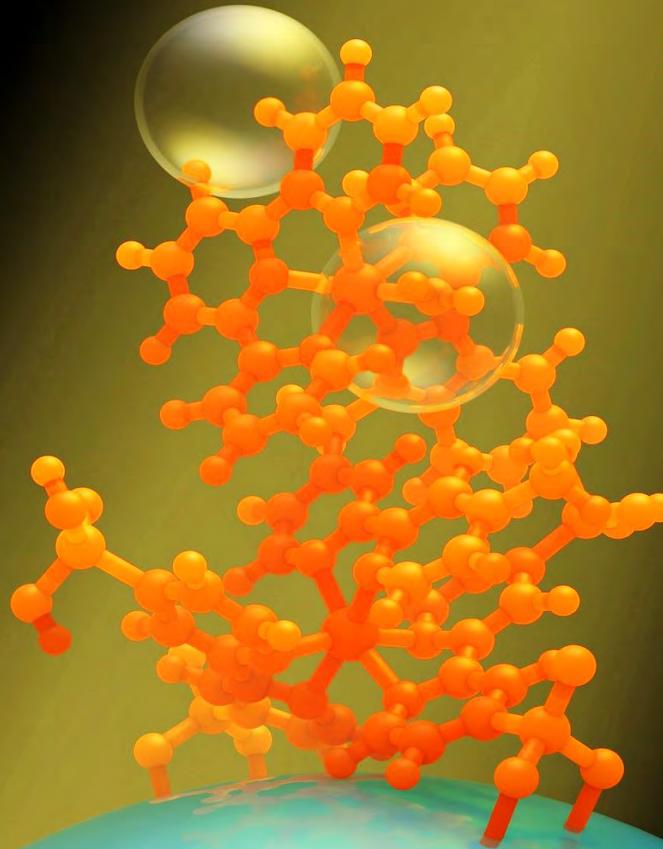


UNC EFRC Center for Solar Fuels: Optimization of Materials and Catalysis for Solar Fuel Production

MISSION

Conduct research on
Dye-sensitized
photoelectrosynthesis
cells (DSPECs) for
water oxidation and
tandem cells for the
reduction of carbon
dioxide to carbon-
based solar fuels



VISION

“Provide the basic
research to enable
a revolution in the
collection and
conversion of
sunlight into
storable solar fuels”

Dec 8, 2016



U.S. DEPARTMENT OF
ENERGY

Office of
Science

Funded by the U.S. Department of Energy, Office of Science,
Office of Basic Energy Sciences under Award DE-SC0001011

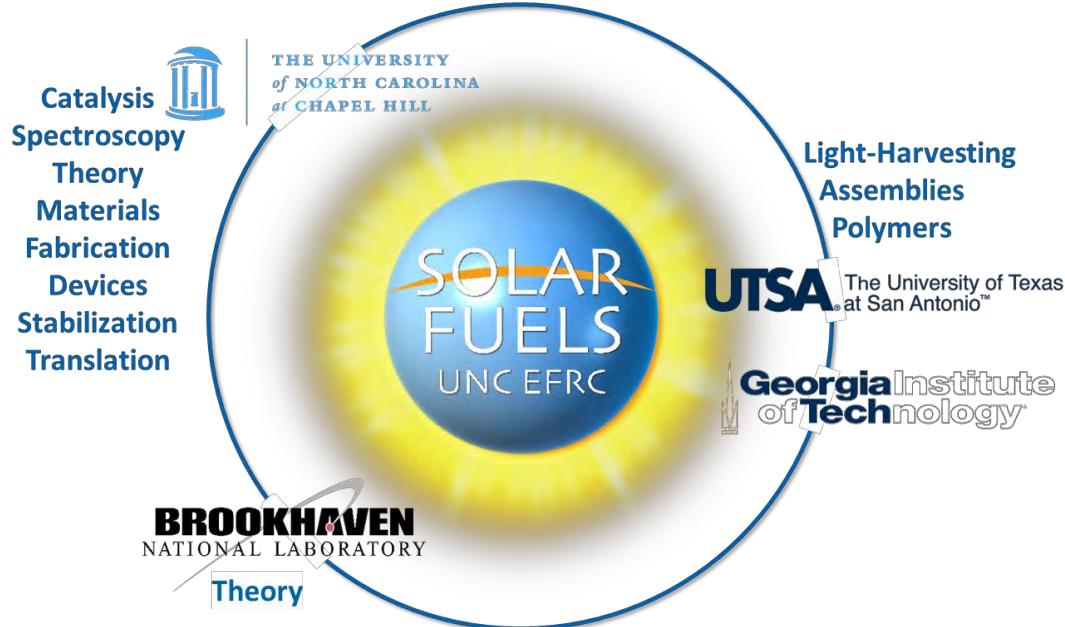
UNC EFRC: CENTER for SOLAR FUELS

4 Research Organizations → 1 Integrated Center

SOLAR
FUELS

UNC EFRC

“Integrating the skills and talents of multiple investigators to enable fundamental research at a level of scope and complexity not possible with individual or small group research projects”

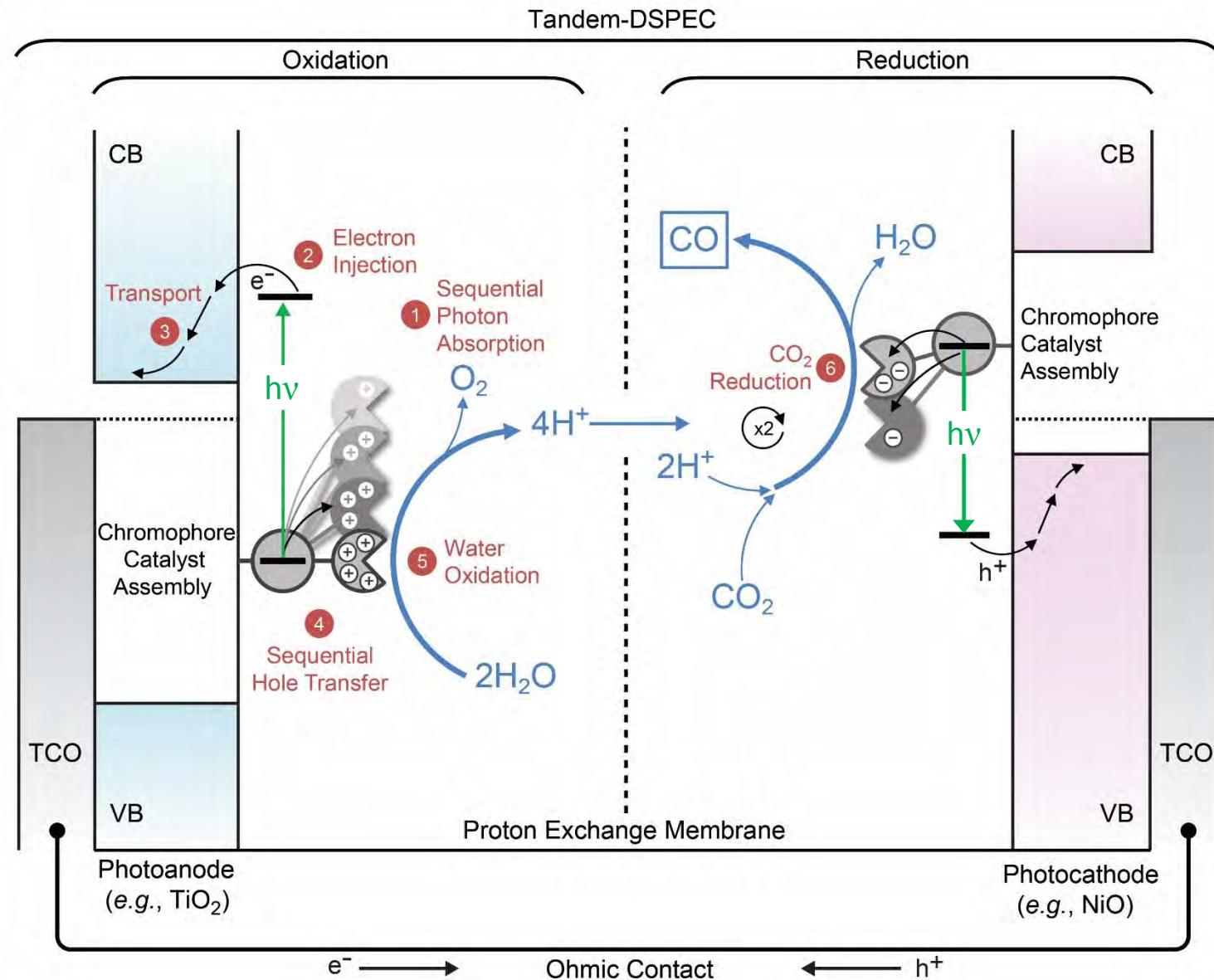


www.efrc.unc.edu

DYE SENSITIZED PHOTOLELECTROSYNTHESIS CELLS (DSPEC) FOR SOLAR FUELS PRODUCTION

- A modular approach to design and optimize for high efficiency solar water oxidation and CO₂ reduction
- Integrate results from research on water oxidation, CO₂ reduction, light-harvesting chromophore arrays, chromophore-catalyst assemblies, mesoporous nanocrystalline semiconductor oxide thin films, and core/shell structures to develop efficient DSPECs

Dye-Sensitized Photoelectrosynthesis Cells (DSPECs)



UNC EFRC INTEGRATED RESEARCH

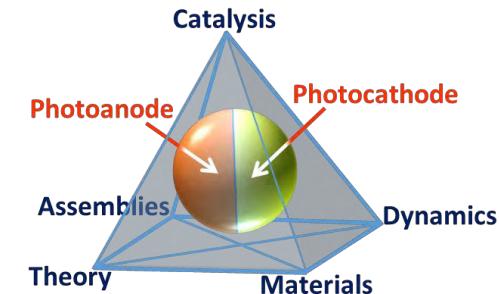
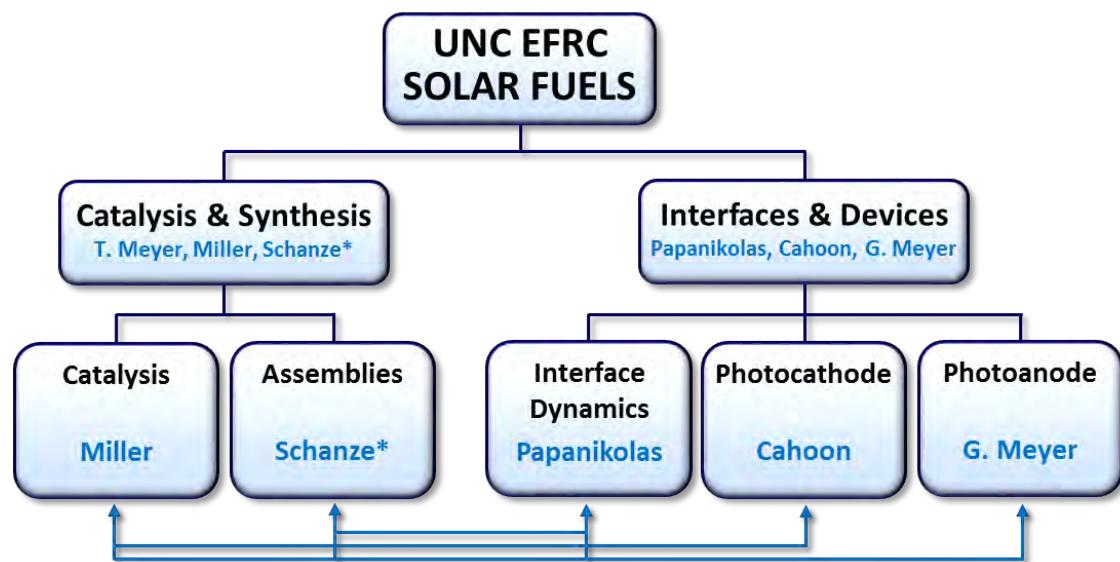
Modular, Team-Based Approach

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Science

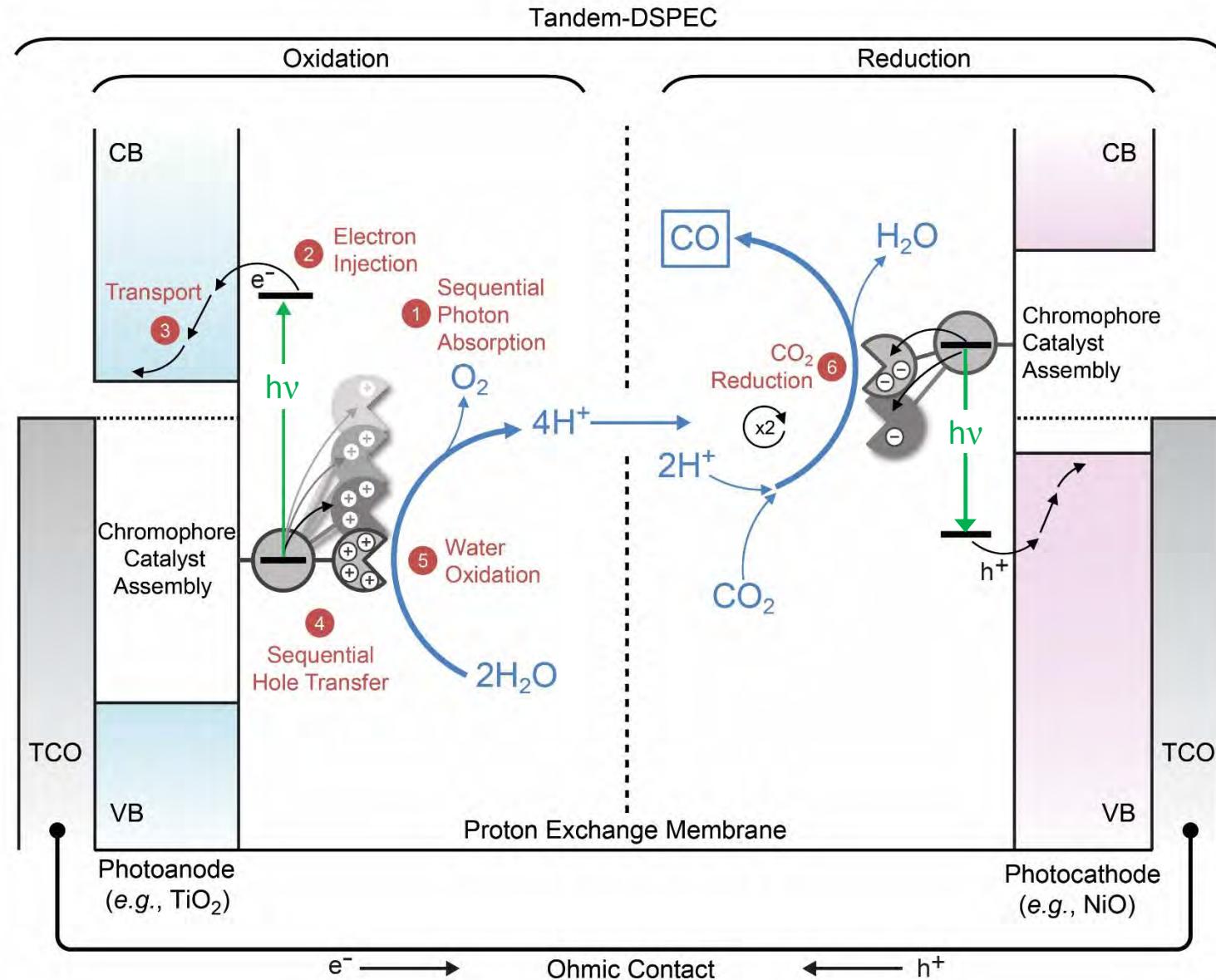


TEAM

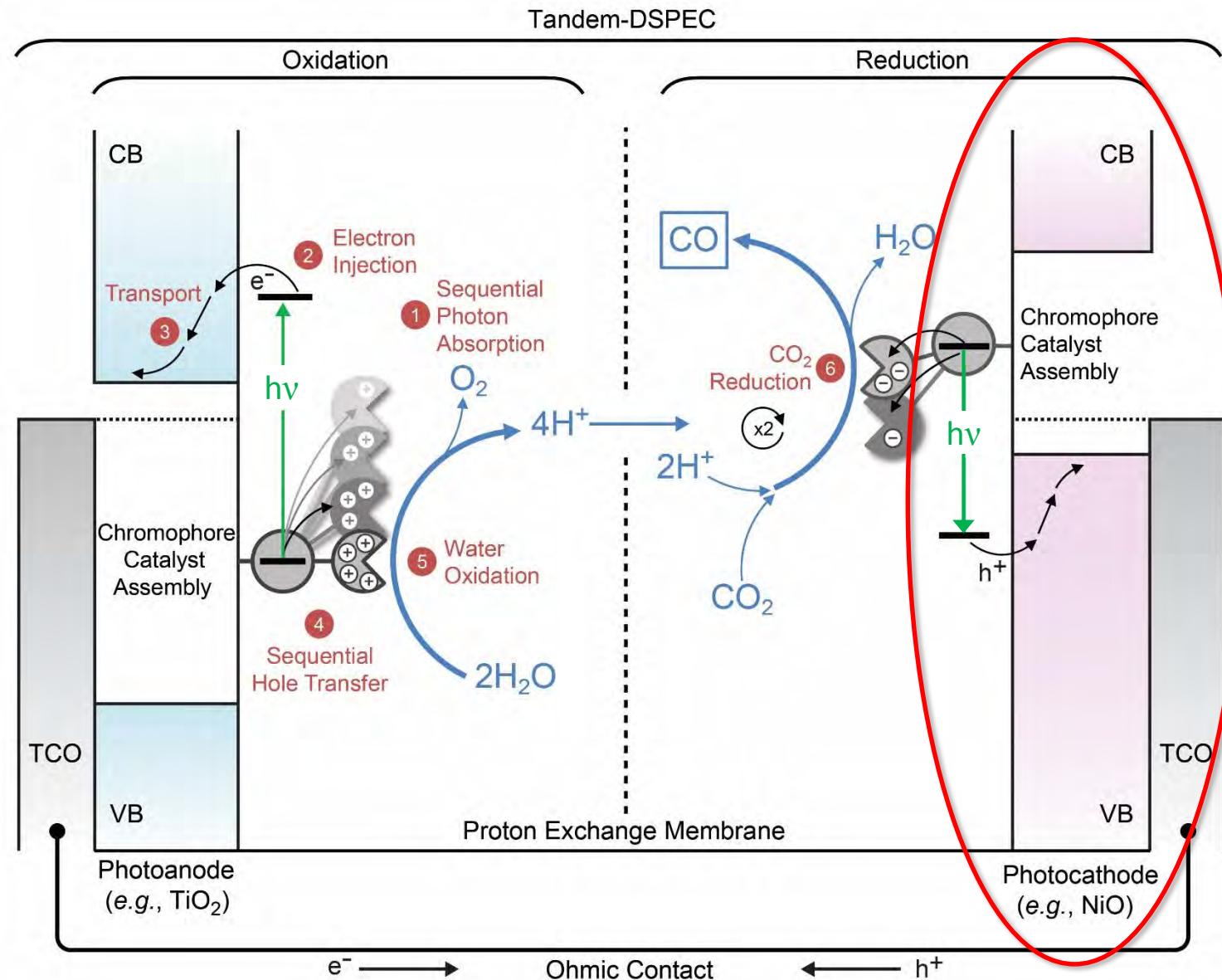
TEAM MISSION & RESEARCH FOCUS

CATALYSIS	Catalyst development and mechanistic studies on solution and interfacial catalysts for water oxidation and CO ₂ reduction. Evaluation of catalysts in assemblies and device prototypes for photoanode and photocathode applications.
ASSEMBLIES	Design, synthesis, and characterization of molecular, oligomer and polymer chromophore-catalyst assemblies for applications in water oxidation and CO ₂ reduction at n- and p-type semiconductors.
INTERFACIAL DYNAMICS	Provide detailed understanding of surface mechanisms that guide design of molecular systems and materials to improve functional performance of DSPEC photoanodes and photocathodes.
PHOTOCATHODE	Development of hole-transporting semiconductor nanomaterials, core/shell structures, and light-absorbing sensitizers for high-performance photocathode applications integrated with molecular catalysts for CO ₂ reduction.
PHOTOANODE	Optimize sunlight driven water oxidation at dye sensitized photoanodes.

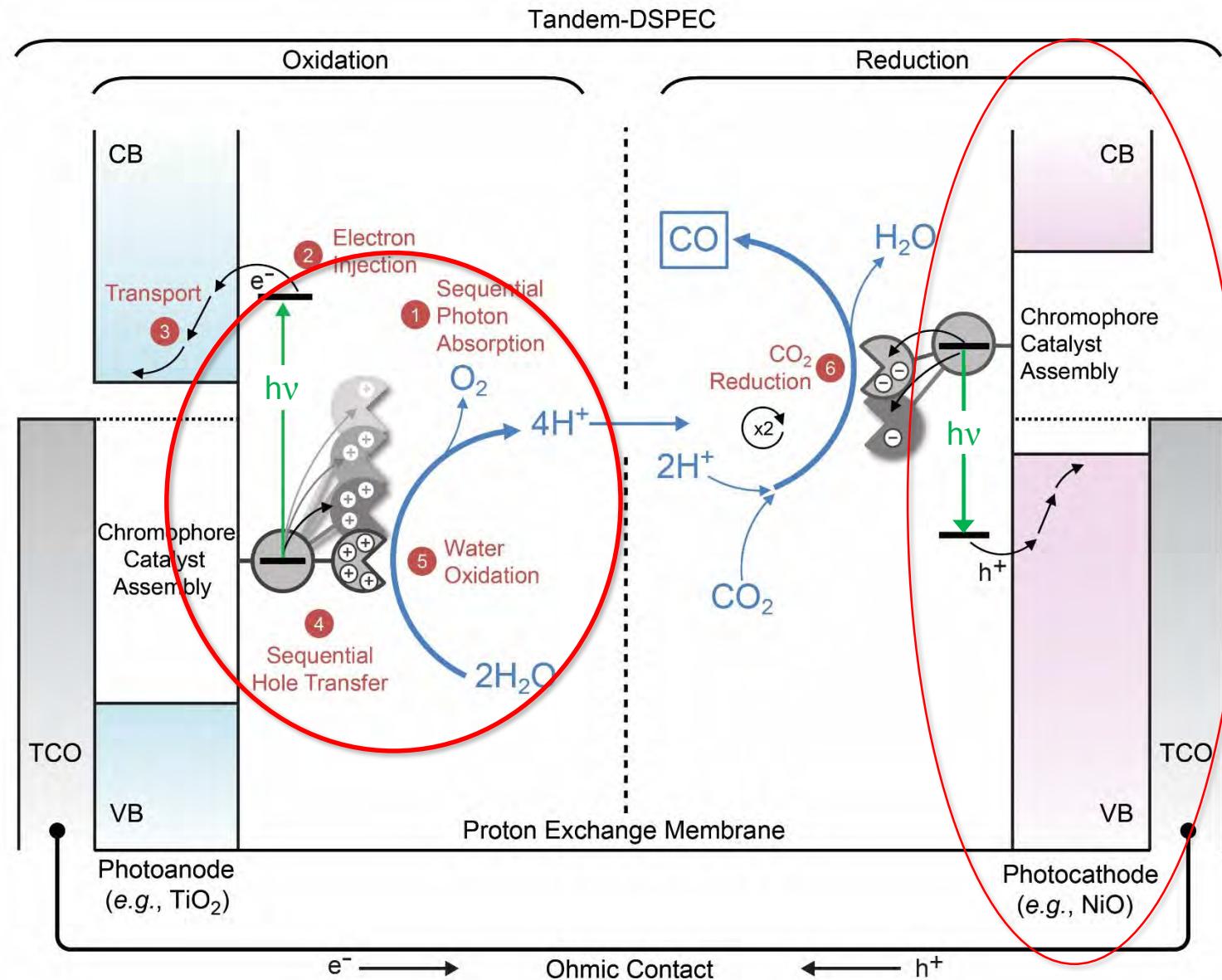
Dye-Sensitized Photoelectrosynthesis Cells (DSPECs)



Dye-Sensitized Photoelectrosynthesis Cells (DSPECs)



Dye-Sensitized Photoelectrosynthesis Cells (DSPECs)



Challenges with NiO

1) Low electrical mobility for holes

	carrier mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)	
	bulk	nanoparticle
NiO	5.3×10^{-1}	6.3×10^{-6}
TiO ₂	1.0	1.7×10^{-2}



2) High defect density

Ni vacancies have a low formation energy and are the cause of the p-type doping, but do they also facilitate recombination?

3) Low dielectric constant

TiO₂ has a high dielectric constant of ~80, but NiO has a low dielectric constant of ~11.

Does this play a role in charge carrier recombination?

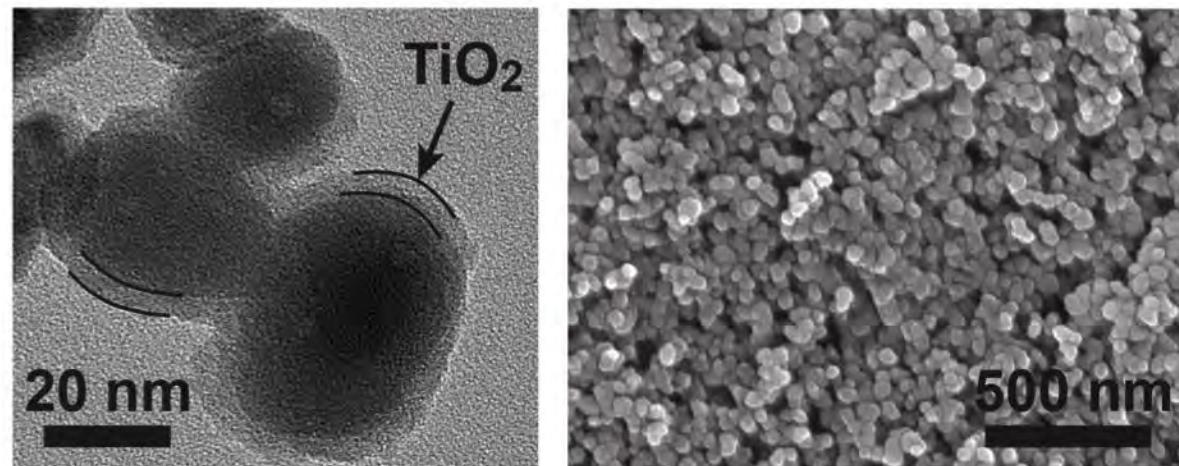
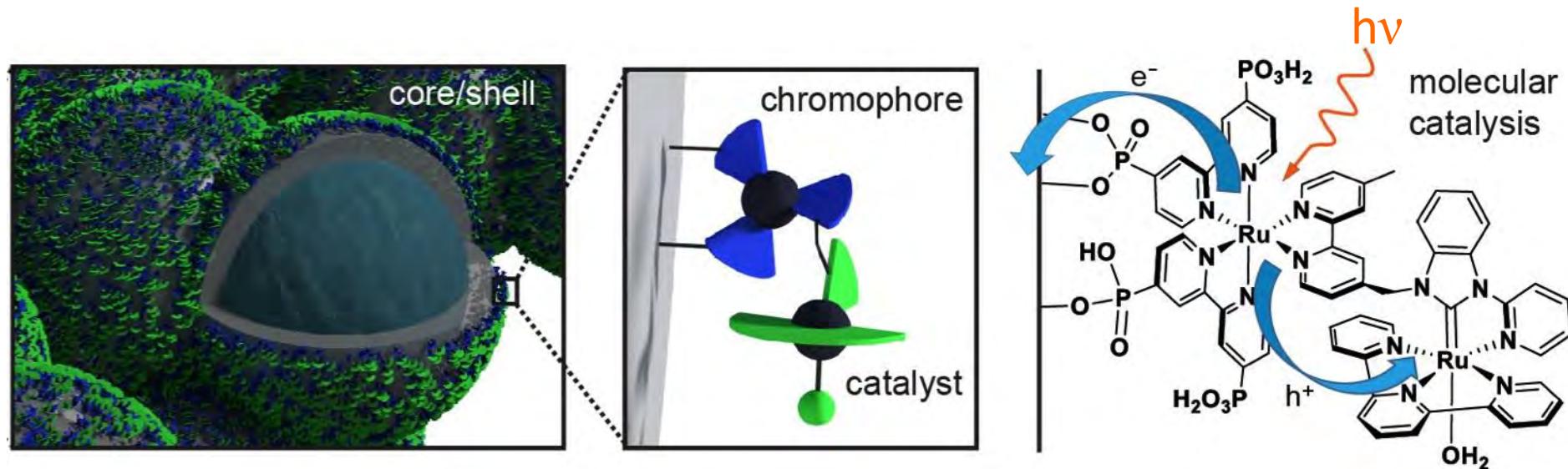


Prof. Jim Cahoon
(UNC Chemistry)

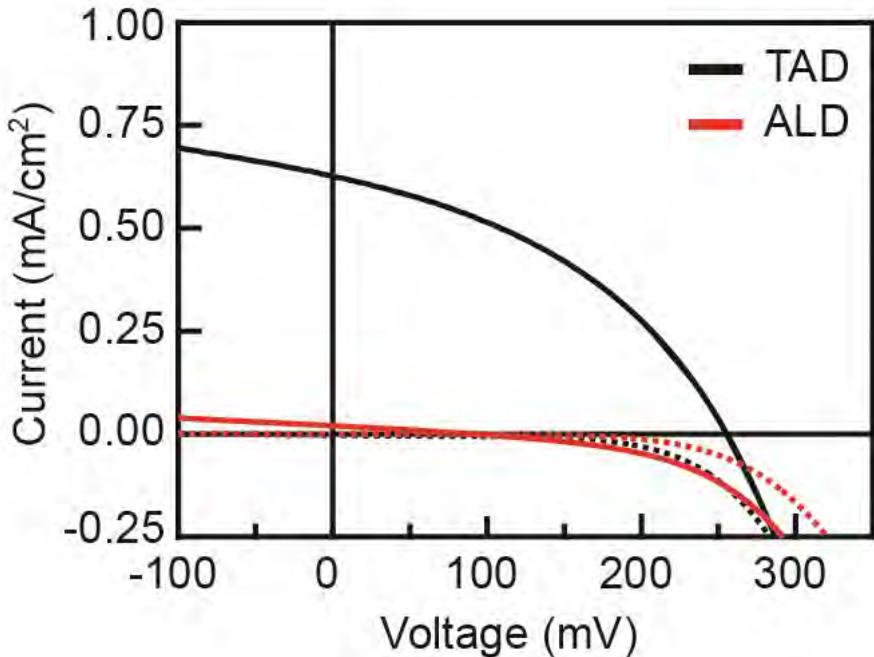


Dr. Cory Flynn
(UNC Chemistry graduate)

High Defect Density Atomic Layer Deposition



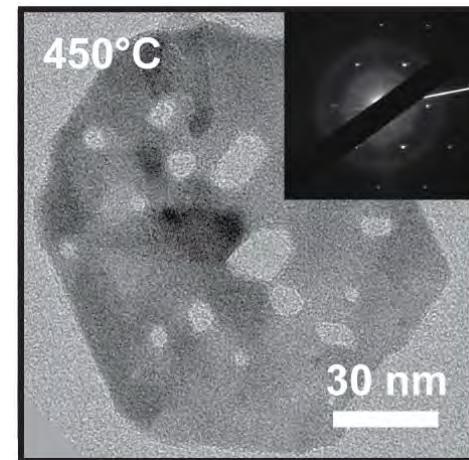
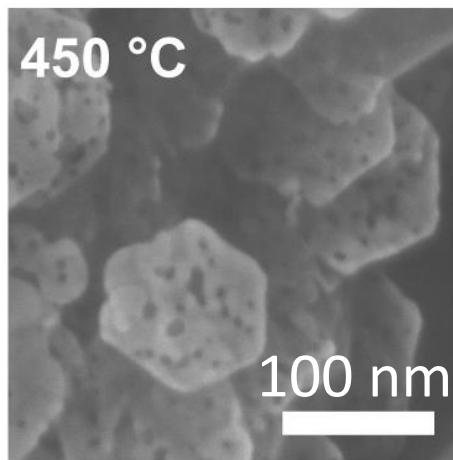
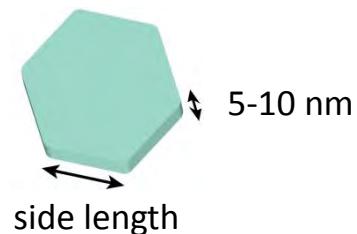
Atomic Layer Deposition ALD



nanoparticle

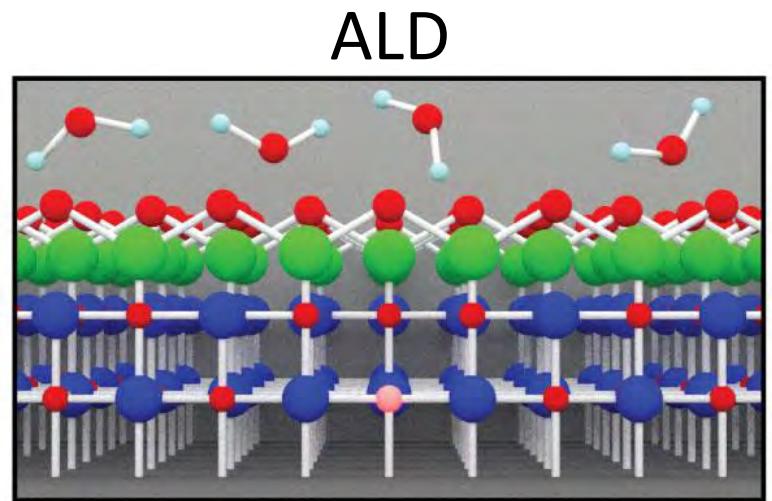
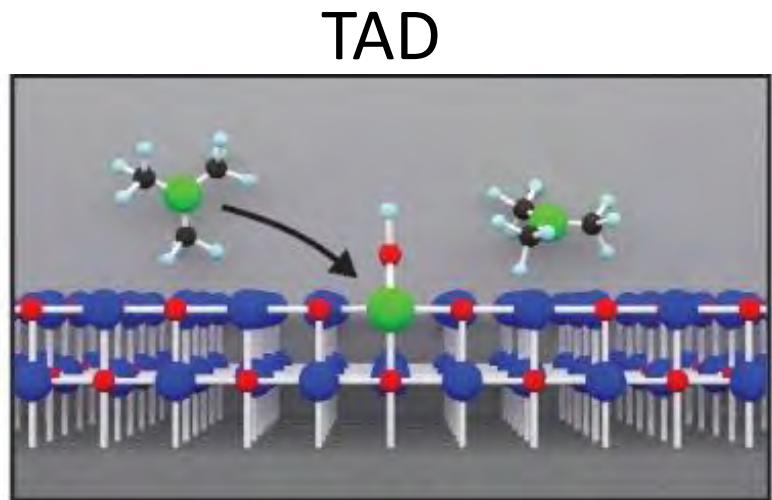
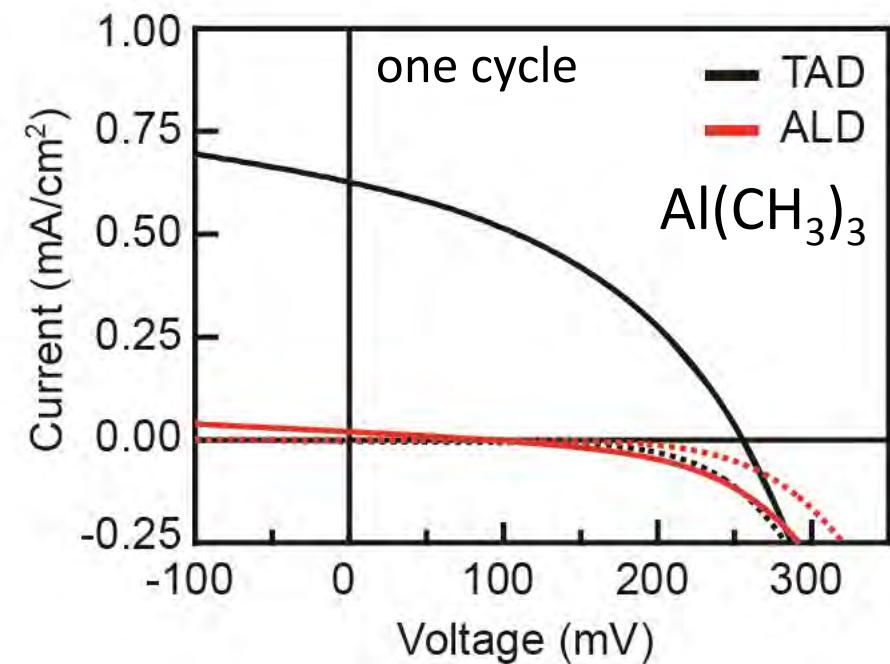


nanoplatelet



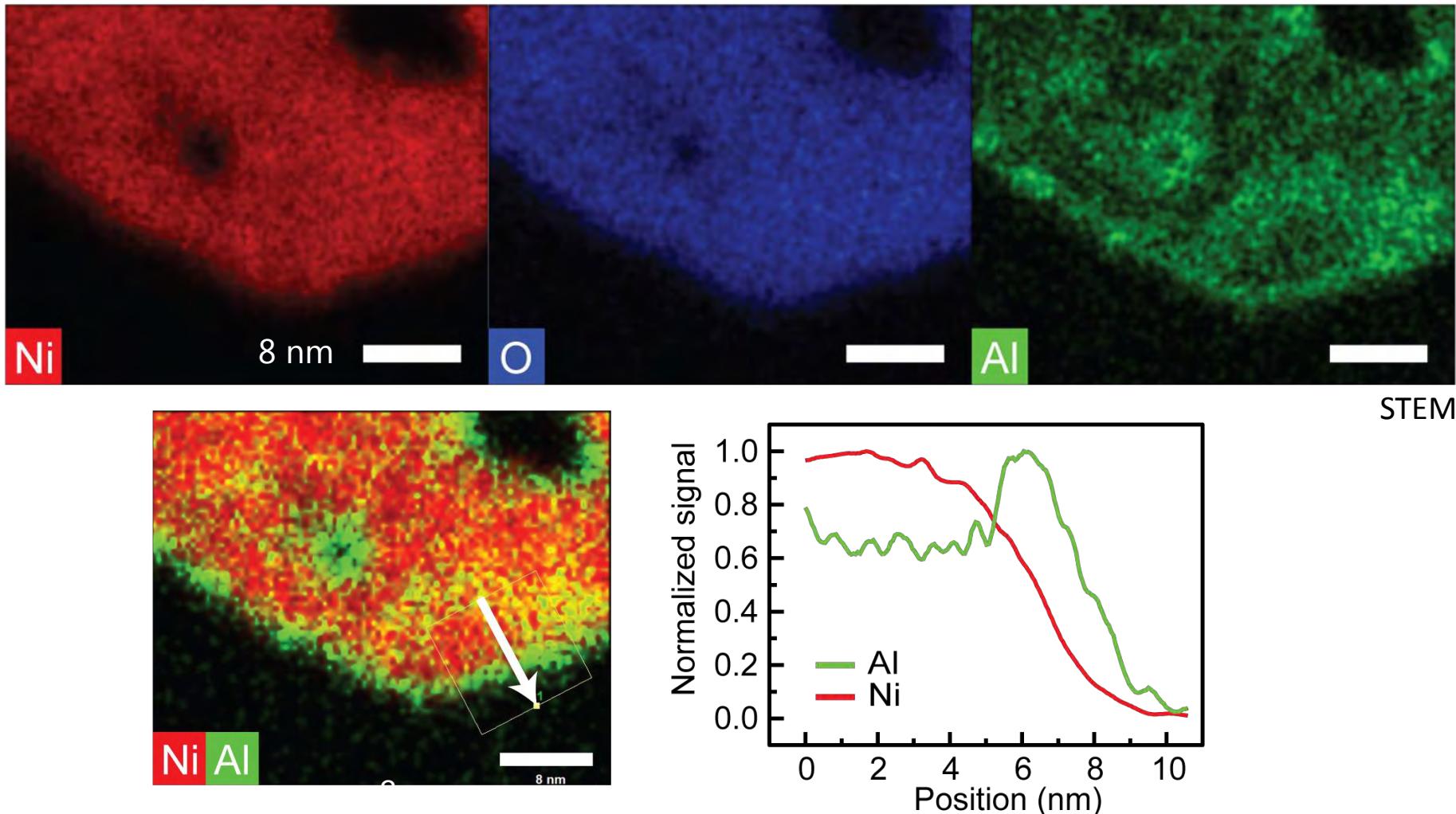
Flynn, Cahoon, et al. *J. Phys. Chem. C* 2014, 118, 14177 – EFRC I

Atomic Layer Deposition



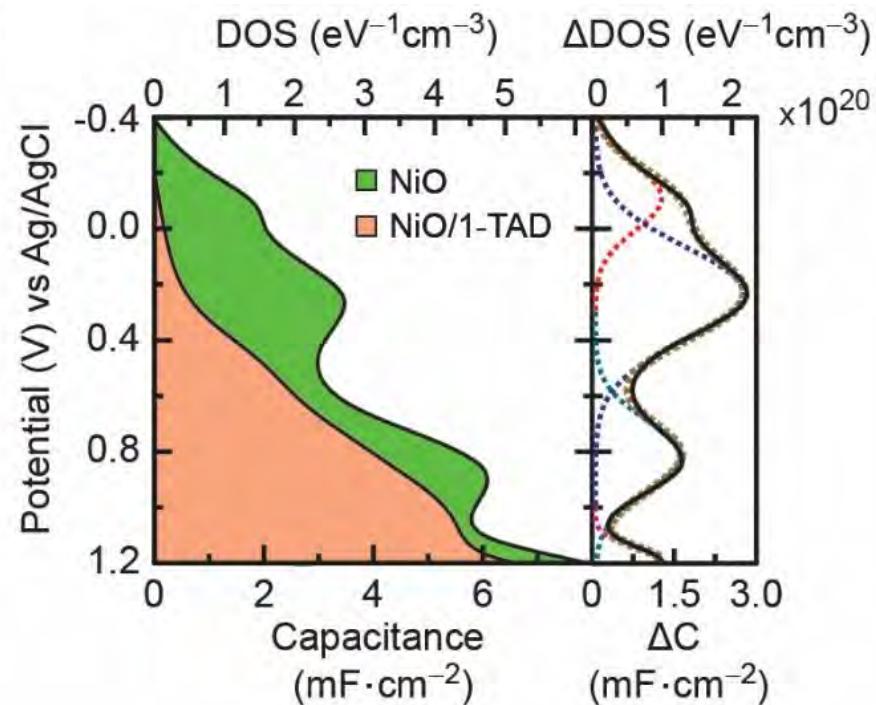
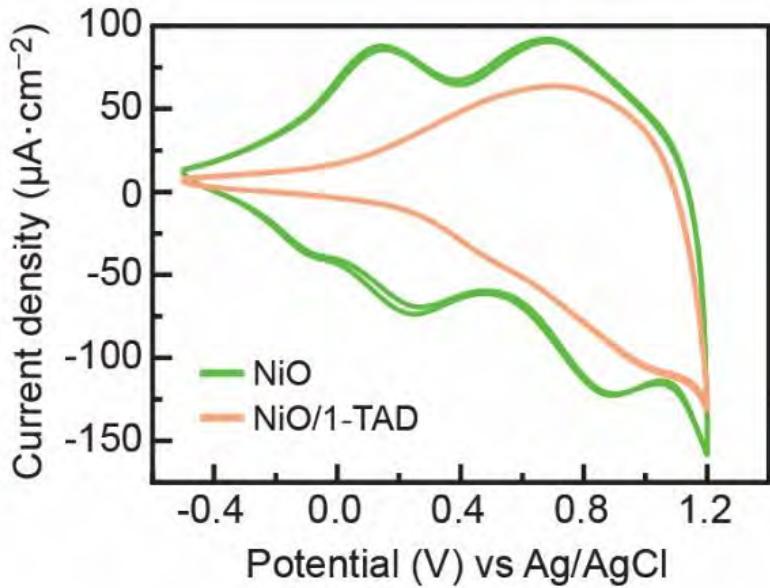
Targeted Atomic Deposition TAD

Mapping Al



Targeted Atomic Deposition

Probing passivated trap states



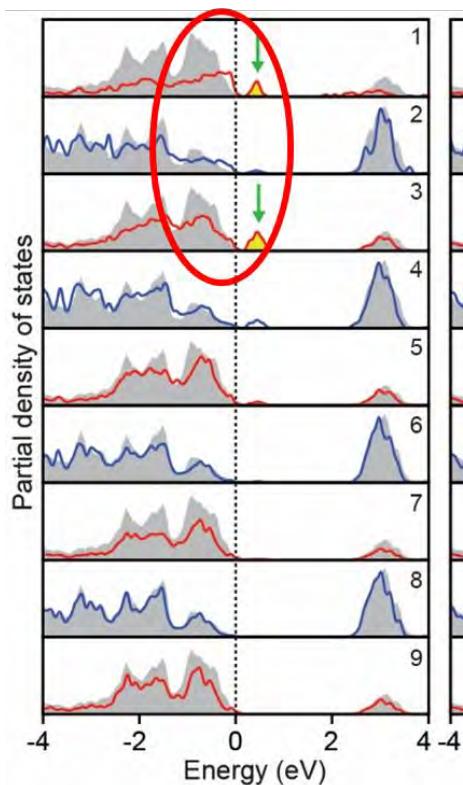
- Flynn, C. J.; McCullough, S. M.; Oh, E. E.; Li, L.; Mercado, C. C.; Farnum, B. H.; Li, W.; Donley, C. L.; You, W.; Nozik, A. J.; McBride, J. R.; Meyer, T. J.; Kanai, Y.; Cahoon, J. F. *ACS Appl. Mater. Interfaces* **2016**, *8* (7), 4754-4761
- Flynn, C. J.; McCullough, S. M.; Li, L.; Donley, C. L.; Kanai, Y.; Cahoon, J. F. *J. Phys. Chem. C* **2016**, *120* (30), 16568-16576

Targeted Atomic Deposition

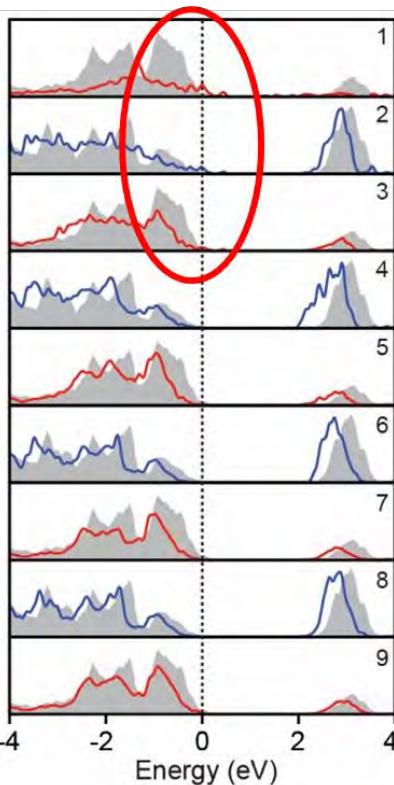
Probing Passivated Trap States

First-principles calculations

Ni vacancy:



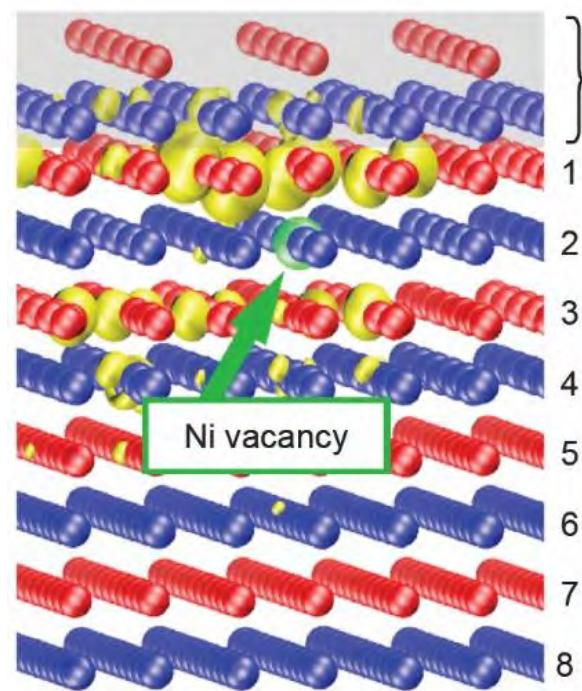
Al passivated vacancy:



Prof. Yosuke Kanai
(UNC Chemistry)



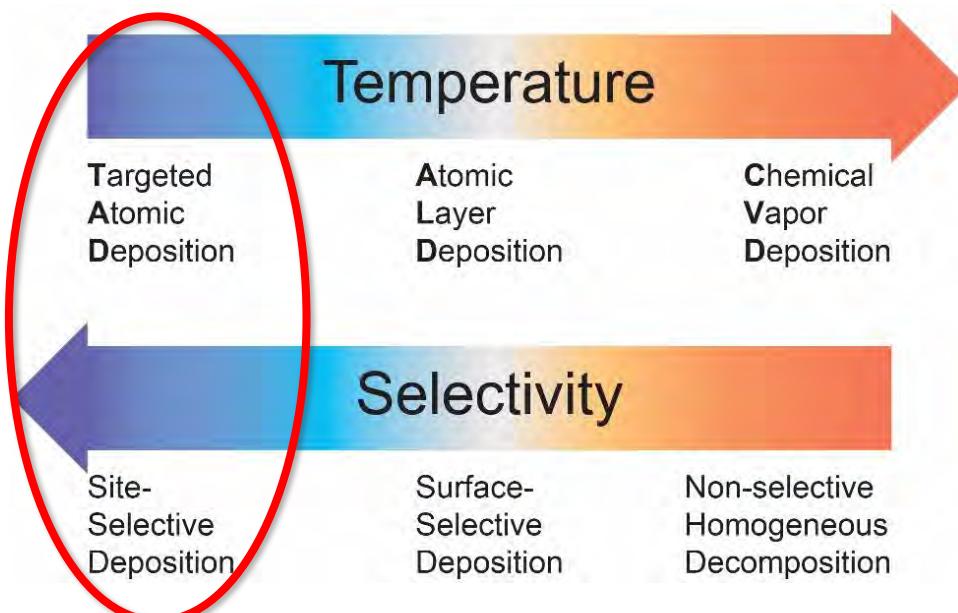
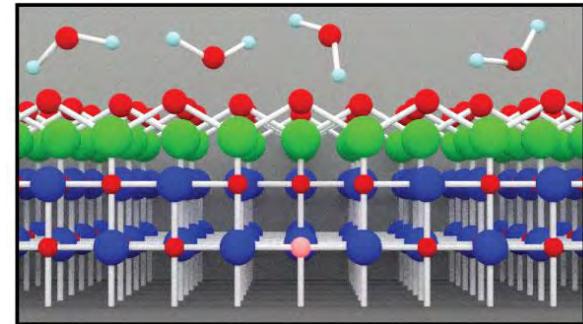
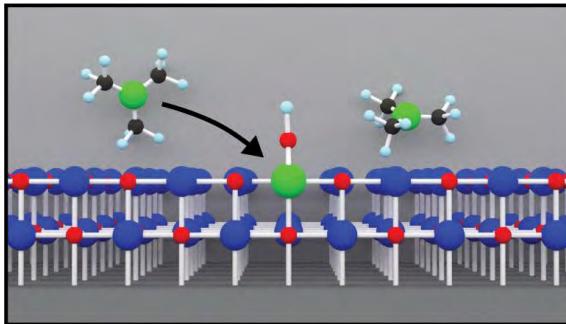
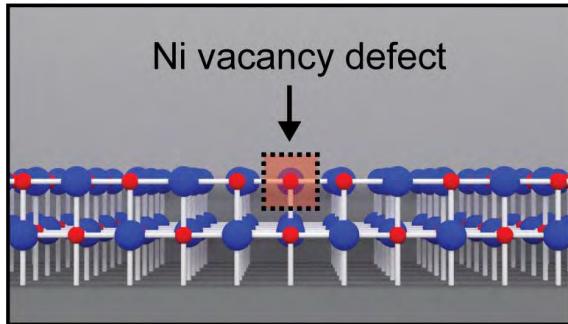
Lesheng Li
(Graduate Student)



Flynn, C. J.; McCullough, S. M.; Oh, E. E.; Li, L.; Mercado, C. C.; Farnum, B. H.; Li, W.; Donley, C. L.; You, W.;
Nozik, A. J.; McBride, J. R.; Meyer, T. J.; Kanai, Y.; Cahoon, J. F. *ACS Appl. Mater. Interfaces* **2016**, *8* (7), 4754-4761

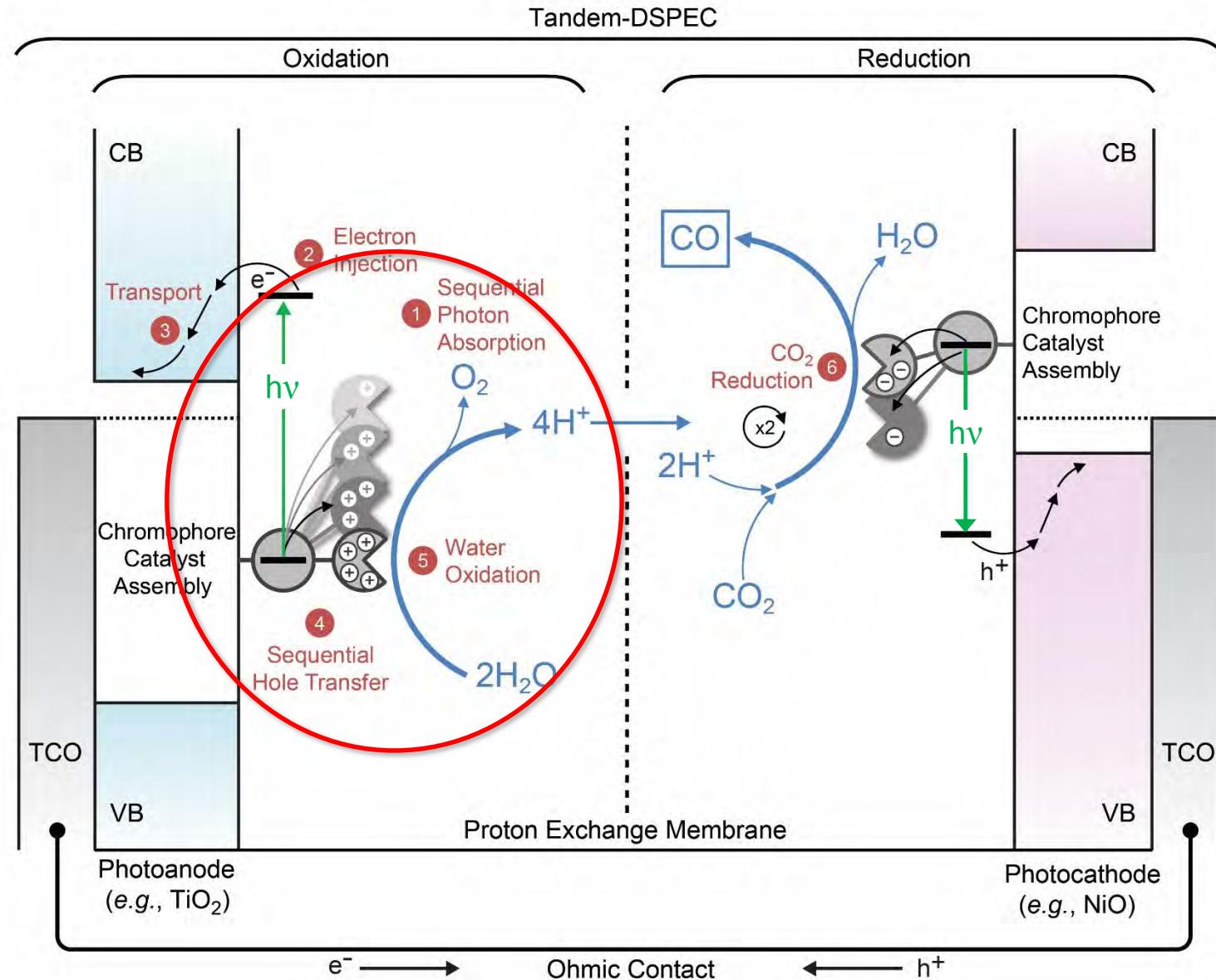
Selective Defect Passivation

Targeted Atomic Deposition (TAD)



- Flynn, C. J.; McCullough, S. M.; Oh, E. E.; Li, L.; Mercado, C. C.; Farnum, B. H.; Li, W.; Donley, C. L.; You, W.; **Nozik, A. J.**; McBride, J. R.; Meyer, T. J.; Kanai, Y.; Cahoon, J. F. *ACS Appl. Mater. Interfaces* **2016**, *8* (7), 4754-4761
- Flynn, C. J.; McCullough, S. M.; Li, L.; Donley, C. L.; **Kanai, Y.**; **Cahoon, J. F.** *J. Phys. Chem. C* **2016**, *120* (30), 16568-16576

Dye-Sensitized Photoelectrosynthesis Cells (DSPECs)

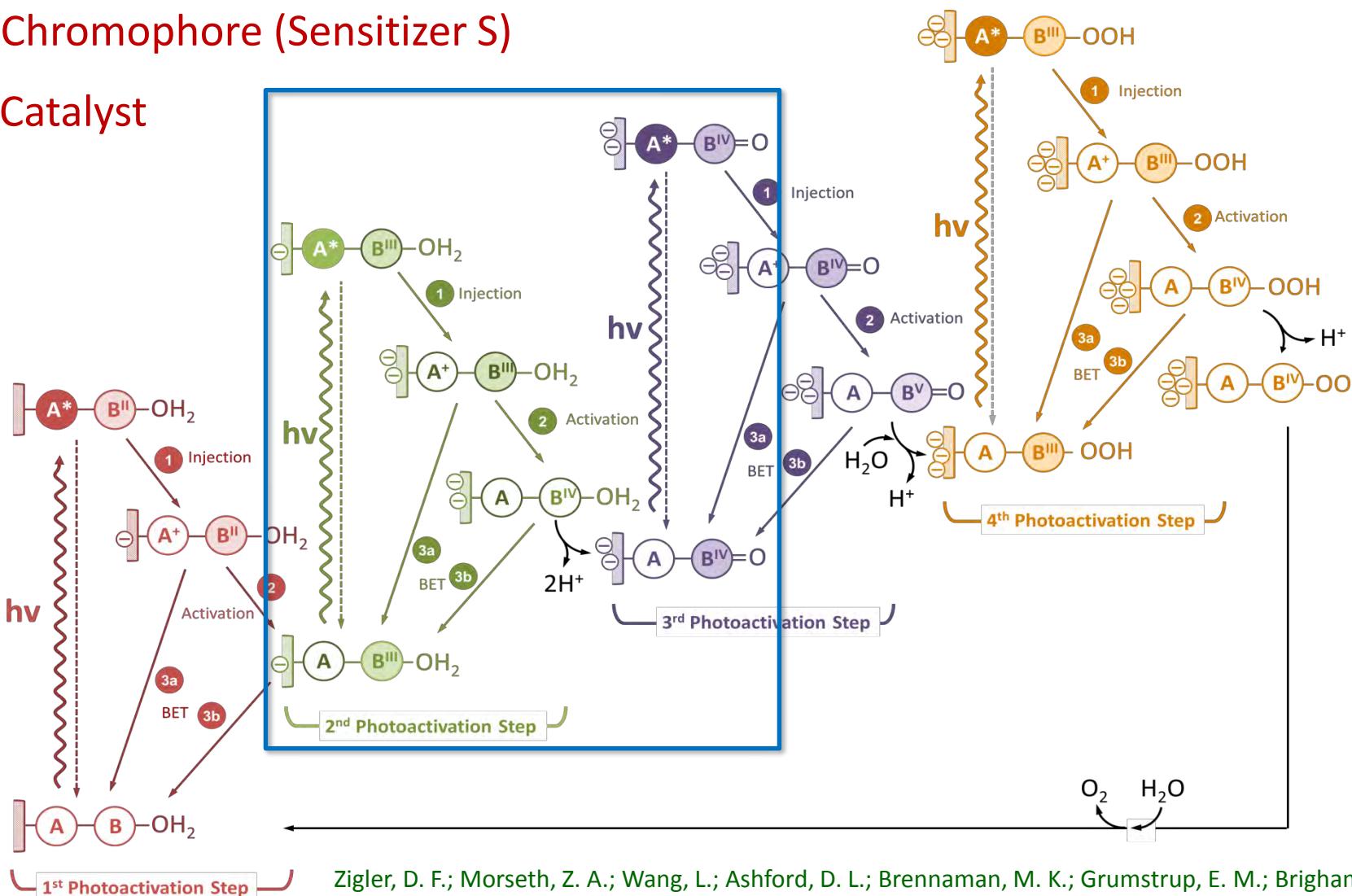


Photoinduced ET Mechanisms of a Chromophore-Catalyst at the Photoanode

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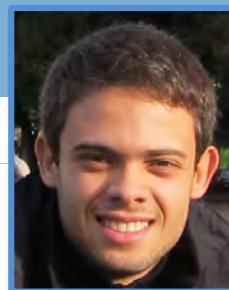
(A) Chromophore (Sensitizer S)

(B) Catalyst



Zigler, D. F.; Morseth, Z. A.; Wang, L.; Ashford, D. L.; Brennaman, M. K.; Grumstrup, E. M.; Brigham, E. C.; Gish, M. K.; Dillon, R. J.; Alibabaei, L.; Meyer, G. J.; Meyer, T. J.; Papanikolas, J. M.
J. Am. Chem. Soc. **2016**, *138* (13), 4426-4438

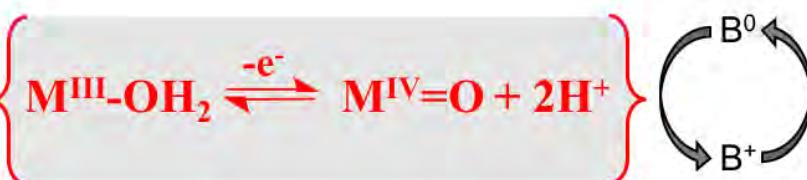
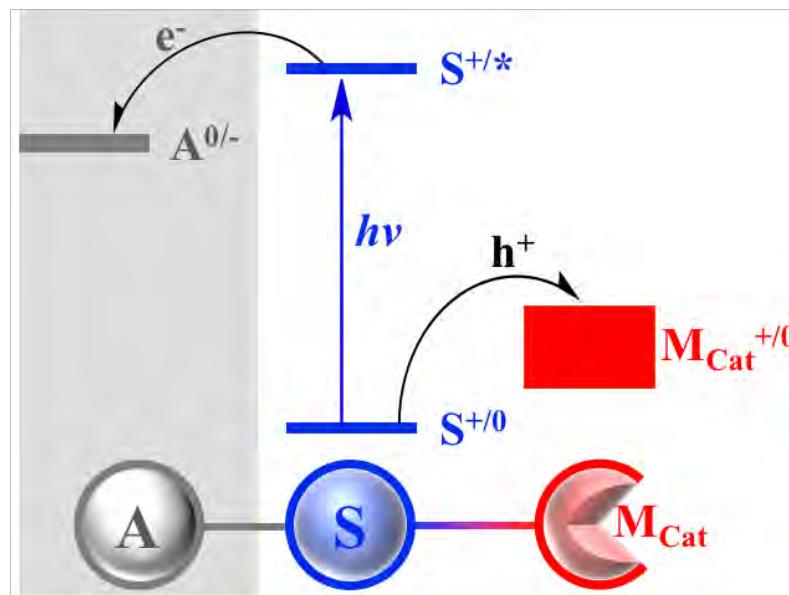
General Approach for Generation of Oxo Catalysts



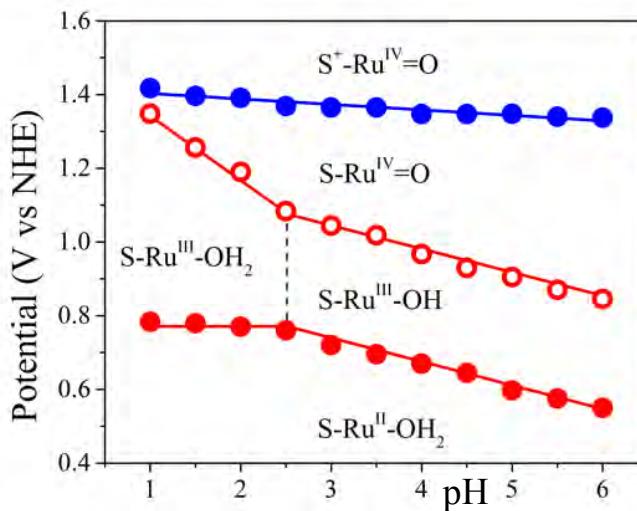
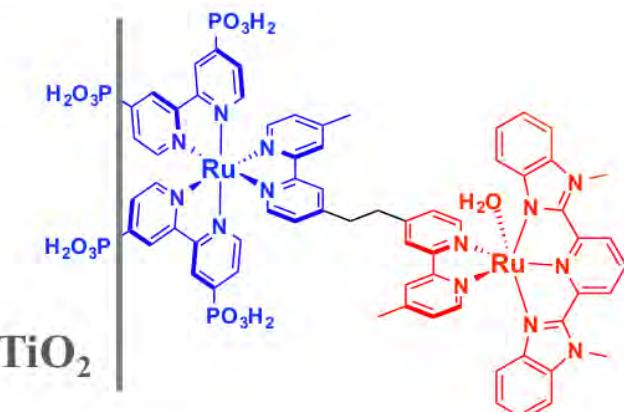
Dr. Renato Sampaio
(Postdoctoral)

Dr. Ke Hu
(Postdoctoral)

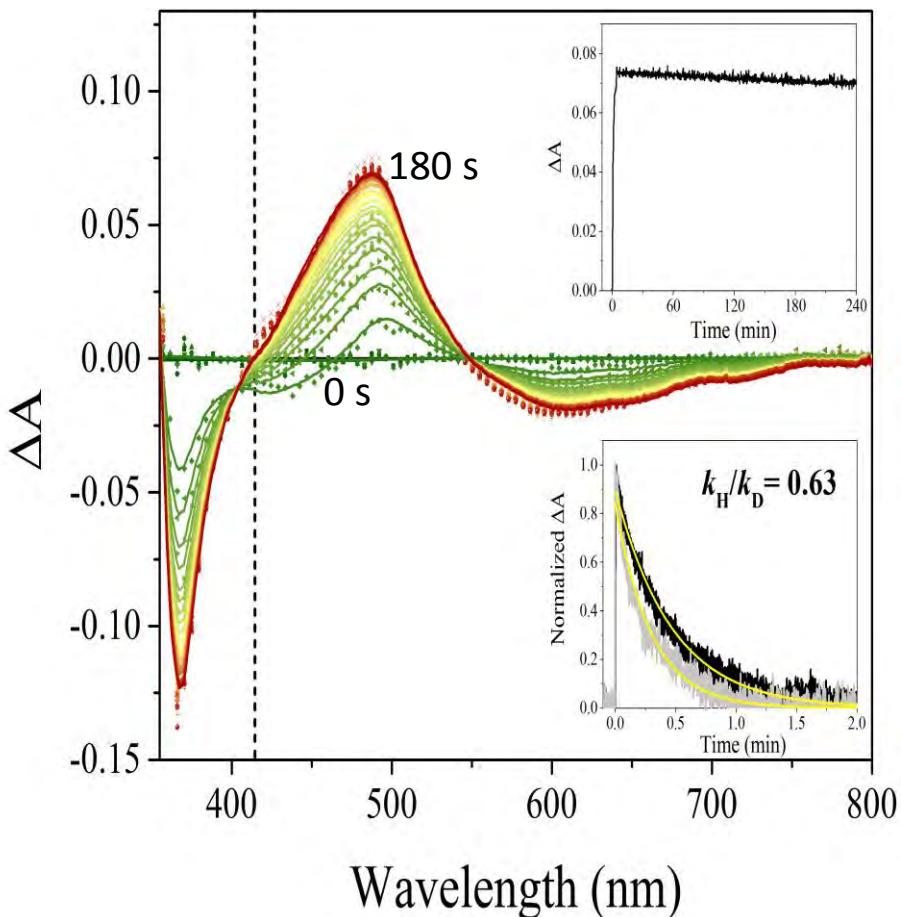
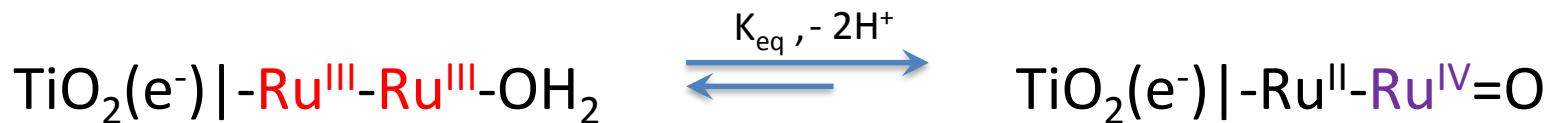
Dr. Kyle Brenneman
(EFRC Senior Scientist)



Hu, K.; Sampaio, R. N.; Marquard, S. L.; Brenneman, M. K.; Tamaki, Y.; Meyer, T. J.; Meyer, G. J. *Nat. Chem.* **2016**, Submitted



Steady State Photolysis Below the Percolation Threshold

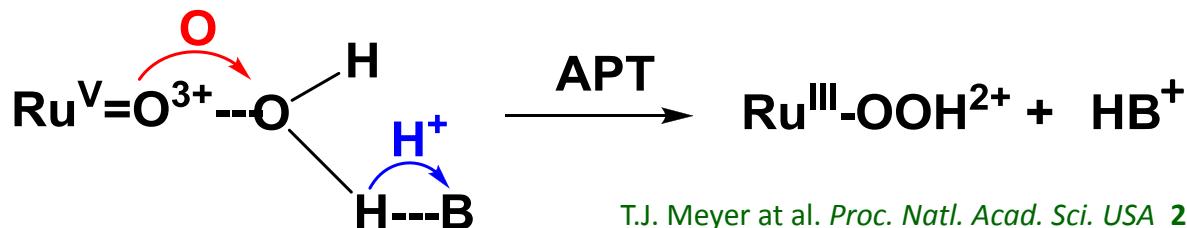


- No precedence for such slow reactivity
- Model for proton transfer on surfaces
- Model for biological PCET
- Raises many questions....
 - How does the reaction proceed?
 - Why is the reaction so slow?
 - Is there a driving force dependence?
 - Can predictive models be developed?
 - **Do buffer bases influence the reaction?**

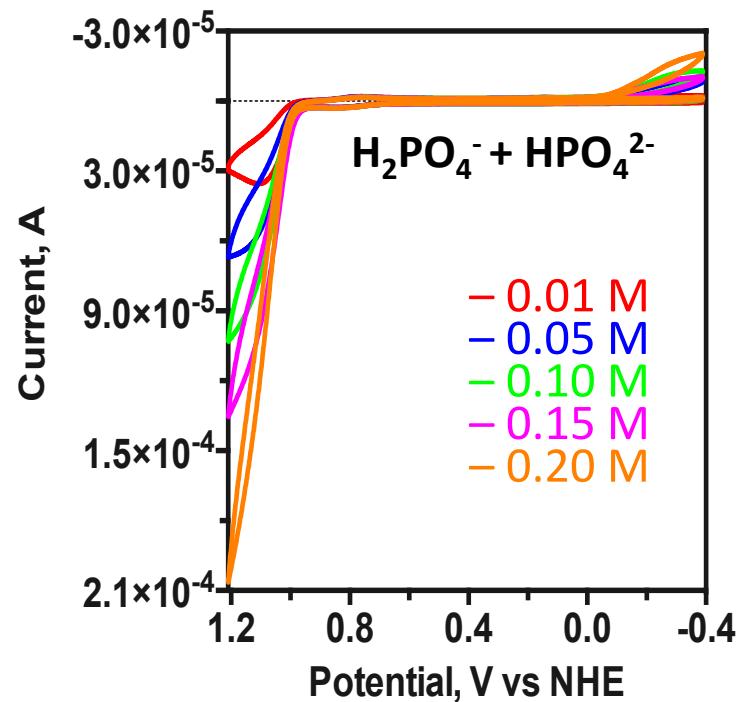
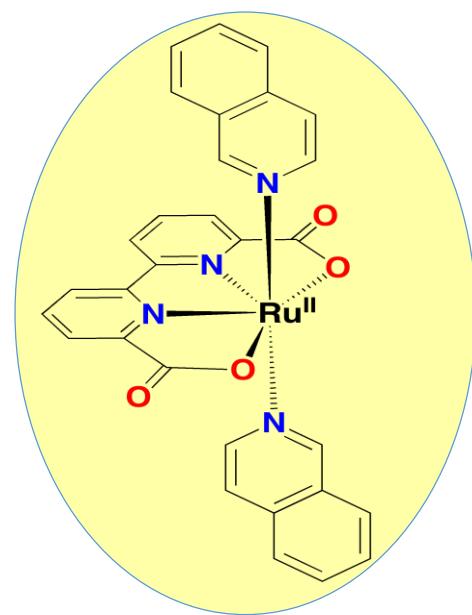
Hu, K.; Sampaio, R. N.; Marquard, S. L.; Brenneman, M. K.; Tamaki, Y.; Meyer, T. J.; Meyer, G. J. *Nat. Chem.* **2016**, Submitted

Buffer Base Water Oxidation Catalysis

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T.J. Meyer et al. *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 7225 — EFRC I



pH 7.0
 $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$
4% CH₃CN; 0.5 M NaClO₄;
20 mV/s

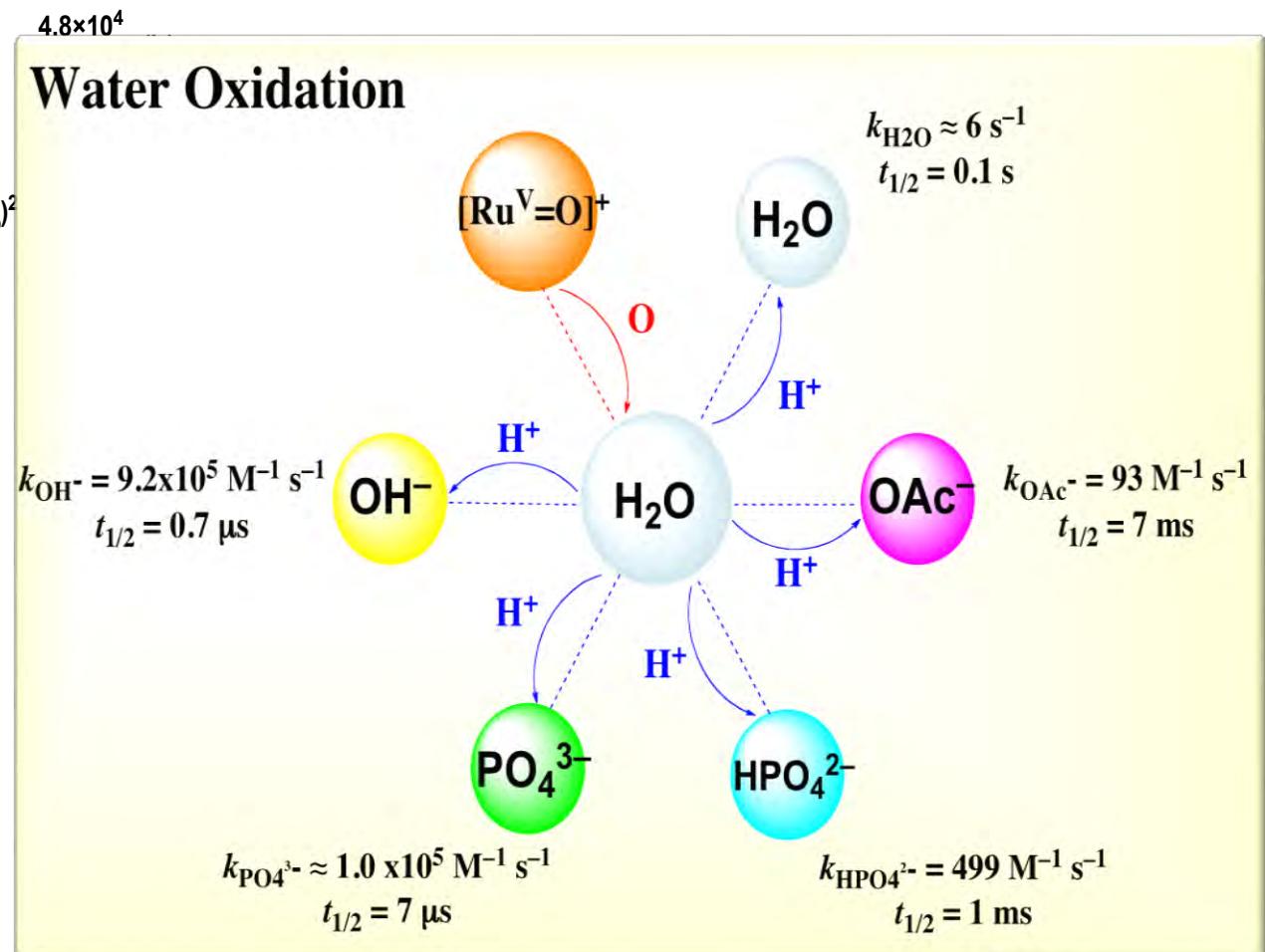
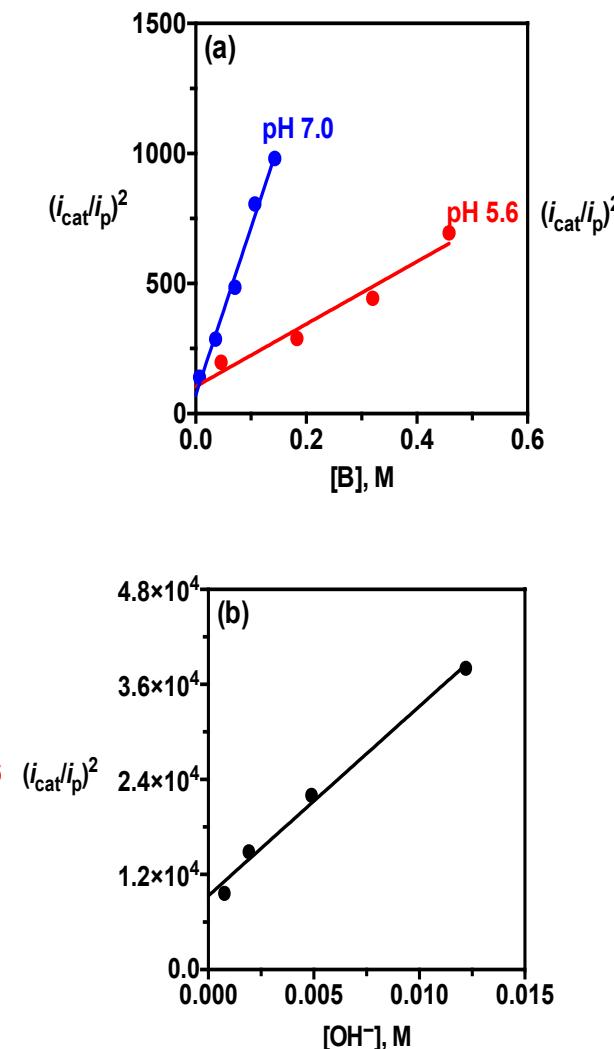


Dr. Na Song
(Postdoctoral)

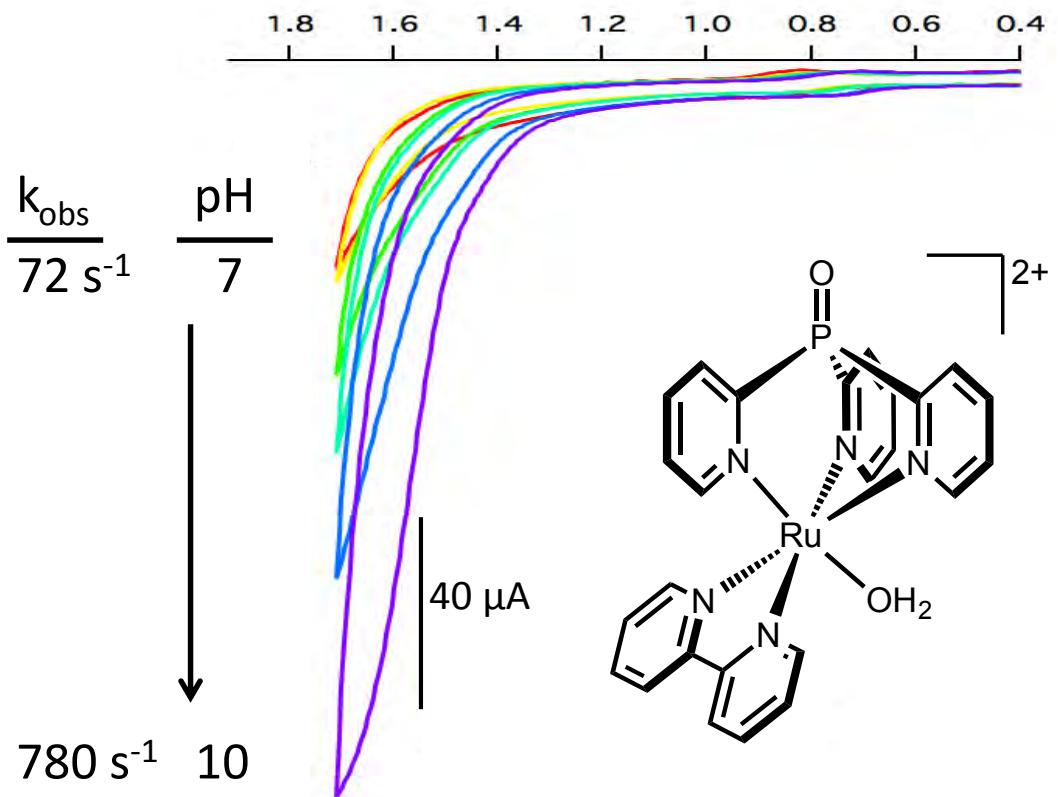
Song, N.; Meyer, T. J. et al. *Proc. Natl. Acad. Sci. USA* **2015**, *112*, 4935-4940

Buffer Base-Enhanced Water Oxidation Catalysis

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Water Oxidation by Tripodal Catalyst



- Observed rate constants increase by over an order of magnitude with pH increase from 7 to 10
- No buffer base enhancements** observed when the pH was fixed with increased base concentration

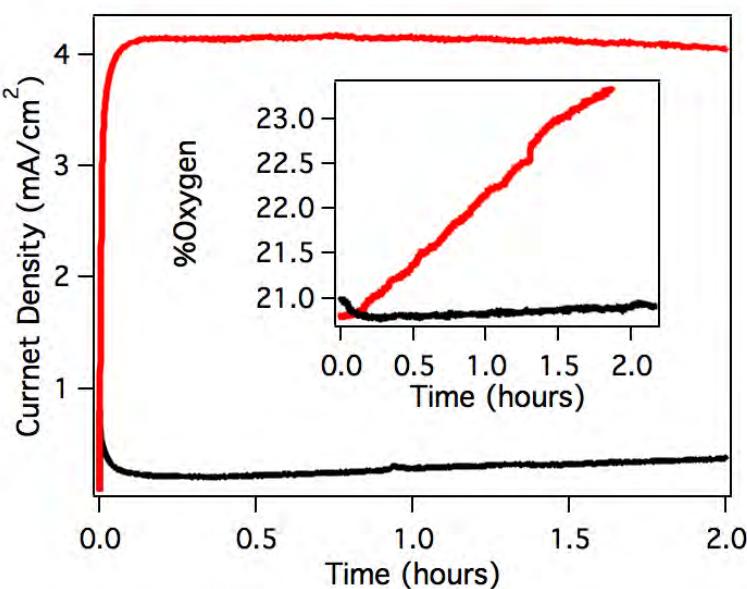
Walden, A. G.; Miller, A. J. M. *Chem. Sci.* **2015**, 6 (4), 2405-2410



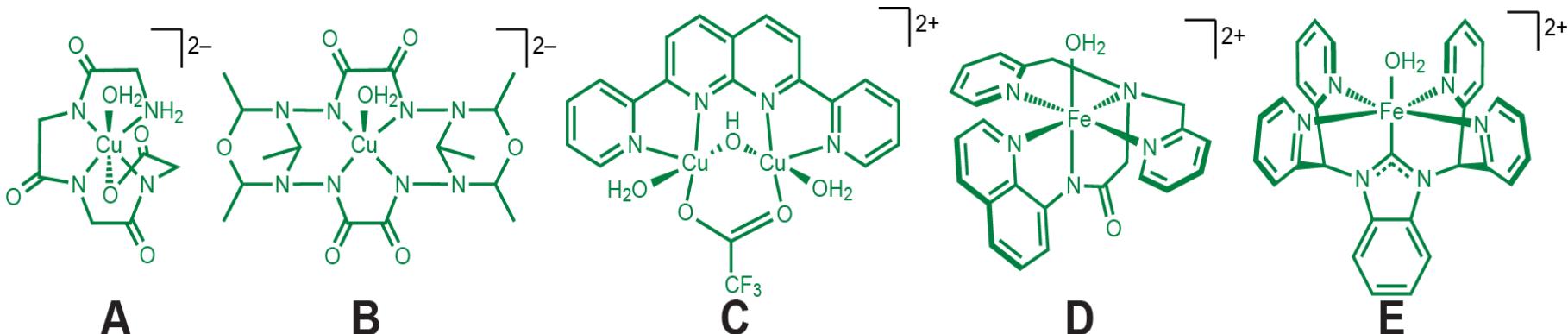
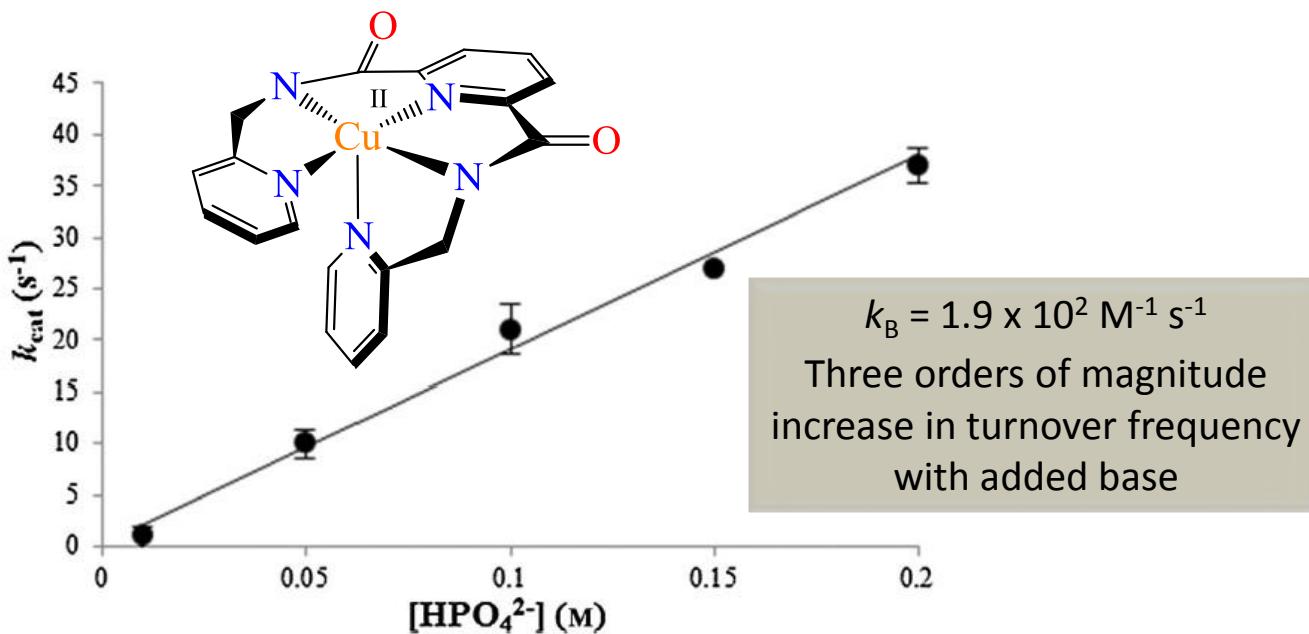
Prof. Alex Miller
(UNC Chemistry)



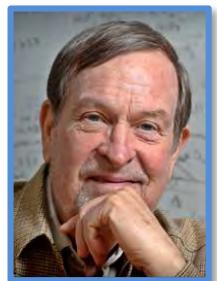
Dr. Andrew Walden
(UNC Chemistry
Graduate)



Water Oxidation by 1st Row Catalysts

**A****B****C****D****E**

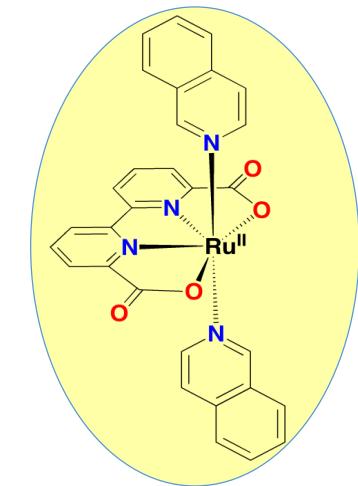
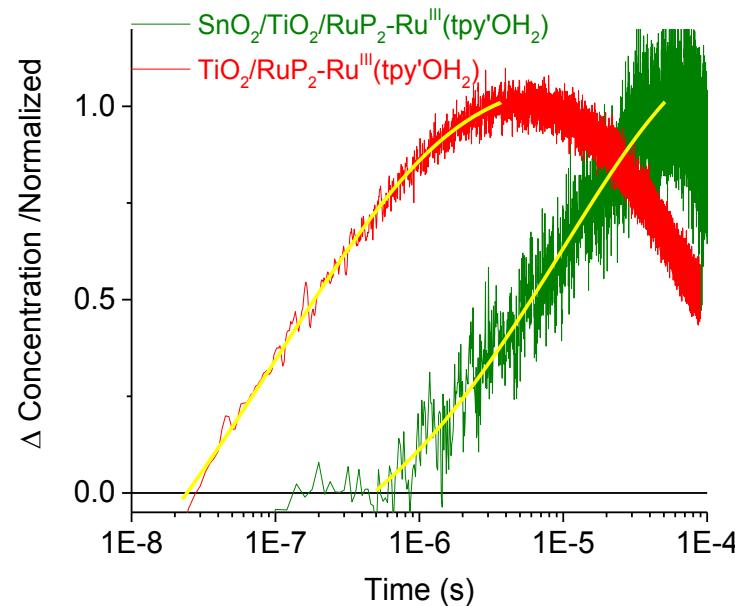
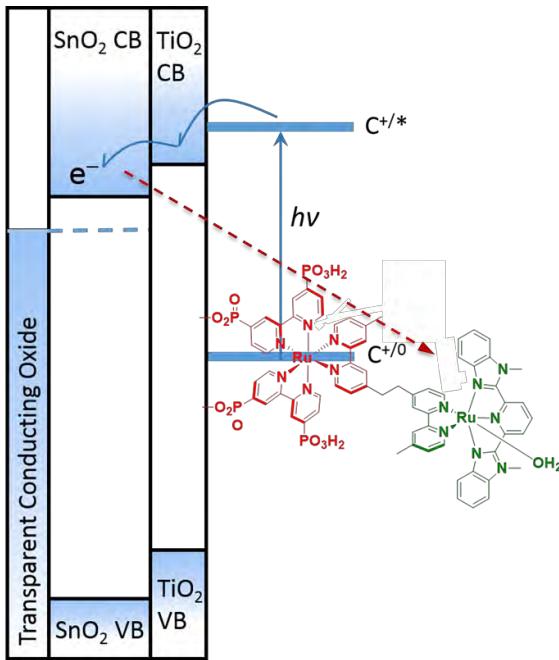
Dr. Michael Coggins Director Tom Meyer
(Postdoctoral) (UNC Chemistry)



- Coggins, M. K.; Meyer, T. J. *et al. Angew. Chem. Int. Ed.* **2014**, 53 (45), 12226-30
- Coggins, M. K.; Meyer, T. J., In *Photoelectrochemical Solar Fuel Production. From Basic Principles to Advanced Devices*, First ed.; Giménez, S.; Bisquert, J., Eds., Springer International Publishing: Switzerland, **2016**; Vol. XXI, Chapter 13, pp 513-548

Base-Catalyzed Water Oxidation Slow Recombination

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Song, N.; Meyer, T. J. et al. *Proc. Natl. Acad. Sci. USA* **2015**, *112*, 4935-4940

$$k_{rec} = 2.1 \times 10^6 \text{ s}^{-1} (\text{TiO}_2)$$

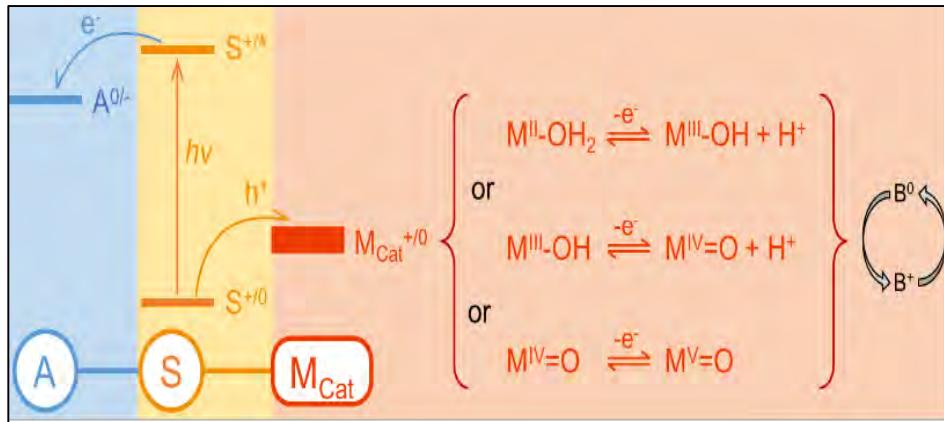
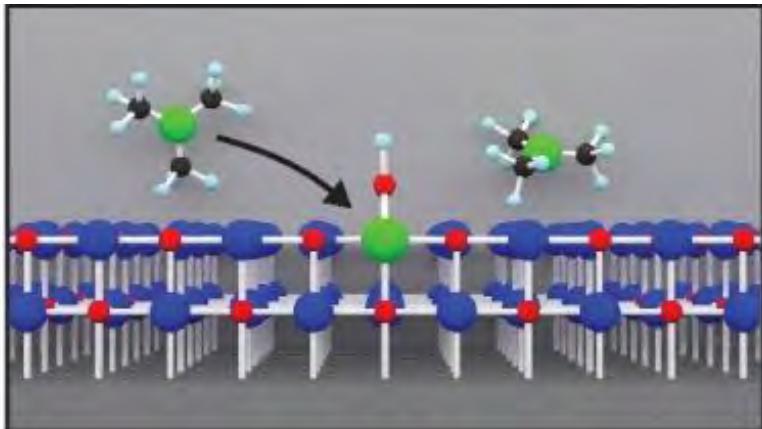
$$k_{rec} = 5.6 \times 10^4 \text{ s}^{-1} (\text{SnO}_2/\text{TiO}_2)$$

$$k_{PO_4^{3-}} = 9.9 \times 10^4 \text{ s}^{-1}$$

$$\phi = \frac{k_{cat}}{k_{cat} + \sum_{i=1}^4 k_{cr}} \approx 0.64$$

Hu, K.; Sampaio, R. N.; Marquard, S. L.; Brenneman, M. K.; Tamaki, Y.; Meyer, T. J.; Meyer, G. J. *Nat. Chem.* **2016**, Submitted

SUMMARY



- Targeted Atomic Deposition (TAD) selectively passivates the most reactive states
- TAD application to NiO resulted in dramatic photoelectrochemical enhancements that were absent in ALD treated NiO
- TAD is a general approach for passivating surface states without the need for an insulating shell layer

- A general approach for the photogeneration of metal oxo catalysts was realized
- Application of this approach reveals kinetically slow 2H^+ , 1e^- transfer reactivity
- Buffer bases enhance proton transfer reactions and water oxidation for some catalysts
- Buffer base catalysis with core-shell oxides may soon result in water oxidation with quantum yields near unity



Thank You! THE UNC EFRC TEAM

