

# Charles Dismukes, 2022 Catalysis & Biocatalysis Research Programs at Rutgers University



2020-2022

## Group Members



Dr. Anders Laursen  
RenewCO<sub>2</sub> LLC



Dr Mahak Dhiman  
postdoc



Krishani Teeluck  
PhD Candidate



Apostolos Zournas  
PhD Candidate



Hengfei Gu  
PhD Candidate



Yifei Li  
PhD Candidate



Christopher Turner  
Grad Student



Zachary Clifford  
PhD Candidate

## Recent Alumni



Shinjae Hwang  
Applied Materials  
Semi-conductor  
Industry



Karin Calvino  
RenewCO<sub>2</sub> LLC  
Start-up



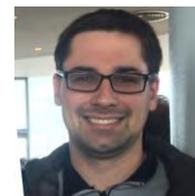
Joshua Flynn  
Chemours  
Chemical Industry



Spencer Porter  
Global Foundry  
Semi-conductor  
Industry



Graeme Gardner  
Visikol  
Start-up



Paul Smith  
Valparaiso U.  
Faculty



Yuan Zhang  
Berkley Nat. Lab  
Postdoc



Colin Gates  
Loyola U.  
Faculty



Dr Gennady Ananyev  
Research Professor



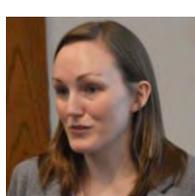
Anagha Krishnan  
Colorado School of  
Mines  
Postdoc



Xiao Qian  
Cipher Gene LLC  
Industry



Tiago Guerra  
A4F  
Start-up



Kelsey McNeely  
Exxon Mobil  
Chemical Industry



Nick Bennette  
Counterbalance  
Capital  
Investment



David Robinson  
BASF  
Environmental  
Catalysis



Jyotishman  
Dasgupta  
TIFR  
Faculty

# Undergraduate Student Alumni (2020-2018)

## Dismukes Laboratories, Rutgers University

**Current 2021:**  
Hiba Shaqra  
Andrew Hsieh  
Gnaneswar Chundi  
Ethan Black  
Julia Burns  
Joyce Yu  
Michael Stringer  
Brooklyn Castillo



Alexander Kim  
2022



Sofia Dvinskik  
2022



Kye Mani  
2021



Mathiaas Miller  
Rutgers MBS



Kyra Yap  
Stanford



Sunjay Melkote  
Stanford National Lab



Devan Solanki  
Yale



Lauren Ostowickz  
Arizona State



Edward Izett  
Opus12



Anika Jalil  
UC Santa Barbara



Tim Goetjen  
Northwestern



Jonah Williams  
McDermott



Jack Weber  
Columbia



Ajay Kashi  
Opus12



**Waksman Institute of Microbiology**

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**Chemistry Dept,**

# Research in Collaboration with....



**Martha Greenblatt:** Solid state materials synthesis and chemistry



**Eric Garfunkel:** novel photovoltaic materials; low power materials for nanoelectronics



**Katherine Ayers:** Electrocatalysis Proton Energy Systems  
Director of Research,



**Todd G. Deutsch:** Tandem Absorbers for Economical Solar H<sub>2</sub> Production & CO<sub>2</sub> reduction



**David Case:** Theoretical chem biomolecules, electronic structure of transition-metal complexes



**Andrew M. Rappe:** Theoretical chemistry of materials



**Sagar Khare:** Computational and experimental studies of molecular recognition



**Petra Fromme:** Biochemistry & Crystallography



**Desmond Lun:** Computer design of microbial metabolism, computational systems biology



**Debashish Bhattacharya:** Algal genomics & Evolution,



**Charles Musgrave:** Theoretical chemistry of electrocatalysis



**Paul G. Falkowski:** Biogeochemical cycles, photosynthesis, biological oceanography



**Laura Fabris:** application of plasmonic nanoparticles



# 2021

## CHANCELLOR'S AWARD FOR PIONEERING RESEARCH

This award honors a faculty member whose research contributions have transformed the field, including highly cited scholarship or practiced patents.



**Charles Dismukes**

*Distinguished Professor*

Chemistry & Chemical Biology

School of Arts and Sciences

## Publications, 2018-2021

1. Hwang, S., S.H. Porter, M. Li, R. Thorpe, A.B. Laursen, A. Safa-ri, M. Greenblatt, E. Garfunkel and G.C. Dismukes, *Thin-film SrNbO<sub>2</sub>N photoanode: in situ synthesis of photo-stable inter-faces and the influence of thickness and roughness on performance* **J. Phys. Chem.**, 2022. **in press**.
2. Gates, C., G. Ananyev, S. Roy-Chowdhury, P. Fromme and G.C. Dismukes, *Quantifying the oxidation states of manganese in the water oxidation cycle of Photosystem II by chemical reduction of ultrapure PSII microcrystals.* **Photosyn. Res** , , 2022. **in preparation**.
3. Gates, C., G. Ananyev, S. Roy-Chowdhury, B. Cullinane, M. Miller, P. Fromme and G.C. Dismukes, *Why Did Nature Choose Manganese Exclusively to Make Oxygen on Earth?* **J. Phys. Chem. C**, 2022. **in press**.
4. Dismukes, G.C., *Beyond biofuels, a need for solutions to overcome Nature's inefficiency.* in review, 2022.
5. Dismukes, G., A. Laursen and K. Calvinho, "Nickel Phosphide Catalysts For Direct Electrochemical Co<sub>2</sub> Reduction To Hydrocarbons", **USPTO**, Editor. 2021 filed.
6. Zournas, A., J.A.E. ten Veldhuis and G.C. Dismukes, *CO<sub>2</sub> throttle-points and bottlenecks in photosynthetic electron transport and their influence on CO<sub>2</sub> carboxylation rate as revealed by chlorophyll fluorescence transients.* **Photosyn. Res.** In preparation, 2021.
7. Mani, K., A. Zournas and G.C. Dismukes, *Bridging the gap between Kok-type and kinetic models of photosynthetic electron transport within Photosystem II.* **Photosynth Res**, 2021. **Aug 16**.

## Publications, 2018-2021

8. Laursen, A.B., K.U. Calvinho, T.A. Goetjen, K.M. Yap, S. Hwang, H. Yang, E. Garfunkel and G.C. Dismukes, *CO<sub>2</sub> electro-reduction on Cu<sub>3</sub>P: Role of Cu (I) oxidation state and surface facet structure in C<sub>1</sub>-formate production and H<sub>2</sub> selectivity. *Electrochimica Acta*, 2021. **391: p. 138889.***
9. Gabr, A., A. Zournas, T.G. Stephens, G.C. Dismukes and D. Bhattacharya, *Evidence for a robust photosystem II in the photosynthetic amoeba Paulinella. *New Phytologist*, 2021. **IN PRESS.***
10. Calvinho, K.U.D., A.W. Alherz, K.M.K. Yap, A.B. Laursen, S. Hwang, Z.J.L. Bare, Z. Clifford, C.B. Musgrave and G.C. Dismukes, *Surface Hydrides on Fe<sub>2</sub>P Electrocatalyst Reduce CO<sub>2</sub> at Low Overpotential: Steering Selectivity to Ethylene Glycol. *J Am Chem Soc*, 2021. **143(50): p. 21275-21285.***
11. ten Veldhuis, M.-C., G. Ananyev and G.C. Dismukes, *Symbiosis extended: exchange of photosynthetic O<sub>2</sub> and CO<sub>2</sub> mutually power metabolism of lichen symbionts. *Photosyn. Res*, 2020 **143: p. 287–299.***
12. Potkay, A., M.C. Ten Veldhuis, Y. Fan, C.R.C. Mattos, G. Ananyev and G.C. Dismukes, *Water and Vapor Transport in Algal-Fungal Lichen: Modeling constrained by Laboratory Experiments, an application for Flavoparmelia caperata. *Plant Cell Environ*, 2020. **43(4): p. 945-964.***
13. Hwang, S., Young, J.L., Mow, R., Garfunkel, E., Dismukes, G.C., *Highly efficient and durable III-V semiconductor-catalyst photocathodes: Via a transparent protection layer. *Sustainable Energy and Fuels*, 2020. **4(3): p. 1437–1442.***

## Publications, 2018-2021

14. Gates, C., G. Ananyev and G.C. Dismukes, *Realtime kinetics of the light driven steps of photosynthetic water oxidation in living organisms by "stroboscopic" fluorometry. Biochim Biophys Acta Bioenerg*, 2020. **1861(8): p. 148212.**
15. Dismukes, G.C., A. Laursen, M. Greenblatt and K. Calvinho, *Continuation in Part to Nickel phosphide catalysts for direct electrochemical CO<sub>2</sub> reduction to hydrocarbons, USPTO, Editor. 2020.*
16. Dismukes, G.C., A. Laursen, M. Greenblatt and K. Calvinho, *Nickel phosphide catalysts for direct electrochemical CO<sub>2</sub> reduction to hydrocarbons, USPTO, Editor. 2020, US Patent 10,676,833.*
17. Calvinho, K.U.D., A.W. Alherz, K.M.K. Yapa, A.B. Laursen, S. Hwang, Z.J.L. Bare, C.B. Musgrave and G.C. Dismukes, *Hydride-driven Electrocatalytic Reduction of CO<sub>2</sub> to Ethylene Glycol on Fe<sub>2</sub>P. submitted, 2020.*
18. Shevela, D., G. Ananyev, A.K. Vatland, J. Arnold, F. Mamedov, L.A. Eichacker, G.C. Dismukes and J. Messinger, *"Birth defects" of photosystem II make it highly susceptible to photodamage during chloroplast biogenesis. Physiologia Plantarum*, 2019. **166(1): p. 165-180.**
19. Kumaraswamy, K.G., A. Krishnan, G. Ananyev, S.Y. Zhang, D.A. Bryant and G.C. Dismukes, *Crossing the Thauer limit: rewiring cyanobacterial metabolism to maximize fermentative H<sub>2</sub> production. Energy & Environmental Science*, 2019. **12(3): p. 1035-1045.**
20. Jalil, A.F., K.U. Calvinho, A.B. Laursen and G.C. Dismukes. *Development of Falling Thin Film Liquid Phase Electrolyzer for CO<sub>2</sub> Reduction. in 2019 AIChE Annual Meeting. 2019. AIChE.*

## Publications, 2018-2021

21. Hwang, S., S.H. Porter, A.B. Laursen, H. Yang, M. Li, V. Manichev, K.U.D. Calvinho, V. Amarasinghe, M. Greenblatt, E. Garfunkel and G.C. Dismukes, *Creating stable interfaces between reactive materials: titanium nitride protects photoabsorber–catalyst interface in water-splitting photocathodes. Journal of Materials Chemistry A*, 2019. **7(5): p. 2400-2411.**
22. Ananyev, G., S. Roy-Chowdhury, C. Gates, P. Fromme and G.C. Dismukes, *The Catalytic Cycle of Water Oxidation in Crystallized Photosystem II Complexes: Performance and Requirements for Formation of Intermediates. Acs Catalysis*, 2019. **9(2): p. 1396-1407.**
23. Vinyard, D.J., G.M. Ananyev and G.C. Dismukes, *Desiccation tolerant lichens facilitate in vivo H/D isotope effect measurements in oxygenic photosynthesis. Biochimica et Biophysica Acta (BBA) - Bioenergetics*, 2018. **1859(10): p. 1039-1044.**
24. Qian, X., Y. Zhang, D.S. Lun and G.C. Dismukes, *Rerouting of Metabolism into Desired Cellular Products by Nutrient Stress: Fluxes Reveal the Selected Pathways in Cyanobacterial Photosynthesis. ACS Synthetic Biology*, 2018. **7(5): p. 1465-1476.**
25. Laursen, A.B., R.B. Wexler, M.J. Whitaker, E.J. Izett, K.U. Calvinho, S. Hwang, R. Rucker, H. Wang, J. Li and E. Garfunkel, *Climbing the volcano of electrocatalytic activity while avoiding catalyst corrosion: Ni<sub>3</sub>P, a hydrogen evolution electrocatalyst stable in both acid and alkali. ACS Catalysis*, 2018. **8(5): p. 4408-4419.**
26. Krishnan, A., X. Qian, G. Ananyev, D.S. Lun and G.C. Dismukes, *Rewiring of cyanobacterial metabolism for hydrogen production: Synthetic biology approaches and challenges. Synthetic Biology of Cyanobacteria, in Adv Exp Med Biol.*, W.Z.a.X. Song, Editor. 2018, Springer: Singapore. p. 171-213.

## Publications, 2018-2021

27. Greenblatt, M. and G.C. Dismukes, *Spinel Catalysts for Water Oxidation/Water Splitting*. 2018.
28. Dismukes, G., K. Calvinho and A. Laursen. *Bioinspired heterogeneous electrocatalysts for CO<sub>2</sub> reduction: Energy-efficient carbon-carbon coupling rivaling enzymes*. in *ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY*. 2018. AMER CHEMICAL SOC 1155 16TH ST, NW, WASHINGTON, DC 20036 USA.
29. Chen, H., G.C. Dismukes and D.A. Case, *Resolving Ambiguous Protonation and Oxidation States in the Oxygen Evolving Complex of Photosystem II*. *The Journal of Physical Chemistry B*, 2018. **122(37): p. 8654-8664**.
30. Chen, H., D.A. Case and G.C. Dismukes, *Reconciling Structural and Spectroscopic Fingerprints of the Oxygen-Evolving Complex of Photosystem II: A Computational Study of the S<sub>2</sub> State*. *The Journal of Physical Chemistry B*, 2018. **122(50): p. 11868-11882**.
31. Calvinho, K.U., A.B. Laursen, K.M. Yap, T.A. Goetjen, S. Hwang, N. Murali, B. Mejia-Sosa, A. Lubarski, K.M. Teeluck and E.S. Hall, *Selective CO<sub>2</sub> reduction to C<sub>3</sub> and C<sub>4</sub> oxyhydrocarbons on nickel phosphides at overpotentials as low as 10 mV*. *Energy & Environmental Science*, 2018. **11(9): p. 2550-2559**.
32. Ananyev, G., C. Gates and G.C. Dismukes, *The multiplicity of roles for (bi)carbonate in photosystem II operation in the hypercarbonate-requiring cyanobacterium *Arthrospira maxima**. *Photosynthetica*, 2018. **56(1): p. 217-228**.

# Artificial Photosynthesis is the path to a sustainable Energy Future

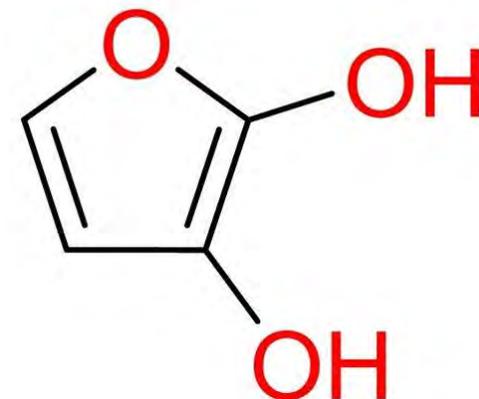
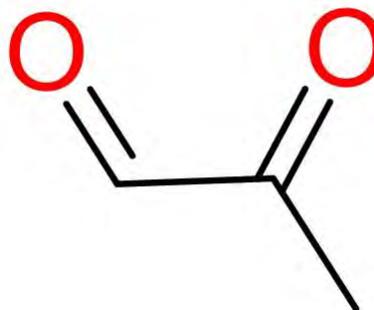
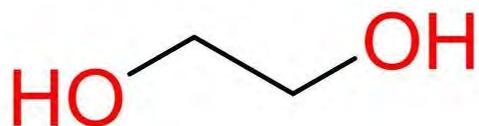
First renewable chemicals



RENEW



Rutgers Startup



Mono-ethylene glycol

Methyl glyoxal

Furandiol



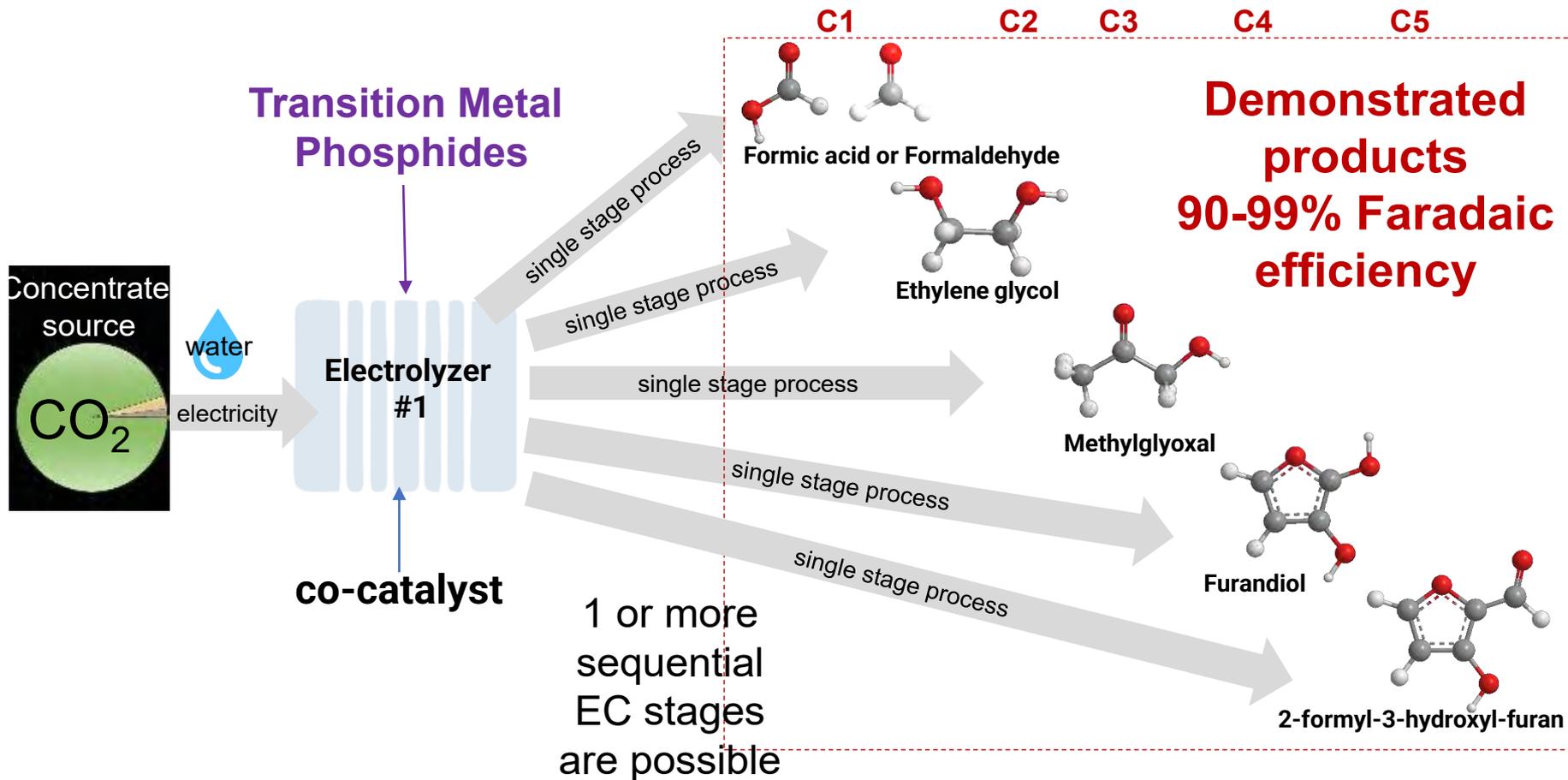
Dr. Anders Laursen  
Research associate &  
CEO RenewCO<sub>2</sub> LLC



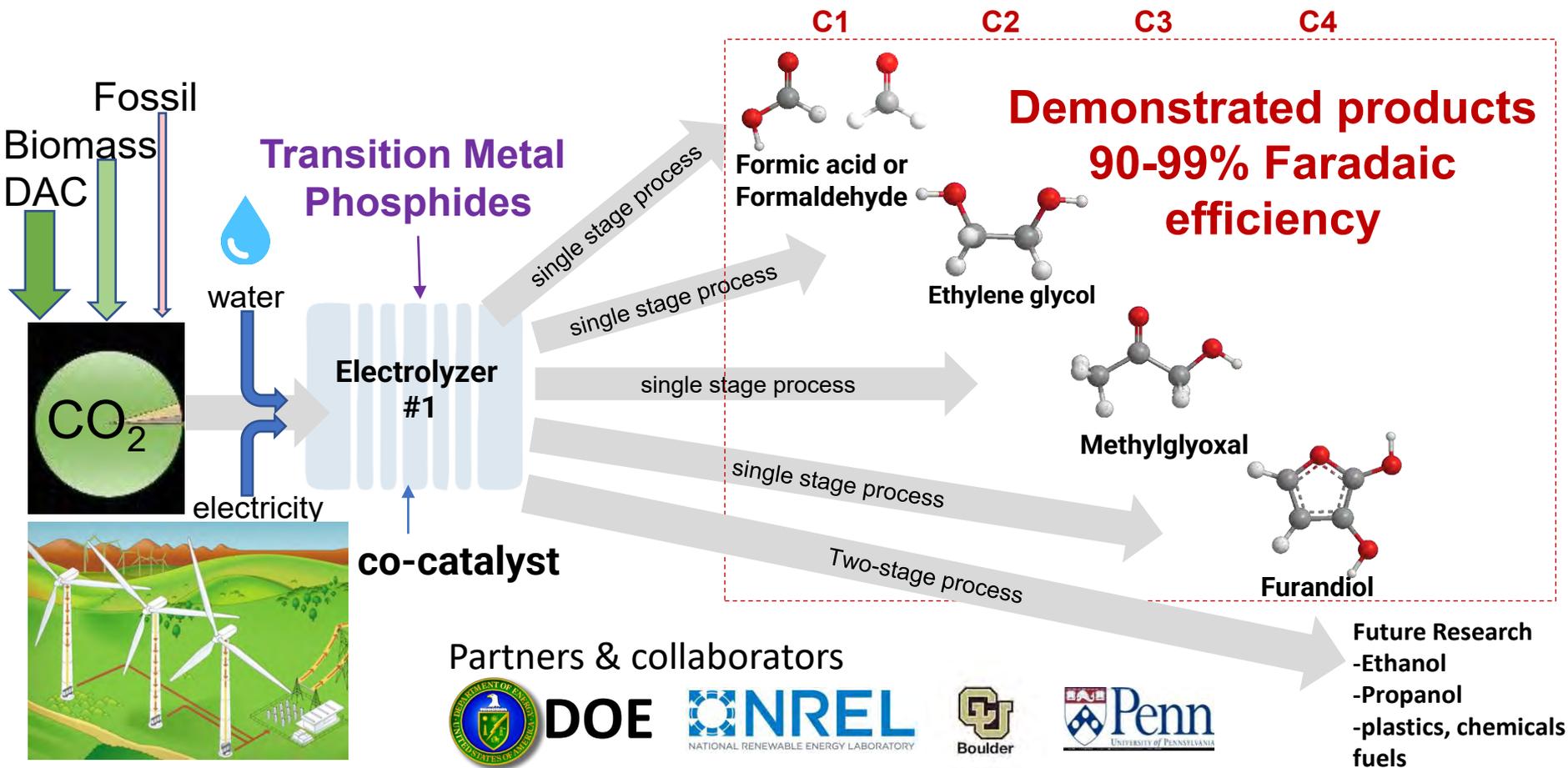
Karin Calvino  
CTO RenewCO<sub>2</sub>

# Artificial Photosynthesis beats Natural Photosynthesis

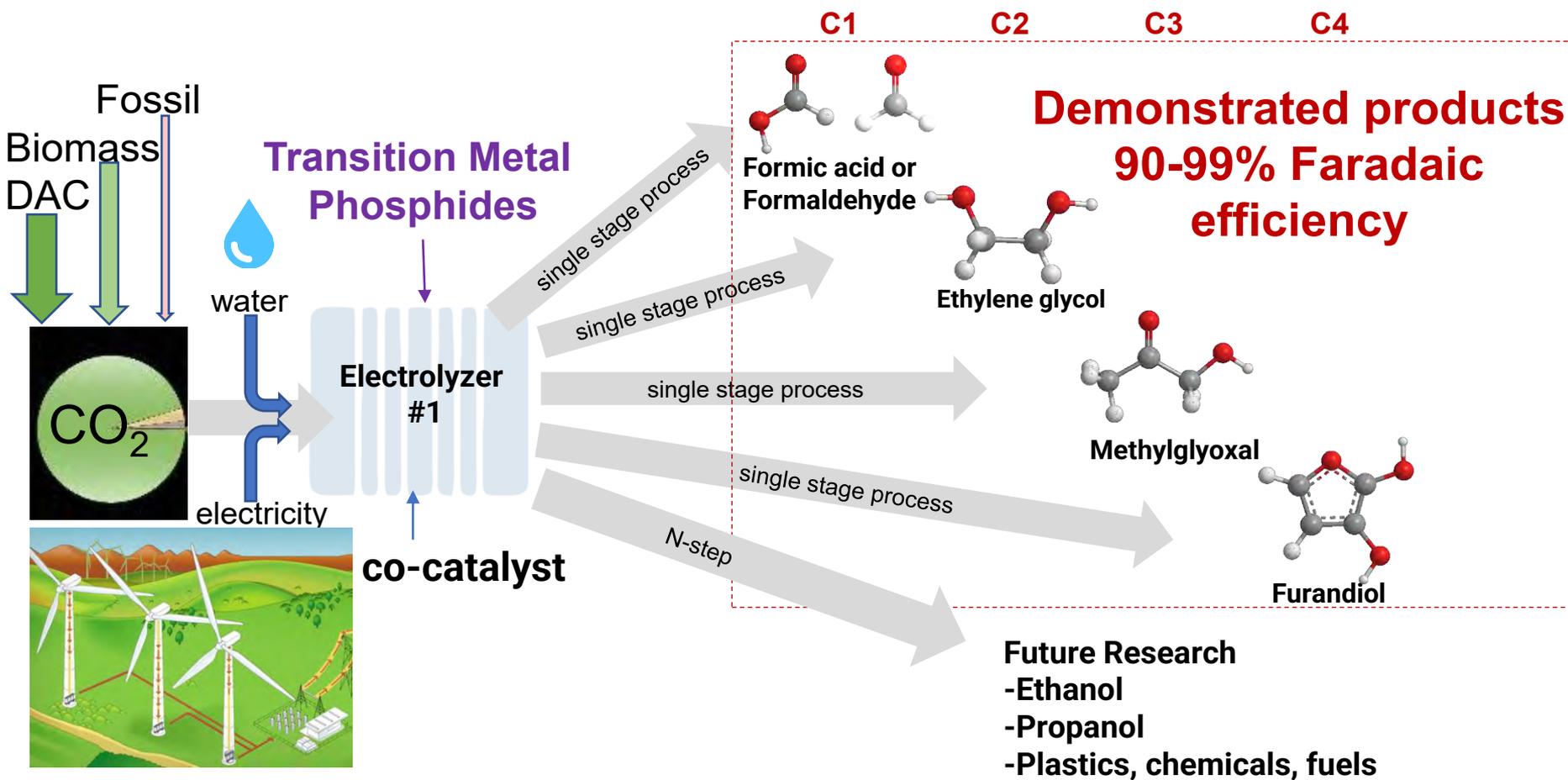
## Rutgers C-negative Technology



# CO<sub>2</sub> → Bulk Chemicals & Fuels : *Rutgers CO<sub>2</sub>-Negative Technology*



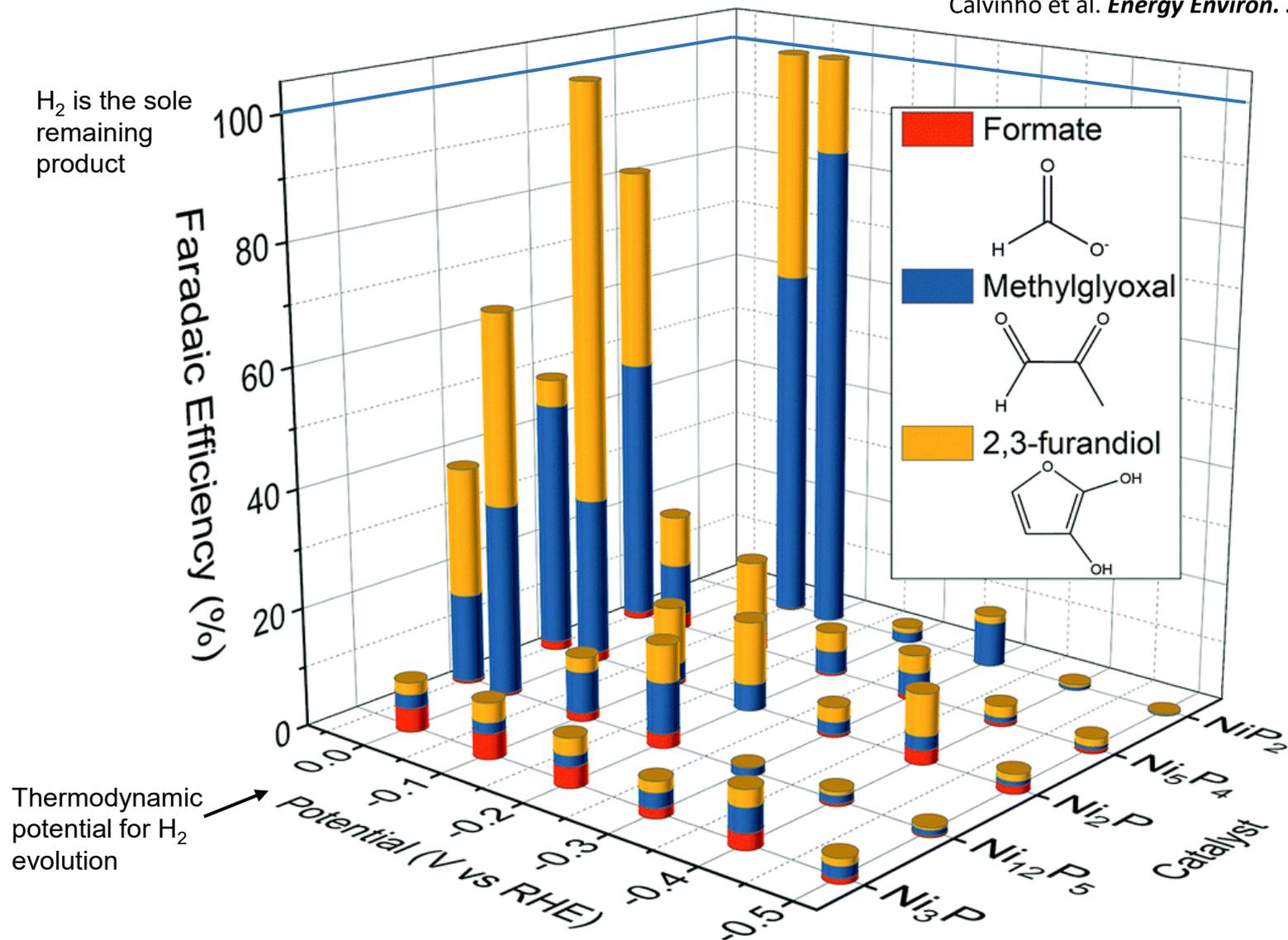
# CO<sub>2</sub> → Bulk Chemicals & Fuels : *Rutgers CO<sub>2</sub>-Negative Technology*



# Saving Planet Earth

## Nickel Phosphides: Bioinspired CO<sub>2</sub> Reduction Catalysts

Calvinho et al. *Energy Environ. Sci.*, 2018,



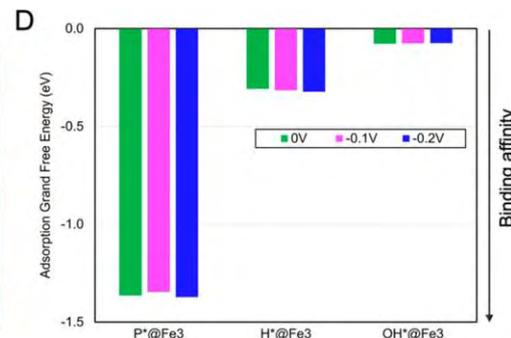
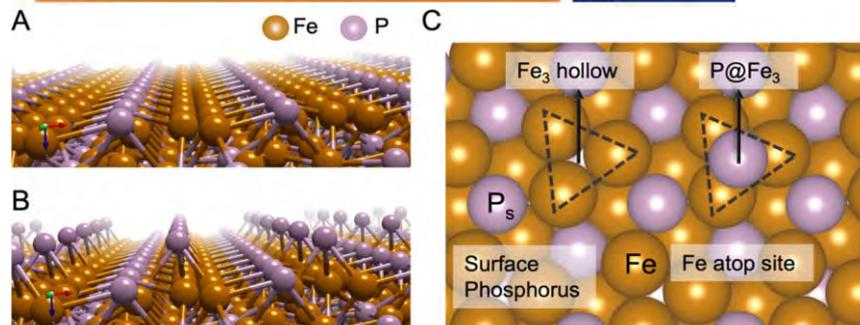
Reaction conditions: pH 7.5, 0.5 M KHCO<sub>3</sub>(aq), 25°C, 1 atm CO<sub>2</sub>

## Surface Hydrides on Fe<sub>2</sub>P Electrocatalyst Reduce CO<sub>2</sub> at Low Overpotential: Steering Selectivity to Ethylene Glycol

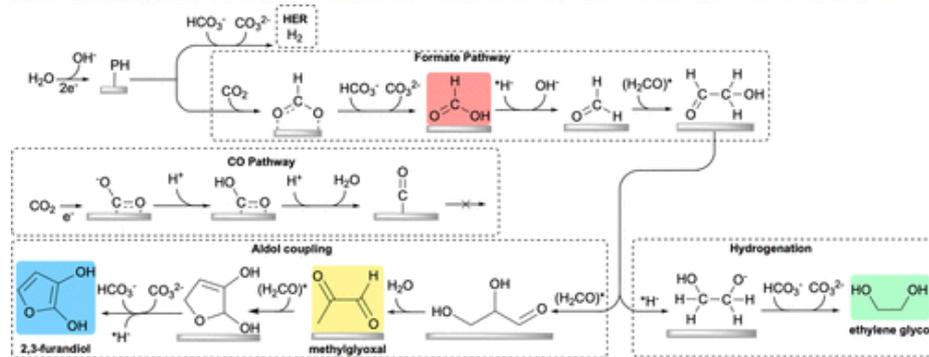
Karin U. D. Calvino,<sup>†</sup> Abdulaziz W. Alherzi,<sup>†</sup> Kyra M. K. Yap,<sup>†</sup> Anders B. Laursen, Shinjae Hwang, Zachary J. L. Bare, Zachary Clifford, Charles B. Musgrave,\* and G. Charles Dismukes\*

Cite This: *J. Am. Chem. Soc.* 2021, 143, 21275–21285

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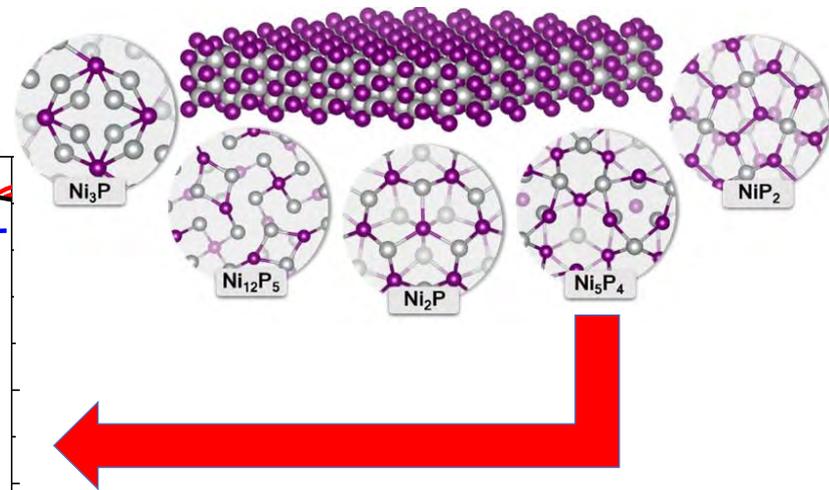
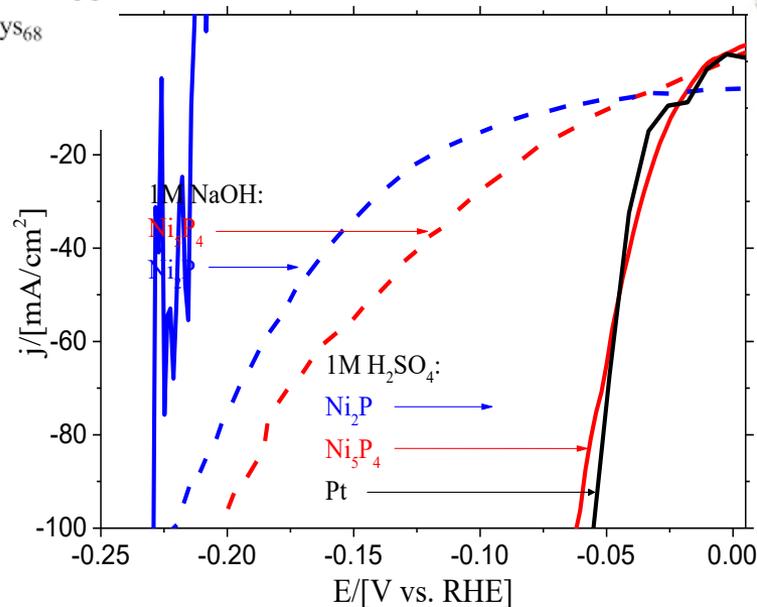
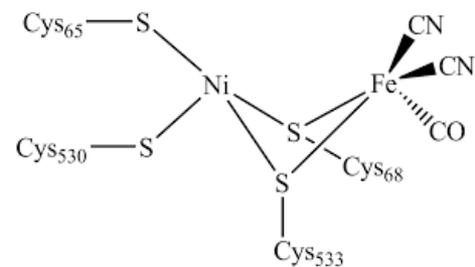
A) Fe<sub>2</sub>P (0001) side view showing the clean surface and (B) reconstructed surfaces. (C) Fe<sub>2</sub>P (0001) top view



\*C<sub>2</sub> precursor to produce ethylene glycol is also the precursor to the C<sub>3</sub> and C<sub>4</sub> products. The \*C<sub>2</sub> aldol precursor (glycolaldehyde) simply reacts faster with \*H to produce more ethylene glycol as the bias decreases than it reacts with the decreasing amount of \*C<sub>1</sub> via a slower, entropically disfavored step

# Transition Metal Phosphides: Bioinspired H<sub>2</sub> Evolution Catalysts

NiFe-Hydrogenase → Ni-organometallic models (fragile) → Ni<sub>x</sub>P<sub>y</sub> solid state catalysts (Robust)



**Activity = PGM performance**

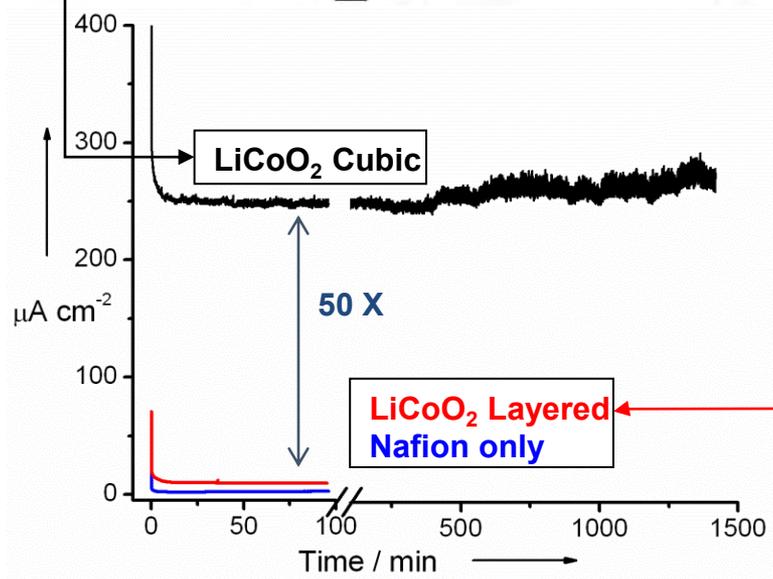
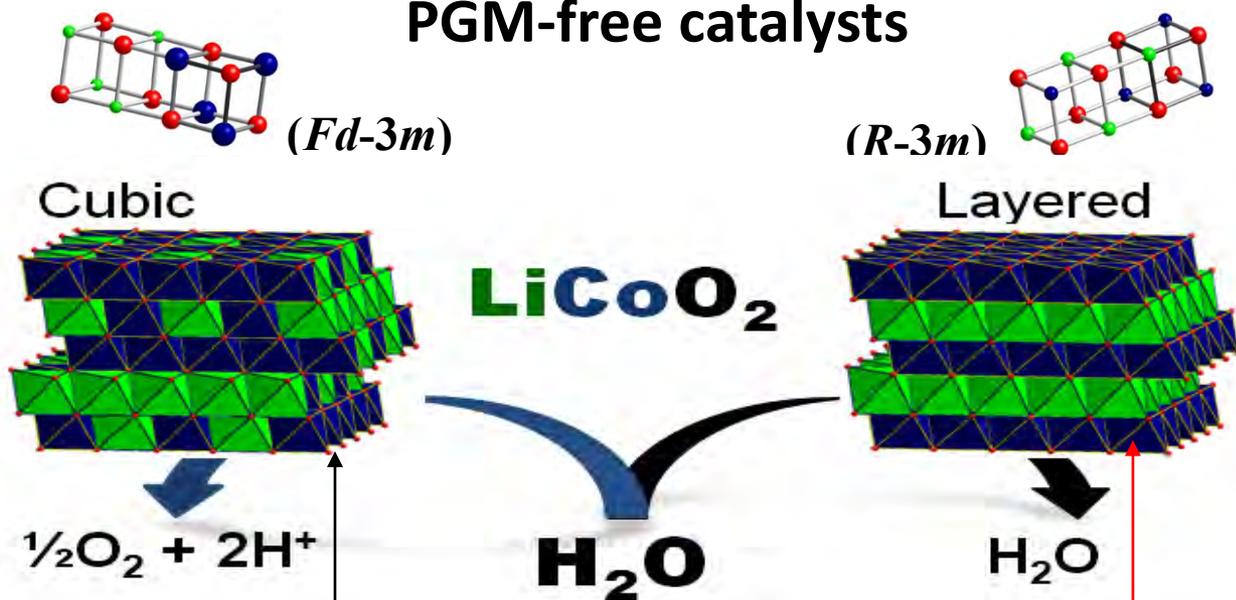
**Stability in both acidic and basic media (>24h, no degradation)**

Laursen, A.B., K.R. Patraju, M.J. Whitaker, M. Retuerto, T. Sarkar, N. Yao, K.V. Ramanujachary, M. Greenblatt and G.C. Dismukes, *Energy & Environmental Science*, 2015. 8: p. 1027-1034.

A. B. Laursen, R. B. Wexler, M. J. Whitaker, E. Izett, R. Rucker, H. Wang, J. Li, M. Greenblatt, A. M. Rappe and G.C. Dismukes, *ACS Catalysis*, 2018(8): p. 4408-4419.



# Water Splitting PGM-free catalysts



Graeme Gardner

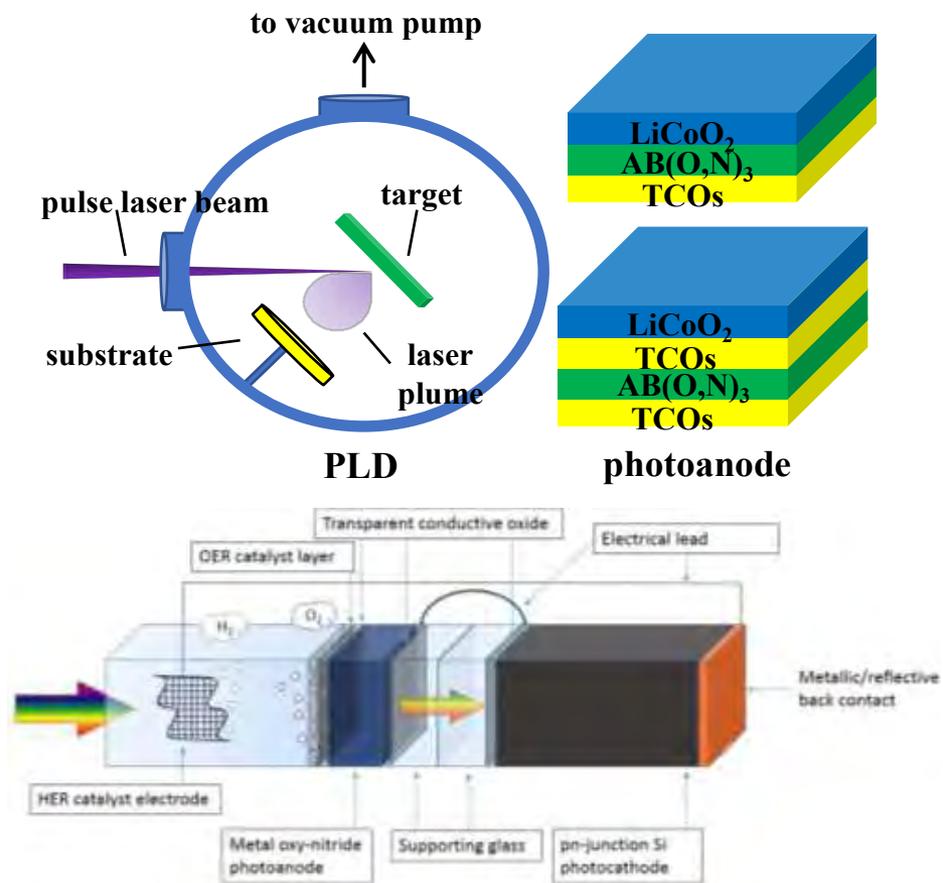
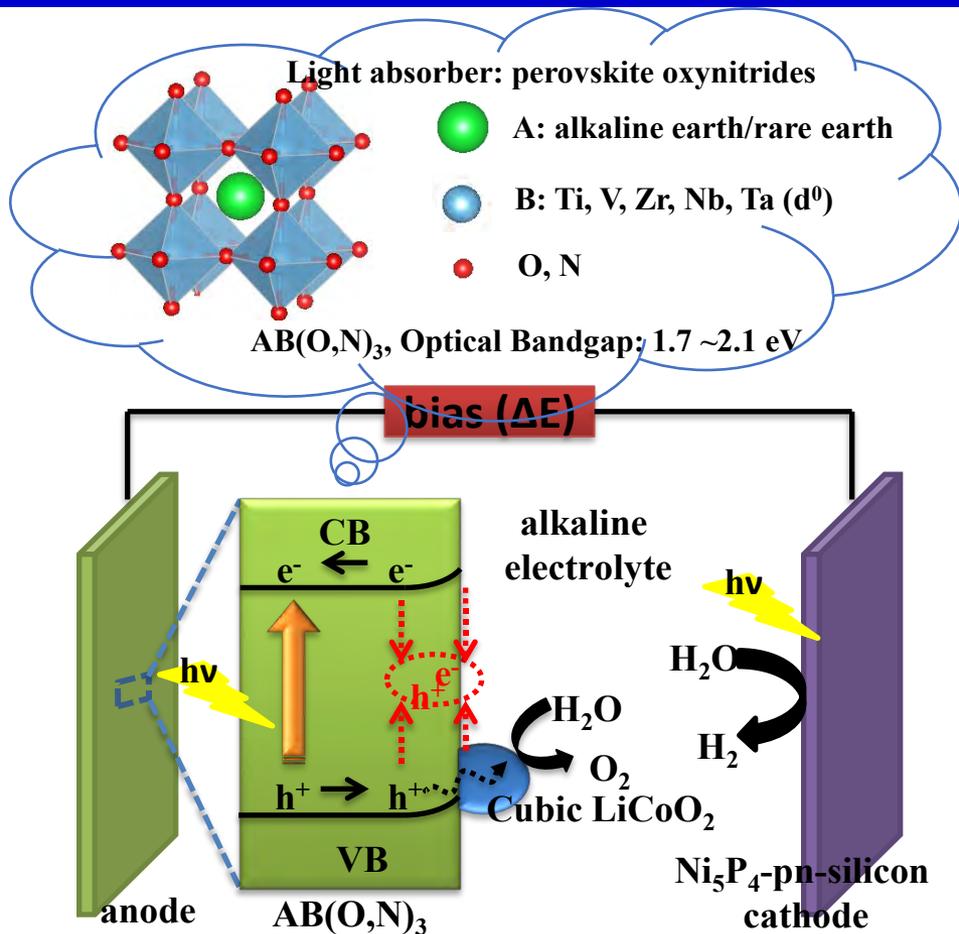
Gardner, Robinson, Smith, Go, Greenblatt, Dismukes (2012) *Angew Chemie*, 51, 1616  
Gardner, Al-Sharab, Danilovic, Go, Ayer, Greenblatt and Dismukes, (2016) *Energy Environ. Sci.*, 9: p. 184--192.



# Hydrogen from Water & Sunlight: Photoanode-Photocathode-Catalysts



GC Dismukes (PI) and E Garfunkel (coPIs), Rutgers University, DOE/NSF-1433492



- Synthesize and investigate selected phase-pure members of perovskite oxynitride series  $AB(O,N)_3$ .
- Characterize the optical bandgaps and photoinduced carrier lifetime of these materials in preparation of attaching OER catalyst.

- Using pulsed laser deposition, prepare photoanode with thin film structures shown above.
- Fabricate photocathode of pn-silicon and  $Ni_5P_4$  HER catalyst
- Investigate two electrolytes system: aqueous alkaline electrolyte solution (pH=14) and alkaline exchange membrane

# **Dismukes Waksman lab projects**

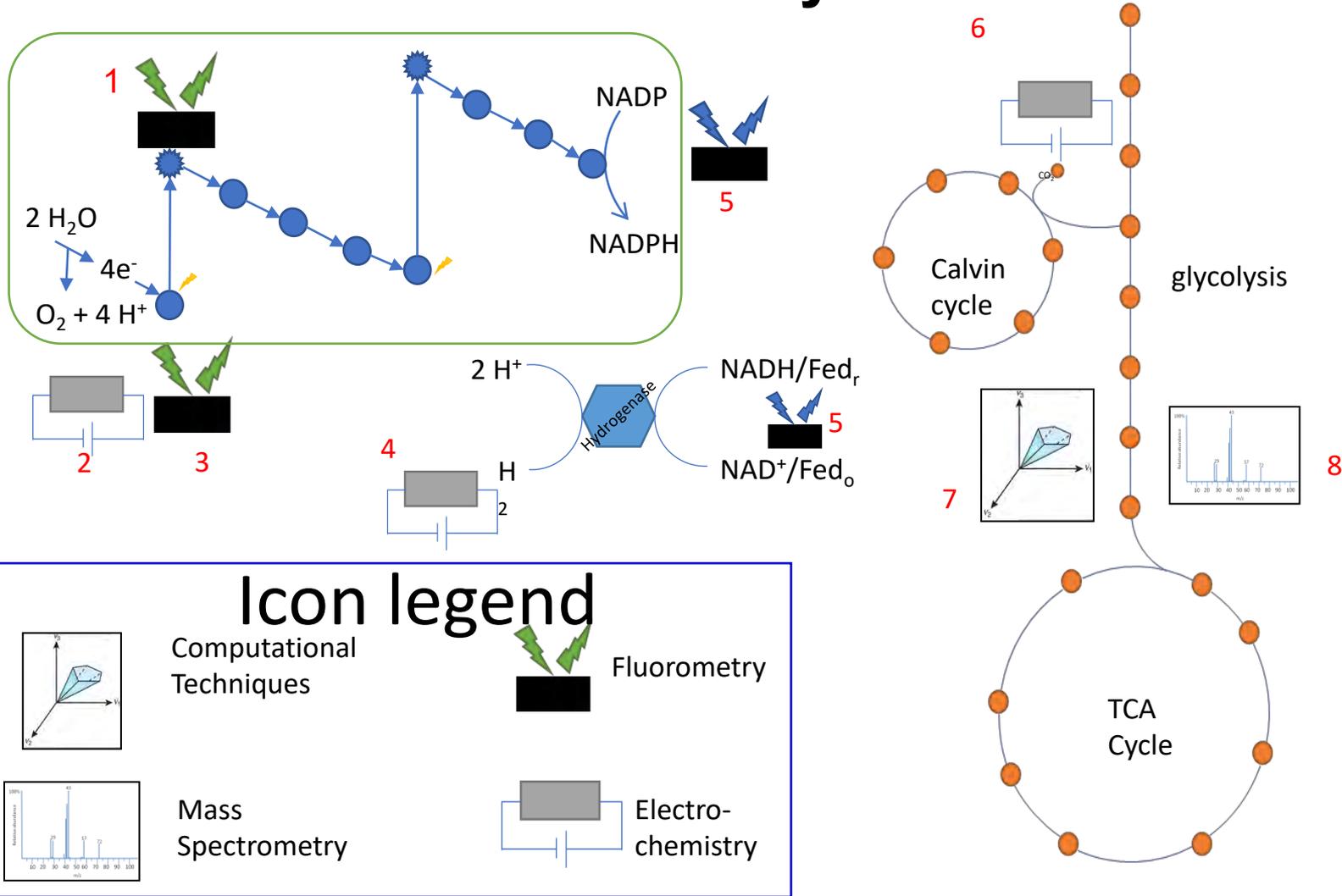
## **Bioenergy from Biomass - Natural Photosynthesis**

- **Photosynthetic Adaptation to Carbon Dioxide**
- **Metabolomics – Experimental Isotopic Fluxes by Mass Spectrometry**
- **Computational Modelling of Metabolism**

## **Biocatalysis**

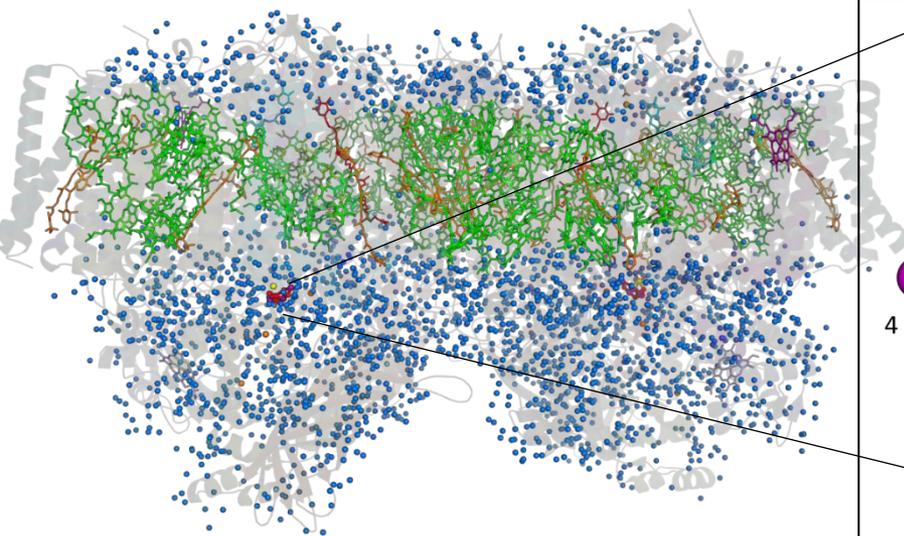
- **Photosystem II and Water Oxidation Catalysis**
- **Overcoming Limitations in Carboxylation**

# Dismukes Waksman lab analytical toolbox

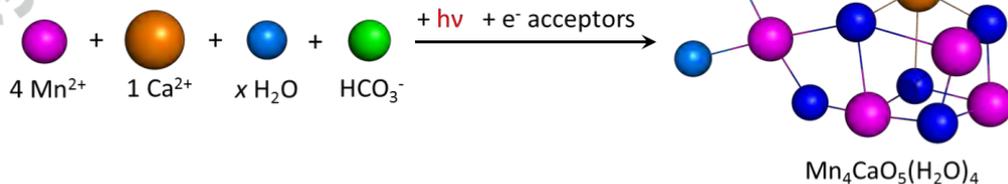


Powerful tools developed in our laboratory offer unique insights into biology

# Bioinorganic Chemistry



## Photo-assembly of the Photosystem II Water-Oxidizing Complex



Understanding the role of bicarbonate ( $\text{HCO}_3^-$ ) in photo-assembly will assist in the development of sources for alternative energy.

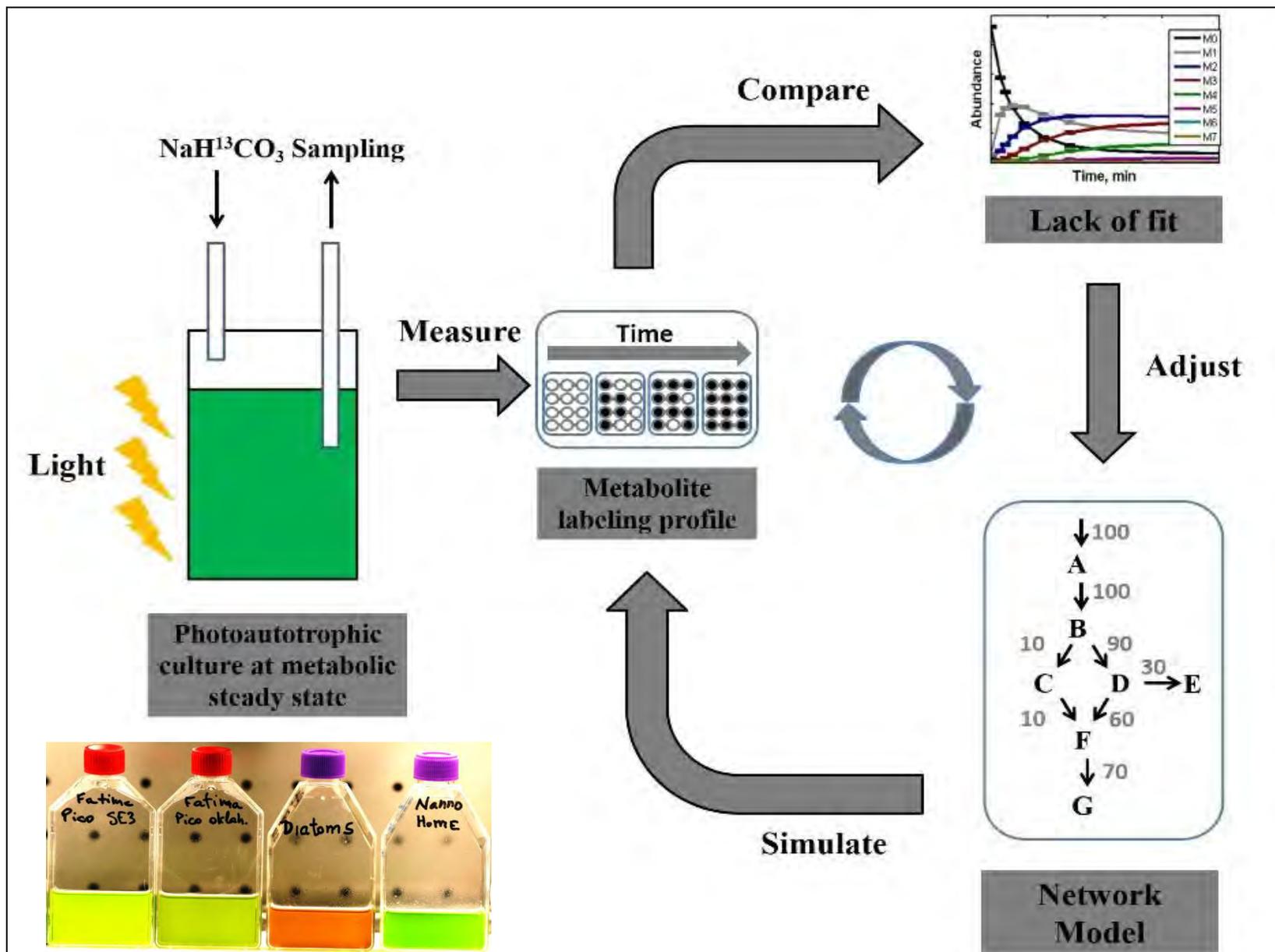
**Credit:** David J. Vinyard & Gerard C. Dismukes

**Project Background:** Photosystem II uses manganese to split water in all oxygenic phototrophs on Earth.

**For the first time we have succeeded in replacing Mn with cobalt in PSII. This opens the door to understanding the chemistry of water oxidation and  $\text{O}_2$  production on Earth.**

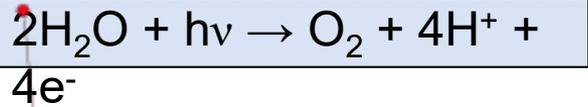
# Can We Unlock the Power of Photosynthetic Metabolism?

## Kinetic Flux Profiling of Photoautotrophic Metabolism

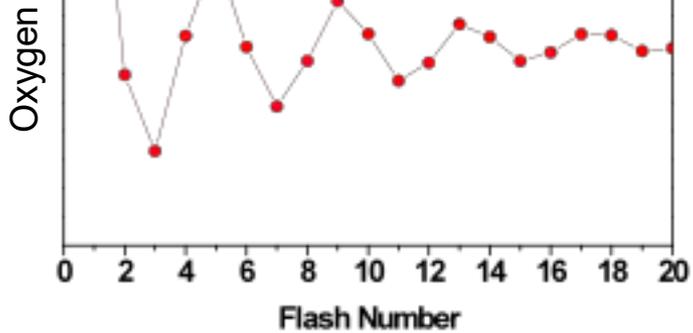


# Oximetry

Flash oxygen electrode (Clark-type),  
membrane-bound platinum-iridium



*A. maxima*

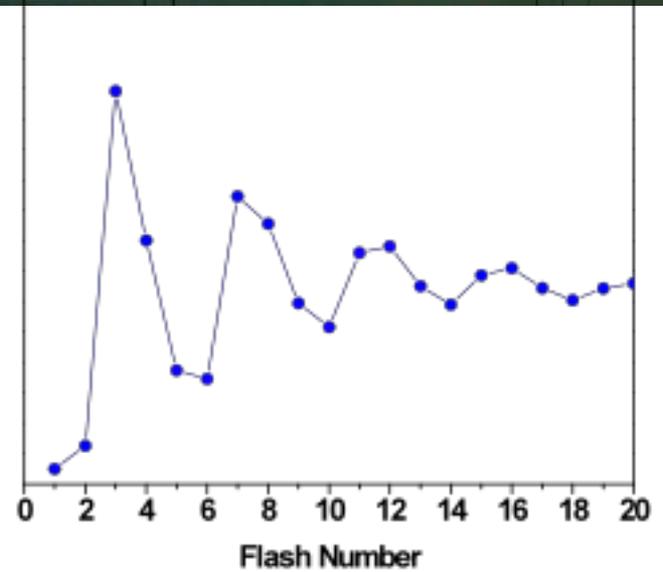


# Chl Fluorescence Induction Fast repetition rate fluorometer



Chl  
Fv/Fm

Variable Fluorescence



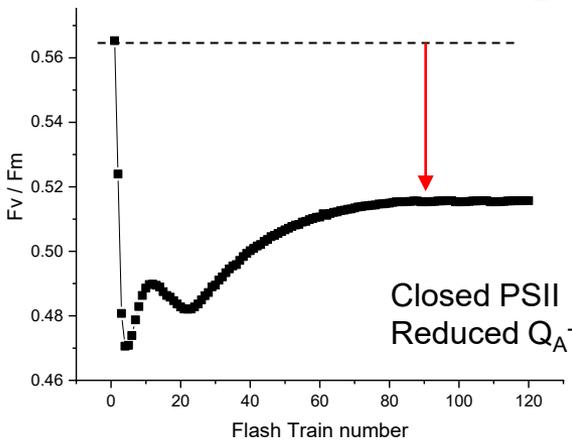
# CO<sub>2</sub>-Dependent Chlorophyll Variable Fluorescence Yield & Rate

Constant growth conditions: Air 0.04% CO<sub>2</sub>

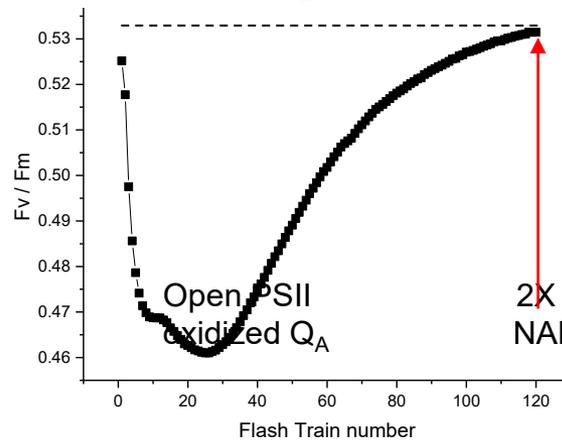
Variable CO<sub>2</sub> in headspace (no bicarb added)

*Nannochloropsis Oceania* –green alga

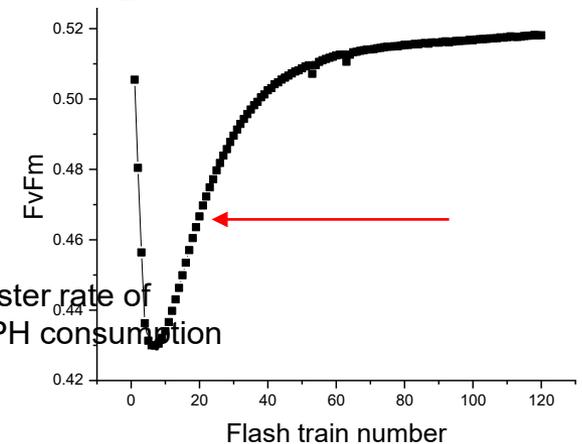
Measure: Air 0.04% CO<sub>2</sub>



2 % CO<sub>2</sub>



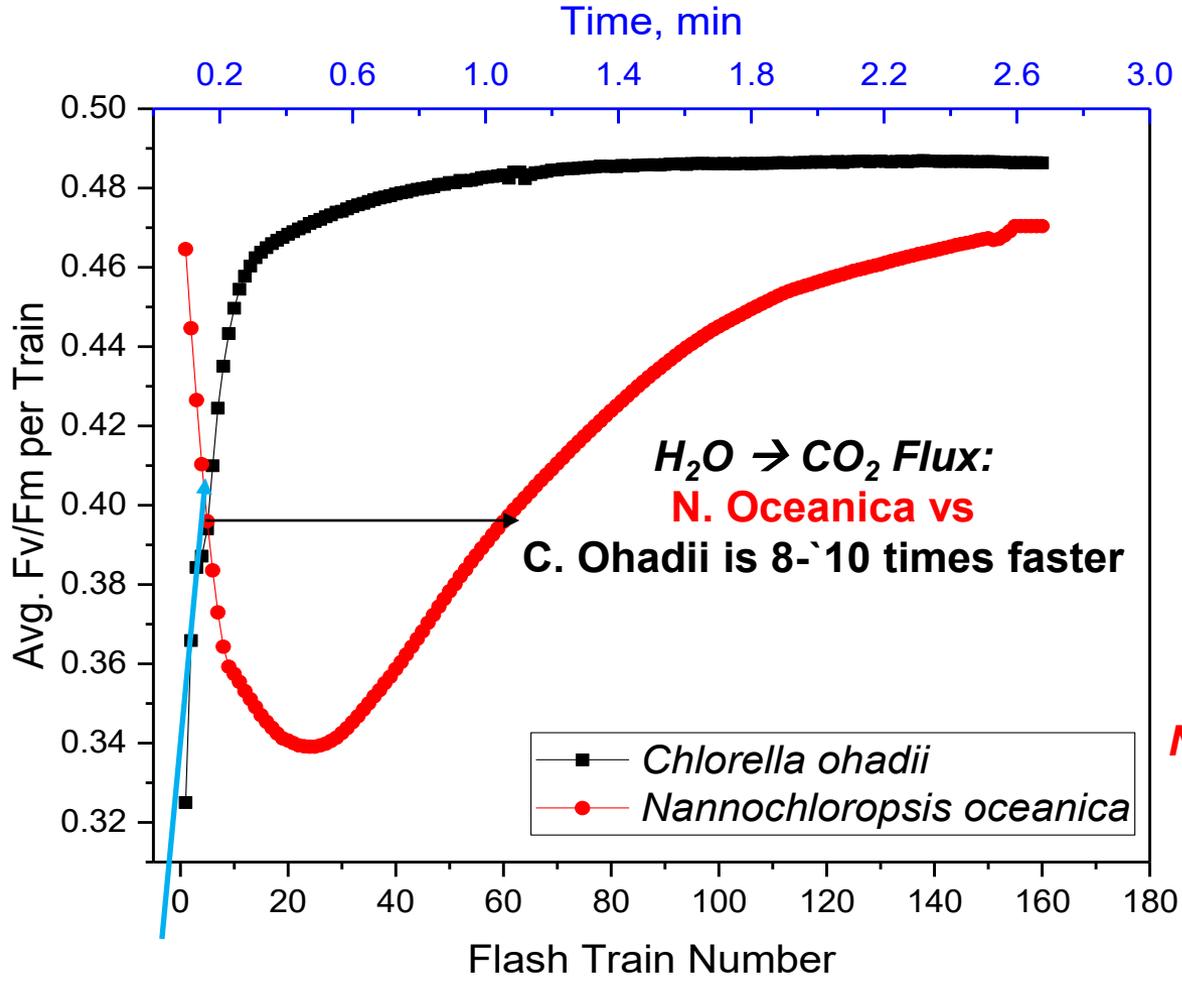
10 % CO<sub>2</sub>



- ✓ 2% + 10% CO<sub>2</sub> opens closed PSII centers (QA-) to the full dark-adapted level
- ✓ 10% CO<sub>2</sub> accelerates the rate of NADPH consumption (~50 → 25 FT)
- ✓ Slow CO<sub>2</sub> diffusion rate
- ✓ RuBisCO is ponderously slow and highly inefficient (+ATP)

# The Usain Bolt of Photosynthesis: *Chlorella Ohadii*

Algal Tree of Life: *Chlorella ohadii* Possesses the Fastest Carbon Fixation Mechanisms Among Eukaryotic Phototrophs:

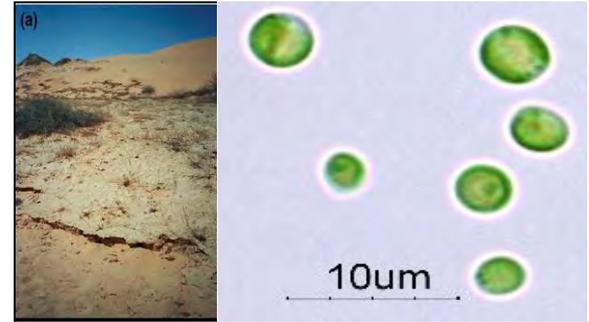


**H<sub>2</sub>O → CO<sub>2</sub> Flux:**  
**N. Oceanica vs**  
**C. Ohadii is 8-10 times faster**

■ *Chlorella ohadii*  
● *Nannochloropsis oceanica*



**C. ohadii:** from the Negev Desert, Israel  
*Treves et al. (2013)*



**N. oceanica:** marine heterokont alga  
**slow growing lipid producer**

# Photosynthetic Adaptation to Carbon Dioxide Gradients in Yellowstone: A glimpse into the future of climate change?

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