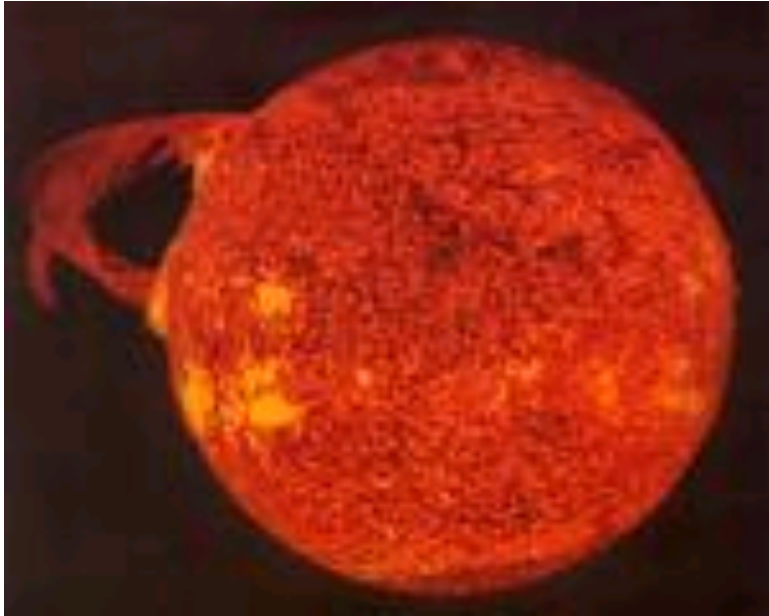


The 21st Century Solar Army

Carl Wamser Symposium 28 September 2012



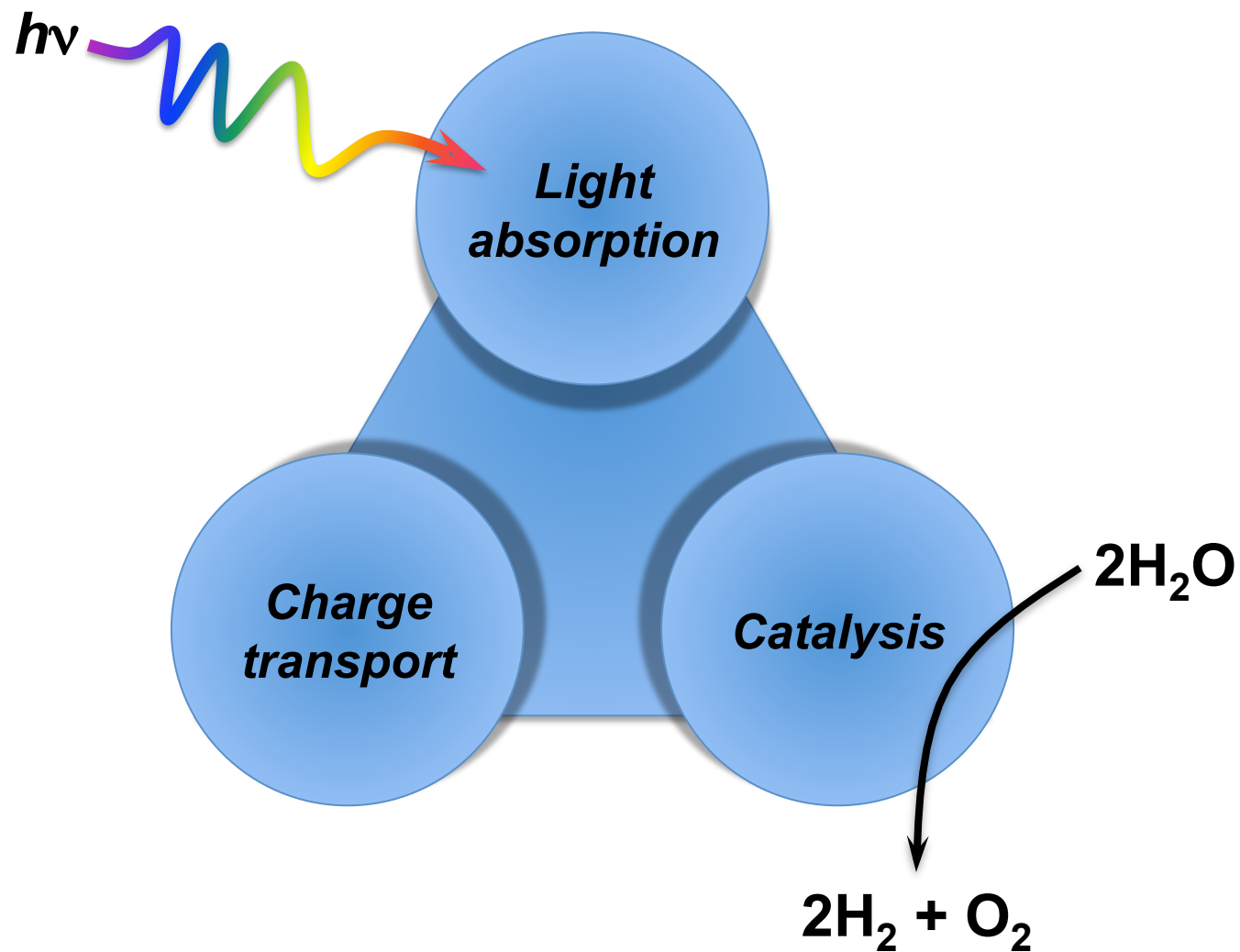
Solar Energy!



- **More energy from sunlight strikes the earth in 1 hour than all the energy consumed on the planet in 1 year!**



Solar Fuels Science



Powering the Planet





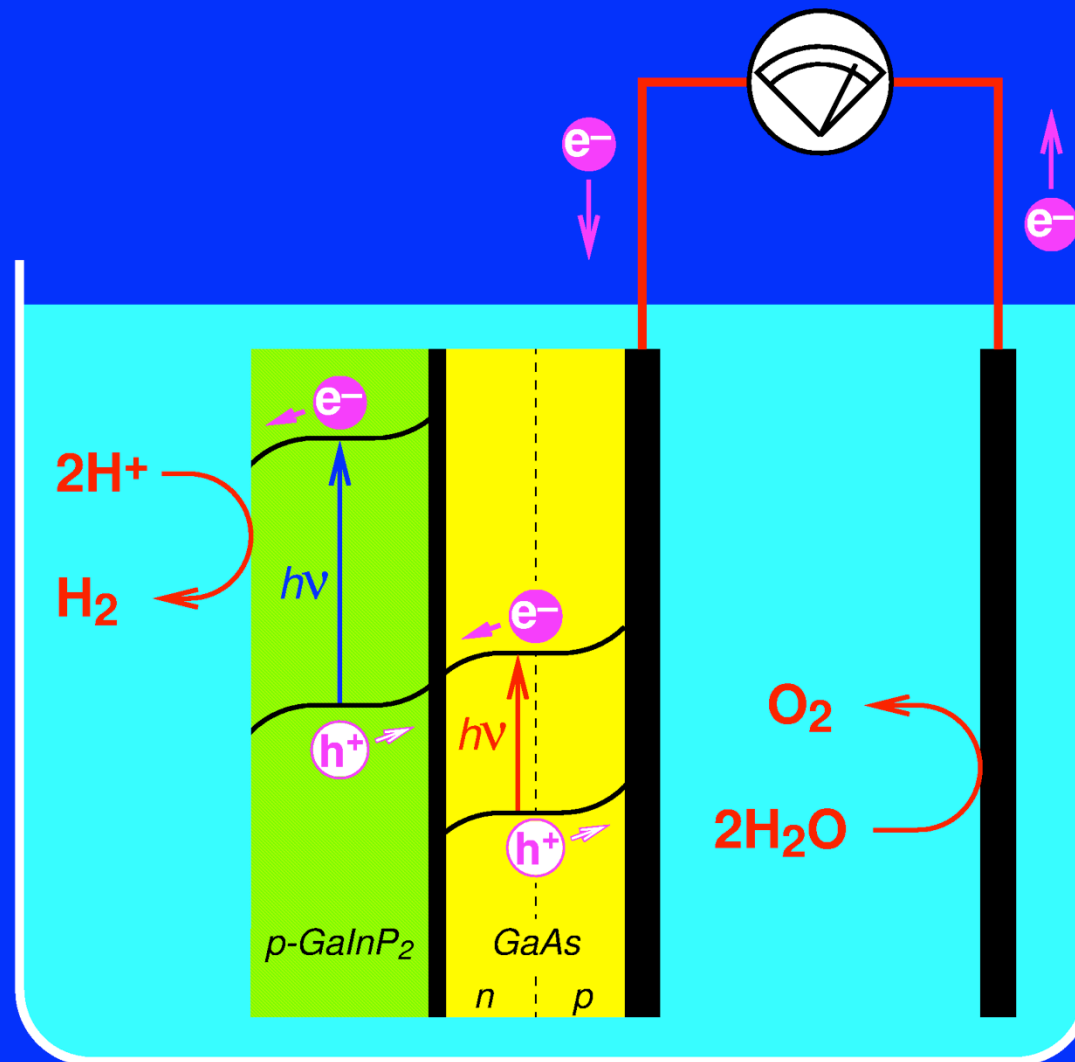
Gray, H. B.; Maverick, A. W.. Solar chemistry of metal complexes. *Science* **1981**, 214, 1201-5.

Khaselev, O.; Turner, J. A. *Science* **1998**, 280, 425-427.

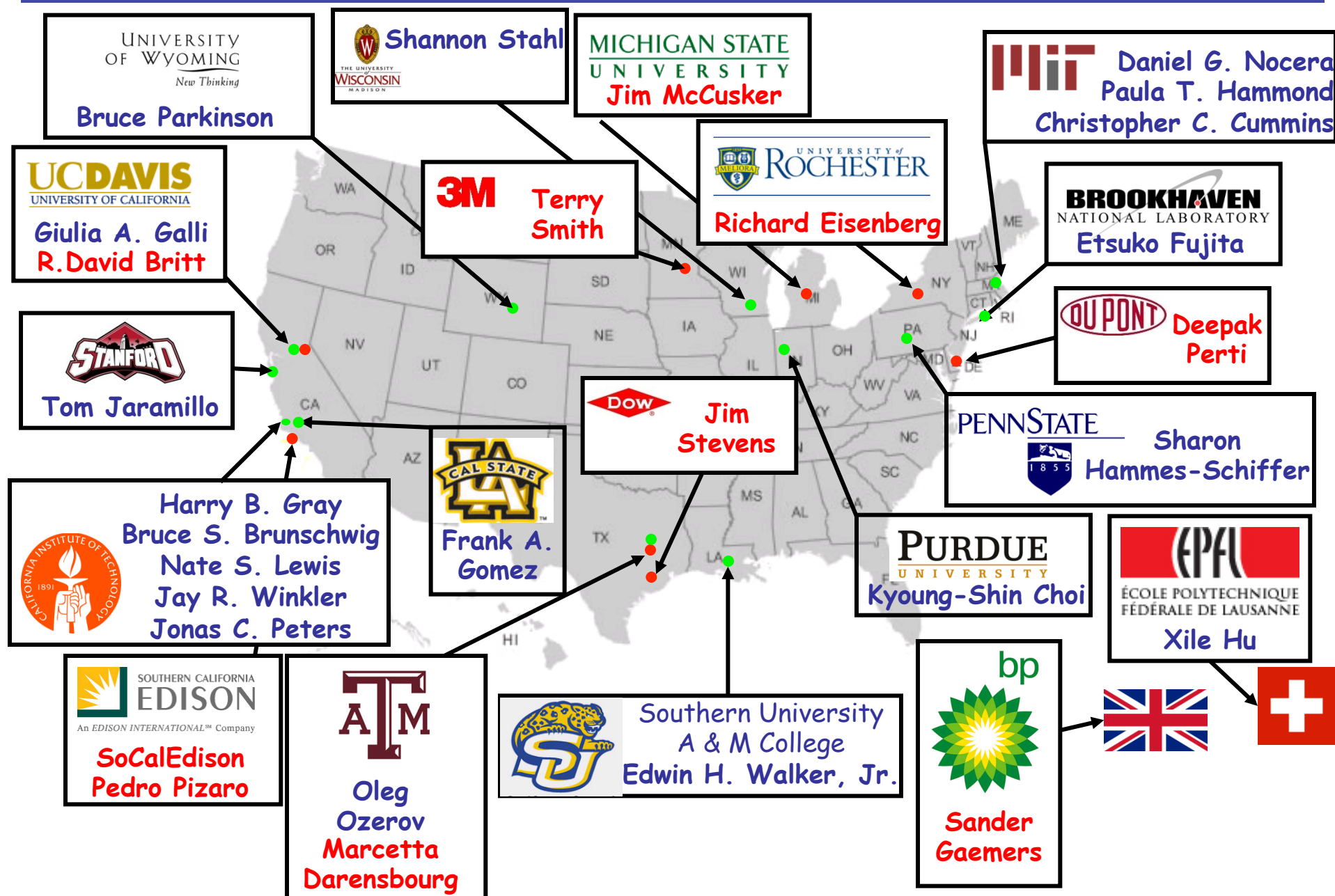
Lewis, N. S.; Nocera, D. G.. Powering the planet: chemical challenges in solar energy utilization. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, 103, 15729-15735.

Gray, Harry B. Powering the planet with solar fuel. *Nat. Chem.* **2009**, 1, 112.

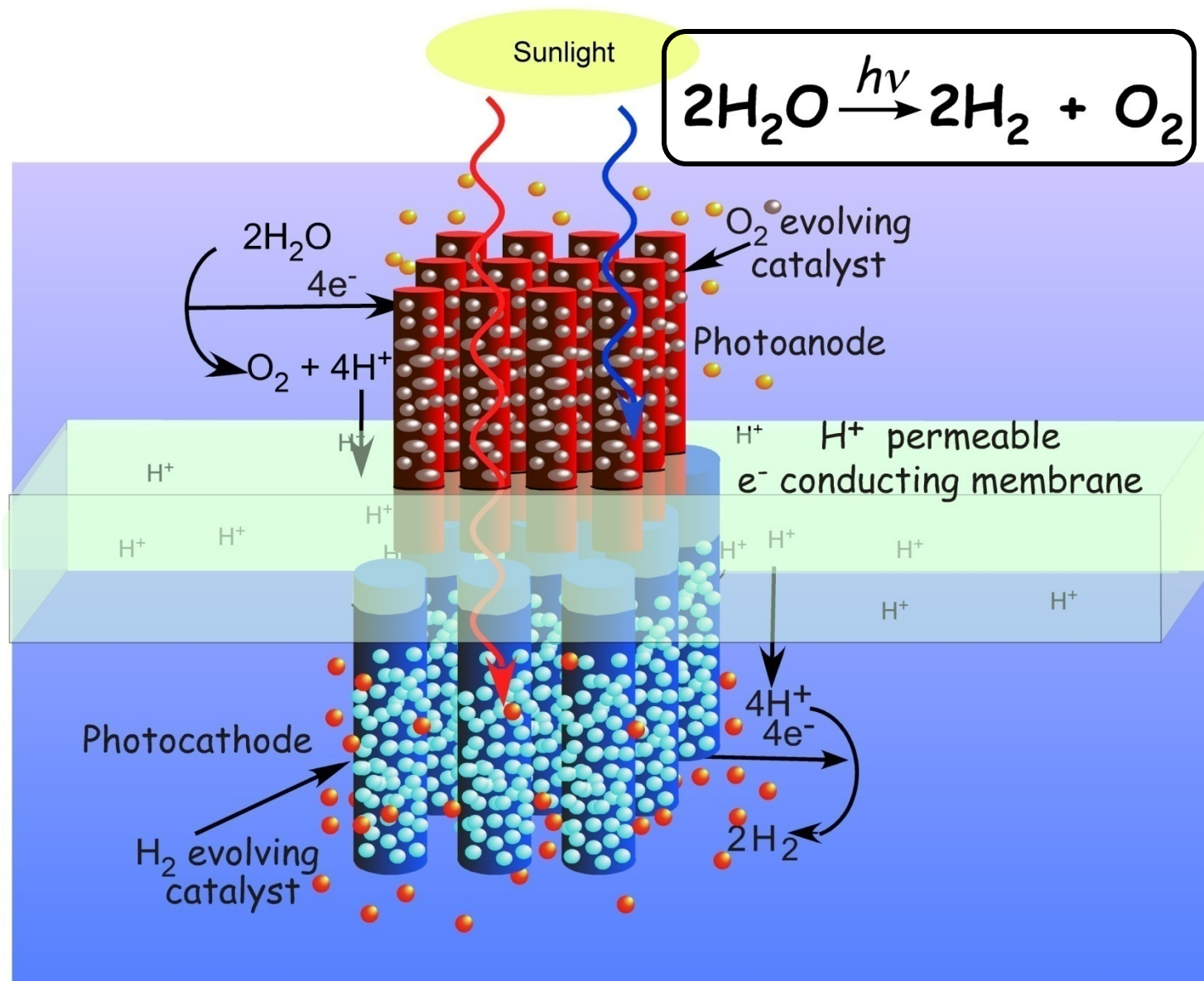
Turner (NREL) Water-Splitting Solar Cell



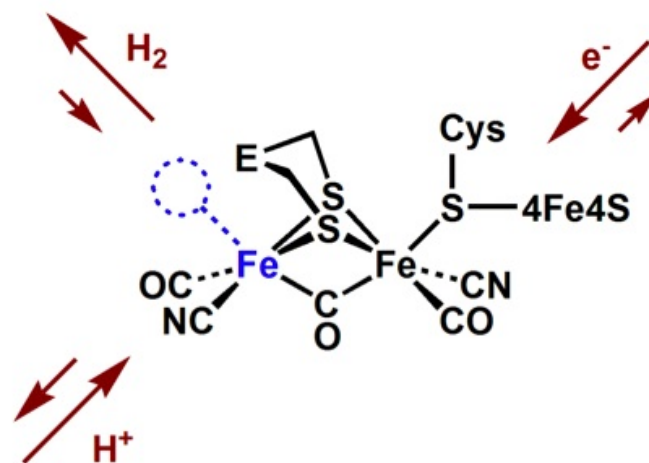
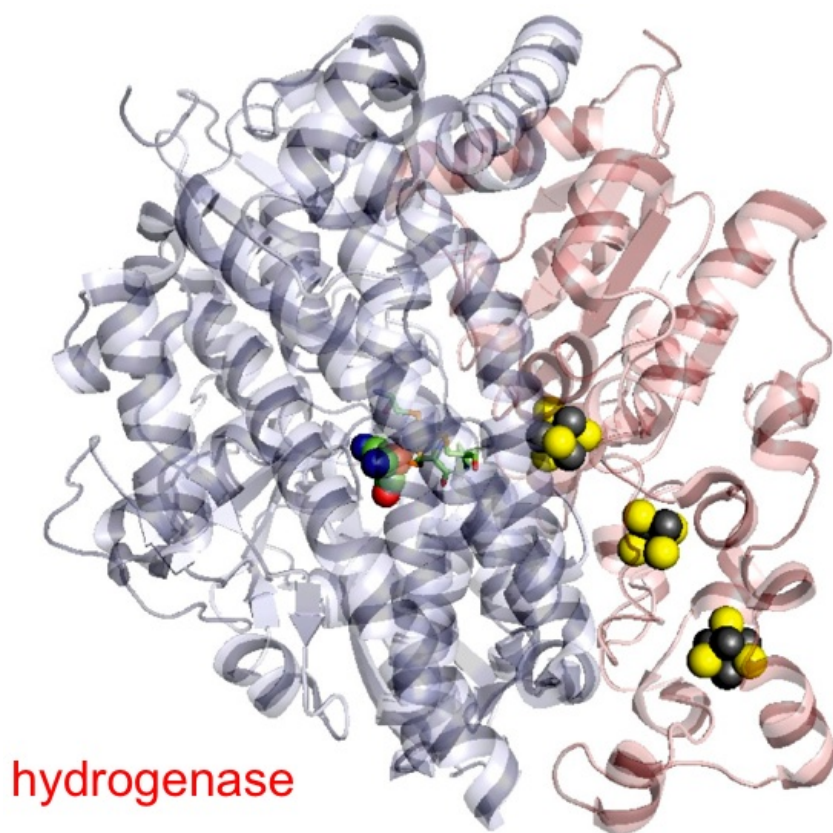
NSF CCI Solar Fuels Program



Powering the Planet: A Center for Chemical Innovation



Biological Catalysis



- Active site of $\text{Fe}_2\text{-H}_2\text{ase}$

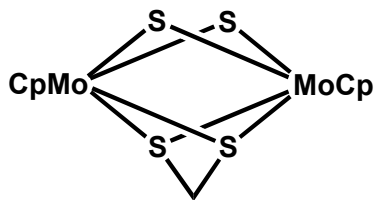
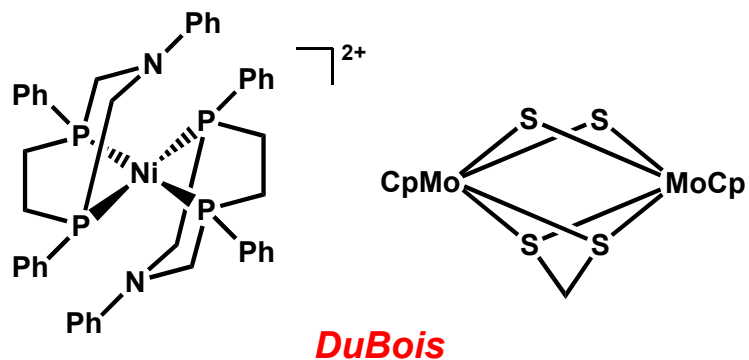
- TOF = 9000 s^{-1} at $30\text{ }^\circ\text{C}$

Frey, M. *ChemBioChem* **2002**, 3, 153.

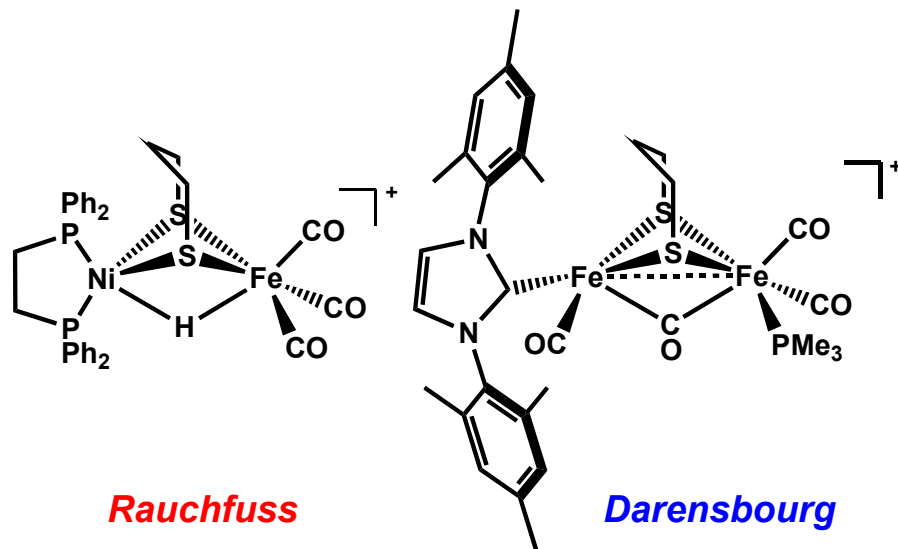
Fontecilla-Camps, J. C.; Volbeda, A.; Cavazza, C.; Nicolet, Y. *Chem. Rev.* **2007**, 107, 4273.

Shriver, D. F.; Atkins, P. W.; Overton, T. L.; Rourke, J. P.; Weller, M. T.; Armstrong, F. A. *Inorganic Chemistry, Fourth Edition* **2006**.

H_2 Evolving Catalysts

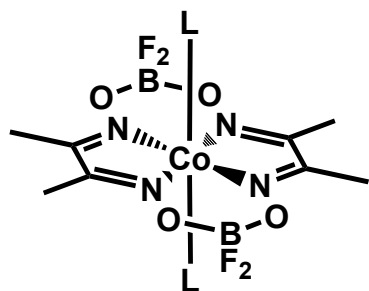


DuBois



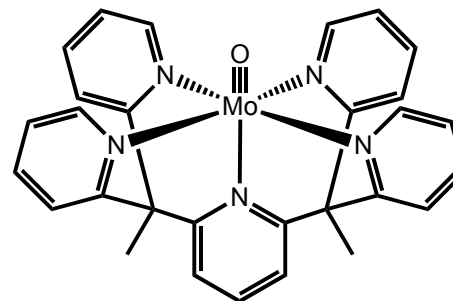
Rauchfuss

Darensbourg



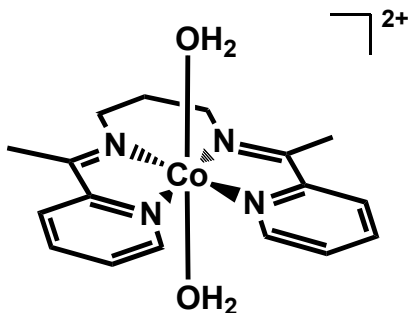
L = MeCN

**Artero,
Espenson,
Fontecave**

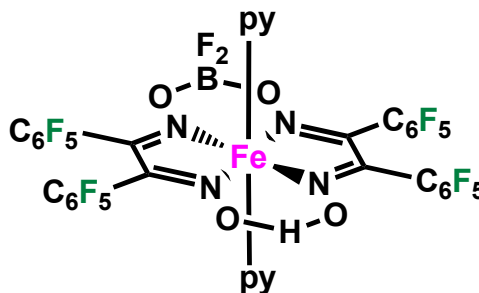


**Chang,
Long**

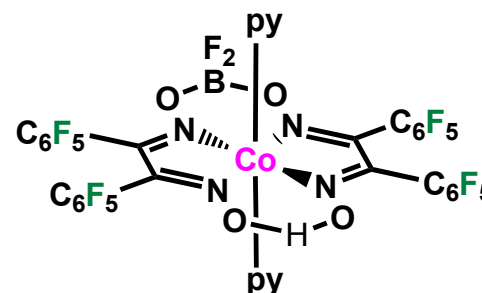
Caltech H_2 Evolving Catalysts



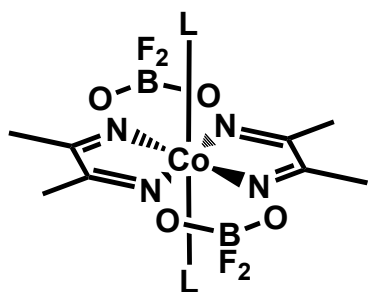
Bryan Stubbert



Mike Rose

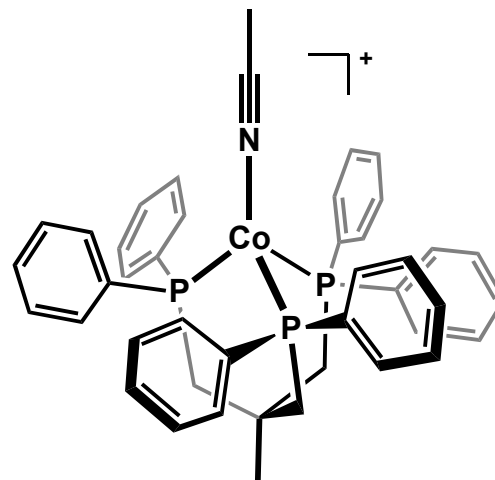


Rocio Mercado



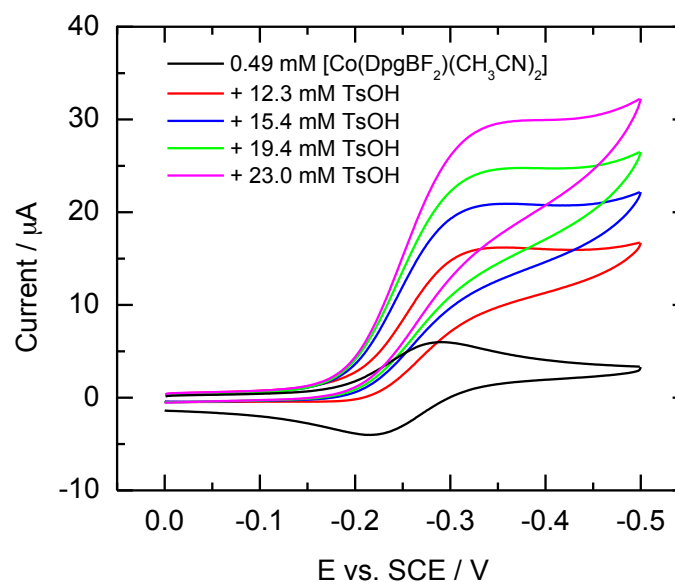
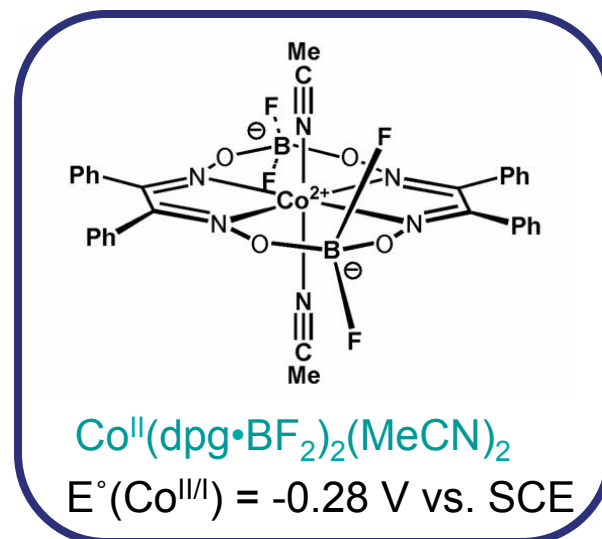
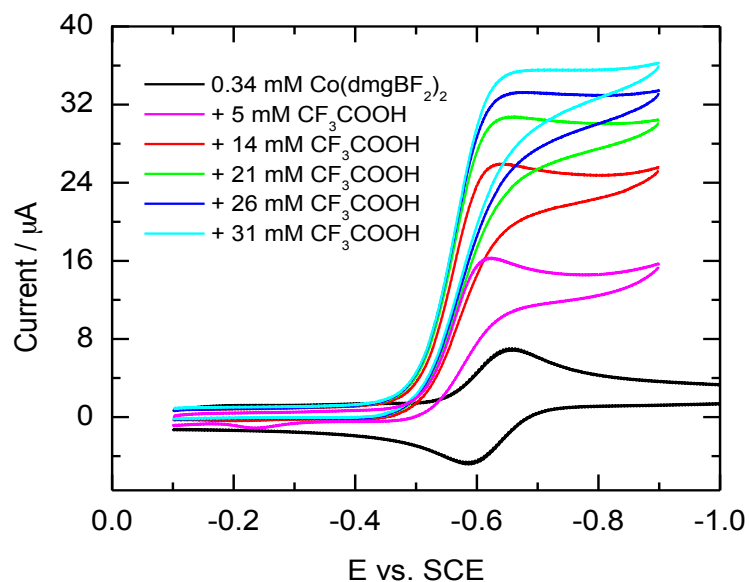
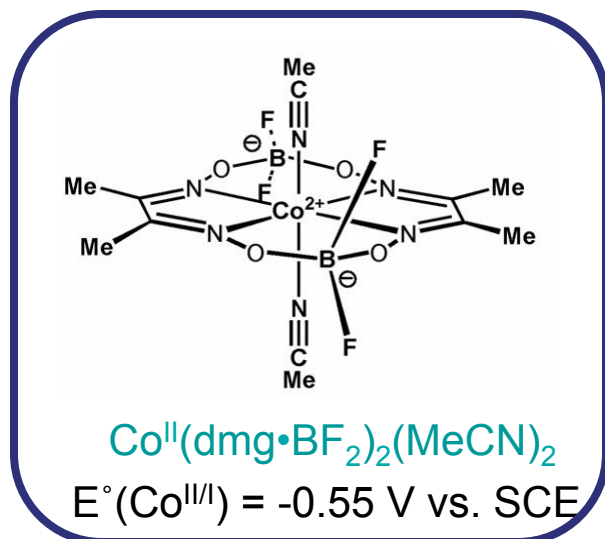
$L = MeCN$

Jillian Dempsey



Smaranda Marinescu

Cobalt Catalyzed H₂ Evolution at Low Overpotentials

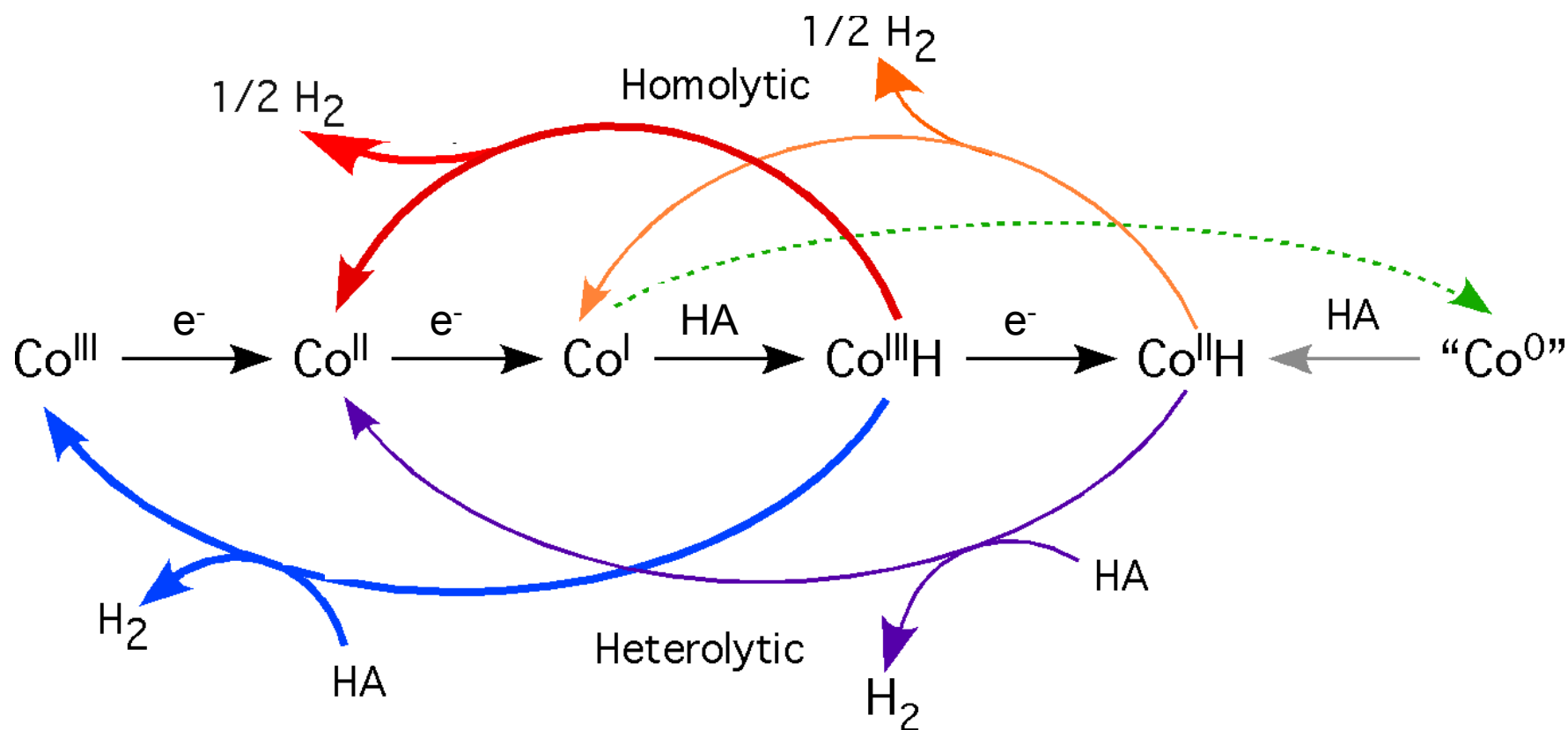


Connolly, P.; Espenson, J.H. *Inorg. Chem.* **1986**, 25, 2684-2688.

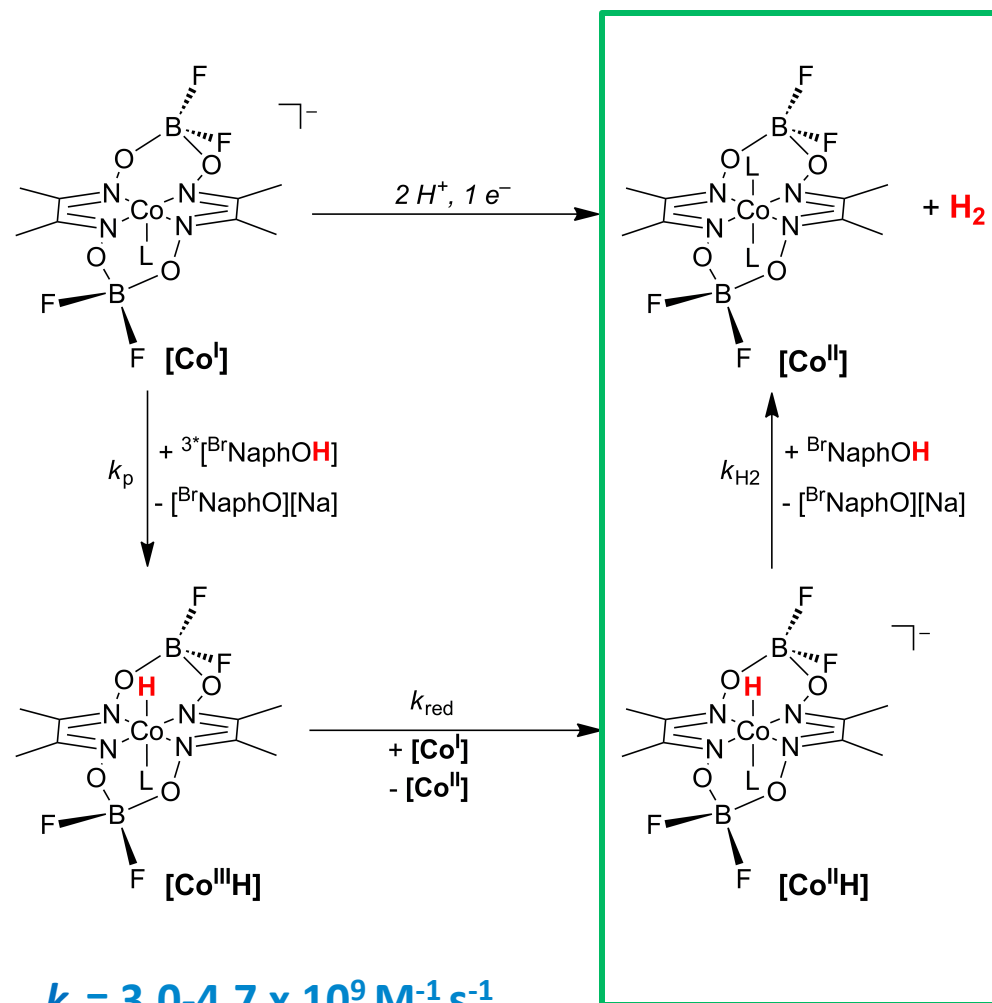
Hu, X.; Cossairt, B.M.; Brunschwig, B.S.; Lewis, N.S.; Peters, J.C. *Chem. Commun.* **2005**, 4723-4725.

Razavet, M.; Artero, V.; Fontecave, M. *Inorg. Chem.* **2005**, 44, 4786-4795.

H₂ Evolution Pathways

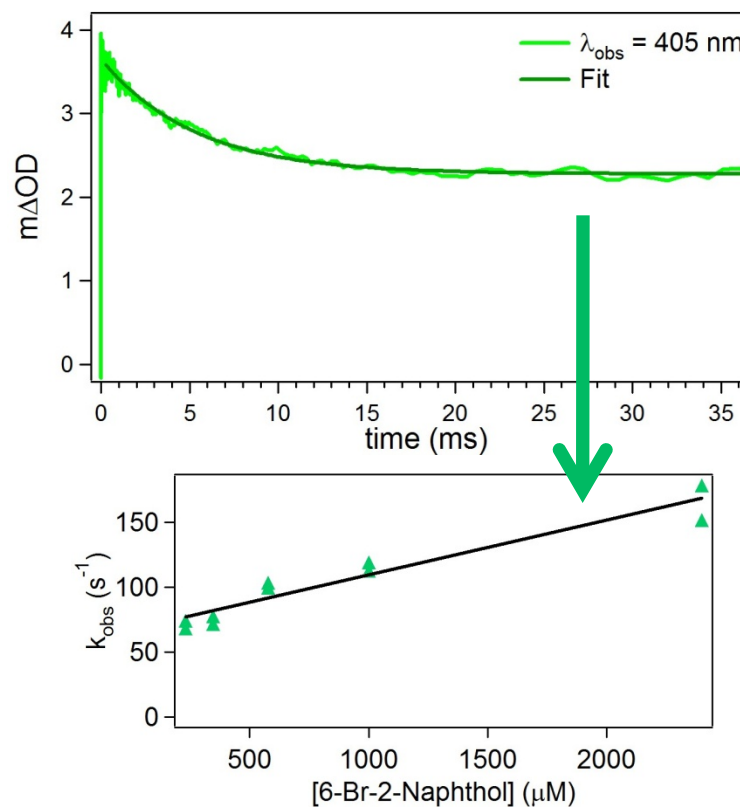


Mechanism of H₂ Evolution



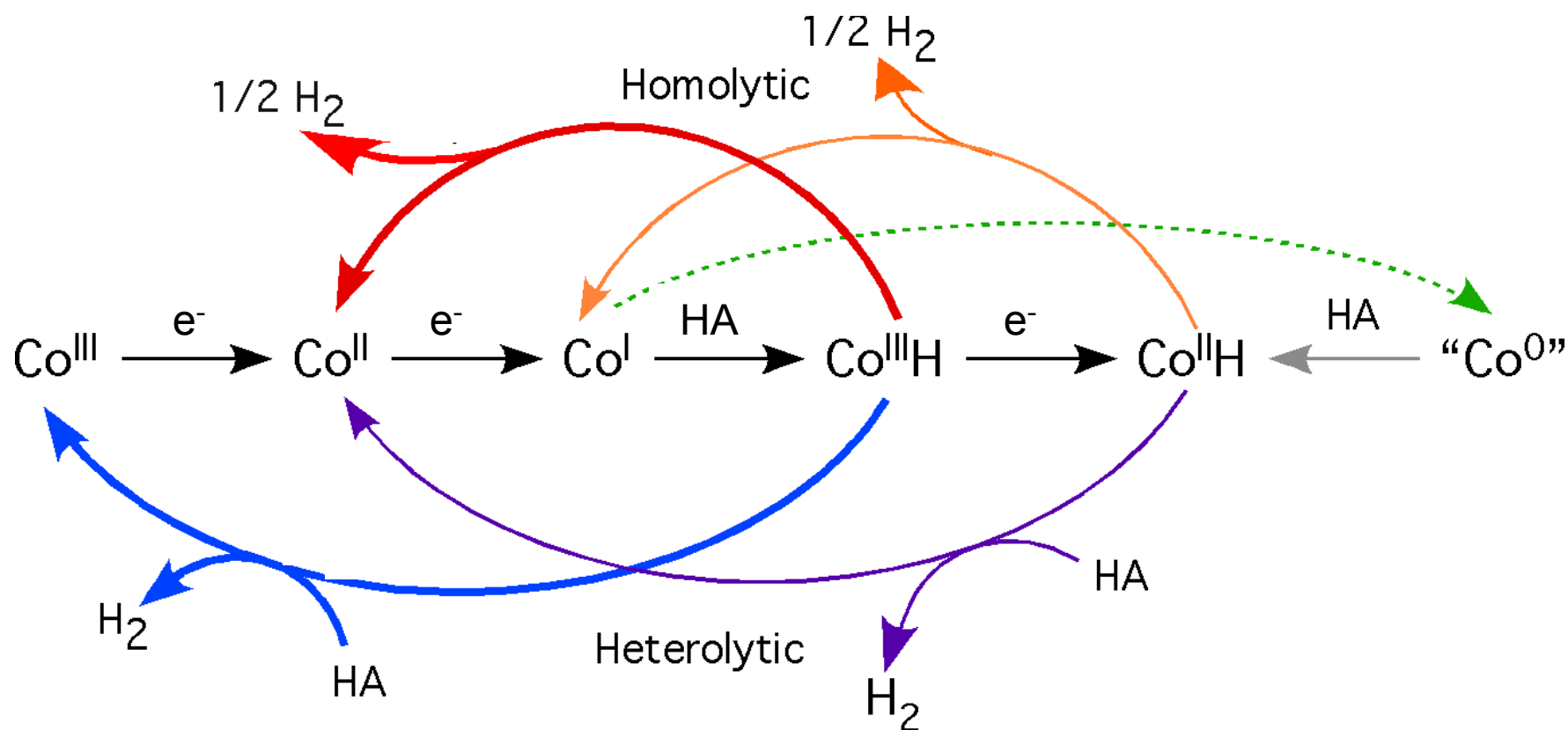
$$k_p = 3.0-4.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{red} = 5.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$

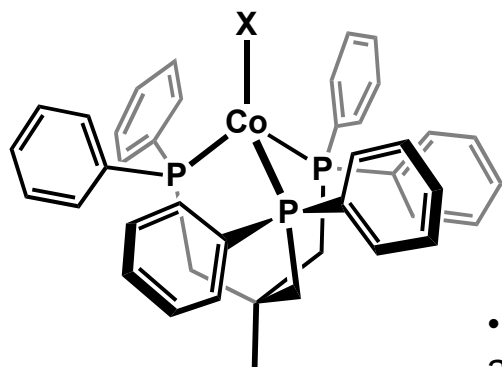


$$k_{H_2} = 4.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$$

H₂ Evolution Pathways

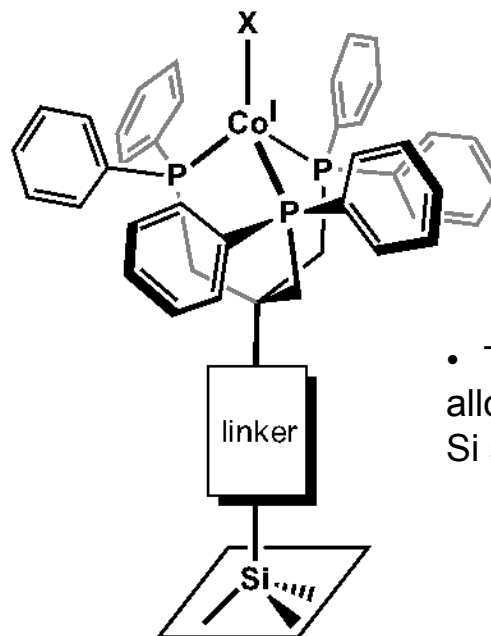


Tripodal Phosphine Cobalt Complexes

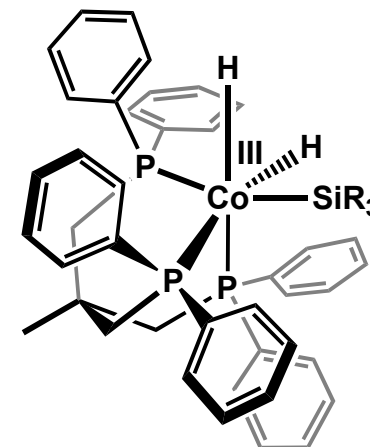
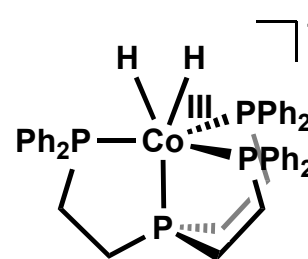
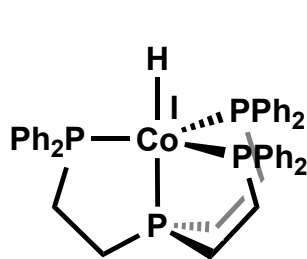
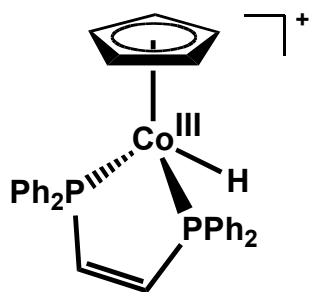
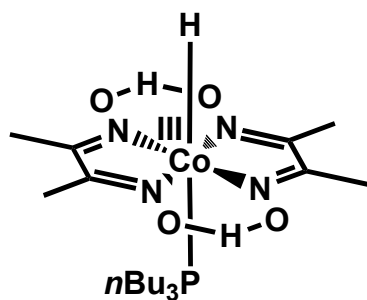


- The ligand framework allows for facile tuning of the reduction potential.

X = anionic ligand

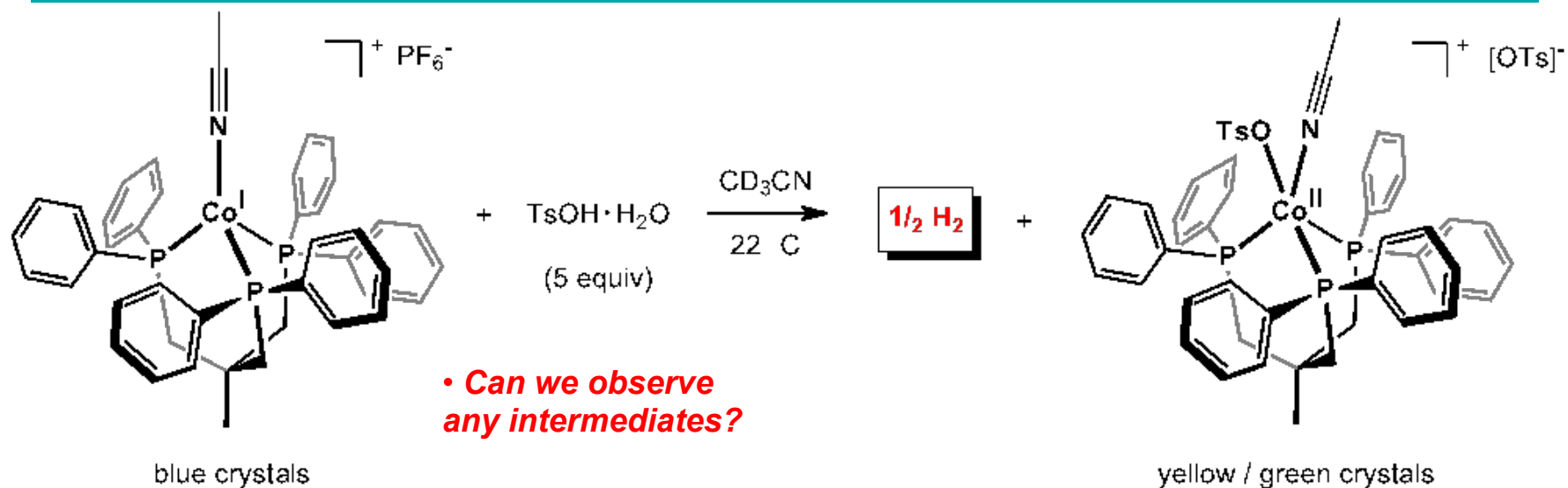


- The ligand framework allows for attachment to Si surface.



Sacconi, L.; Ghilardi, C. A.; Mealli, C.; Zanobini, F. *Inorg. Chem.* **1975**, *14*, 1380.
 Heinze, K.; Huttner, G.; Zsolnai, L.; Schober, P. *Inorg. Chem.* **1997**, *36*, 5457.
 Ghilardi, C. A.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1975**, *14*, 1790.
 Bianchini, C.; Mealli, C.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 8725.
 Heinekey, D. M.; Liegeois, A.; van Roon, M. *J. Am. Chem. Soc.* **1994**, *116*, 8388.
 Mautz, J.; Heinze, K.; Wade, H.; Huttner, G. *Eur. J. Inorg. Chem.* **2008**, 1413.
 Winterhalter, U.; Zsolnai, L.; Kircher, P.; Heinze, K.; Huttner, G. *Eur. J. Inorg. Chem.* **2001**, 89.
 Koelle, U.; Ohst, S. *Inorg. Chem.* **1986**, *25*, 2689.

Reduction of Protons by Cobalt(I)



Selected distances (Å):

Co(1)–N(1) = 1.919(2) Å

Co(1)–O(1) = 1.9849(17) Å

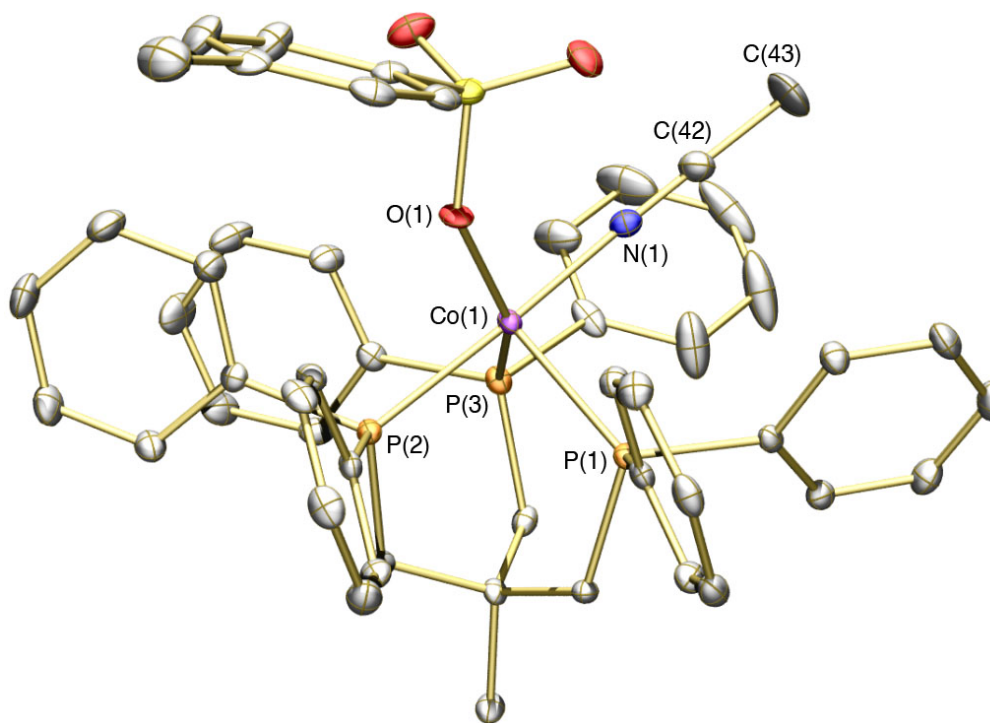
Co(1)–P(1) = 2.2788(8) Å

Co(1)–P(2) = 2.2101(8) Å

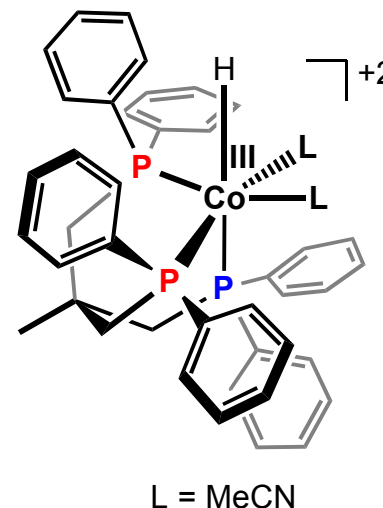
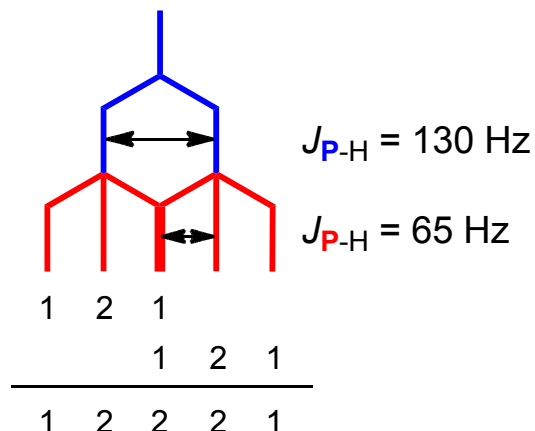
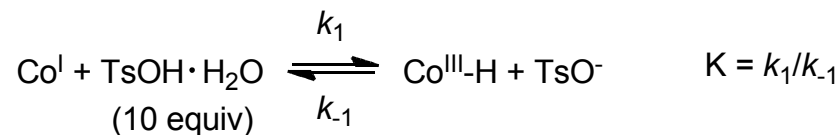
Co(1)–P(3) = 2.2207(8) Å

N(1)–C(42) = 1.133(3) Å

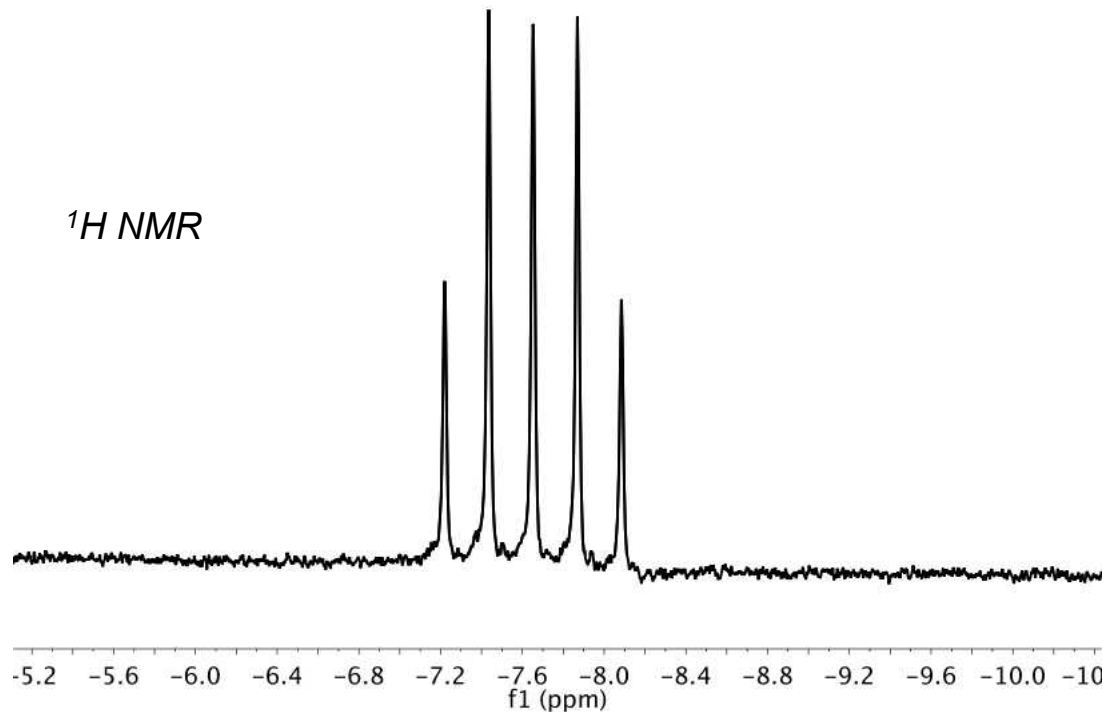
C(42)–C(43) = 1.452(4) Å



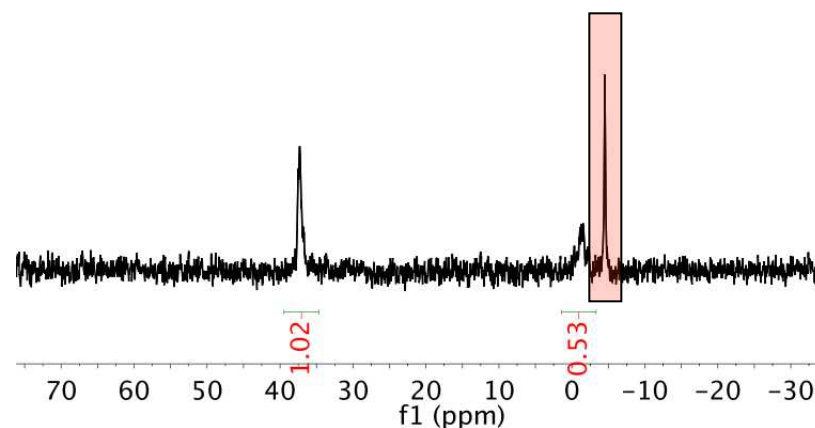
NMR Spectroscopic Evidence for $\text{Co}^{\text{III}}\text{-H}$



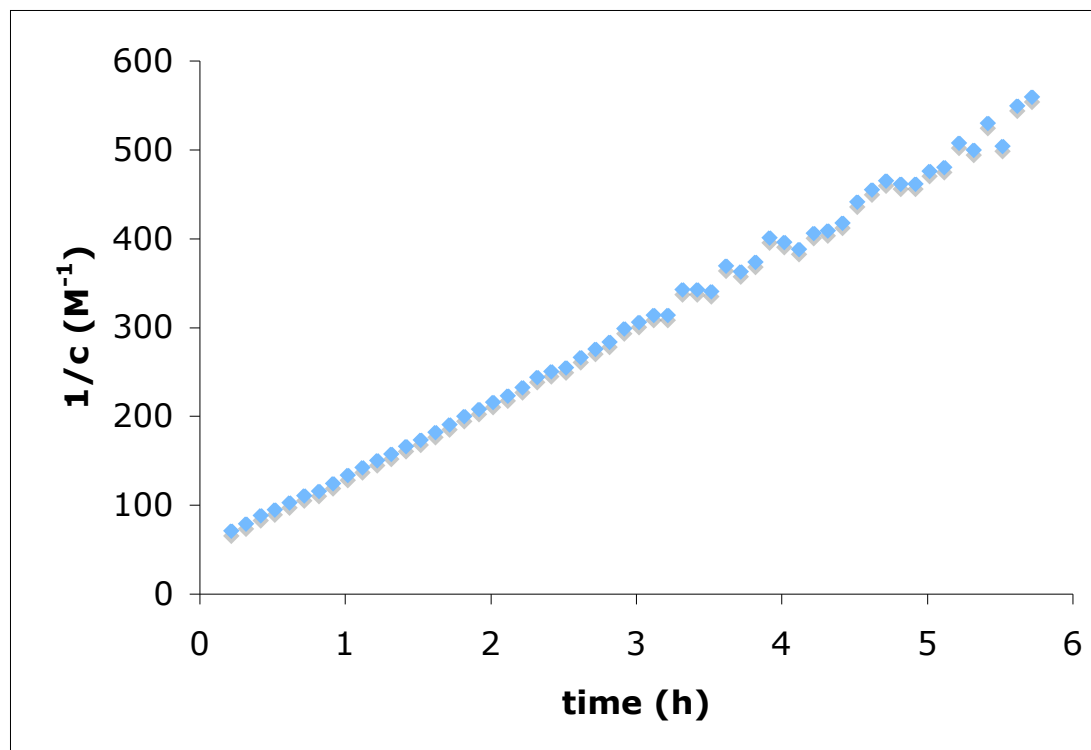
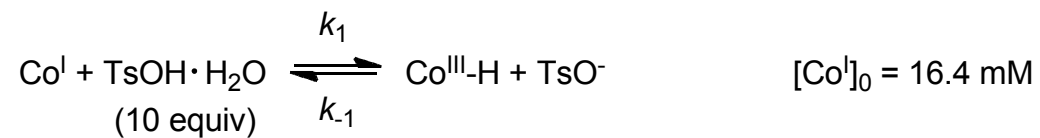
^1H NMR



^{31}P NMR

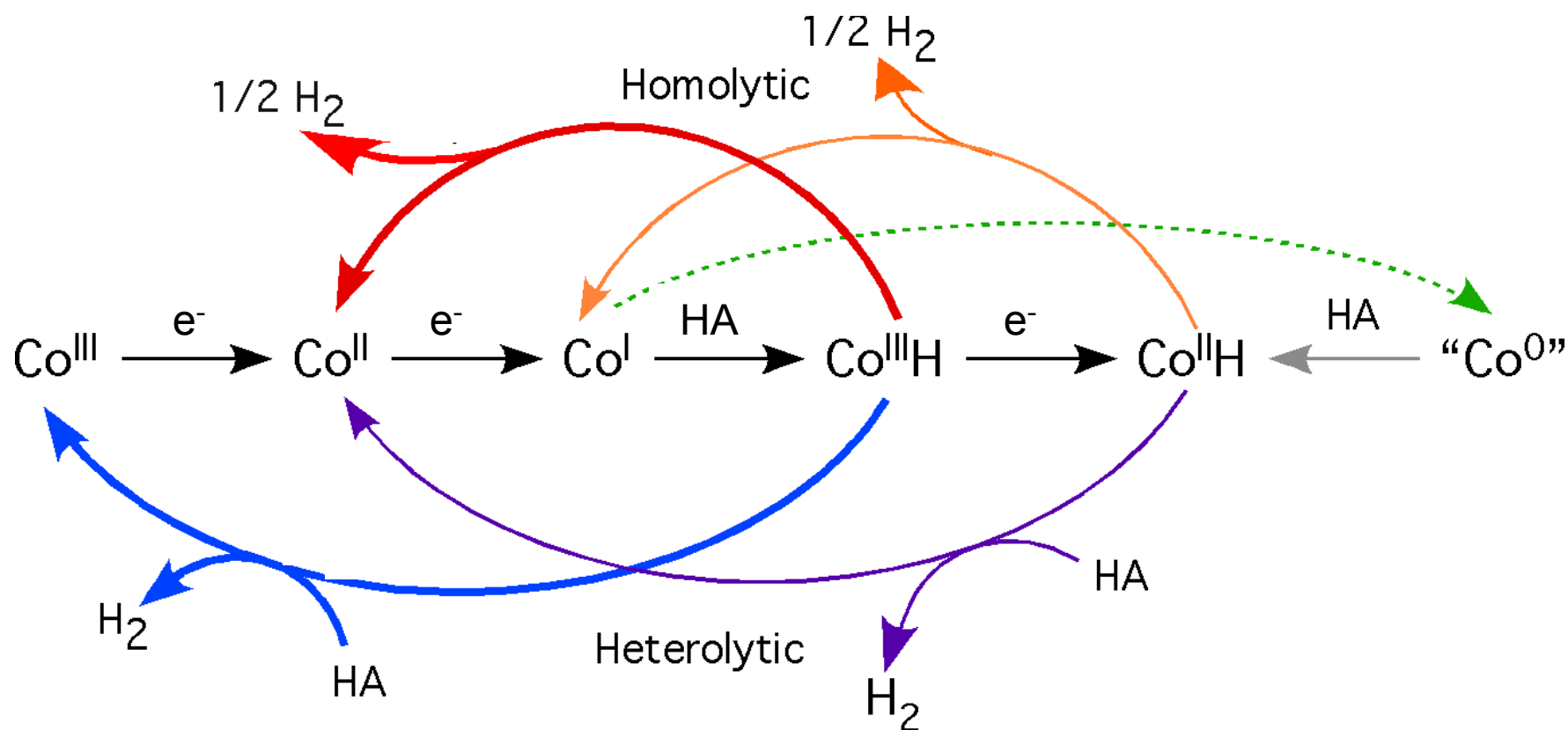


Second Order Decay of $\text{Co}^{\text{III}}\text{-H}$



- 2nd order dependence on $[\text{Co}^{\text{III}}\text{-H}]$

H₂ Evolution Pathways



Catalysis

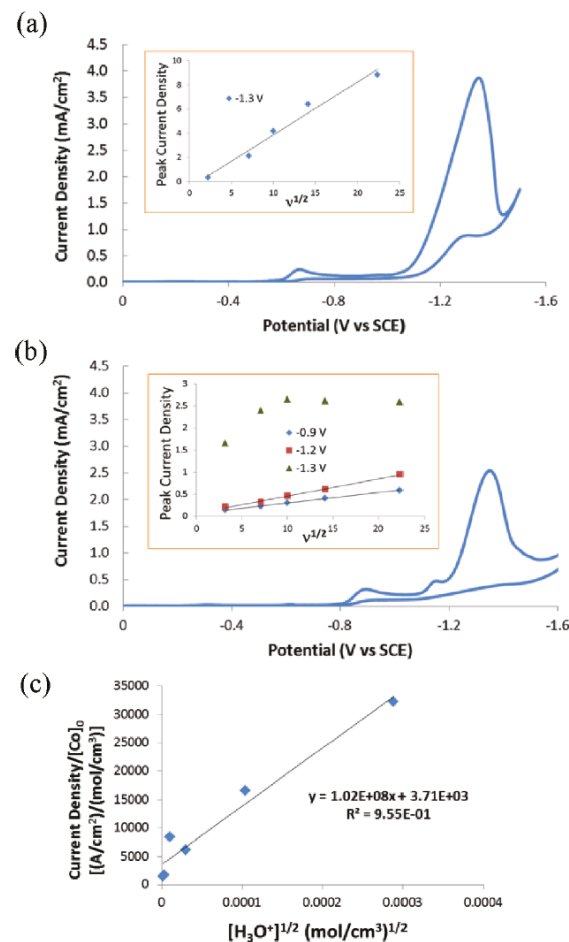
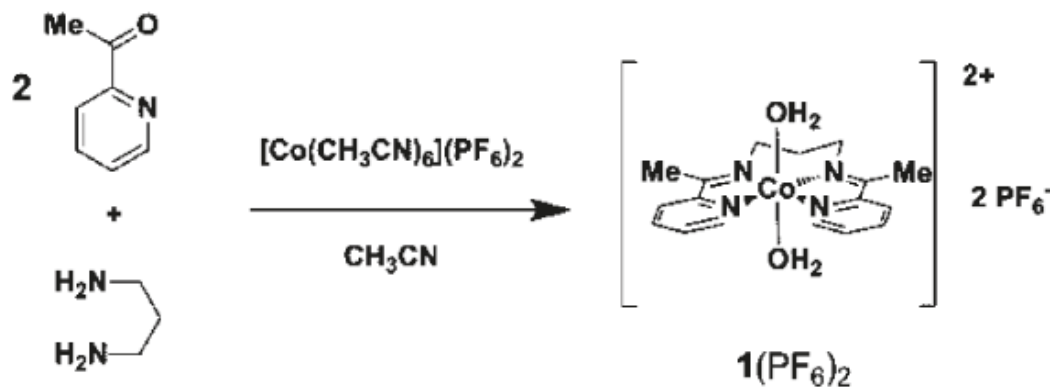
J|A|C|S
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

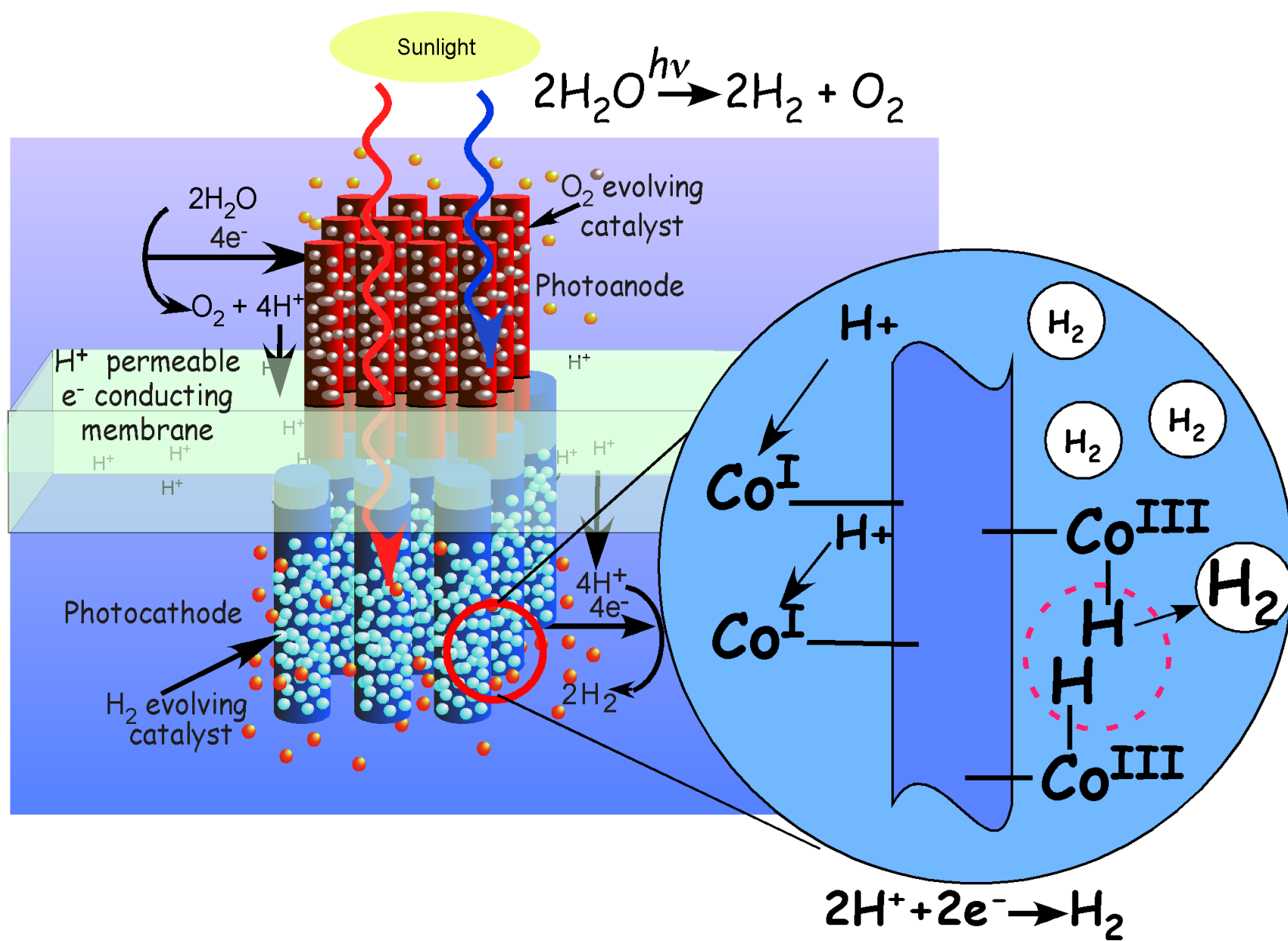
Rapid Water Reduction to H₂ Catalyzed by a Cobalt Bis(iminopyridine) Complex

Bryan D. Stubbett, Jonas C. Peters,* and Harry B. Gray*



Powering the Planet





Integrated Systems

Energy & Environmental Science

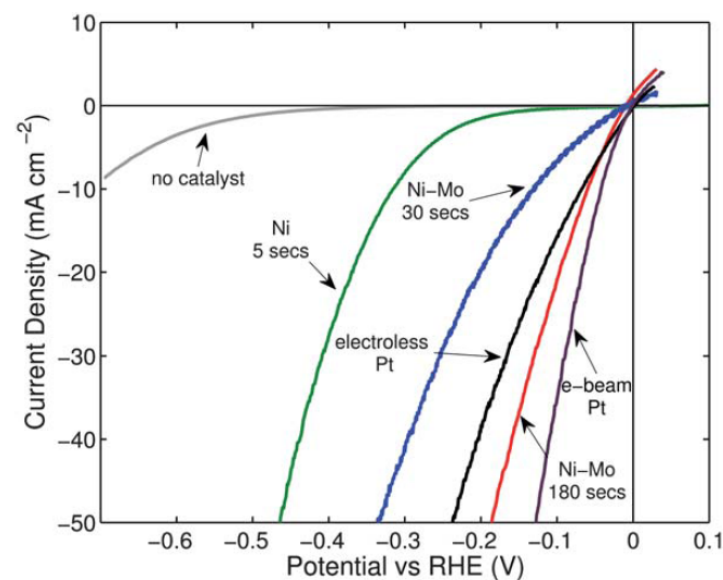
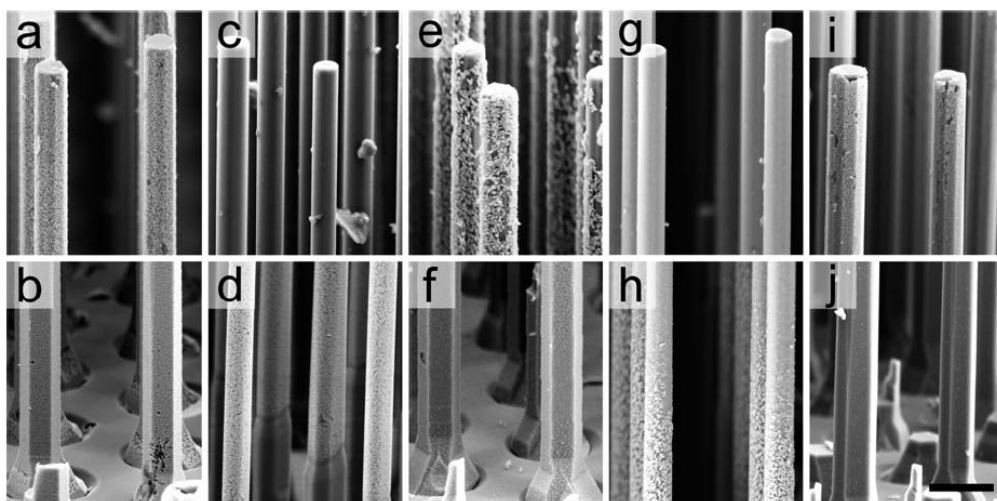
Cite this: *Energy Environ. Sci.*, 2011, **4**, 3573

www.rsc.org/ees

PAPER

Evaluation of Pt, Ni, and Ni–Mo electrocatalysts for hydrogen evolution on crystalline Si electrodes[†]

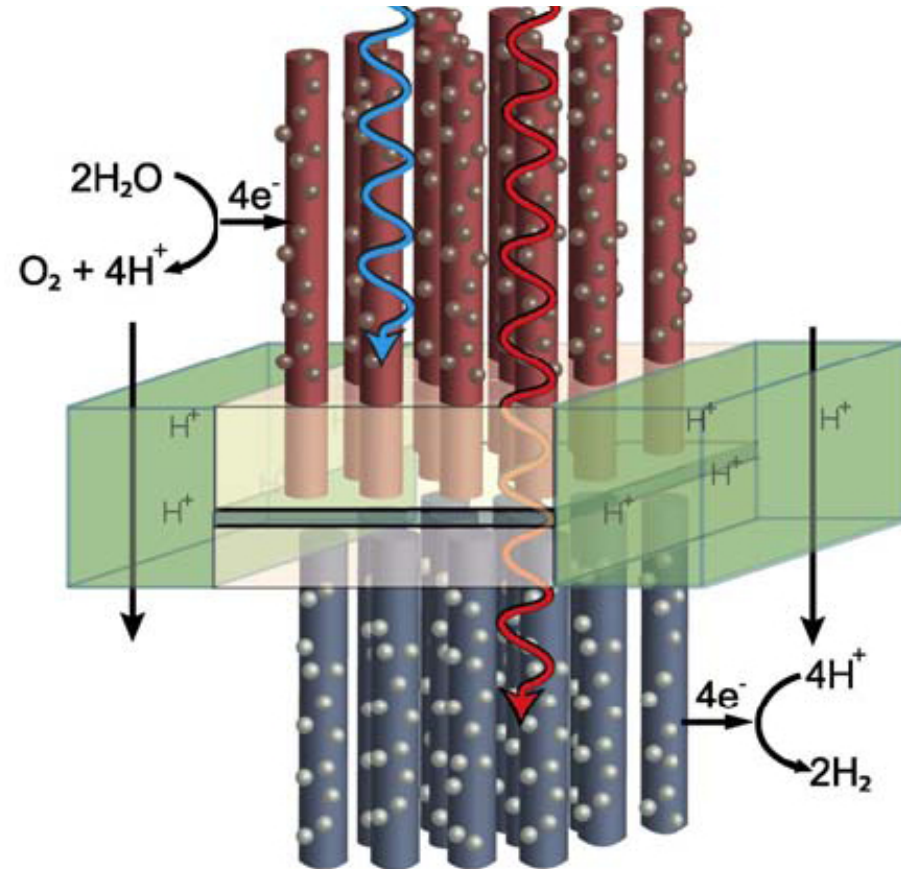
James R. McKone, Emily L. Warren, Matthew J. Bierman, Shannon W. Boettcher,[‡] Bruce S. Brunschwig, Nathan S. Lewis^{*} and Harry B. Gray^{*}



Powering the Planet



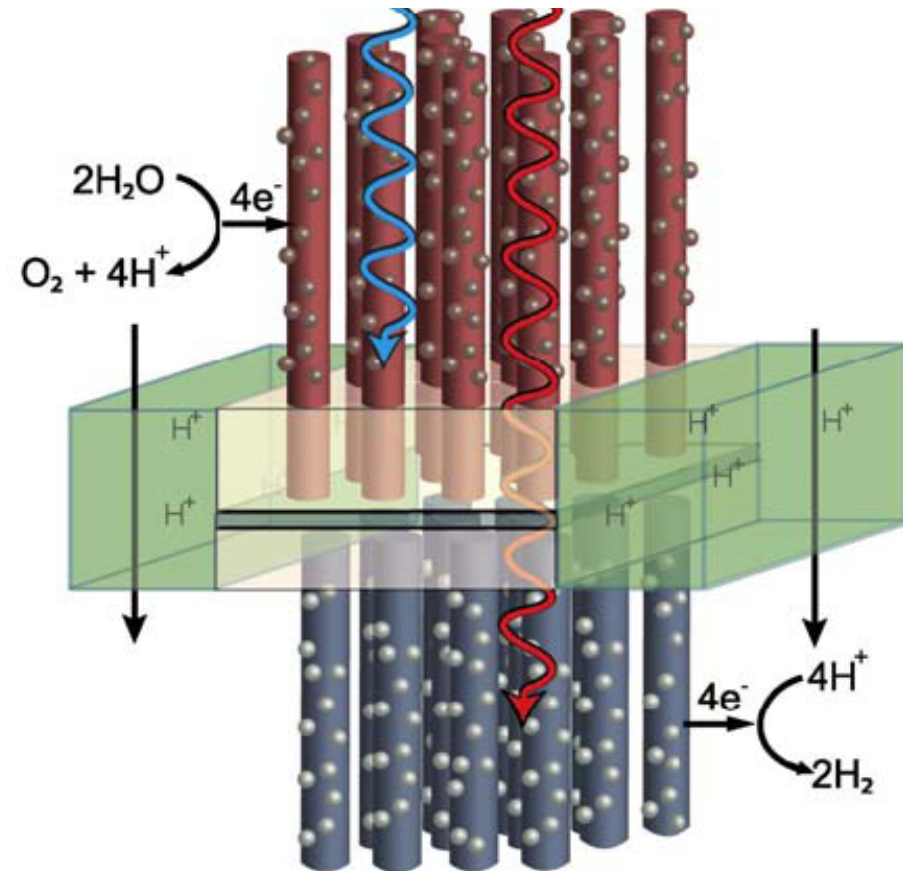
Challenge: Water Oxidation!!



Powering the Planet



Tungsten Oxide Photoanodes



Powering the Planet



Water vs Anion Oxidation

Energy & Environmental Science

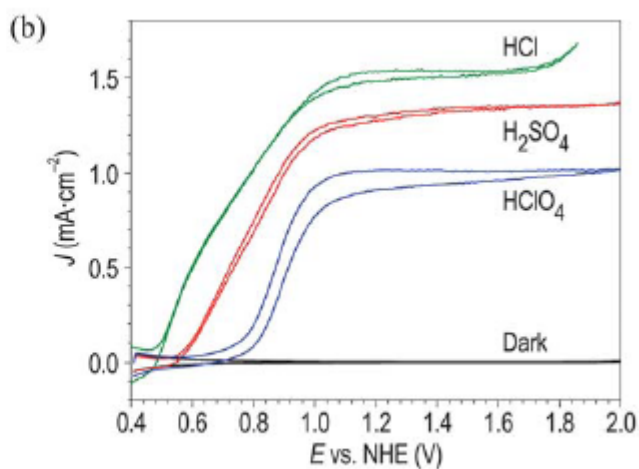
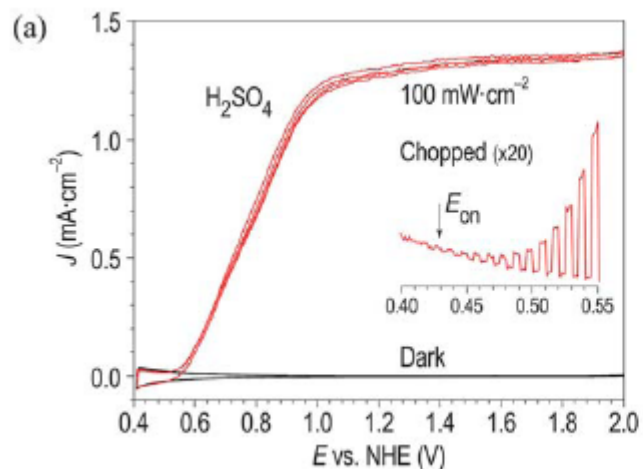
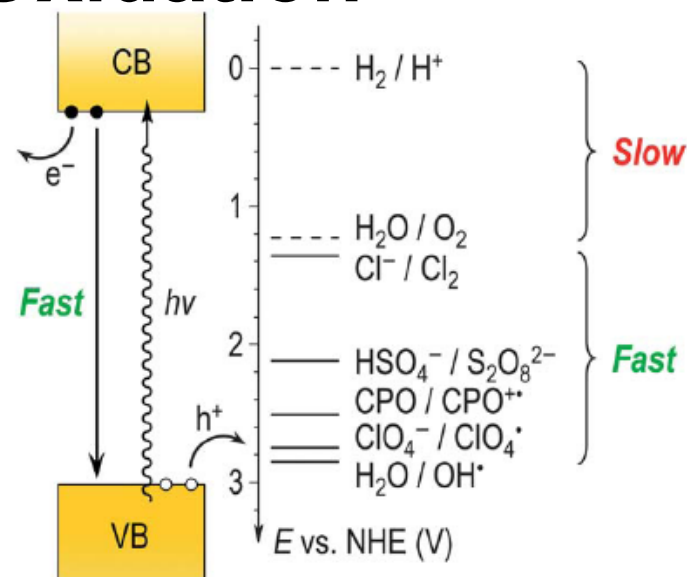
Cite this: *Energy Environ. Sci.*, 2012, **5**, 5694

www.rsc.org/ees

PAPER

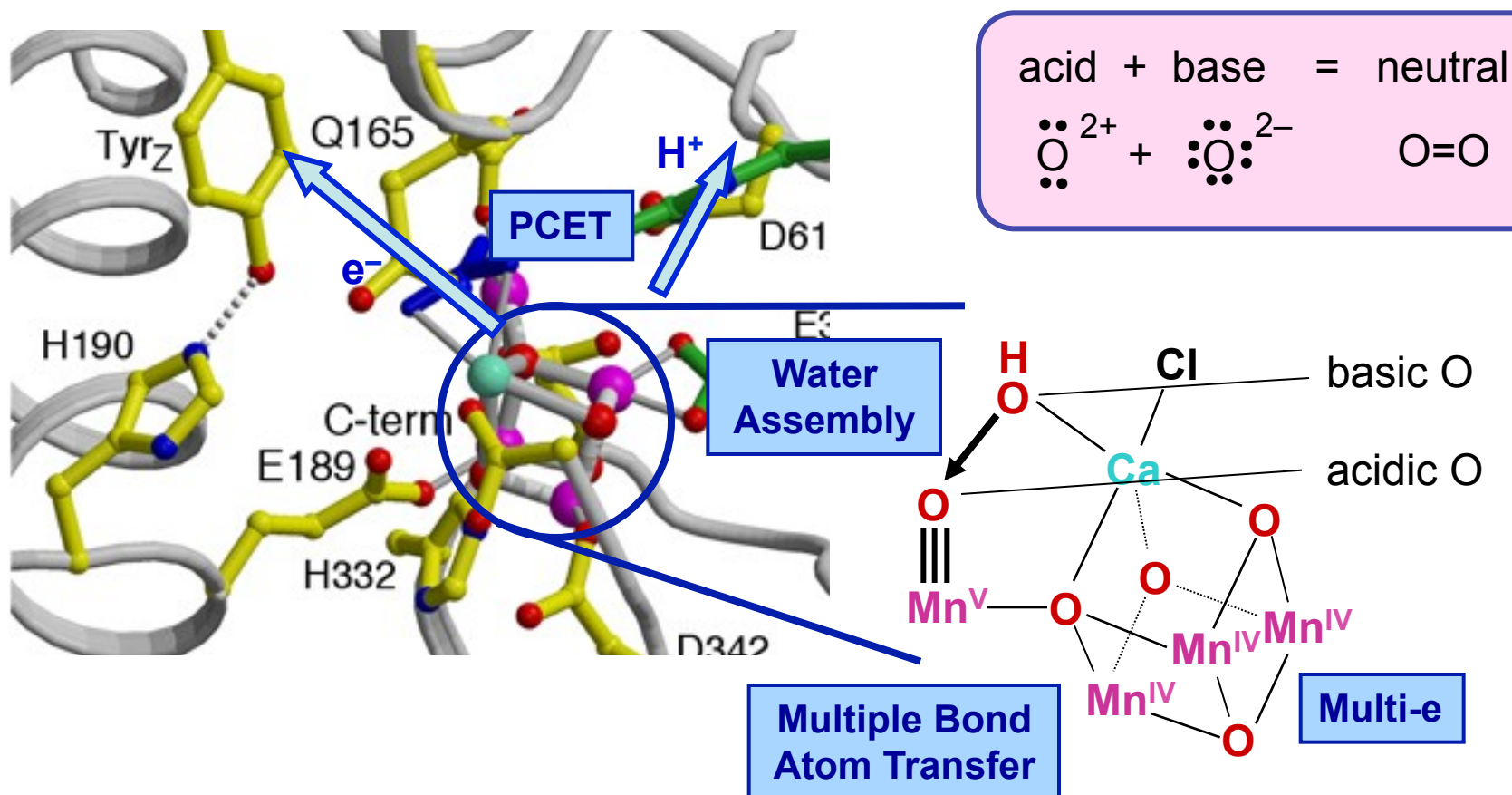
A quantitative assessment of the competition between water and anion oxidation at WO_3 photoanodes in acidic aqueous electrolytes

Qixi Mi, Almagul Zhanaidarova, Bruce S. Brunshwig, Harry B. Gray* and Nathan S. Lewis*



Oxos in Nature

The OEC Active Site of PSII (Imperial College structure)

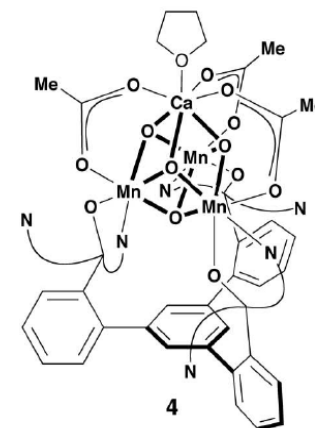


Solar Fuels



A Synthetic Model of the Mn_3Ca Subsite of the Oxygen-Evolving Complex in Photosystem II

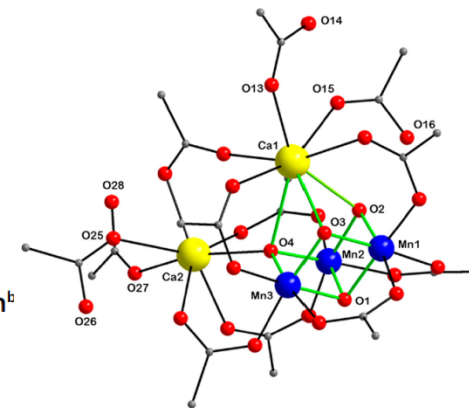
Jacob S. Kanady, Emily Y. Tsui, Michael W. Day, Theodor Agapie*



PNAS Early Edition

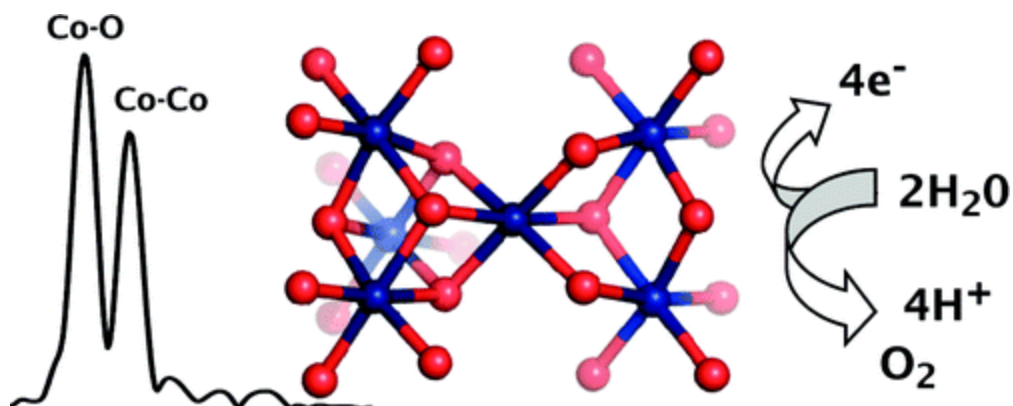
Synthetic model of the asymmetric $[\text{Mn}_3\text{CaO}_4]$ cubane core of the oxygen-evolving complex of photosystem II

Shreya Mukherjee^a, Jamie A. Stull^b, Junko Yano^c, Theocharis C. Stamatatos^a, Konstantina Pringouri^a, Troy A. Stich^b, Khalil A. Abboud^a, R. David Britt^b, Vittal K. Yachandra^c, and George Christou^{a,1}

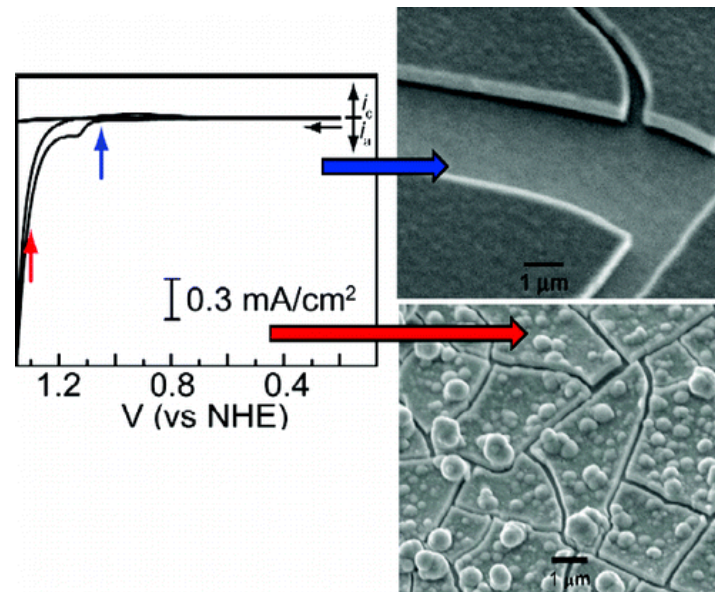


Water Oxidation

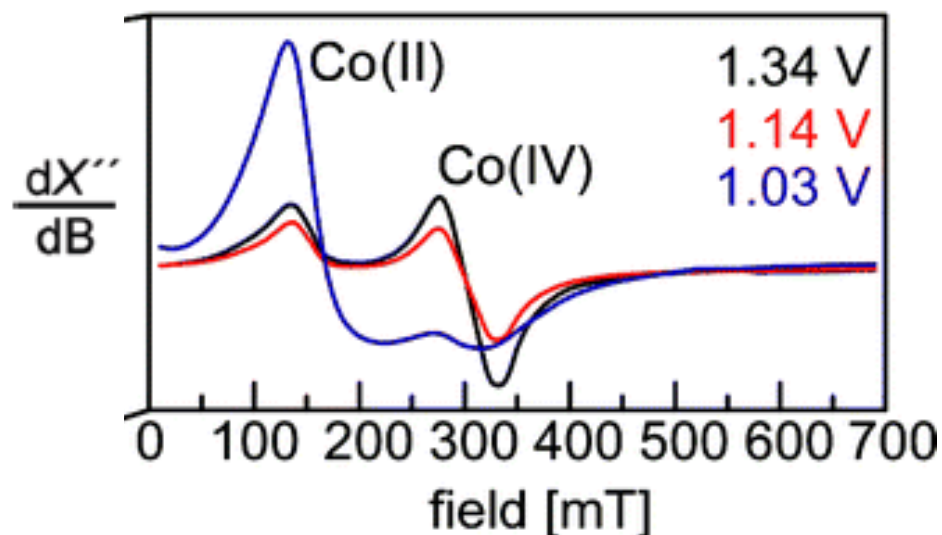
Kanan, M. W.; Nocera, D. G. **In Situ Formation of an Oxygen-Evolving Catalyst in Neutral Water Containing Phosphate and Co^{2+}** *Science*, **2008**, 321, 1072-1075.



McAlpin, J. G.; Surendranath, Y.; Dinca, M.; Stich, T. A.; Stoian, S. A.; Casey, W. H.; Nocera, D. G.; Britt, R. D. **EPR Evidence for Co(IV) Species Produced During Water Oxidation at Neutral pH.** *J. Am. Chem. Soc.*, **2010**, 132, 6882-6883.



Risch, M.; Khare, V.; Zaharieva, I.; Gerencser, L.; Chernev, P.; Dau, H. **Cobalt-Oxo Core of a Water-Oxidizing Catalyst Film.** *J. Am. Chem. Soc.* **2009**, 131, 6936-6937..



Water Oxidation

CHEMISTRY OF
MATERIALS

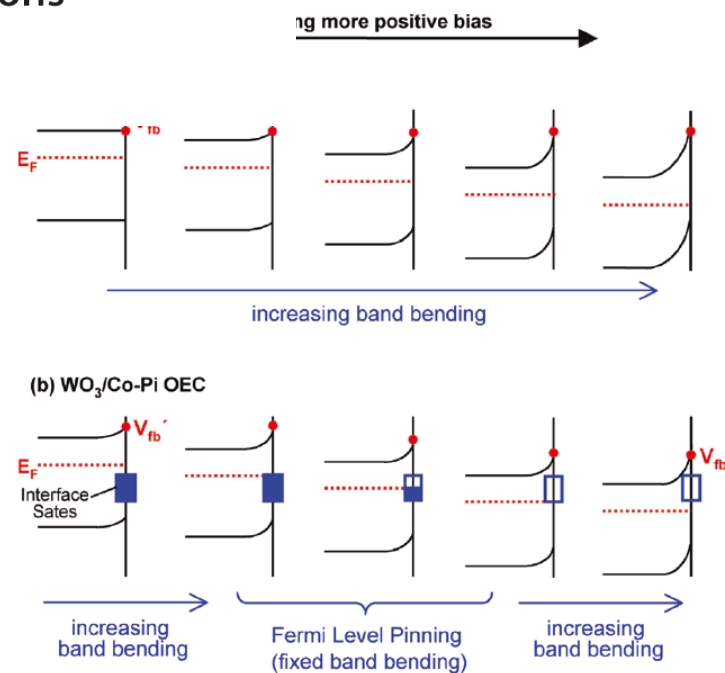
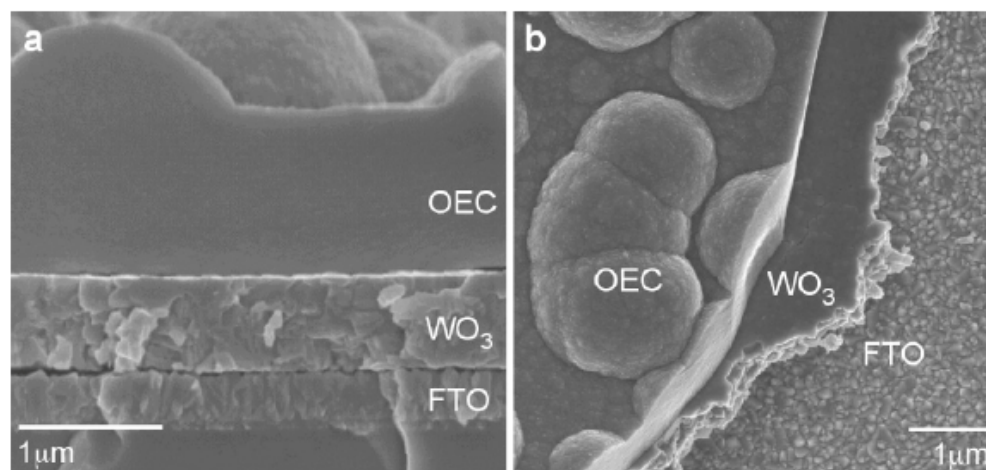
ARTICLE

pubs.acs.org/cm

Chem. Mater. 2011, 23, 1105–1112

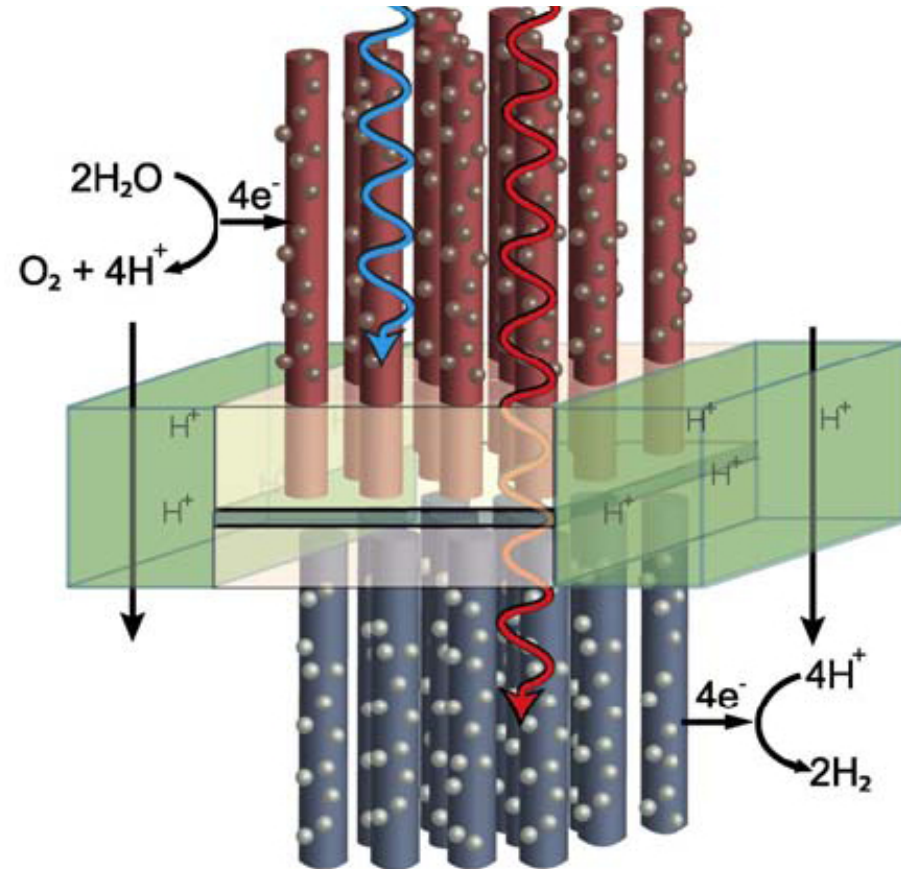
Effect of a Cobalt-Based Oxygen Evolution Catalyst on the Stability and the Selectivity of Photo-Oxidation Reactions of a WO_3 Photoanode

Jason A. Seabold and Kyoung-Shin Choi*



^a E_F = Fermi level, V_{fb} = flat band potential.

Better Catalysts?



Powering the Planet



hydrogen 1 H 1.0079																	helium 2 He 4.0026														
lithium 3 Li 6.941	beryllium 4 Be 9.0122															boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180										
sodium 11 Na 22.990	magnesium 12 Mg 24.305															aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948										
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.88	vanadium 23 V 50.942	chromium 24 Cr 52.00	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.69	copper 29 Cu 63.546	zinc 30 Zn 65.38	gallium 31 Ga 69.723	germanium 32 Ge 72.64	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80														
rubidium 37 Rb 85.468	strontium 38 Sr 87.62															cadmium 48 Cd 112.415	indium 49 In 114.818	tin 50 Sn 118.710	antimony 51 Sb 121.757	tellurium 52 Te 127.6	iodine 53 I 126.905	xenon 54 Xe 131.29									
caesium 55 Cs 132.91	barium 56 Ba 137.33	lanthanum 57 La 138.905	cerium 58 Ce 140.12	praseodymium 59 Pr 140.908	neodymium 60 Nd 144.24	promethium 61 Pm [144.9126]	europium 62 Eu 151.964	gadolinium 63 Gd 157.25	terbium 64 Tb 158.925	dysprosium 65 Dy 162.50	holmium 66 Hm 164.930	erbium 67 Er 167.259	thulium 68 Tm 168.930	ytterbium 69 Yb 173.054	lutetium 70 Lu 174.967	hafnium 72 Hf 178.49	tantalum 73 Ta 180.948	tungsten 74 W 183.84	rhenium 75 Re 186.207	osmium 76 Os 190.23	iridium 77 Ir 192.222	platinum 78 Pt 195.084	gold 79 Au 196.967	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]	
francium 87 Fr [223]	radium 88 Ra [226]	actinium 89 Ac [227]	thorium 90 Th 232.038	protactinium 91 Pa 231.036	uranium 92 U 238.029	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 Nb [259]	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	darmstadtium 110 Ds [271]	roentgenium 111 Rg [272]	copernicium 112 Cn [277]	ununtrium 113 Uut [284]	unquadium 114 Uuq [289]	unpentium 115 Uup [288]	unsextium 116 Uus [289]	unseptium 117 Uus [289]	unoctium 118 Uuo [289]

Millions of Combinations!

Millions of Combinations!

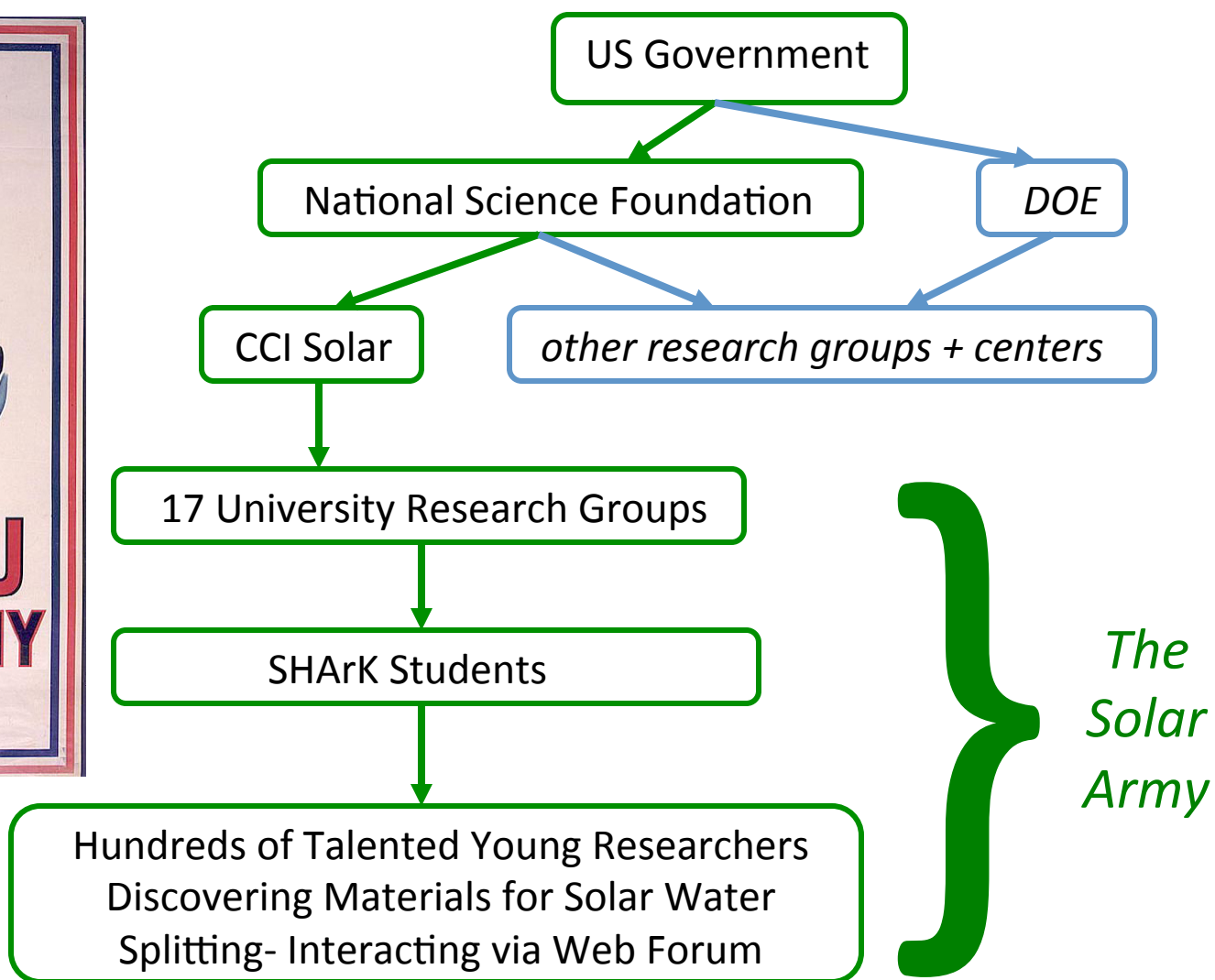


Robust Catalysts



THE SOLAR ARMY

Powering the Planet



CCI Solar A Center for Chemical Innovation

Solar Army Brigades

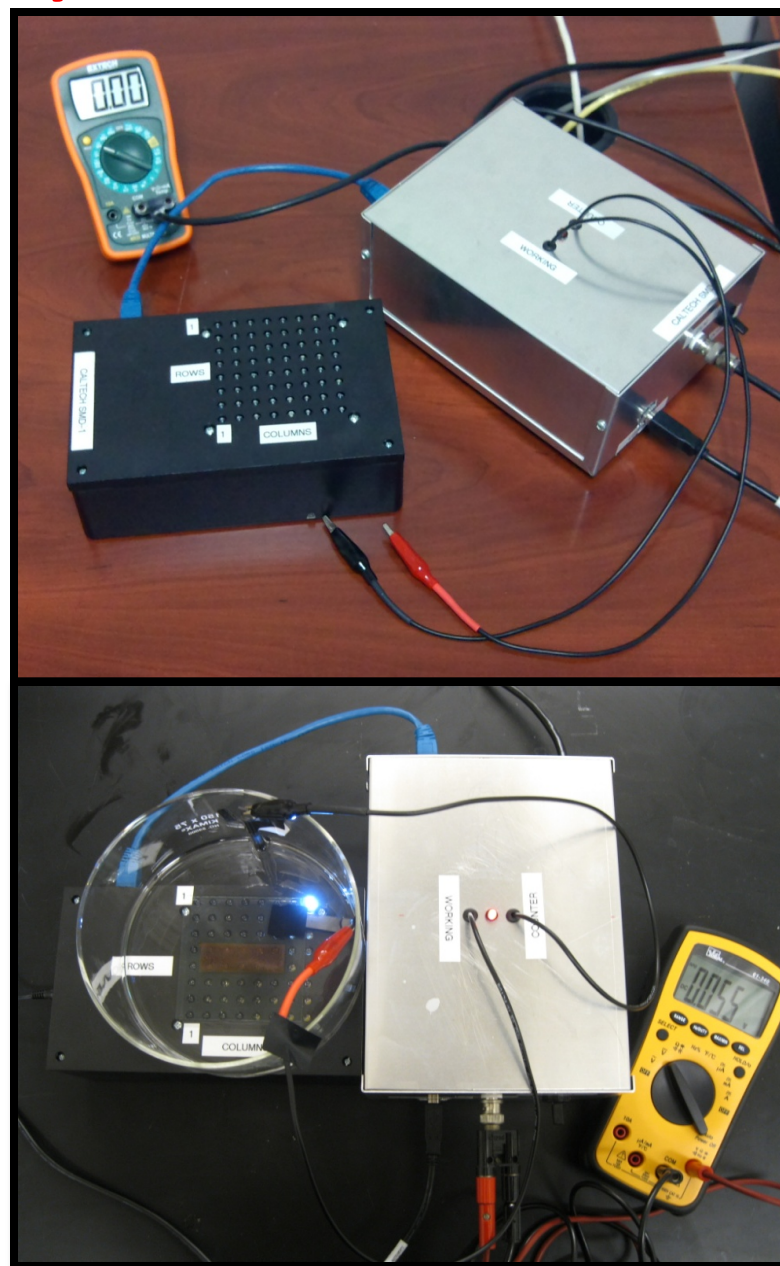


Summer 2010 Caltech Solar Army Brigade

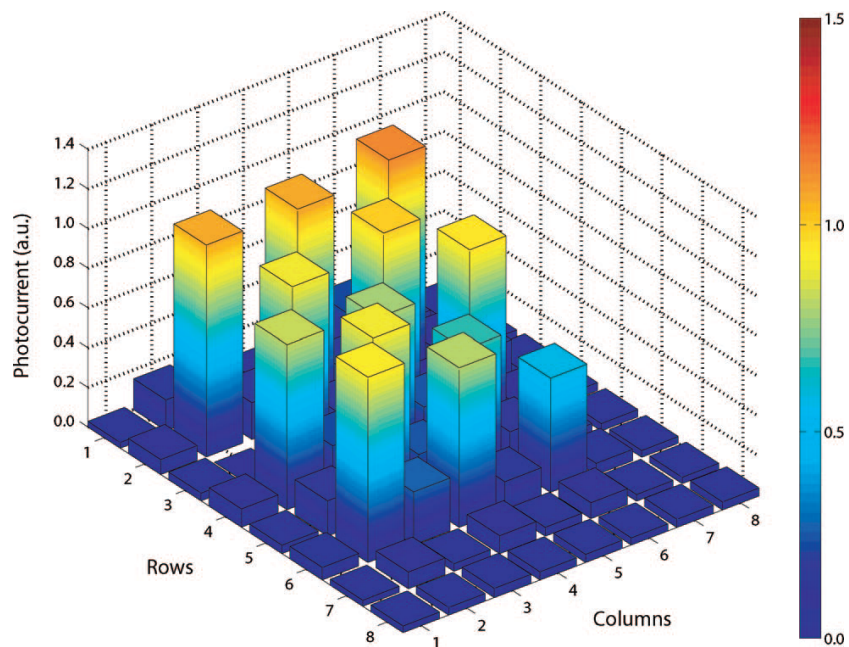


Solar Army Kit

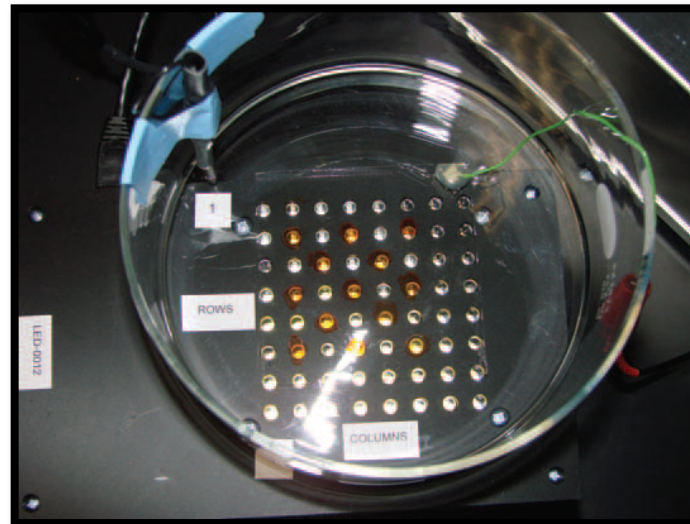
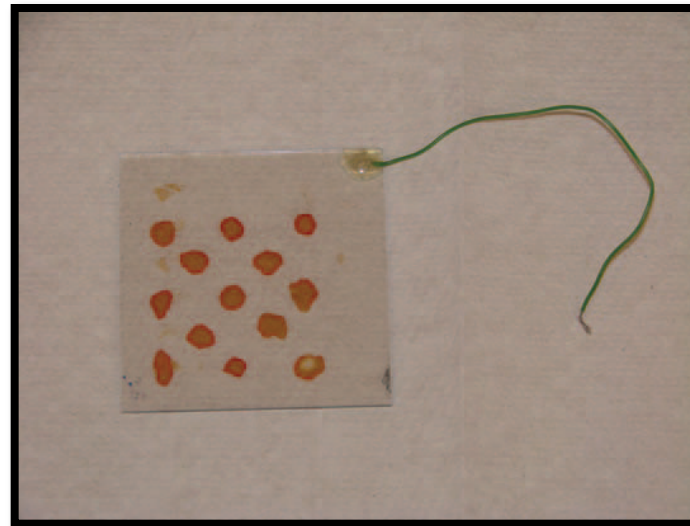
- Metal precursors are deposited onto FTO-conductive glass
 - Pipetting or spray deposition
- Metal precursors are pyrolyzed to metal oxides
 - Fired at 500°C for 2-12 hrs
- Photoactivity is determined
 - LED scan station



Results



Signal-averaged data from ten scans of the iron oxide test plate. The applied potential was 0.1 V.



Solar Materials Discovery Website

Solar Materials Discovery - Mozilla Firefox

File Edit View History Bookmarks Tools Help

Back Forward New Tab Reload Stop Home

http://bilrc.caltech.edu/solmatdisc/ten-best.php

http://bilrc.caltech.edu/solmatdisc/ten-best.php

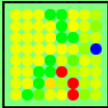
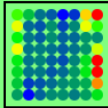
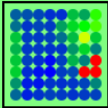
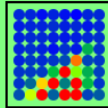
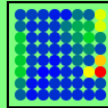
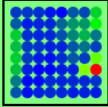
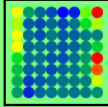
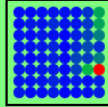
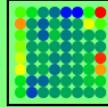
Solar Materials Discovery

CALTECH SOLAR MATERIALS DISCOVERY PROJECT

TEN BIGGEST HITS IN THE SolMatDisc DATABASE

(Dark Values < 1 V)

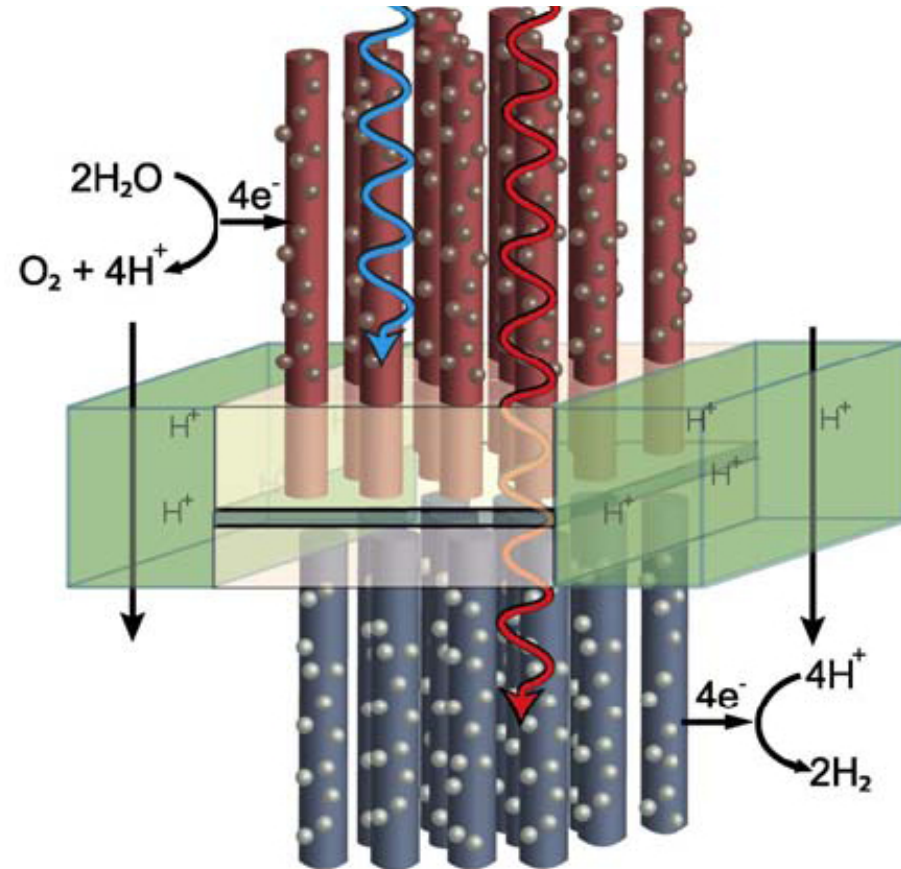
SELECT A DATA SET TO VIEW

Bismuth:Cobalt:Zinc Ch3X_Winter_2011_Wednesday_Afternoon_Section Depositor: G1S1DBLue_array2test View Data 	Copper:Iron:Bismuth Ch3X_Winter_2011_Wednesday_Evening_Section Depositor: Liana & Hima View Data 	Copper:Iron:Bismuth Ch3X_Winter_2011_Wednesday_Evening_Section Depositor: Liana & Hima View Data 	Copper:Zinc:Bismuth Ch3X_Winter_2011_Thursday_Morning_Section Depositor: Singh Suraesh View Data 	Copper:Iron:Bismuth Ch3X_Winter_2011_Wednesday_Evening_Section Depositor: Liana & Hima View Data 
Copper:Iron:Bismuth Ch3X_Winter_2011_Wednesday_Evening_Section Depositor: Hima & Liana View Data 	Copper:Iron:Bismuth Ch3X_Winter_2011_Wednesday_Evening_Section Depositor: Liana & Hima View Data 	Iron Ch3X_Fall_2010_Monday_Evening_Section Depositor: J2K View Data 	Lanthanum:Zirconium:Bismuth Ch3X_Winter_2011_Wednesday_Afternoon_Section Depositor: Okamoto and Coryell View Data 	Copper:Iron:Bismuth Ch3X_Winter_2011_Wednesday_Evening_Section Depositor: Liana & Hima View Data 

[RETURN](#)

Done

Better Photoanodes?



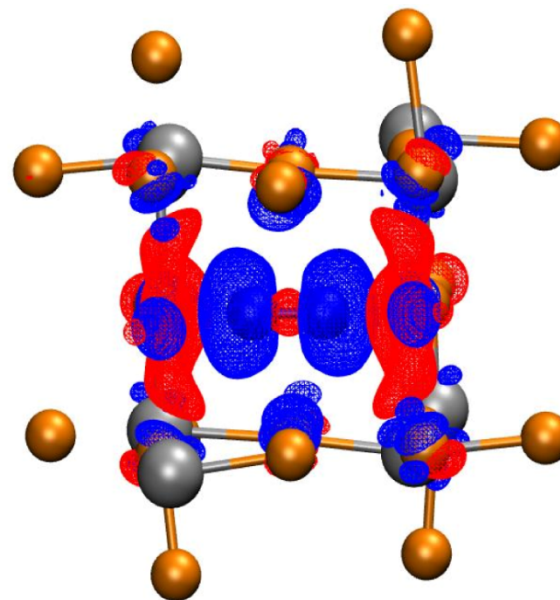
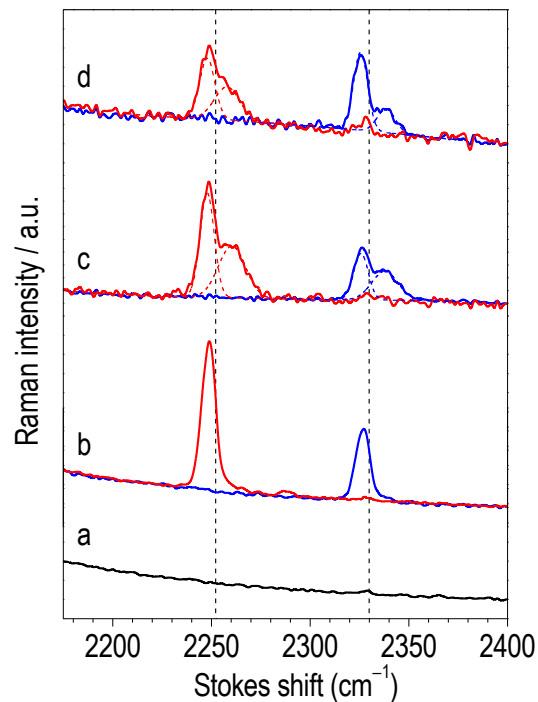
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Band Gap Tuning

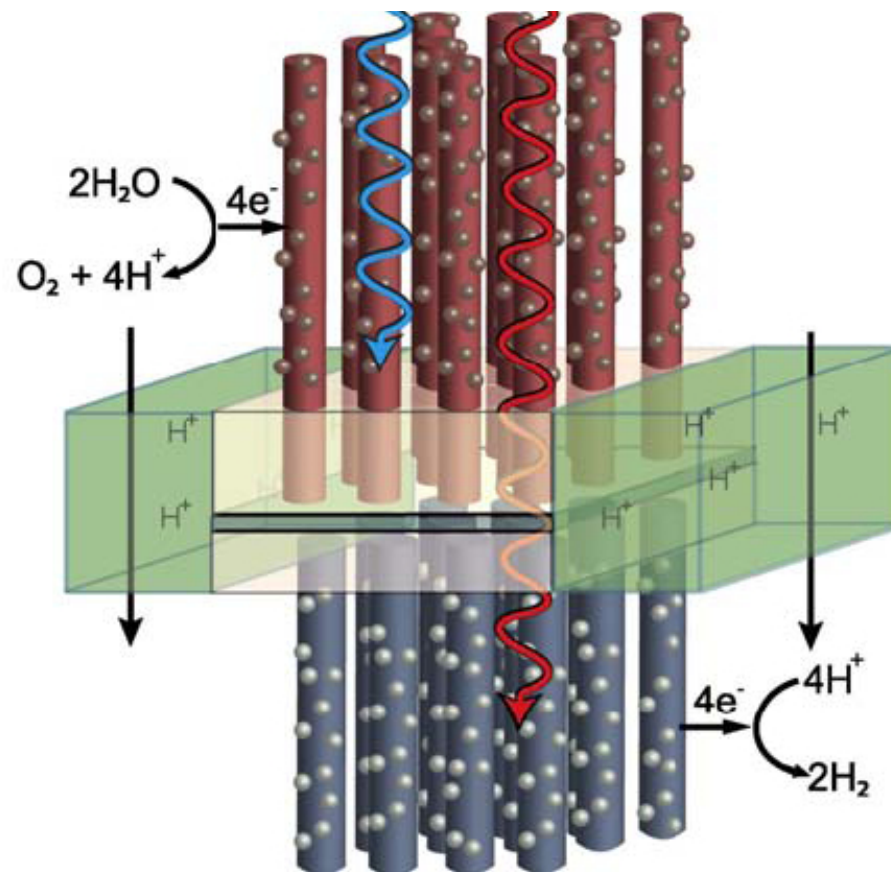
Optical and Photoelectrochemical Properties of Thermally Stable Clathrates of Dinitrogen in Tungsten Trioxide

Qixi Mi,¹ Yuan Ping,² Yan Li,³ Bruce S. Brunschwig,¹ Giulia A. Galli,^{2,} Harry B. Gray^{1,*}
and Nathan S. Lewis^{1,*}*



Making Cobalt Oxide Nanoparticle Catalysts

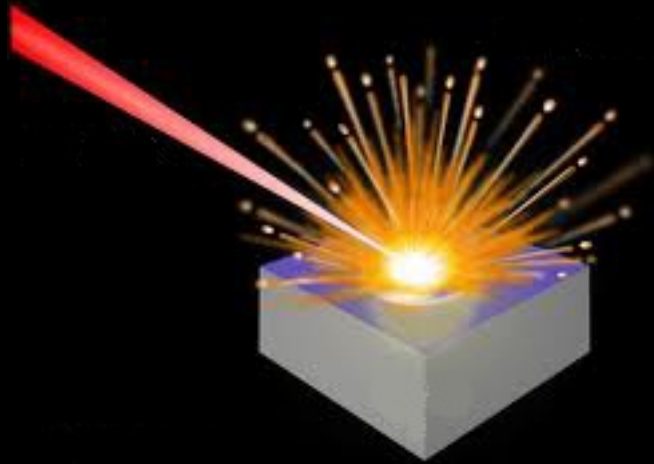
Astrid Mueller, Daniel Konopka, Tania Darnton, Jay Winkler, Bruce Brunschwig



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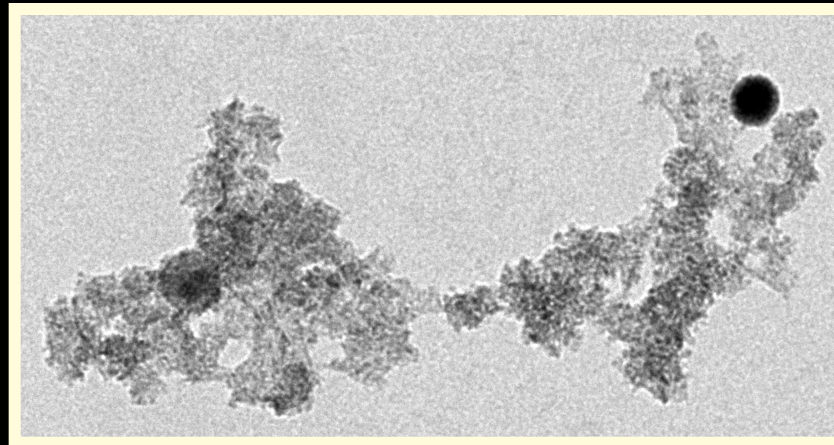
Pulsed Laser Ablation in Liquids



Pulsed laser hits solid target

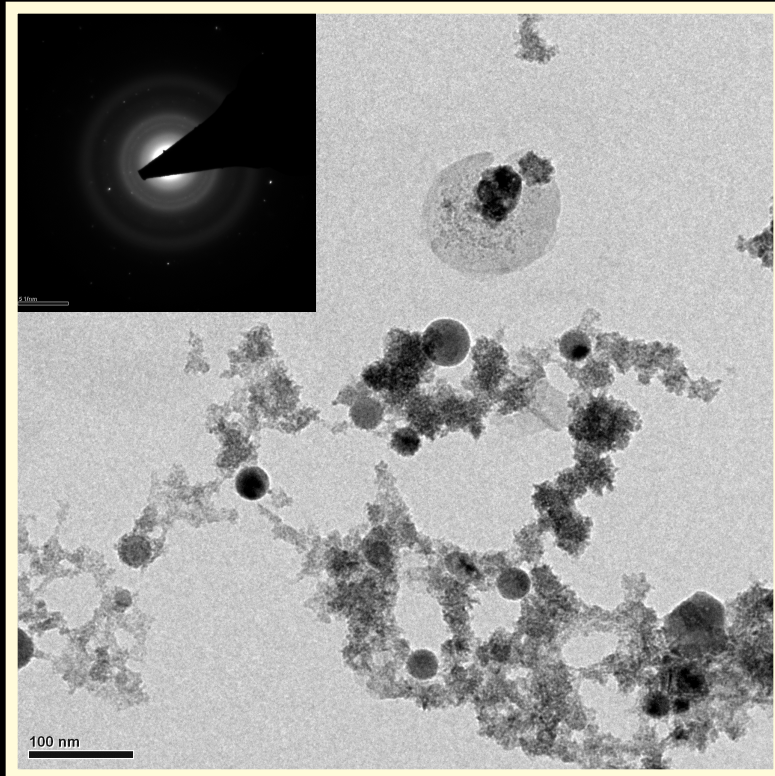


Plasma confined by liquid:
 $\sim 5000\text{K}$, $\sim 10\text{GPa}$

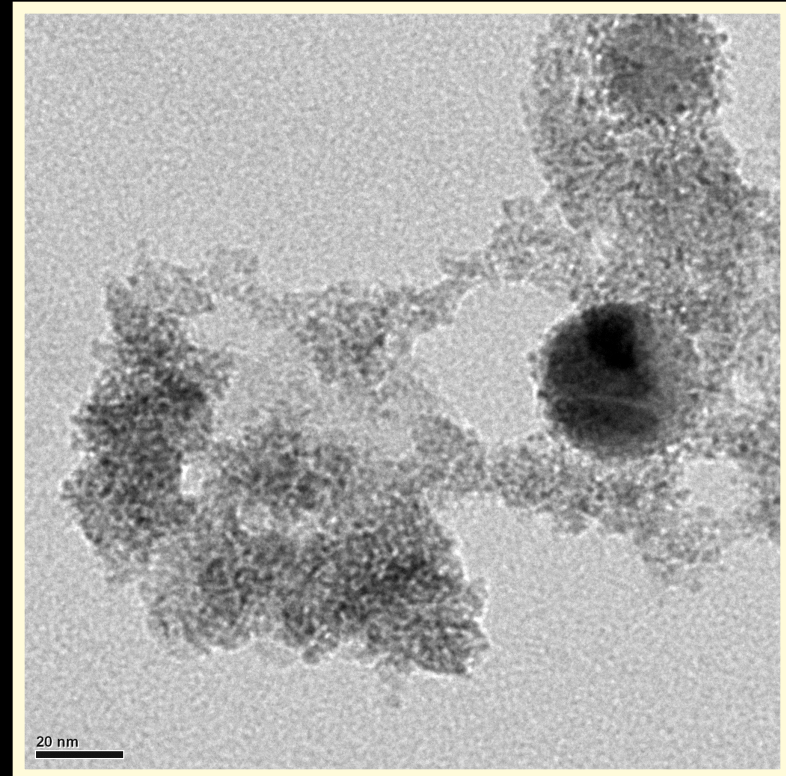


Condensation of nanoparticles
when plasma expands

TEM & ED of Co_3O_4 NPs



100 nm



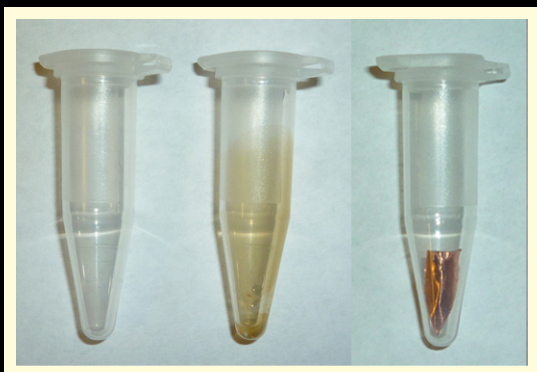
20 nm

⇒ aggregated <10 nm particles
⇒ randomly oriented crystals

Nd:YAG laser: 355 nm, 8 ns pulse length, 30mJ/pulse

XPS of Cobalt Oxide NPs

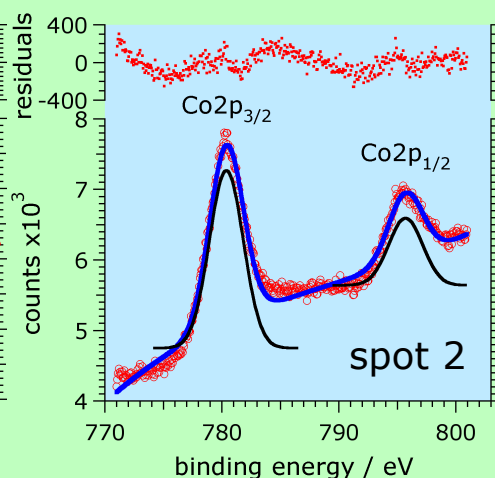
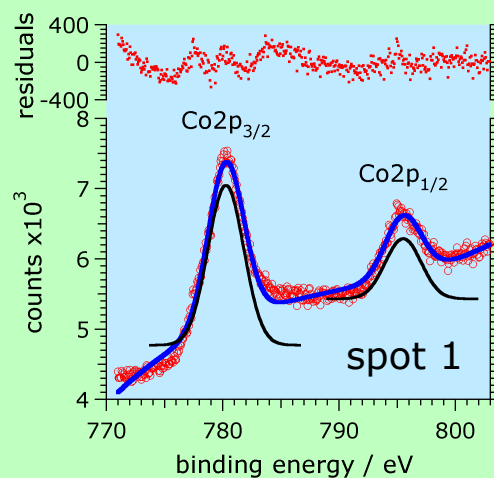
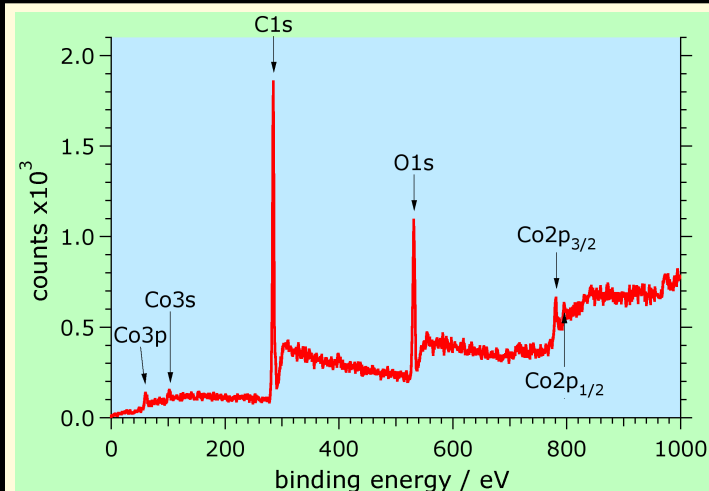
sample preparation



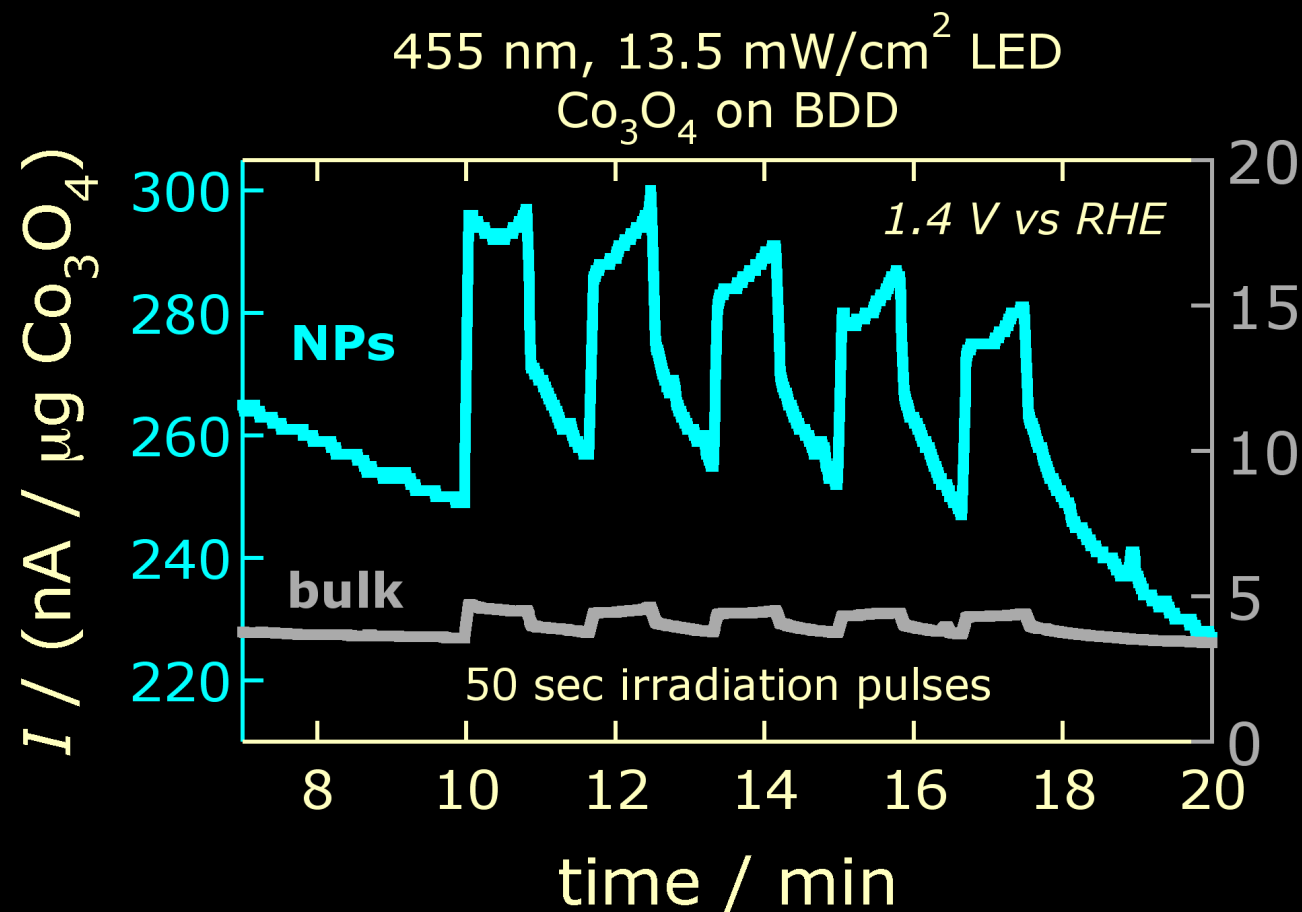
BE / eV	Co2p _{3/2}	sat-2p _{3/2}	Co2p _{1/2}	sat-2p _{1/2}
CoO lit.	780.5	785.5	796.6	802.1
Co ₃ O ₄ lit.	779.8	–	795.7	–
NPs	780.3	–	795.6	–

⇒ **Co₃O₄**

MA Langell, *J. Vac. Sci. Technol. A* **2004**, 22, 1690.

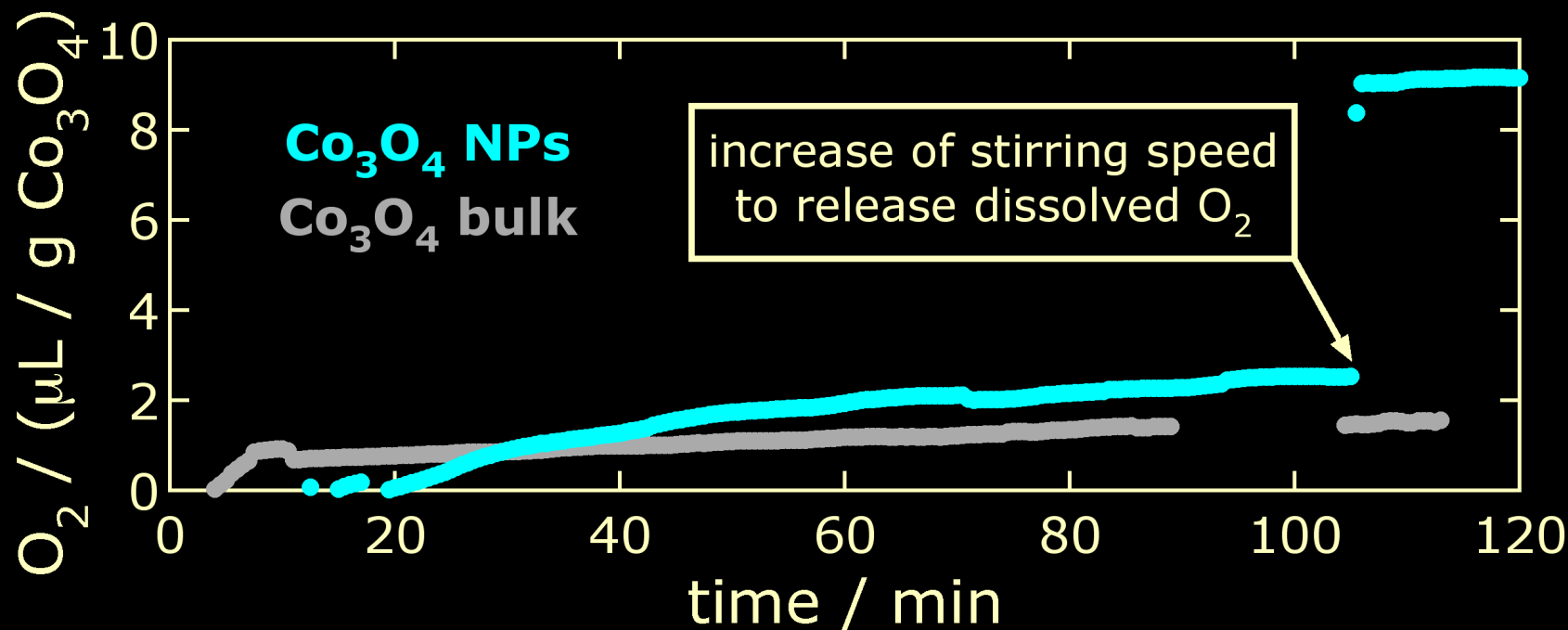


OER Photoelectrochemistry



NP synthesis: 355 nm Nd:YAG laser,
8 ns pulse length, 30mJ/pulse

Making Oxygen



Conditions: $\lambda_{\text{exc}} = 455 \text{ nm}$ (LED), Neofox[®] O₂ sensor

6 mL H₂O, $1.1 \times 10^{-4} \text{ M}$ Ru(bpy)₃Cl₂, $1.0 \times 10^{-2} \text{ M}$ Na₂S₂O₈,

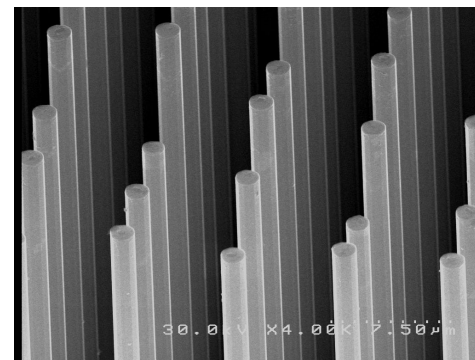
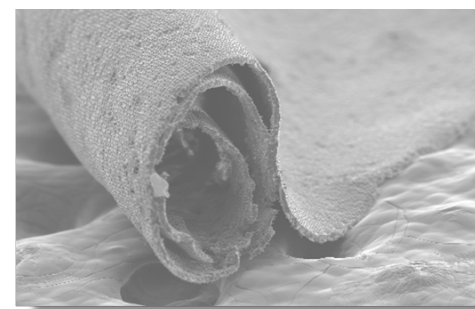
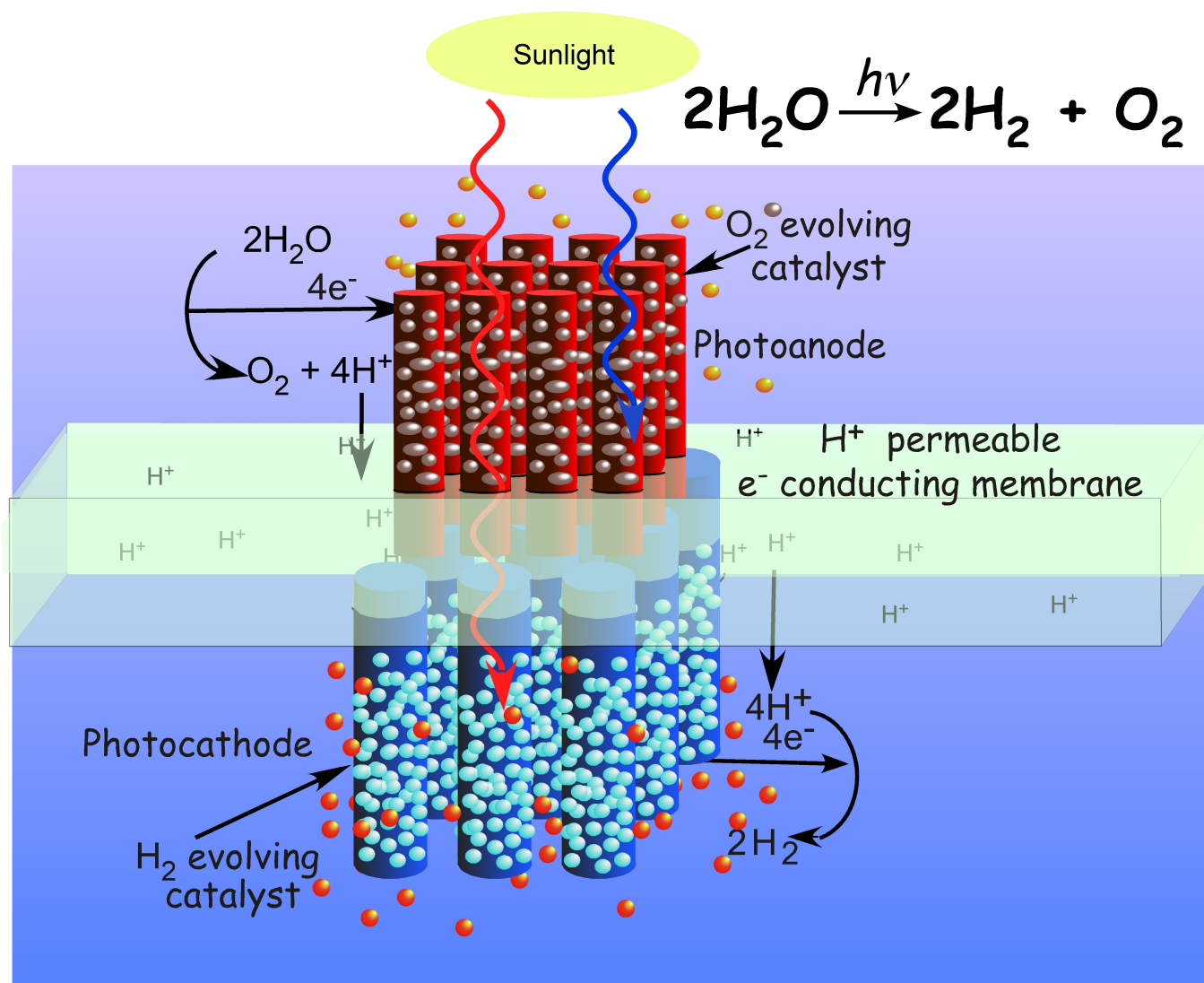
$5.0 \times 10^{-2} \text{ M}$ NaSO₄, 240 mg/L Co₃O₄ powder,

153 mg/L Co₃O₄ NPs, pH 5.5, 6 mL headspace

Method: A. Harriman *et al.*, *J. Chem. Soc., Faraday Trans. 1*, 84, 2795 (1988).

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