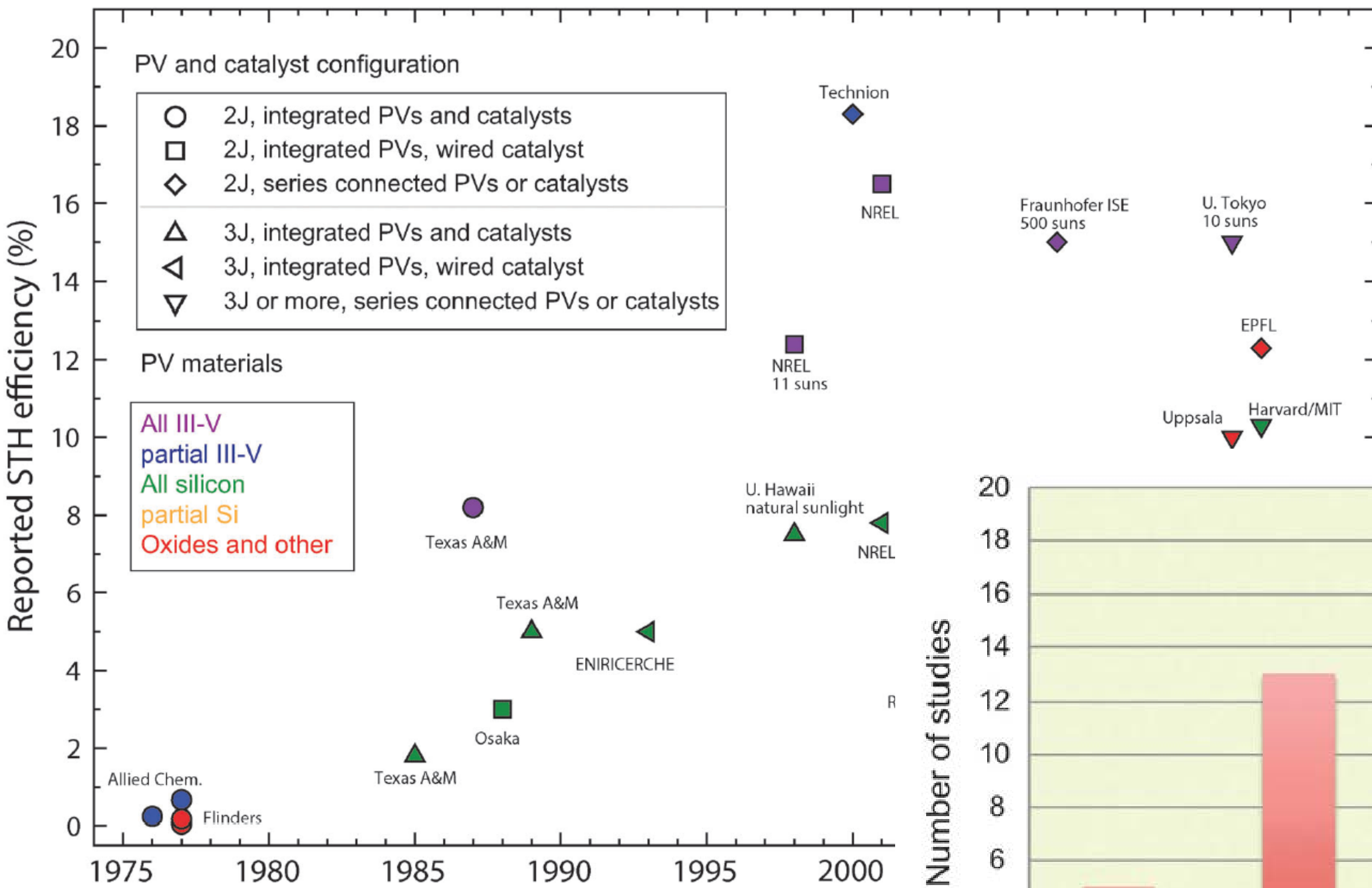
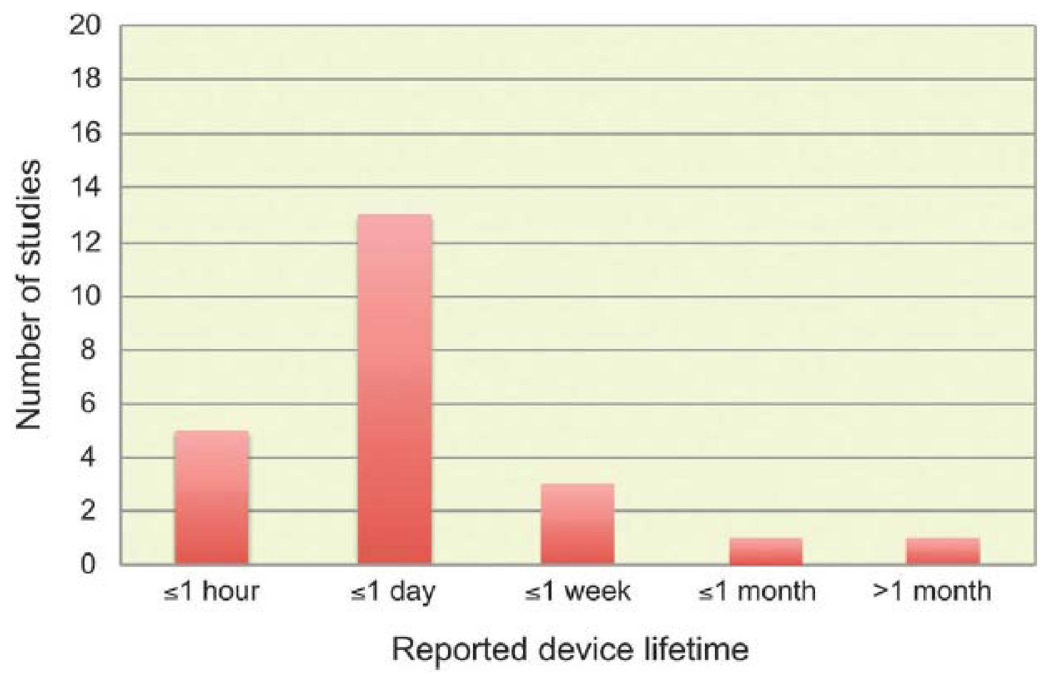
dv. Energy Mater. 7, 1602791 (2017)

State of the Art

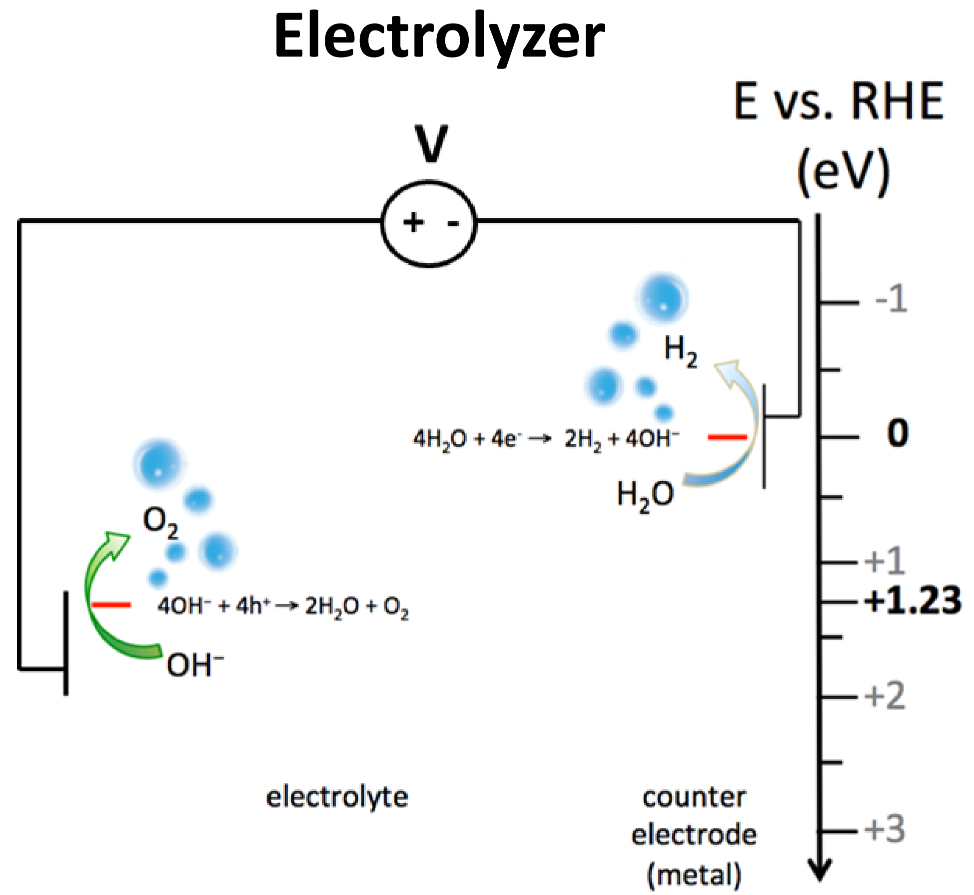




Shaner *et al*. Energy Eniron. Sci **8**, 2811 (2015).

Water Splitting Electrolysis

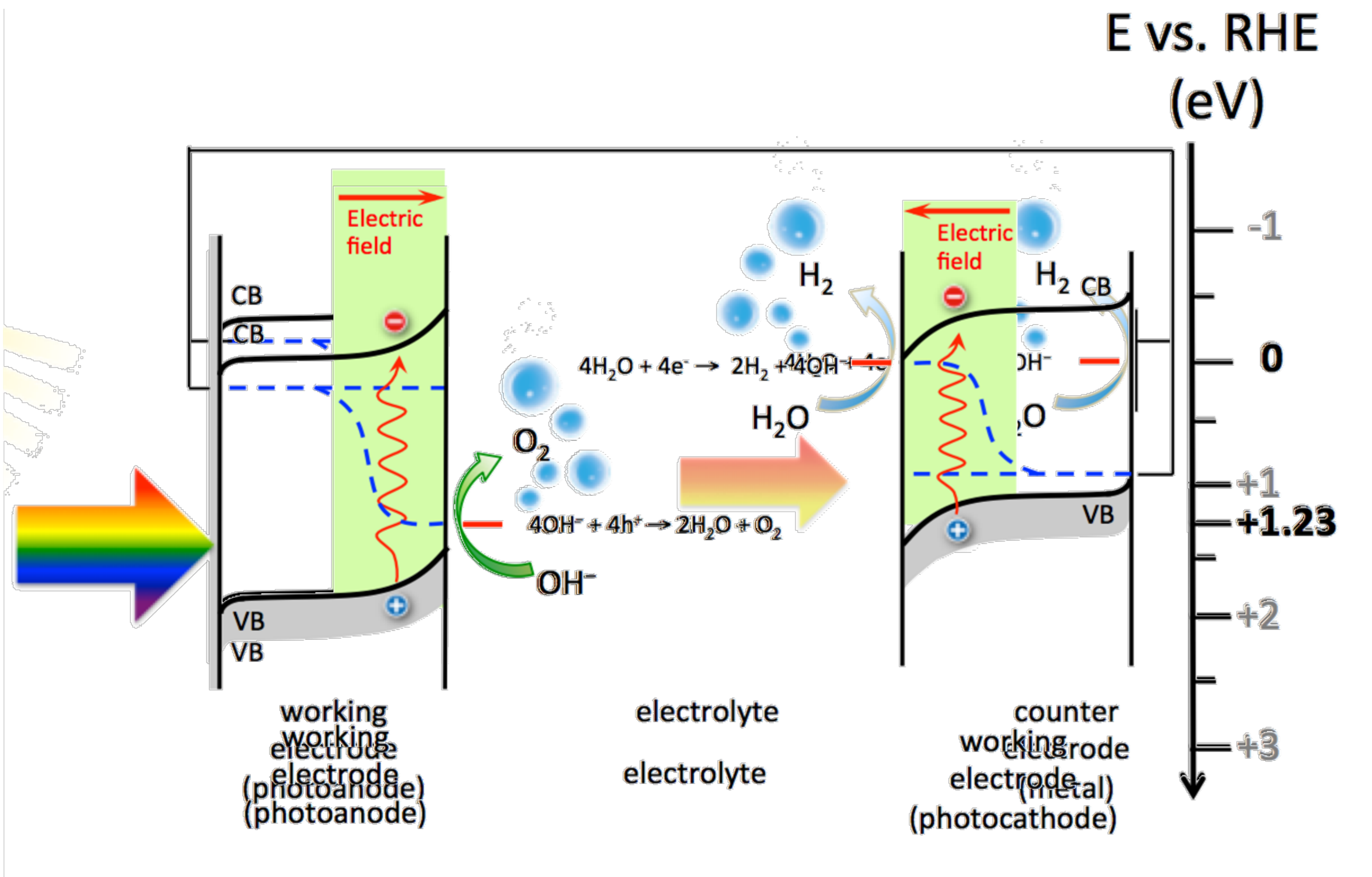
- Thermodynamic potential required: 1.23 V
- Including kinetic factors and loss processes: ~1.7 – 1.8 V



Smith, Sharp, et al., Energy Environ. Sci. **8**, 2851 (2015)

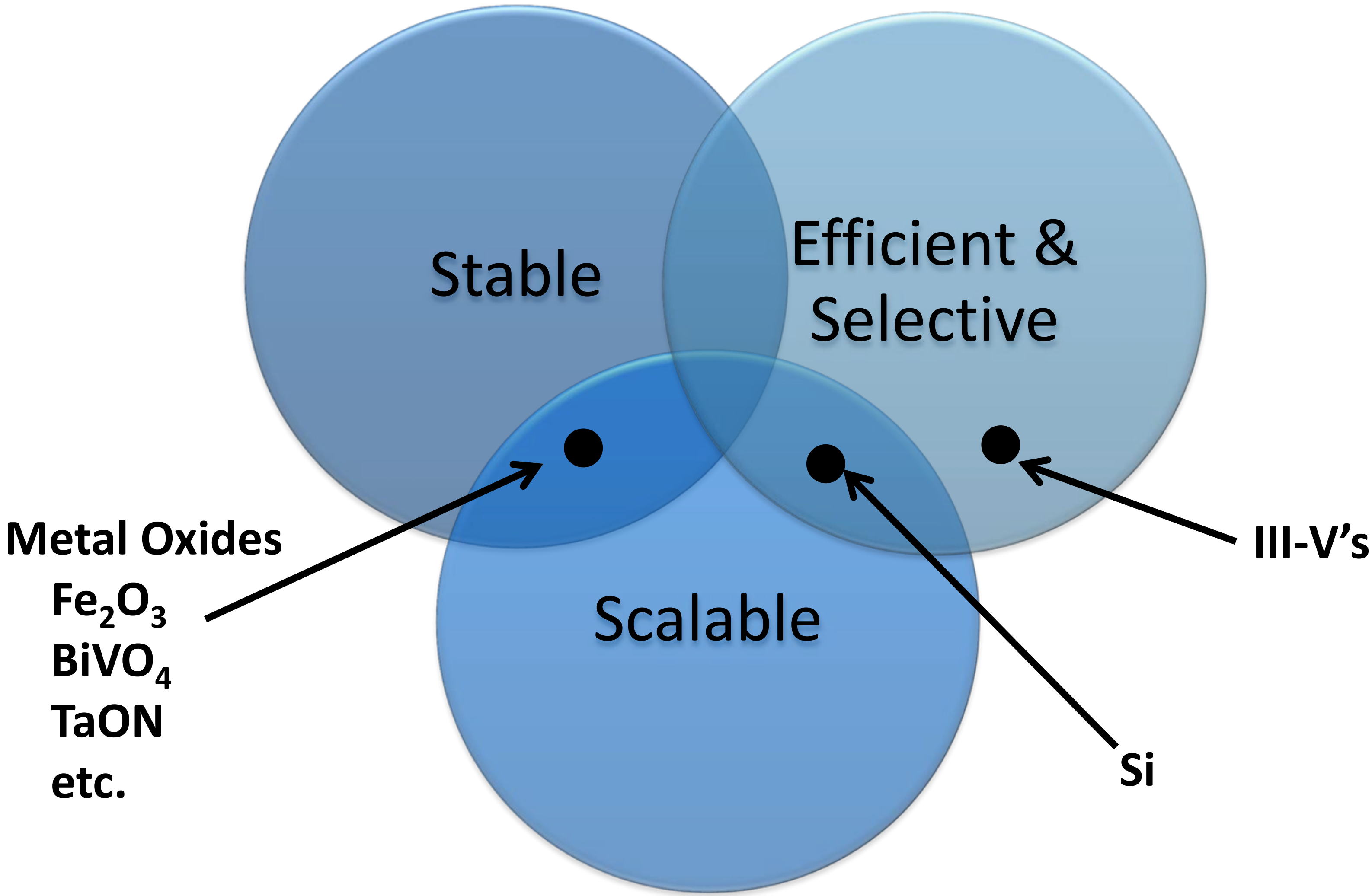
Semiconductor Solar Photoelectrochemistry

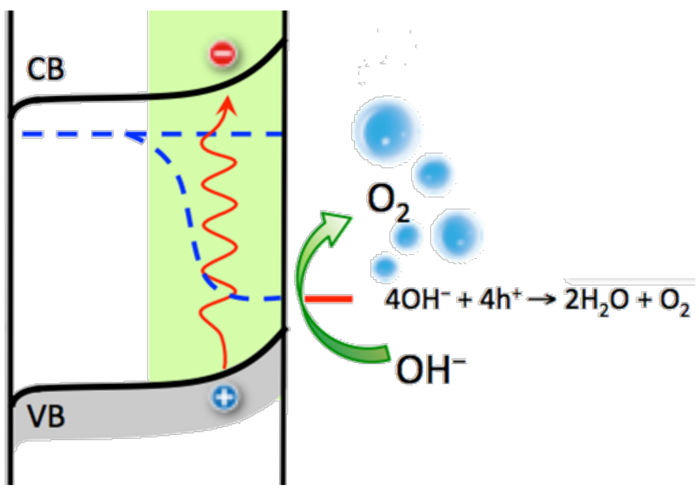
- Charge separation at semiconductor-electrolyte junctions
- Water: Only sufficiently abundant proton and electron source
- Tandem design for matching solar spectrum



Smith, Sharp, et al., Energy Environ. Sci. **8**, 2851 (2015)

The Materials Challenge

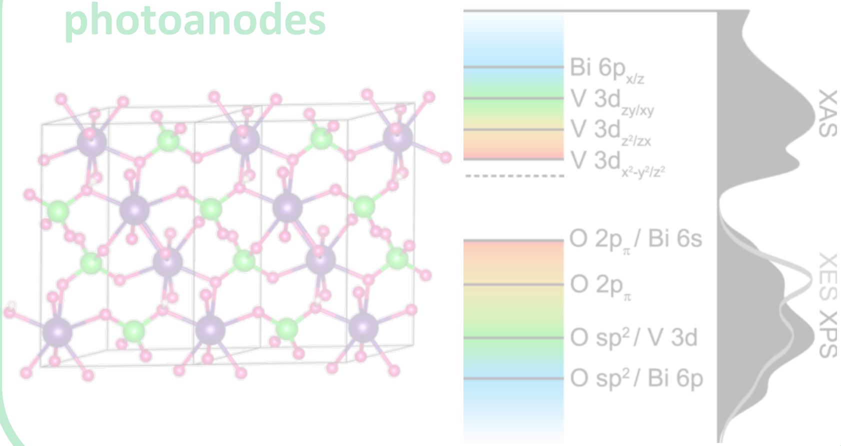




Two Approaches:

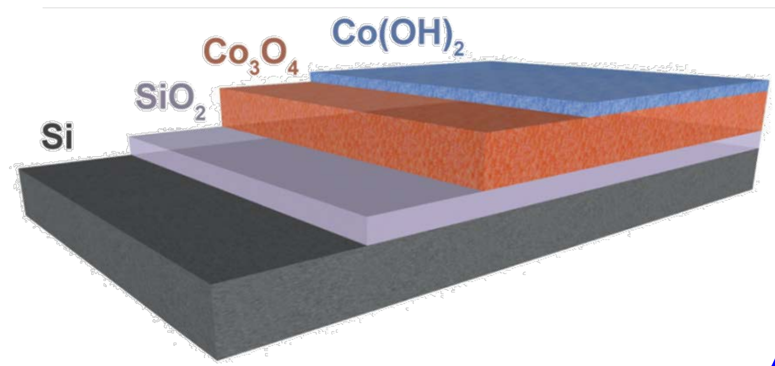
1) Stabilization of otherwise unstable photoelectrodes
2) Discovery of intrinsically stable semiconductors

Advancing thin film metal oxide photoanodes



Stable → Efficient

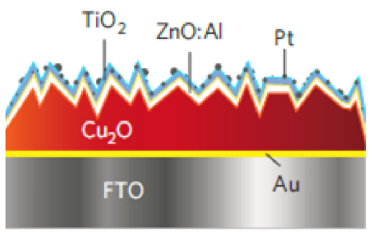
Stabilization with conformal coatings



Efficient → Stable

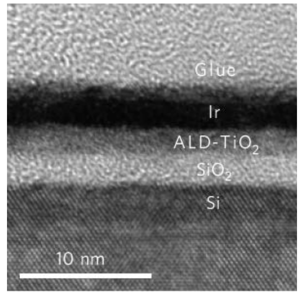
Emergence of a Suite of Viable Corrosion Protection Strategies

Photocathodes



Graetzel *et al.* Nature Mater. **10**, 456 (2011)

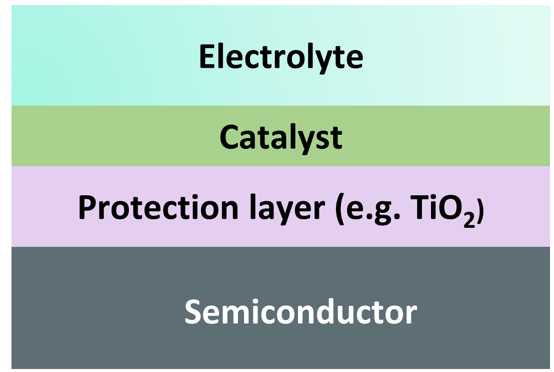
Photoanodes



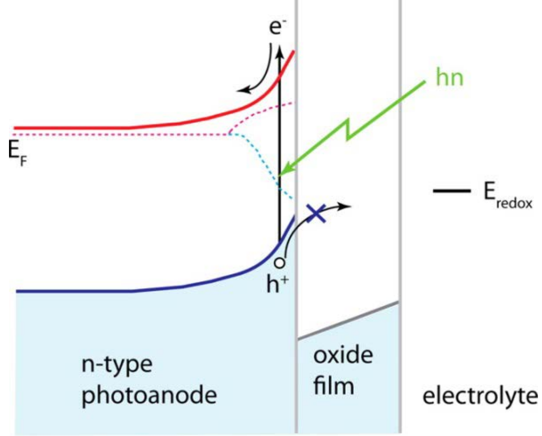
McIntyre, *et al.* Nature Mater. **10**, 539 (2011)

Protected Major Semiconductor Classes:

- Group IV, III-V, II-VI; MOx
- Planar, nanostructured, poly- and single-crystalline

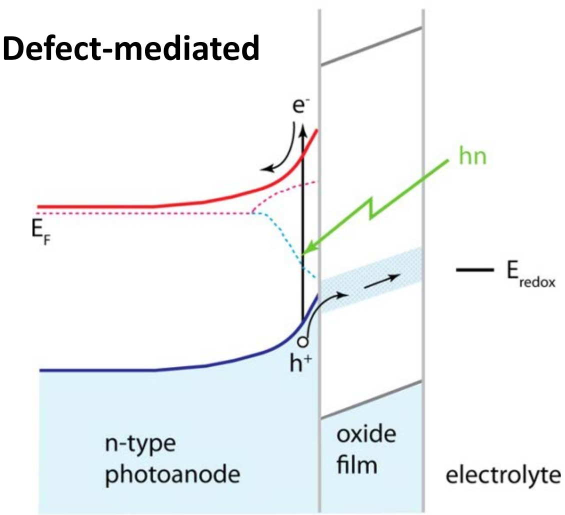


Tunneling



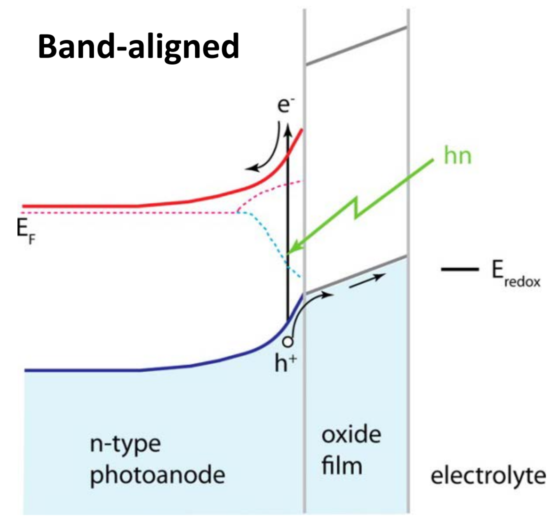
McIntyre *et al.*, Nature Mater. **10**, 539 (2011)

Defect-mediated



Hu *et al.*, Science, **344**, 1005 (2014)

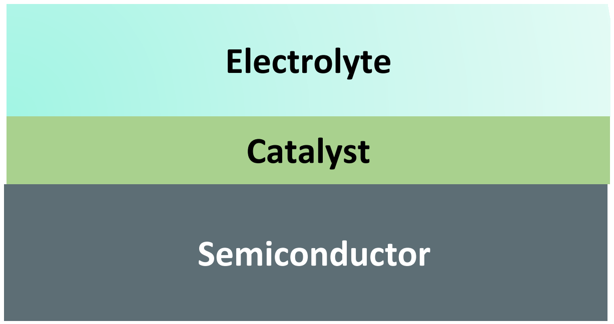
Band-aligned



Chen *et al.*, JACS **137**, 9595 (2015)

Strategies for Stabilizing Semiconductors

Chemically Inactive Interfacial Layers

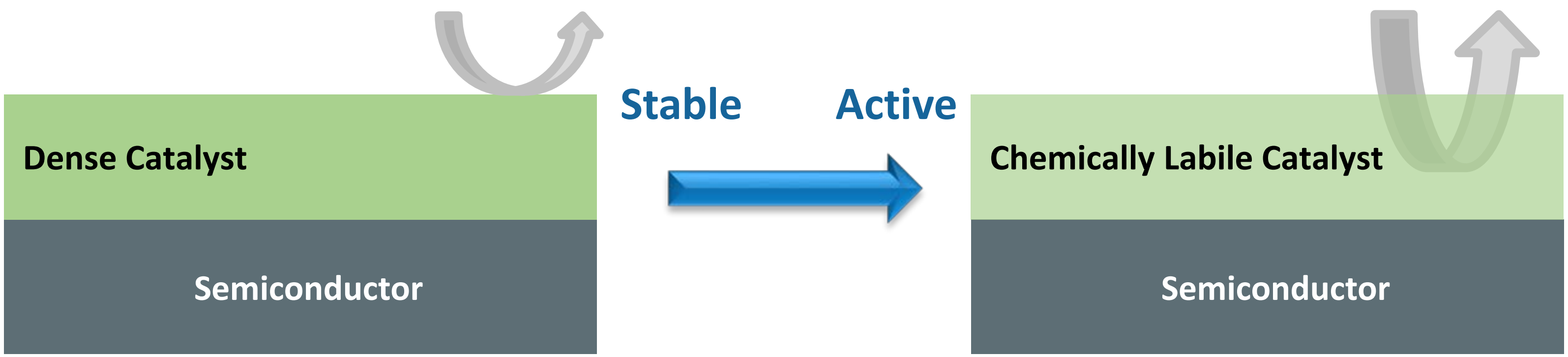


Can we use the catalyst itself to stabilize the semiconductor?

Can we use the atomic precision of ALD to create more active catalysts?

Model System:
PE-ALD of CoO_x on Si photoanodes

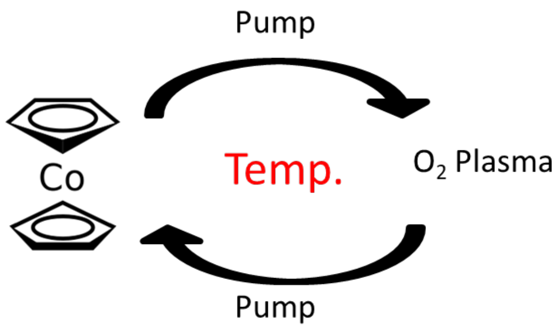
Competing Properties

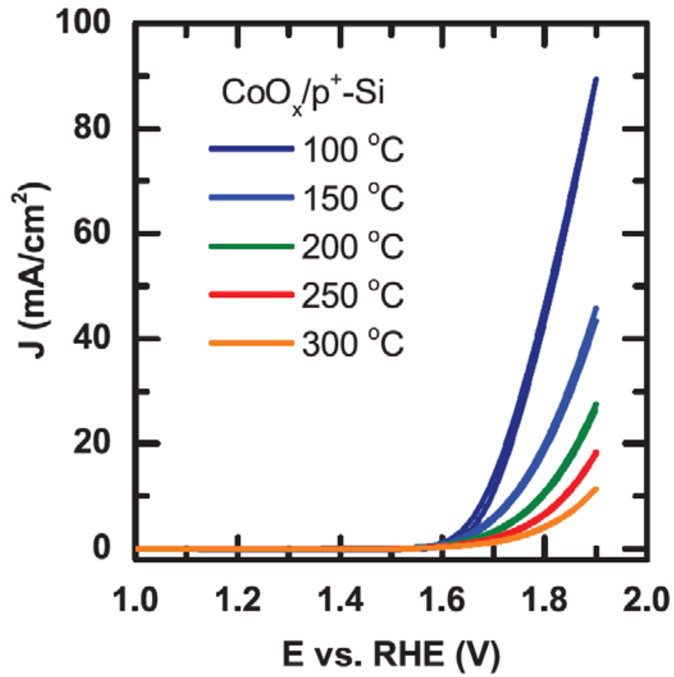


Dense Catalyst	Chemically Labile Catalyst
Ordered	Disordered
Surface Active	Volume Active
Physically and chemically robust	Ion permeable
Isolated interface	Exposed interface

Functional Nanoscale Materials with Plasma-Enhanced ALD

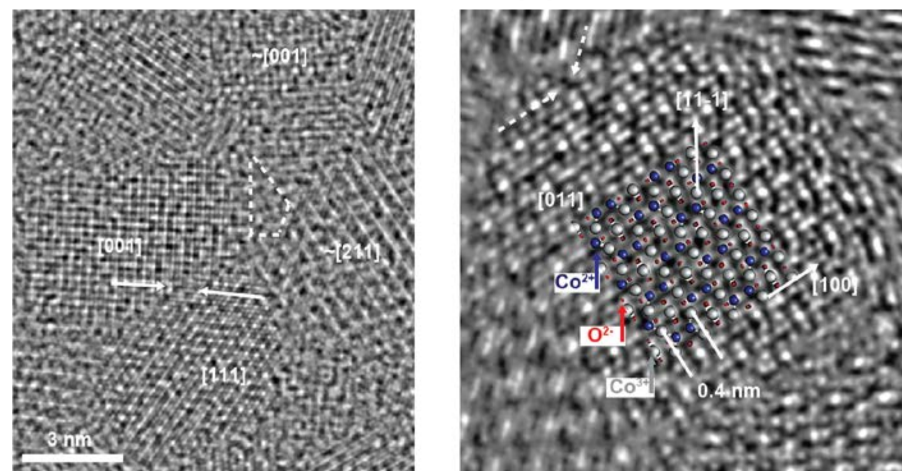
- Conformal coatings
- Non-thermal activation
- Flexible composition, structure, morphology control





Objective: Improve catalytic activity by controlling (dis)order

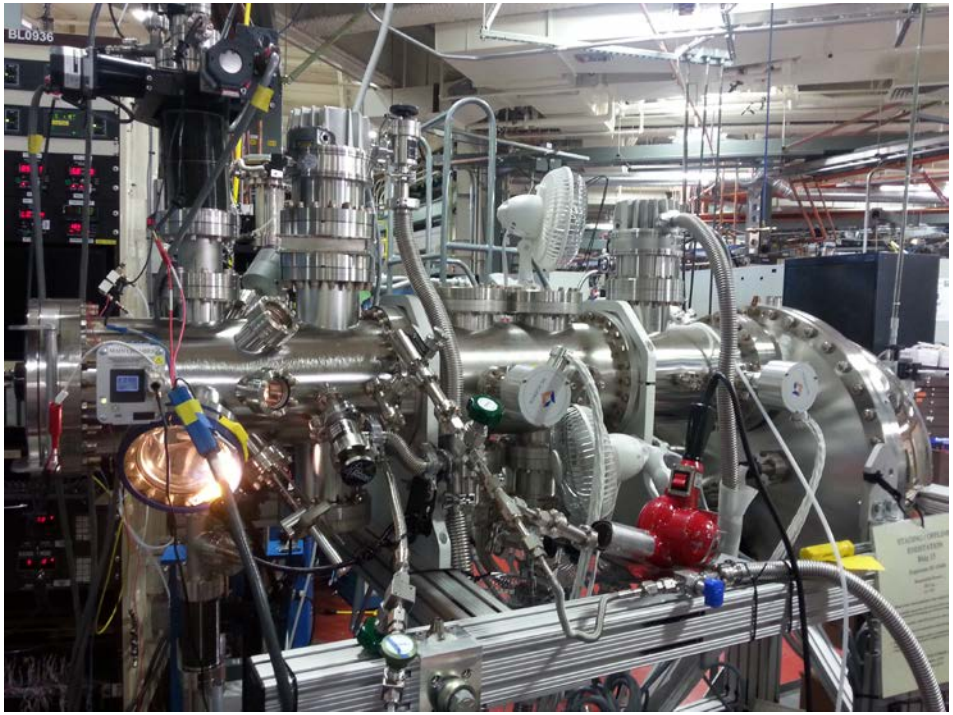
Approach: Create new materials and engineer interfaces with control at the atomic level

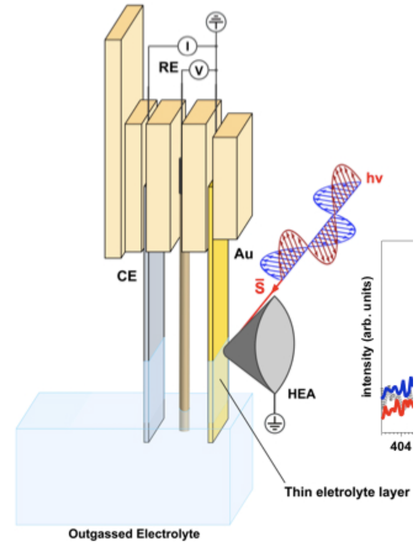


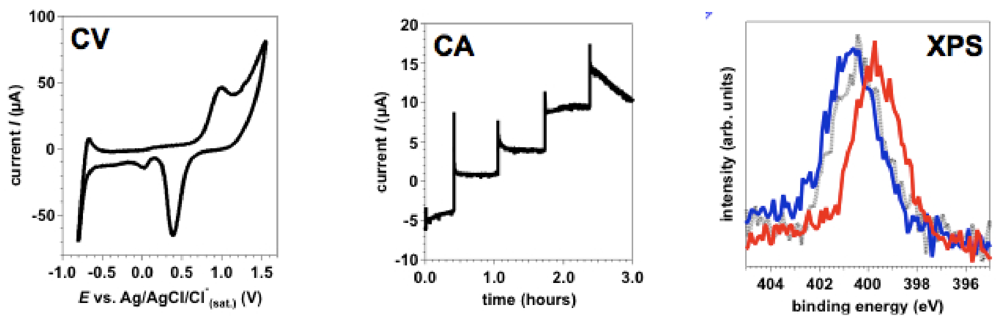
Yang *et al.*, Nature Mater. **16**, 335 (2017)

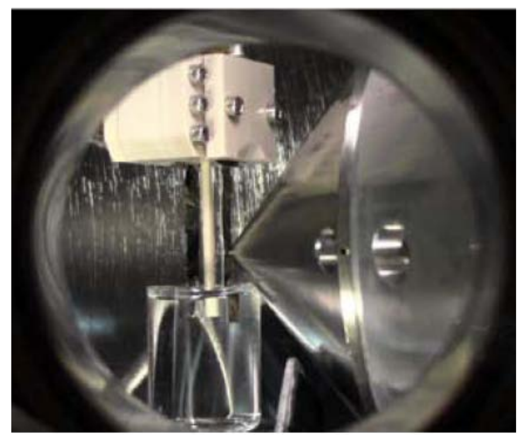
Operando XPS Characterization of Cobalt Oxide Coatings

APXPS @ BL 9.3.1. Electrochemical set up and dip and pull method









Favaro, *et al.*, JACS **139**, 8960 (2017)

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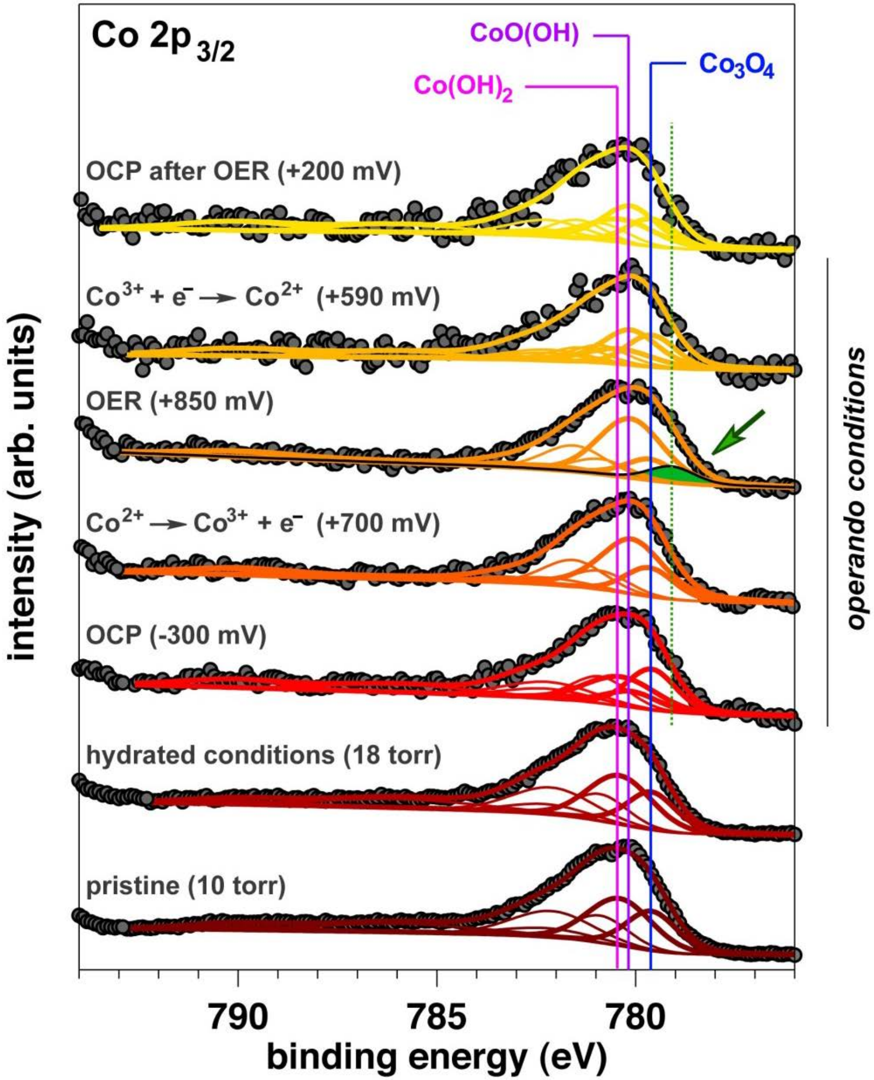

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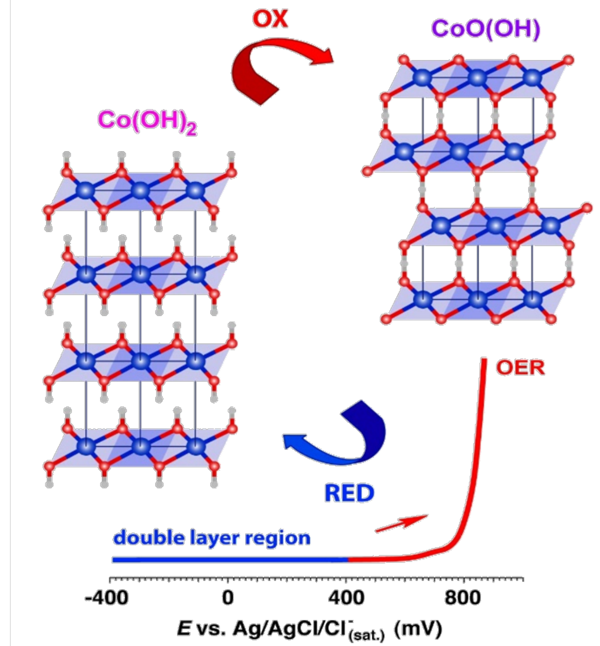
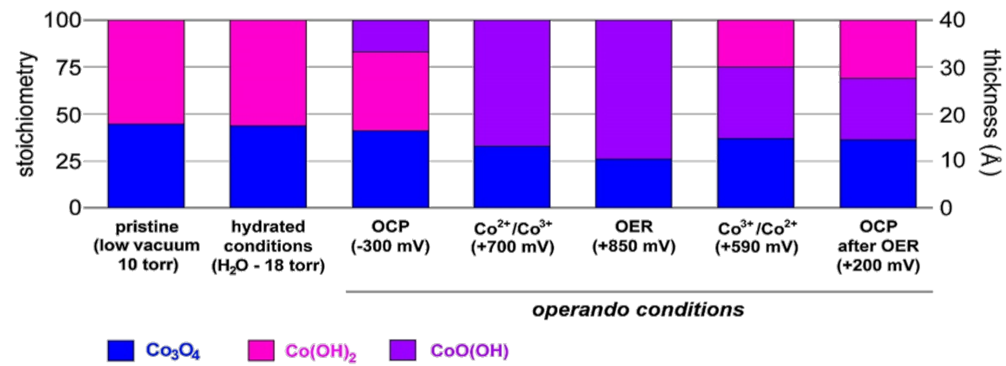
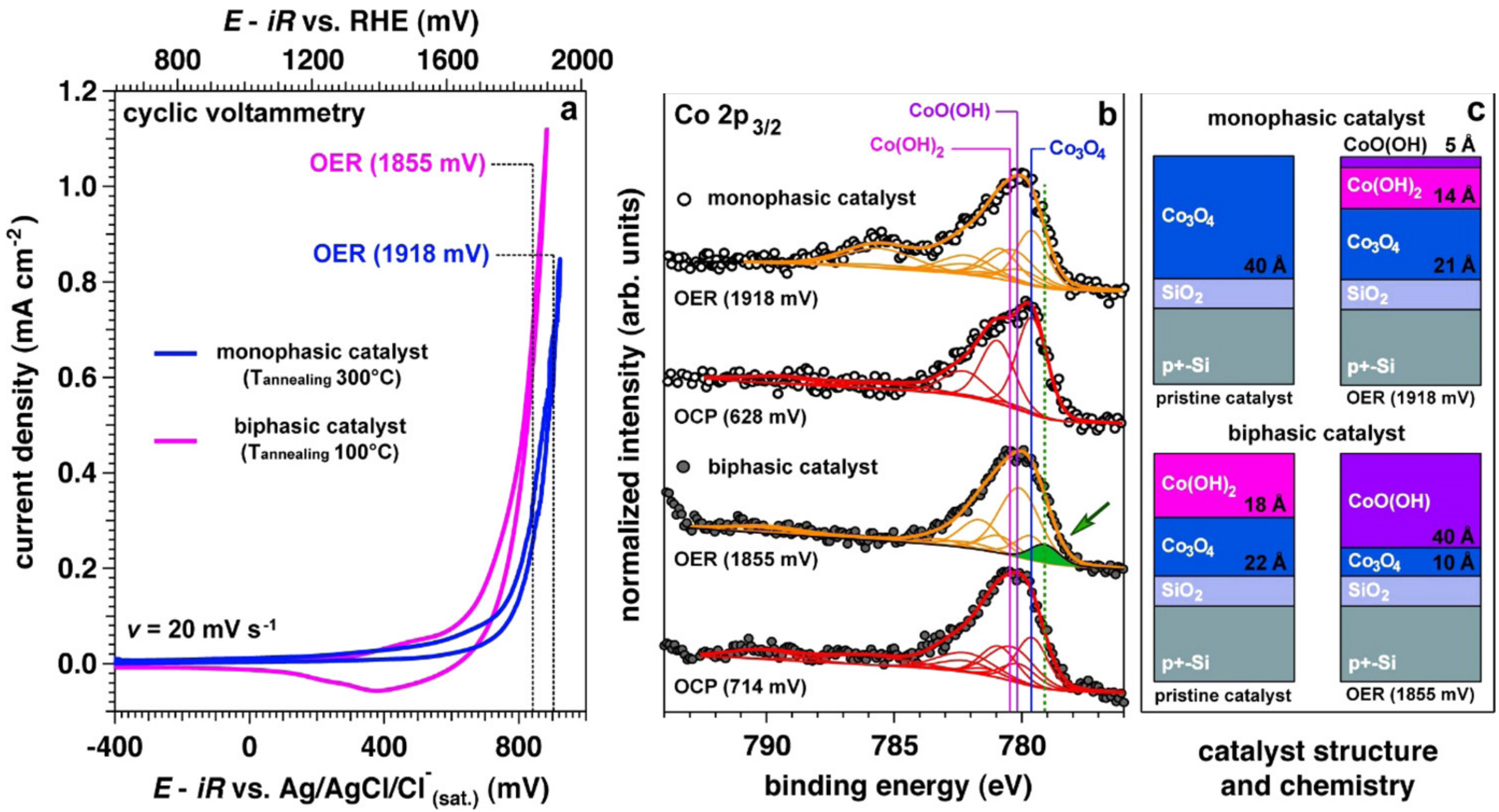




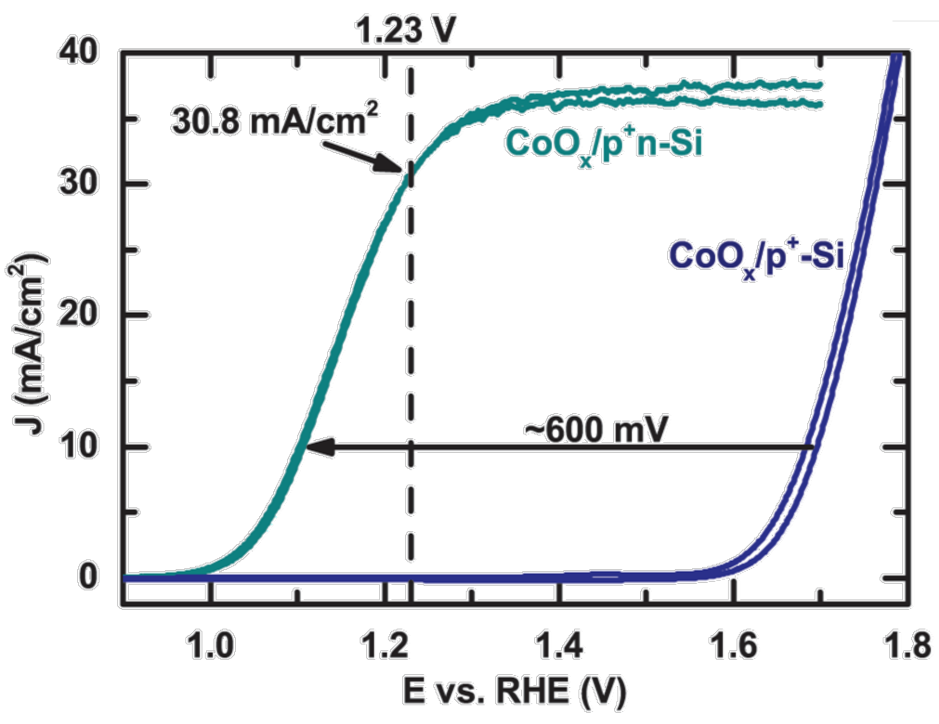
Mechanism discovery by *operando* probing of transformations in complex environments

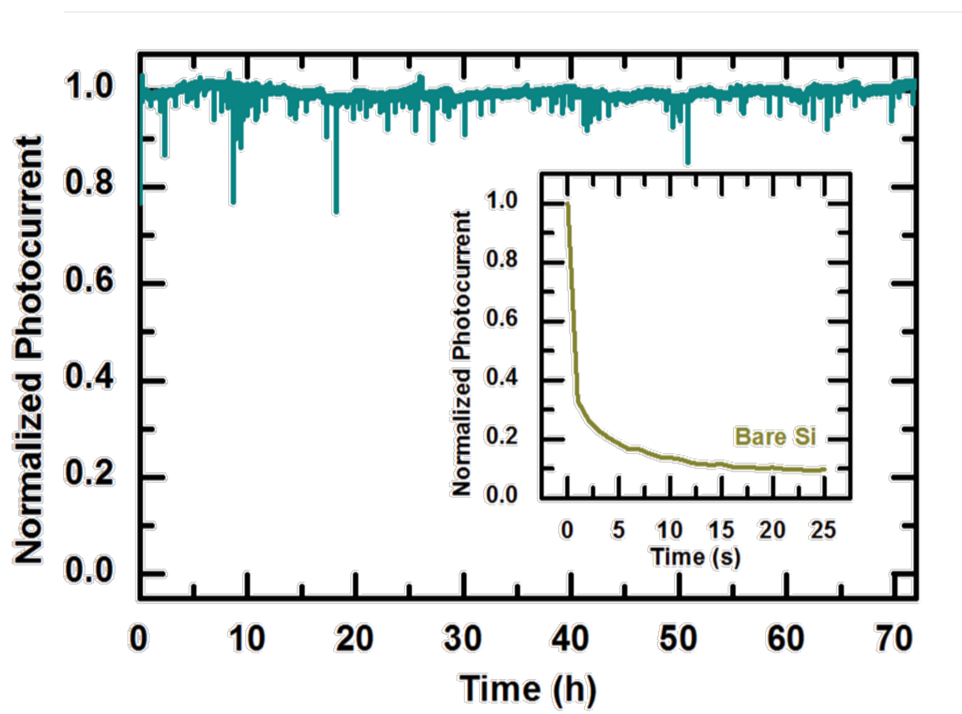
Operando XPS Characterization of Mono- vs. Bi-Phasic Coatings



- **Transformation to CoO(OH) phase provides high activity and is promoted by the presence of $Co(OH)_2$ in as-deposited material**
- **Co^{4+} only observed on highly active films under OER conditions**

Integration into High Performance Silicon Photoanodes





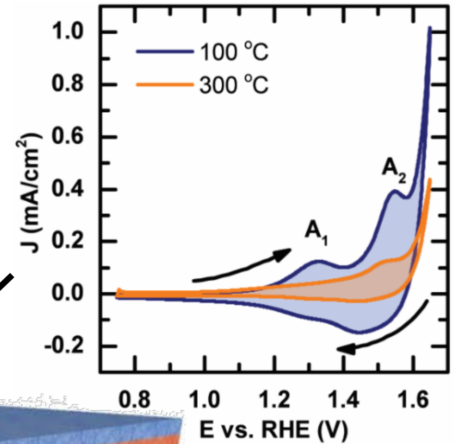
- Improved catalytic activity translates to improved PEC performance
- >30 mA/cm^2 @ 1.23 V vs. RHE
- Photocurrent onset < 1.0 V vs. RHE
- Stable operation for >72 h in 1 M KOH

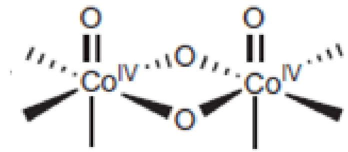
Yang *et al.*, Nature Mater. **16**, 335 (2017)

Biphasic Coatings for Improved Stability and Performance

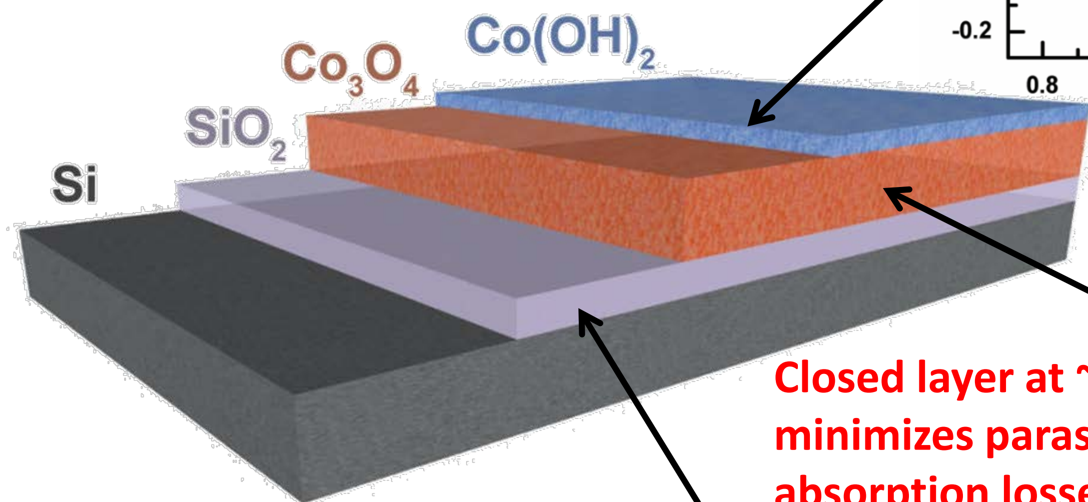
$Co(OH)_2$ volume transformation promotes high concentration of active sites for OER: Co(IV)-Co(IV)

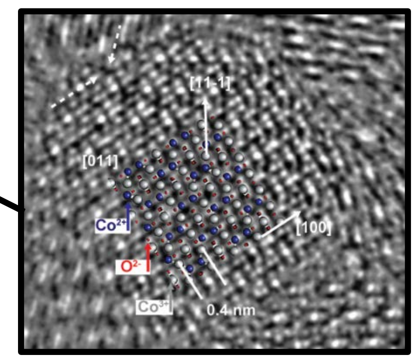
Yang, *et al.,* Nature Mater. **16**, 335 (2017)
Favaro, *et al.*, JACS **139**, 8960 (2017)





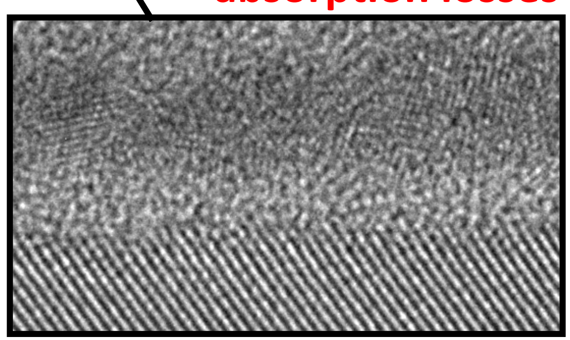
Favaro, *et al.*, JACS **139**, 8960 (2017)





Closed layer at ~4 nm minimizes parasitic absorption losses

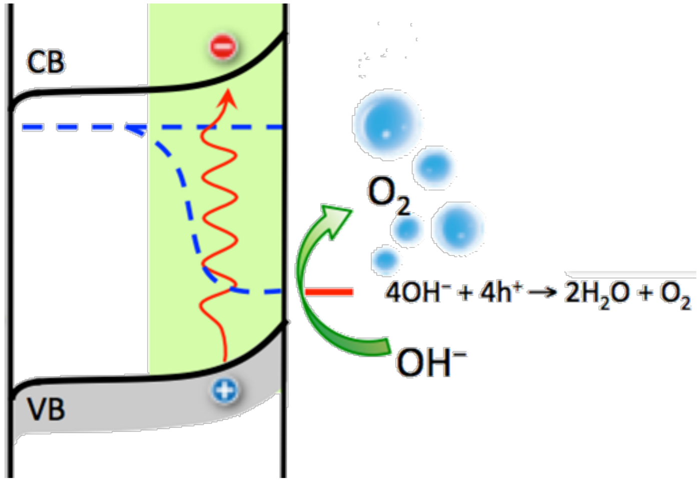
SiO_2 provides electronically passivated interface, while permitting charge transfer



Yang, *et al.*, JACS **131** 6191 (2014)

Spinel Co_3O_4 thin film resists transformation and protects substrate

Yang, *et al.,* Nature Mater. **16**, 335 (2017)
Kieselowski *et al.*, accepted (2016)



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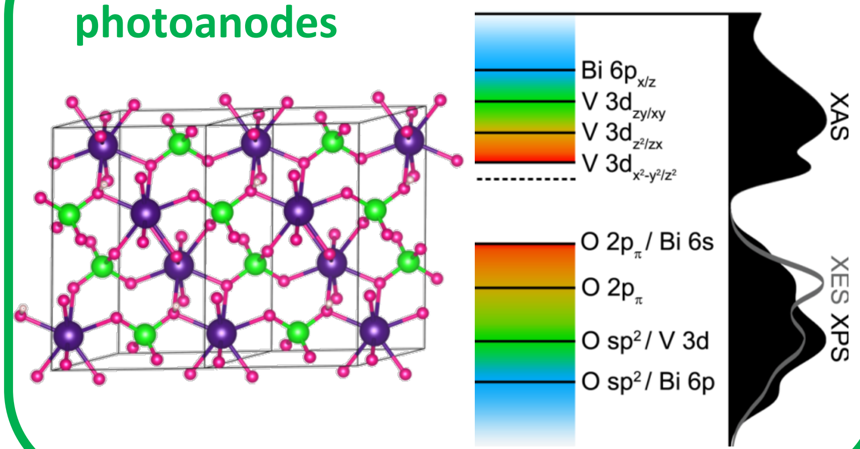
Advancing thin film metal oxide photoanodes

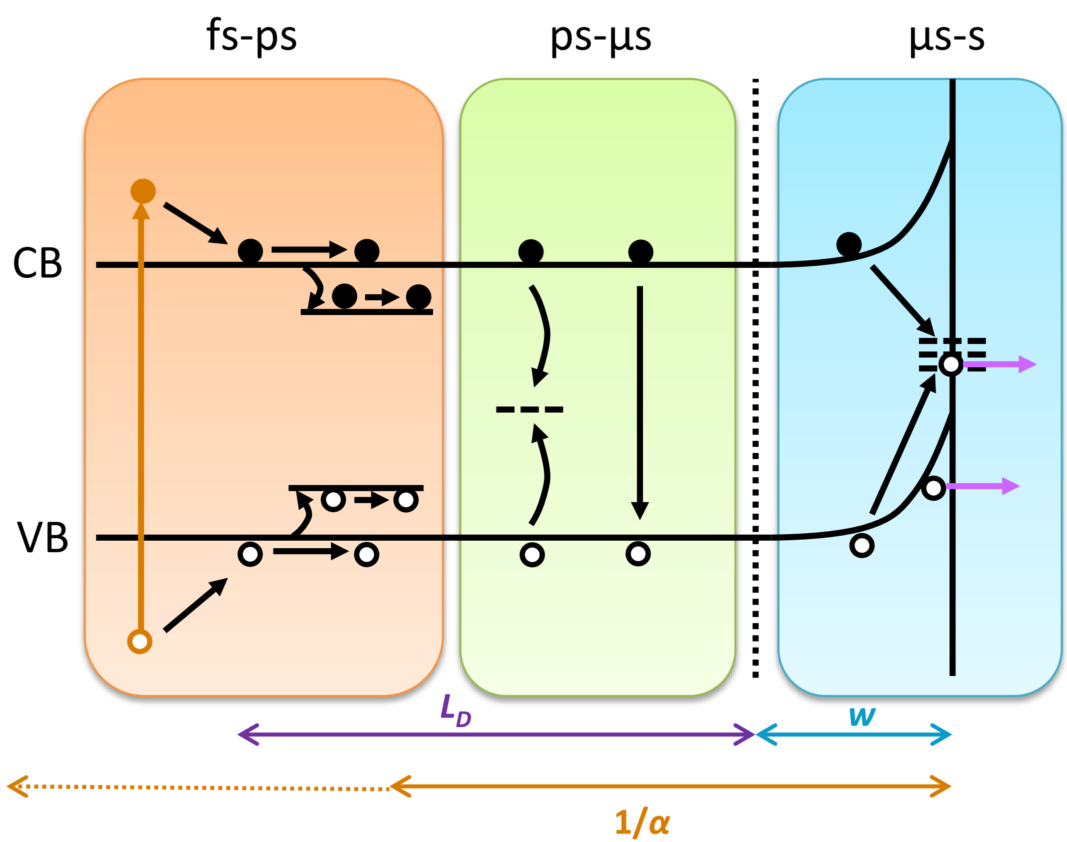


Stable → Efficient

Stabilization with conformal coatings

Efficient → Stable

Competition between reaction and recombination



$1/\alpha \leq L_D + w$ Balanced

$1/\alpha > L_D + w$ Unbalanced

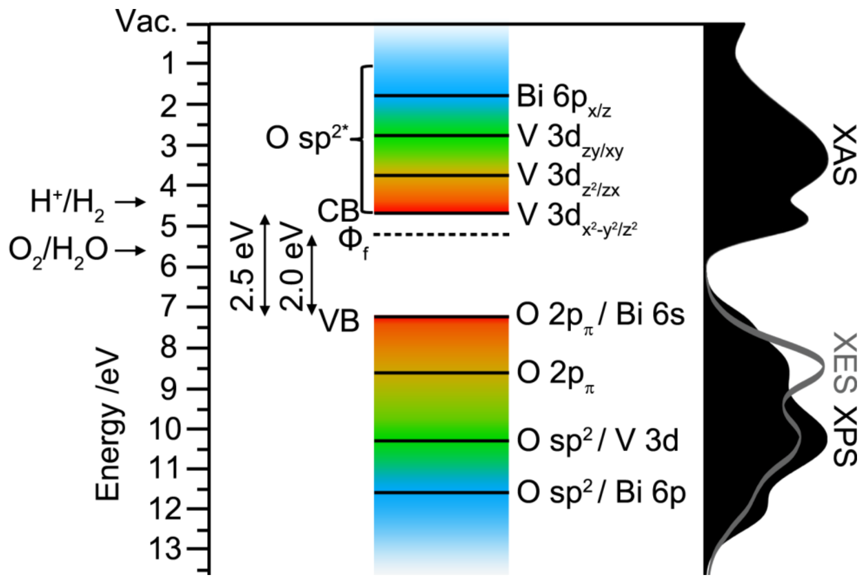
Understanding and controlling energy conversion mechanisms requires characterization over various length and time scales

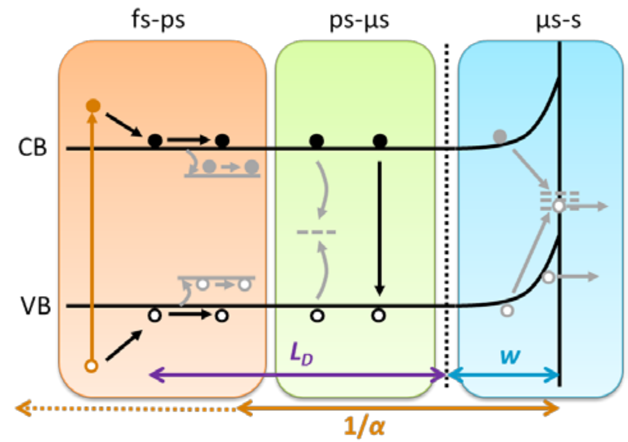
Light interaction with matter
- *Electronic structure*
- Physical structure

Transport mechanisms
- *Electronic structure*
- Photocarrier dynamics
- Defect trapping and recombination

Chemical pathways
- *Electronic structure*
- Interfacial energetics
- Phyical and chemical transformations
- Interface defect states
- Catalytic mechanisms

Electronic Structure of $BiVO_4$

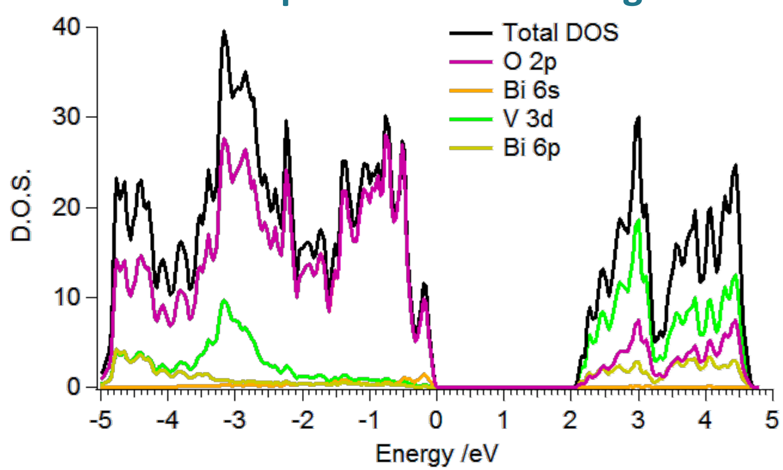


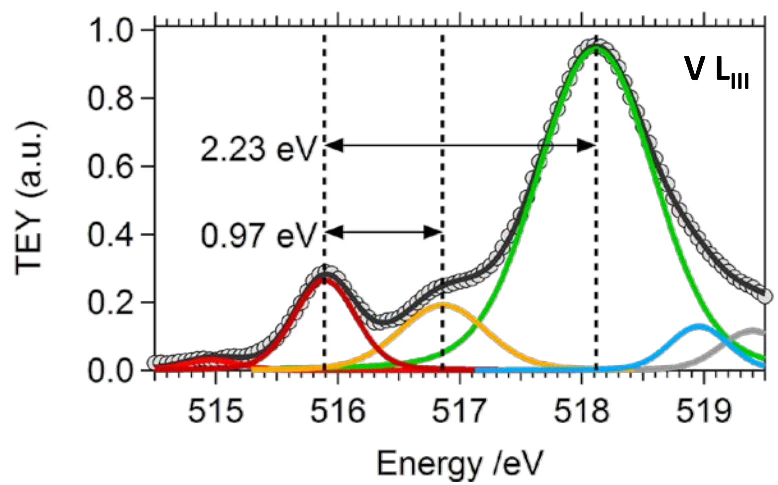


Insights into basic function and limitations of light absorber

Computational Modeling

X-ray and Optical Spectroscopy



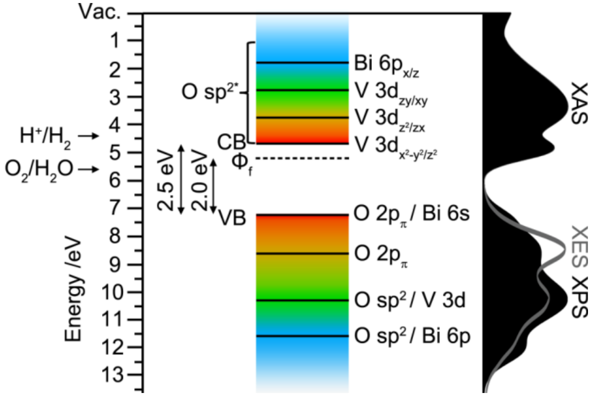


Cooper *et al.*, Chem. Mater. **26**, 5365 (2014)

Cooper *et al.*, JPC C, **119**, 2969 (2015)

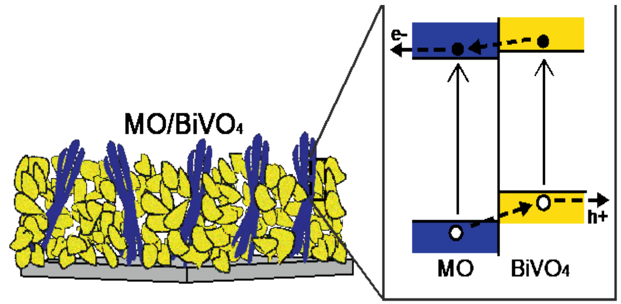
A Comprehensive Approach to Advanced Photoanodes: $BiVO_4$

Electronic Structure



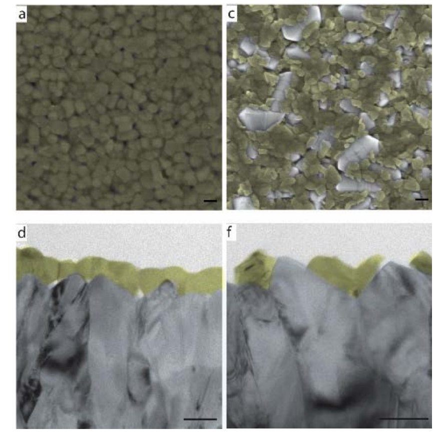
Cooper *et al.*, Chem. Mater. **26**, 5365 (2014)
Cooper *et al.*, JPC C **119**, 2969 (2015)

Photocarrier Dynamics & Novel Mesoscale Architectures



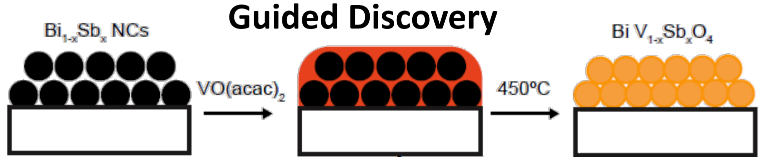
Loiudice, *et al.* Nano Lett. **15** 7347 (2015)
Hess, *et al*. Nano Energy **34**, 375 (2017)
Cooper *et al*. in preparation (2016)

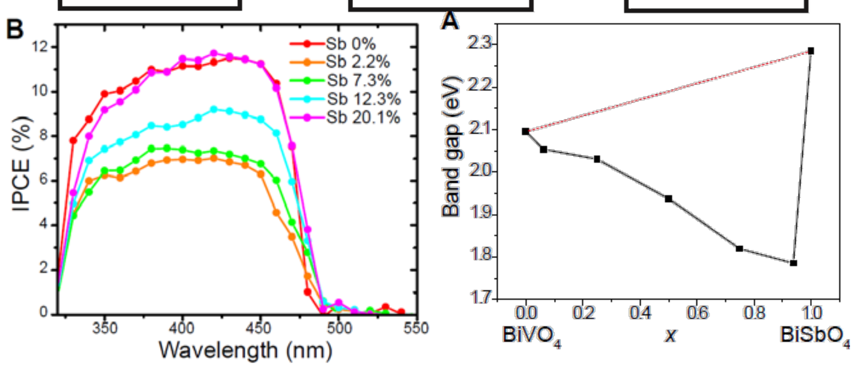
Stability & Photocorrosion



Toma, *et al*. Nature Comm. **7** 12012 (2016)
McDowell *et al*. **118**, JPCC, 19618 (2014)

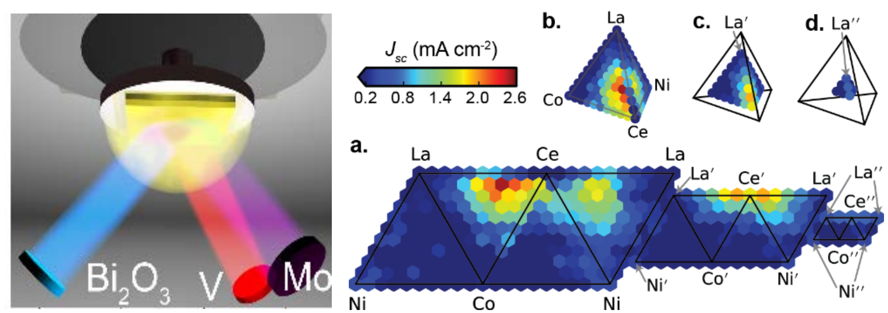
Guided Discovery





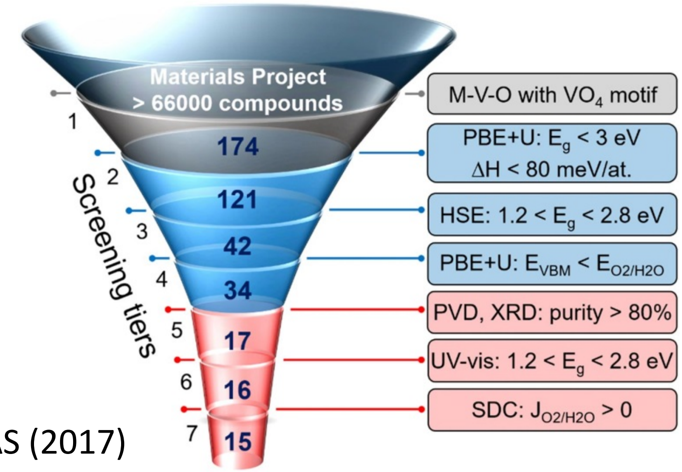
Loiudice, *et al.* Adv. Mater., **11**, 6733 (2015)
Jiang *et al*. Chem. Mater. **29**, 3334 (2017)

Doping, Defects, & Catalyst Integration

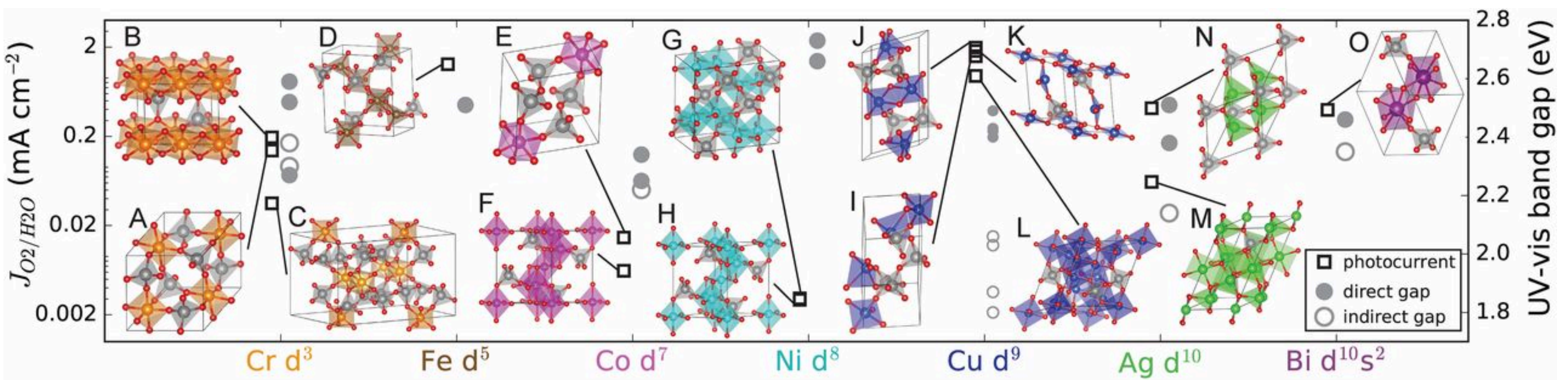


Cooper *et al*. Chem. Mater. **28**, 5761 (2016)
Shinde *et al.*, ACS Appl. Mater. Interf. **8**, 23696 (2016)
Guevarra *et al*. Energy Environ. Sci **9**, 565 (2016)
Chen *et al.,* ChemSusChem **8**, 1066 (2015)
Chen *et al.*, JPC C **117**, 21635 (2013)

An Era of Discovery… That Outpaces Understanding



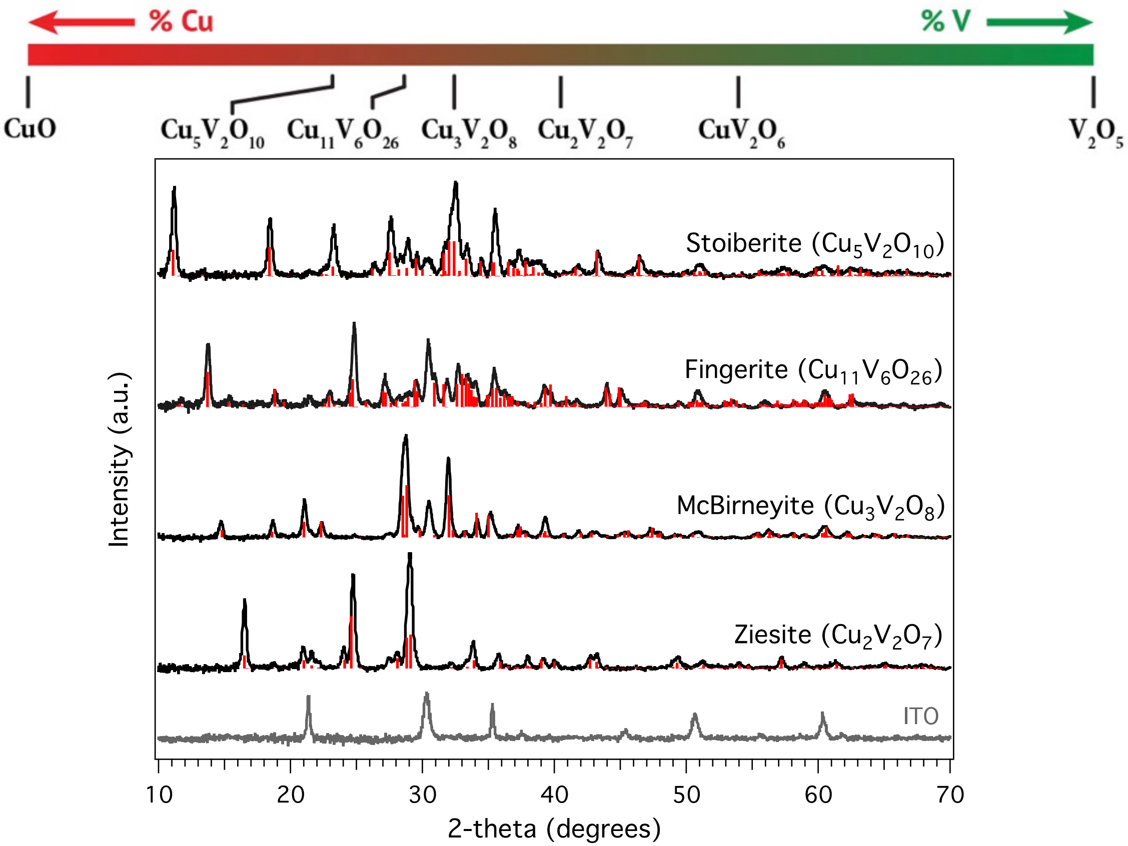
Persson, Gregoire, Neaton, *et al*. PNAS (2017)

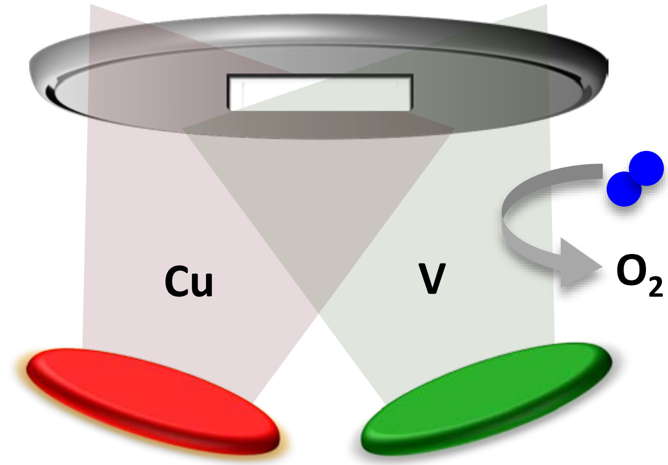


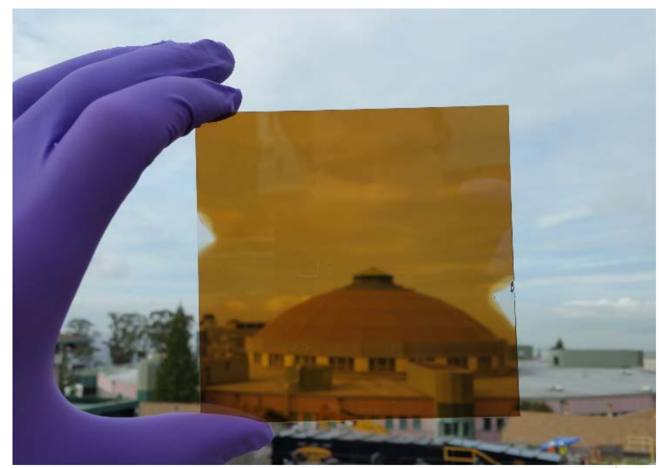
- Worldwide discovery efforts have identified dozens of new semiconductors with desirable bandgaps (**mostly transition metal oxides**)
- Basic factors affecting solar energy conversion efficiencies are poorly understood

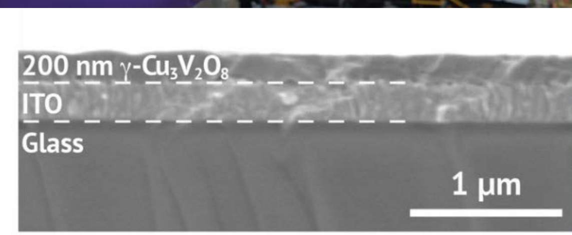
Targeted Synthesis within Complex Phase Space

- **Copper vanadate as an emerging semiconductor**
  - Approx. 1.8 eV bandgap
  - Long-term chemical stability
- Tunable CVO phases by reactive rf co-sputtering



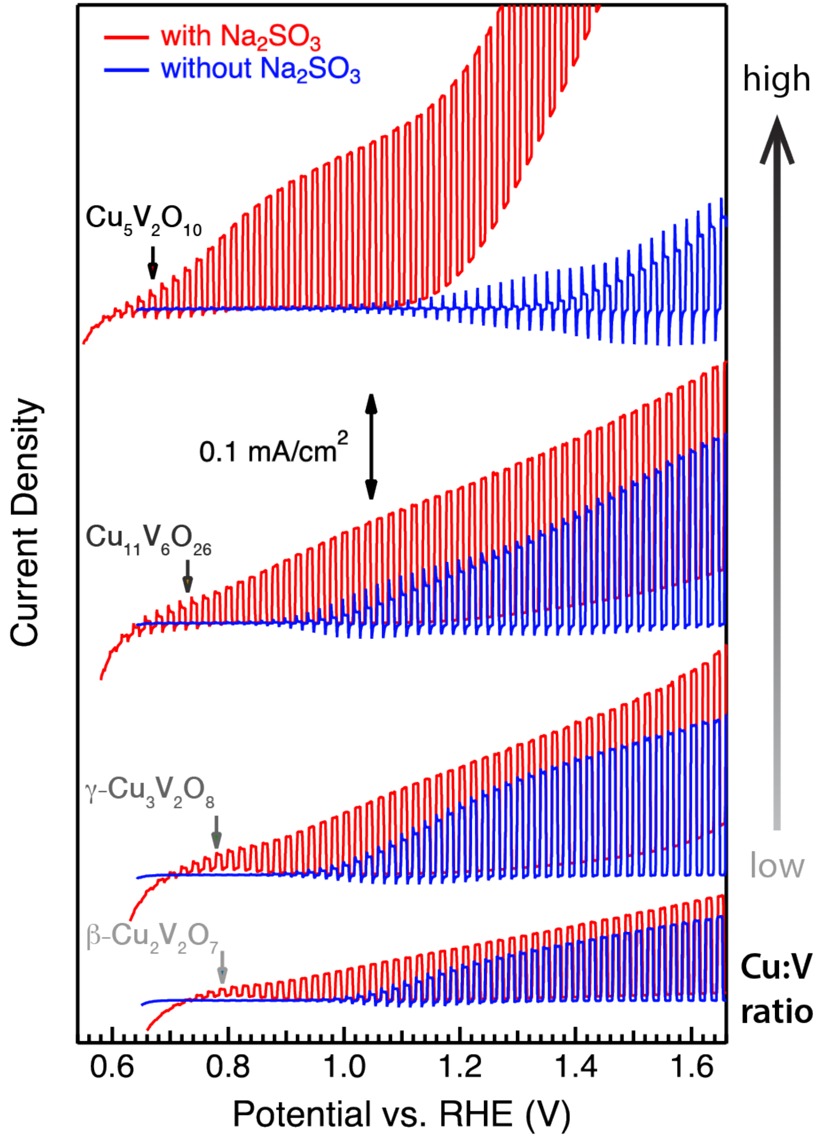


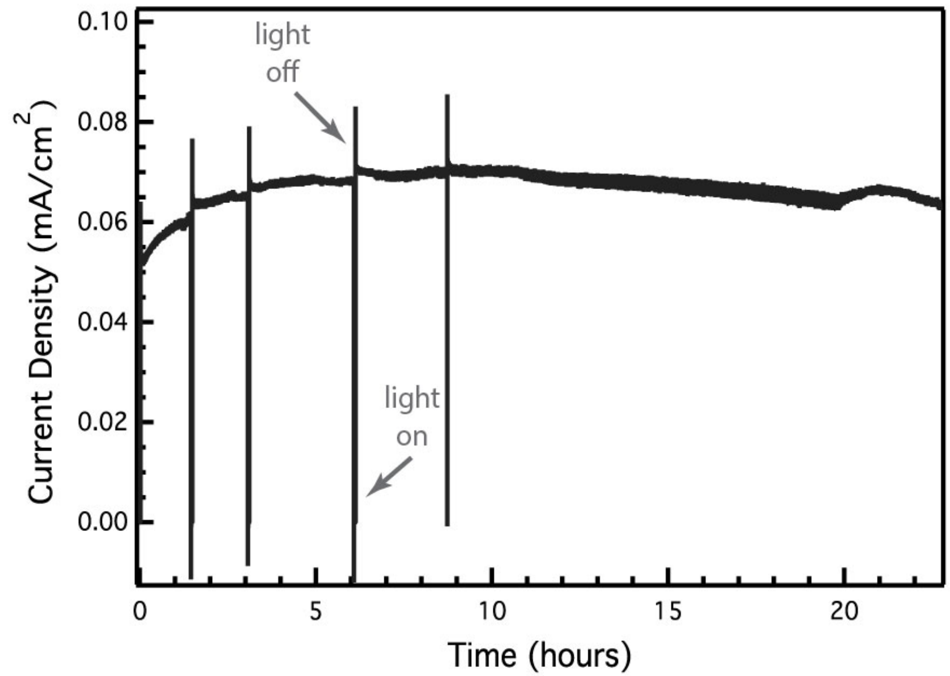




Jiang, *et al*, Chem. Mater. **29**, 3334 (2017)

Photoelectrochemical Function of CVO



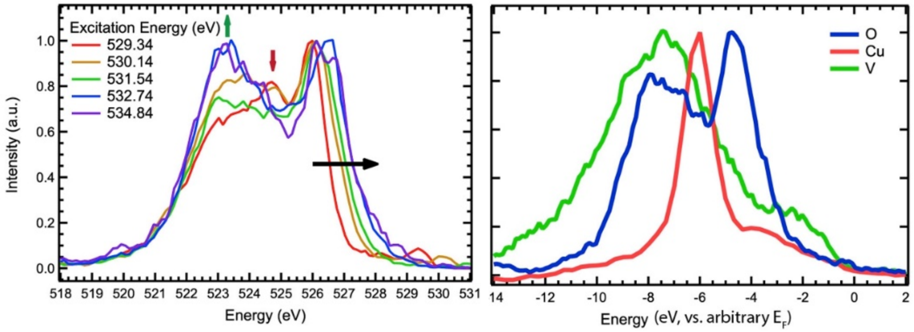


Photoelectrochemically active and stable, but highly inefficient

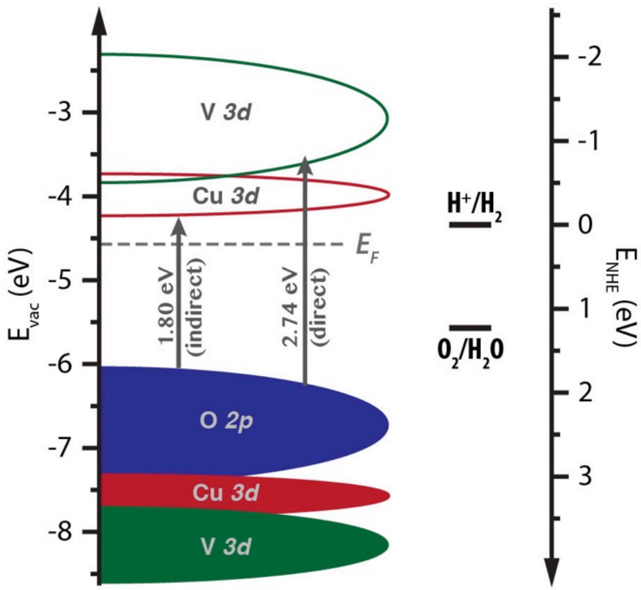
Jiang *et al.*, ACS Appl. Mater. Interfaces *in press* (2018)

Understanding Photoconversion Limitations

Synchrotron X-Ray Characterization of Electronic Structure

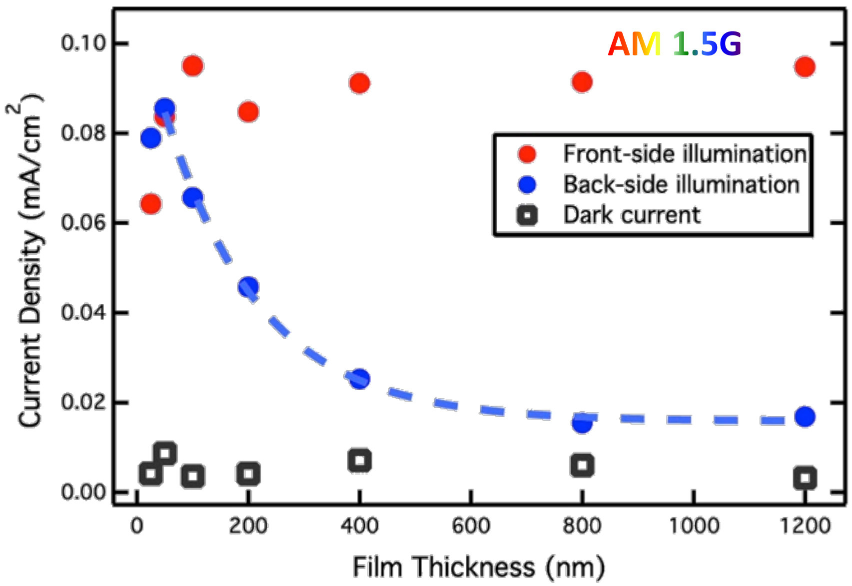


Charge transfer insulator



Expect PEC performance to be limited by electron transport

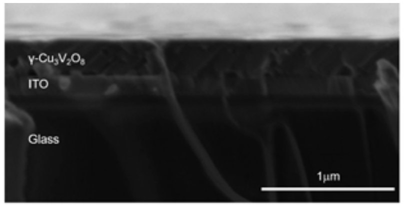
Functional Characterization of Photoelectrochemical Properties



Photocurrent generation limited by minority carrier holes

Jiang *et al.*, Chem. Mater. **29**, 3334 (2017)

SCE of Copper Vanadate Photoanodes



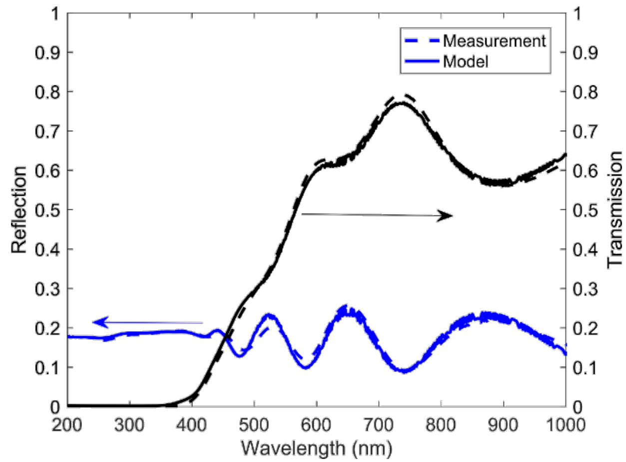
Planar CVO Thin Films

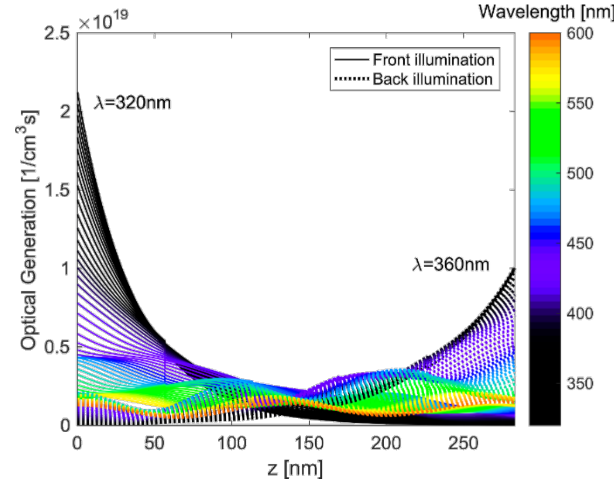
+

Variable Angle Spectroscopic Ellipsometry

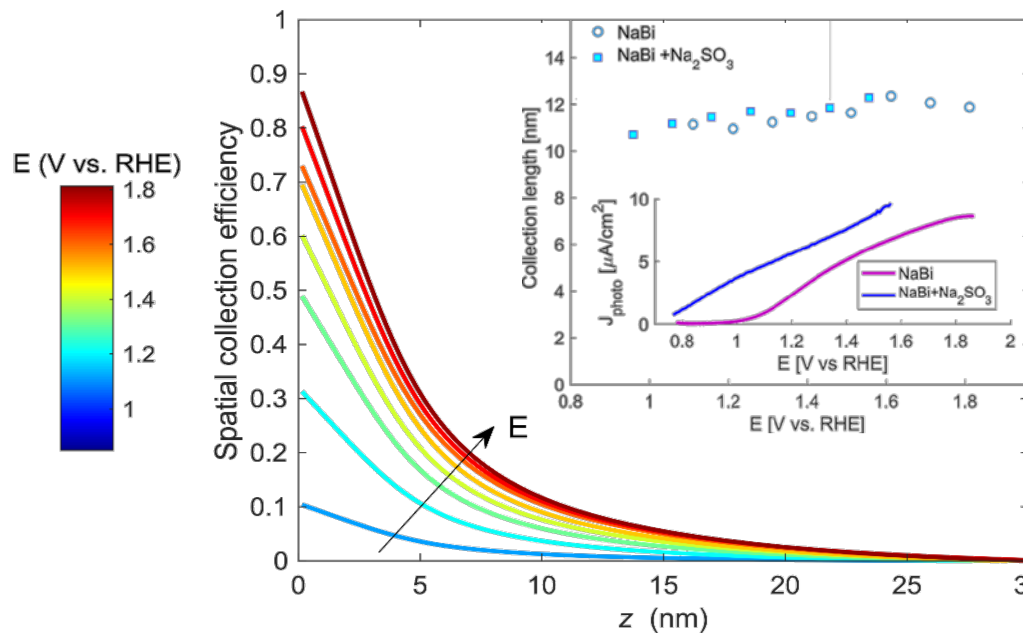
+

Optical Modelling (Transfer Matrix Method)





- Extremely short charge extraction lengths
- Strong surface Fermi level pinning
- Surface passivation, defect engineering, nanostructuring



Segev, *et al*. *EES* in press (2018)

Towards a Next Generation of Semiconductor Light Absorbers

Characterization ⟷ Understanding ⟷ Control

Characterization

X-ray: XAS/XES/RIXS/PES
Optical spectroscopy

Defect spectroscopy
ESR/EDMR

Transient optical: TA/TR

In situ Methods

Photocarrier Transport

Understanding

Intrinsic Limits
- Electronic Structure
- Polaron formation

Extrinsic Limits
- Defects
- Interfaces

Control

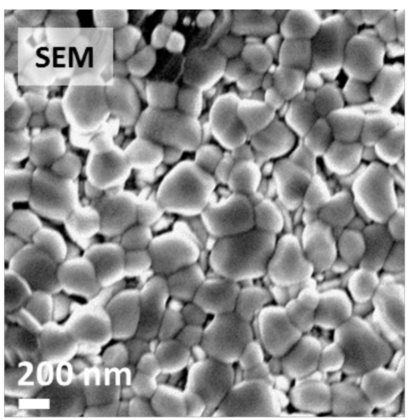
Nanoscale Architecture
Stimulated Transport

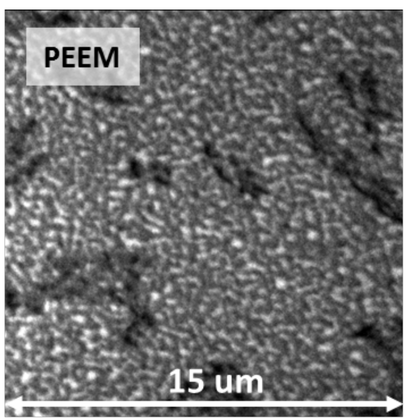
Rational Synthesis
Passivation
Interface Engineering

PEC Performance

The Challenge:

Reliance on disordered polycrystalline thin films that impede mechanistic understanding





The Opportunity:

Application of advanced deposition methods to control disorder at the atomic scale

- Moleular beam epitaxy (MBE)
- Pulsed laser deposition (PLD)
- Plasma-Enhanced Atomic Layer Deposition (PE-ALD) and epitaxy (ALE)
- Bulk crystals

Towards a Next Generation of Semiconductor Light Absorbers

Characterization ⟷ Understanding ⟷ Control

Characterization

X-ray: XAS/XES/RIXS/PES
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Transient optical: TA/TR

In situ Methods

Photocarrier Transport

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Control

Nanoscale Architecture
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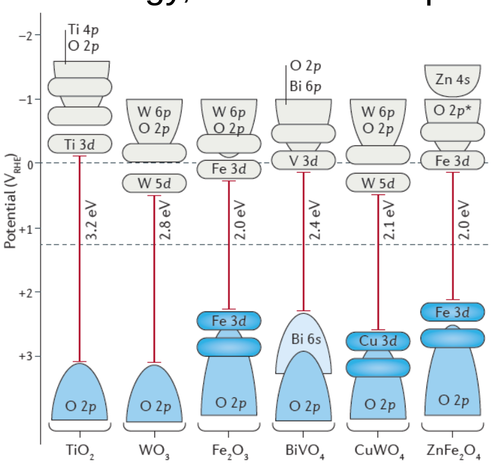
Interface Engineering

PEC Performance

The Challenge:

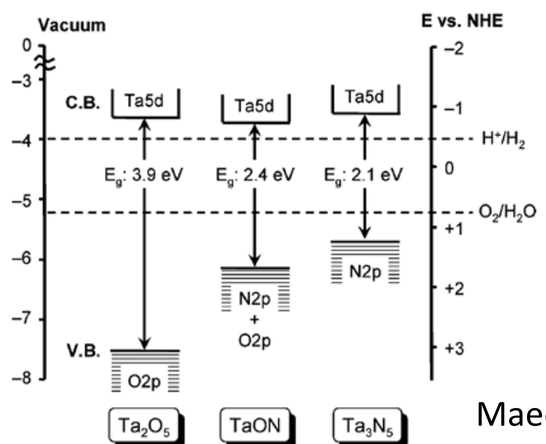
Bandgap engineering of oxides limited to CB energy, at the cost of photovoltage



Sivula & van de Krol, Nature Rev. Mater. 15010 (2016)

The Opportunity:

Expansion to nitride and oxynitride semiconductors



Requires advanced deposition methods (e.g. MBE, ALD) to precisely control composition and defects

Maeda & Domen, JPC C **111**, 7851 (2007)

Towards a Next Generation of Semiconductor Light Absorbers

Characterization ⟷ Understanding ⟷ Control

Characterization
- X-ray: XAS/XES/RIXS/PES
- Optical spectroscopy
- Defect spectroscopy
- ESR/EDMR
- Transient optical: TA/TR
- *In situ* Methods

Photocarrier Transport

Understanding

Intrinsic Limits
- Electronic Structure
- Polaron formation

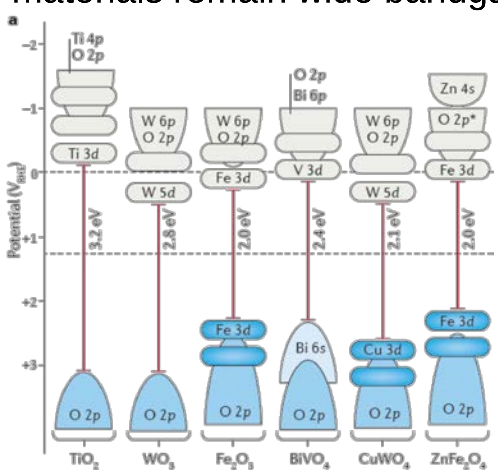
Extrinsic Limits
- Defects
- Interfaces

Control
- Nanoscale Architecture
- Stimulated Transport
- Rational Synthesis
- Passivation
- Interface Engineering

PEC Performance

The Challenge:

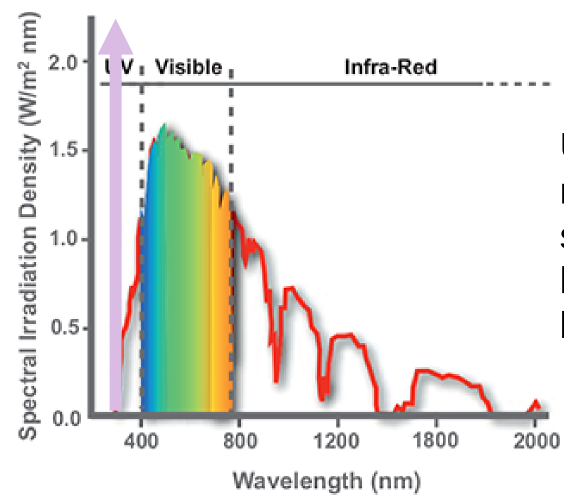
High stability, high quantum efficiency materials remain wide bandgap



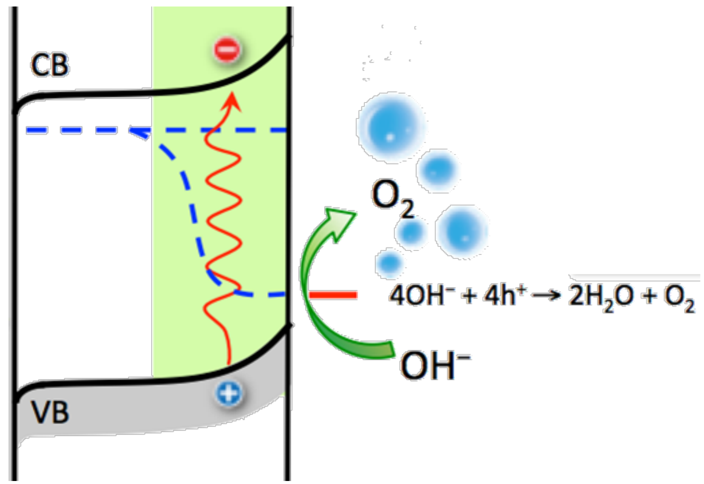
Sivula & van de Krol, Nature Rev. Mater. 15010 (2016)

The Opportunity:

Spectral upconversion with advanced III-N semiconductors



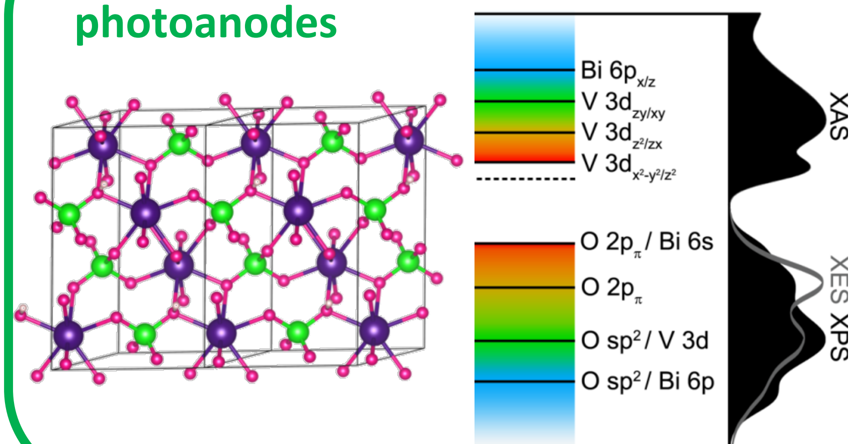
Unlike molecular and nanocrystalline sensitizers, III-N's have high efficiencies over broad power range



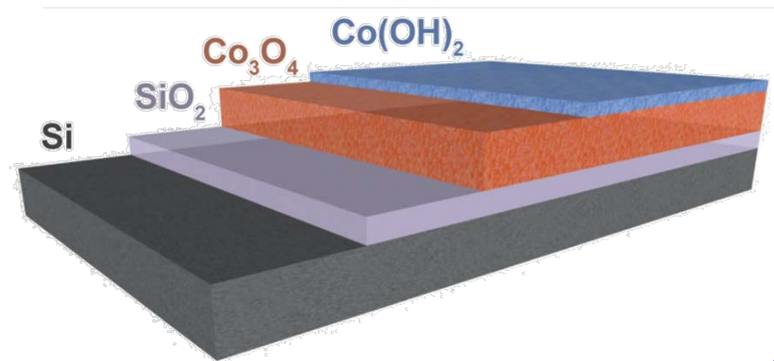
Two Approaches:

1) **Stabilization of otherwise unstable photoelectrodes**
2) **Discovery of intrinsically stable semiconductors**

Advancing thin film metal oxide photoanodes



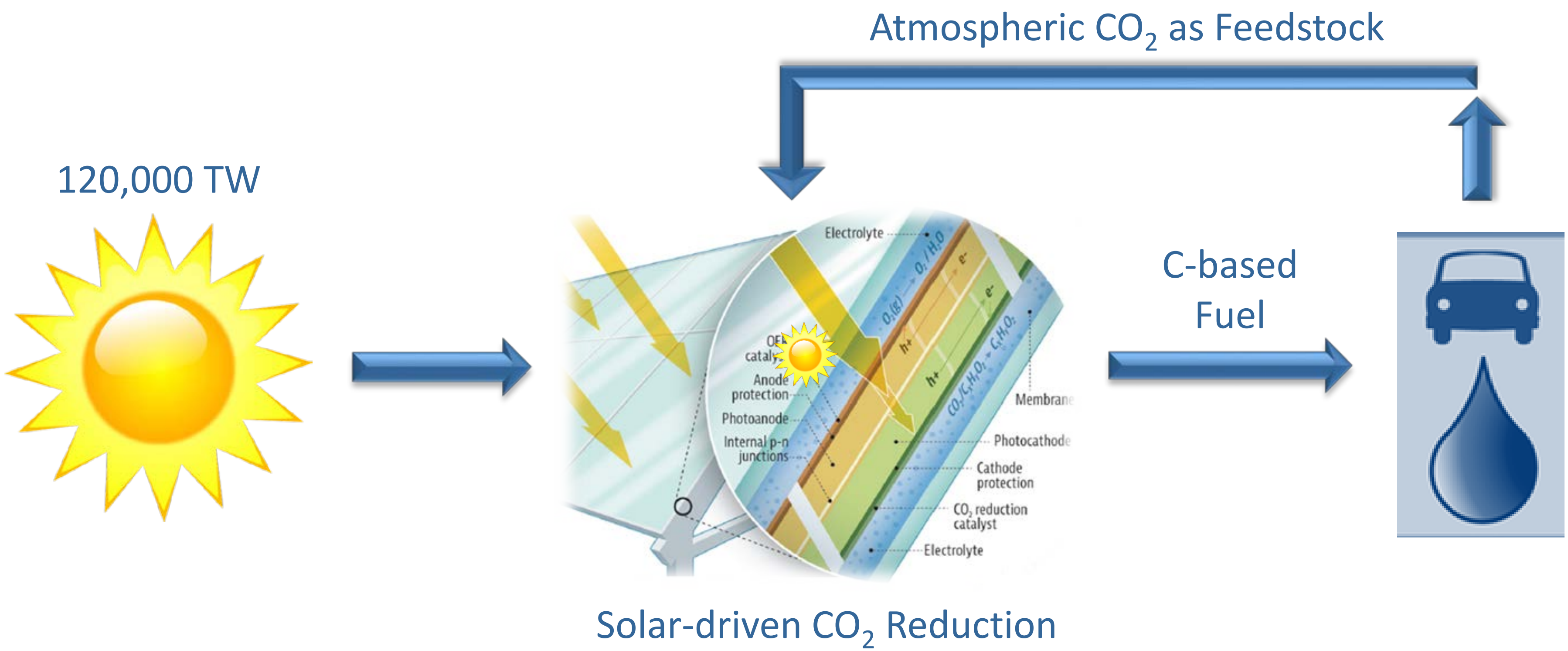
Stabilization with conformal coatings



Stable → Efficient

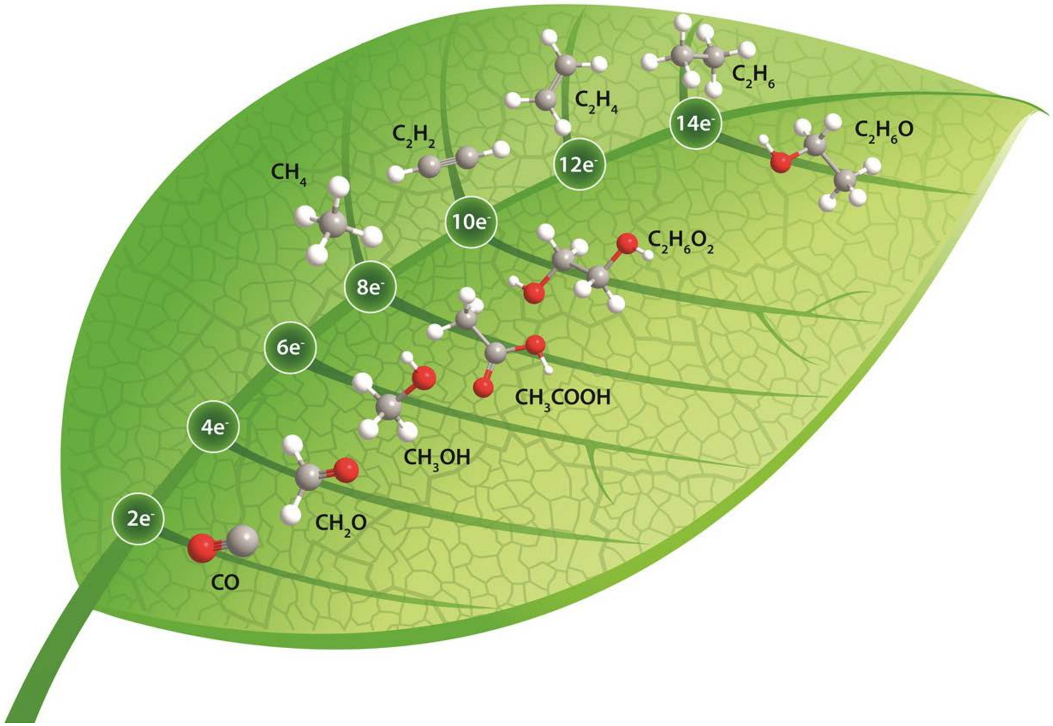
Efficient → Stable

Towards Photoelectrochemical Reduction of CO_2



- **Efficiency** relies on efficient charge separation and extraction across interfaces
- **Stability** under highly reducing aqueous photoelectrochemical conditions
- **Selectivity** depends on potential, energetics, defects, light intensity, etc.

The Selectivity Challenge



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Oxygen Forming Reaction

Oxygen evolution reaction (OER)

$H_2O \longrightarrow ½O_2\,(g) + 2H^+ + 2e^-$

Fuel Forming Reactions

Hydrogen evolution reaction (HER)

$2H^+ + 2e^- \longrightarrow H_2(g)$

CO_2 reduction reaction (CO2RR)

$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH + ½O_2$

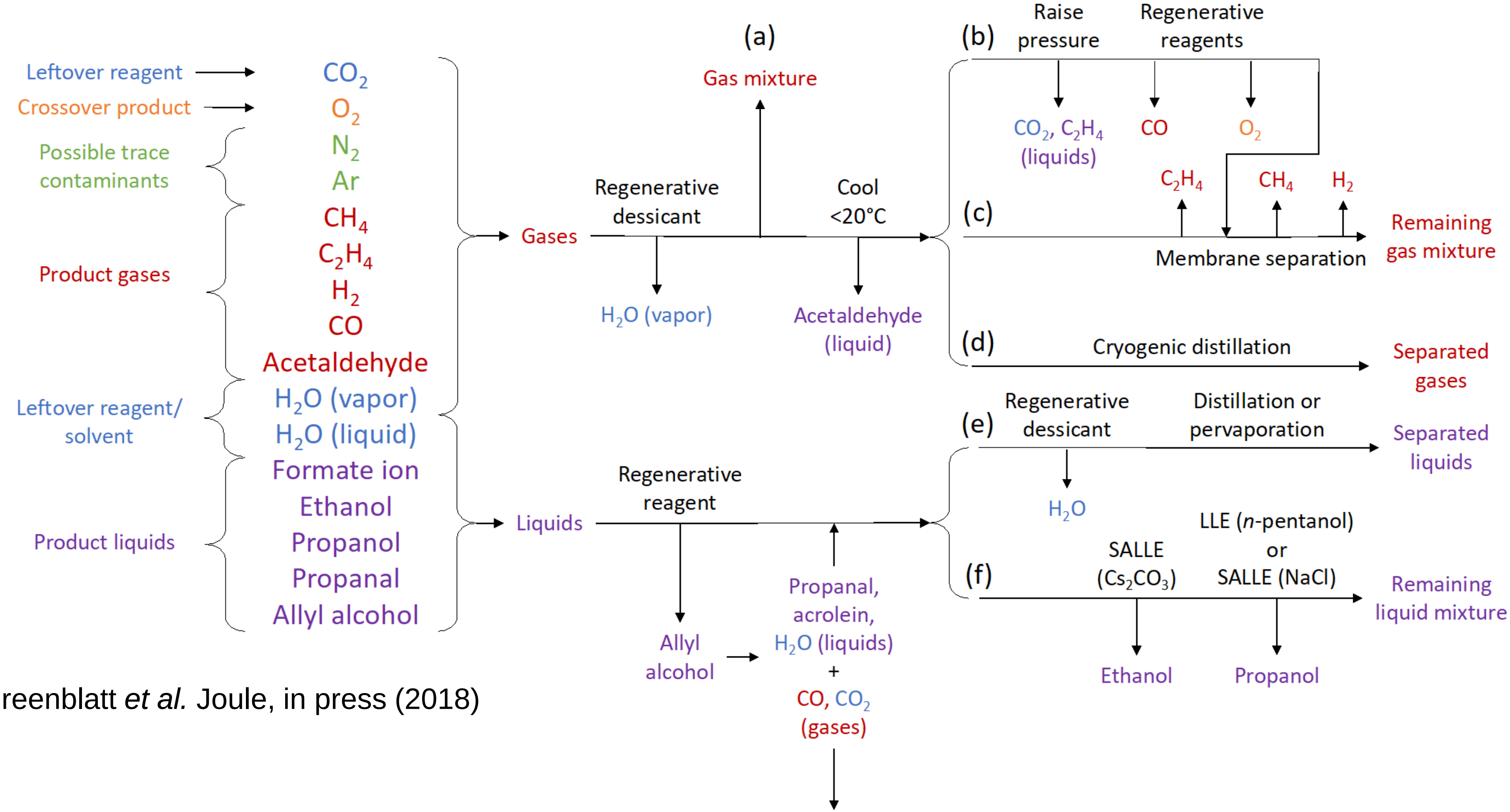
$CO_2 + 4H^+ + 4e^- \longrightarrow HCHO + O_2$

$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + 3/2O_2$

$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2\,H_2O$

etc.

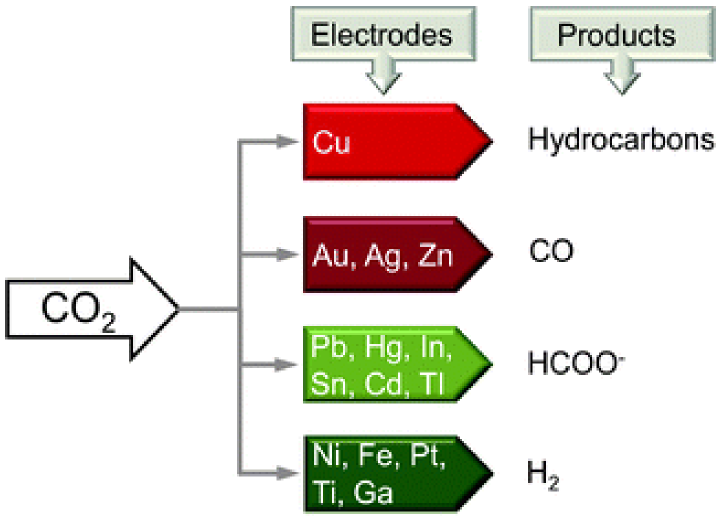
The Separations Challenge



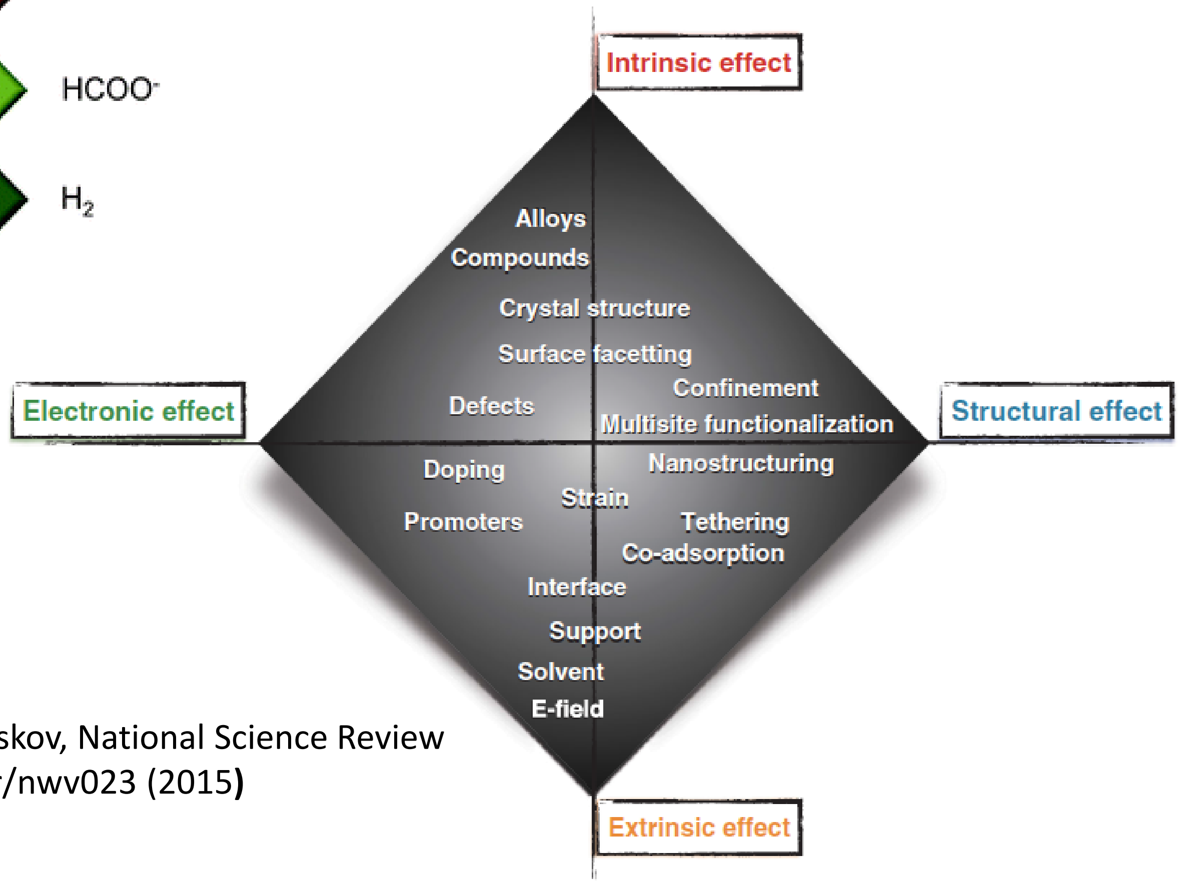
Greenblatt *et al.* Joule, in press (2018)

Reaction selectivity is essential for minimizing energetic separations

Selectivity: Materials Discovery and Development



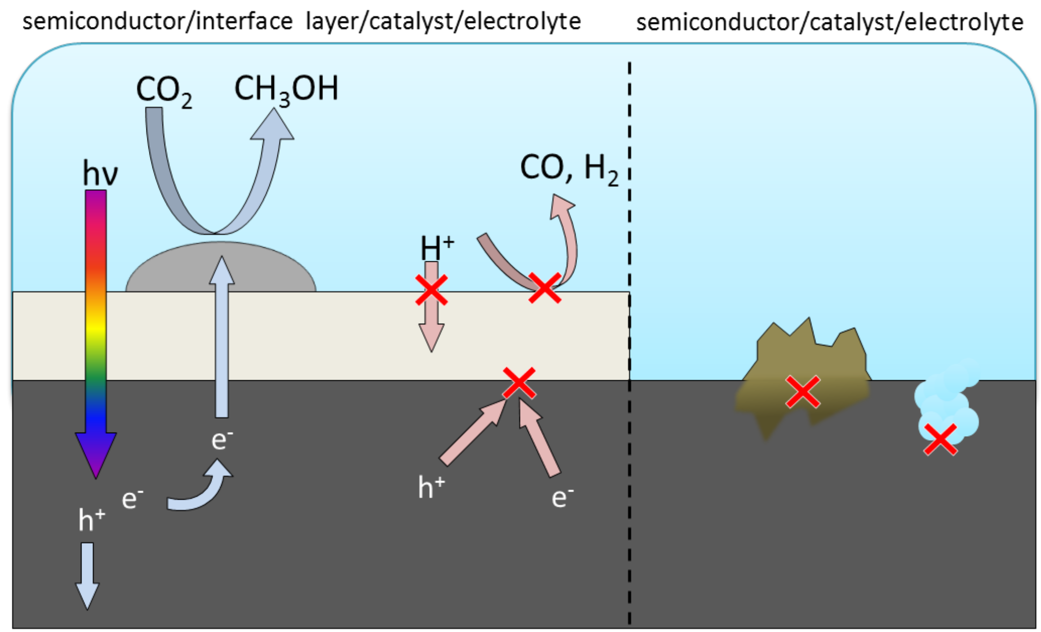
Kondratenko *et al.*
Energy Environ. Sci., 2013,**6**, 3112



A. Vojvodic and J.K. Nørskov, National Science Review 00: 1–4doi: 10.1093/nsr/nwv023 (2015**)**

The Interface Challenge

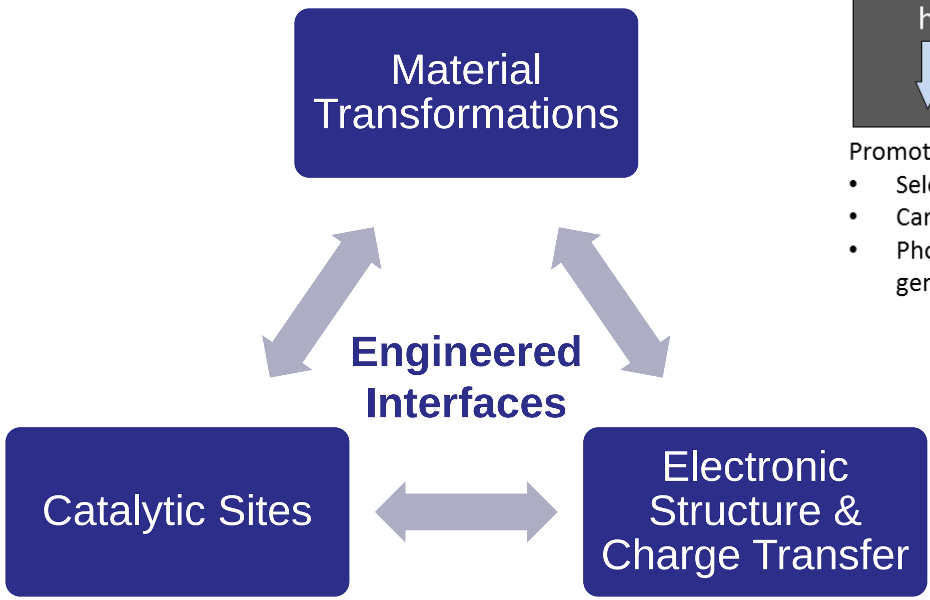
Multi-functional interfaces that promote efficiency and selectivity while inhibiting undesired materials interactions, failure modes, and recombination pathways



Promoting:
- Selective catalysis
- Carrier transport
- Photovoltage generation

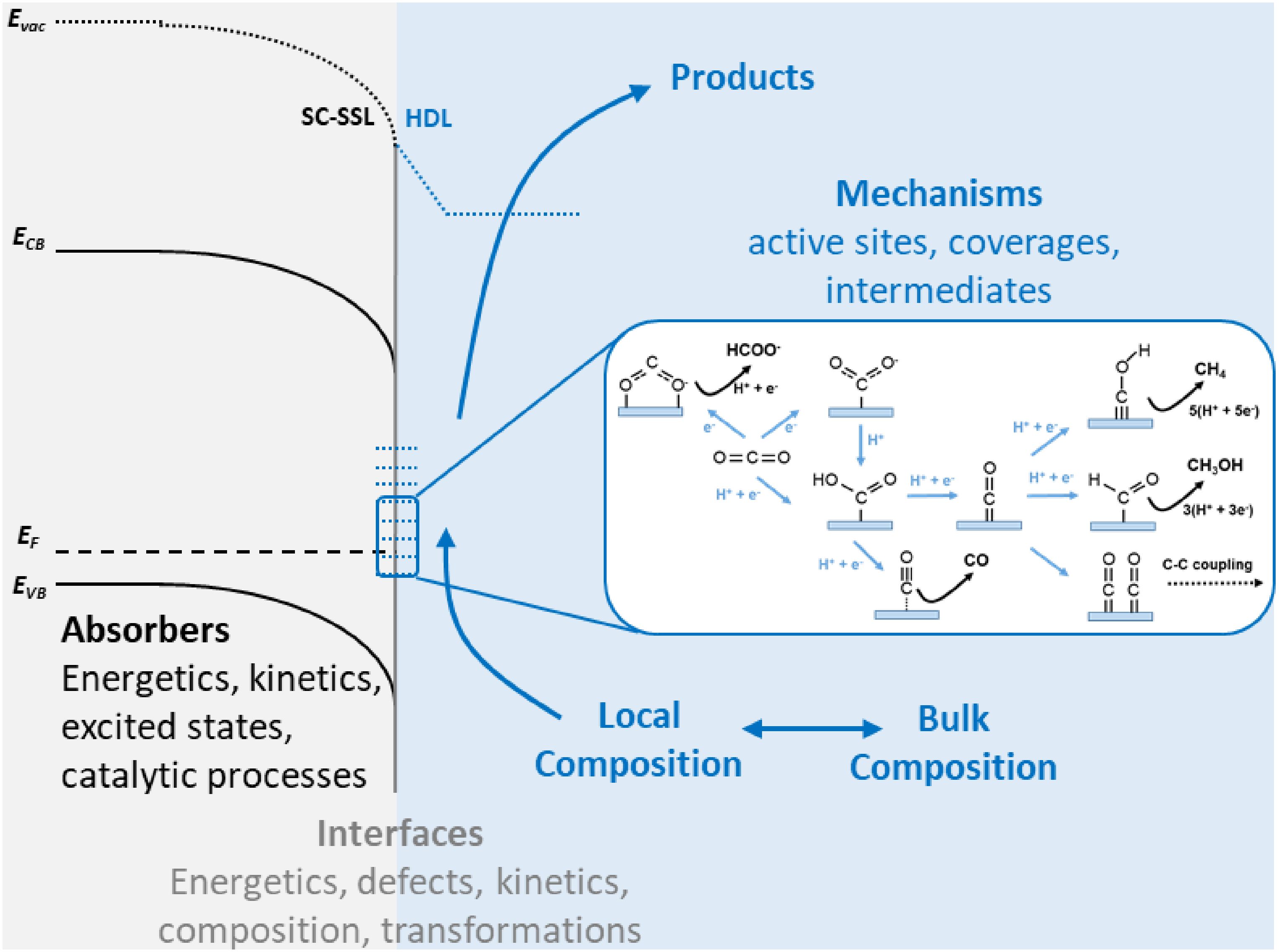
Inhibiting:
- Carrier recombination
- Proton migration
- Side-product formation

Eliminating:
- Corrosion
- Undesired material interactions



Multi-modal *in situ/operando* probes will be essential for mechanism discovery and materials design

The Characterization Challenge



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