

# SHArK (Solar Hydrogen Activity Research Kit) with Pipette Method:

Effect of Varying Metal Precursor Concentration and Drop Size  
on Photocurrent Response of Ternary Metal Oxide Combinations

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Justin Hibbard  
Ella H. Wong  
Professor Carl C. Wamser  
PSU- Chemistry, September 2009



# Abstract

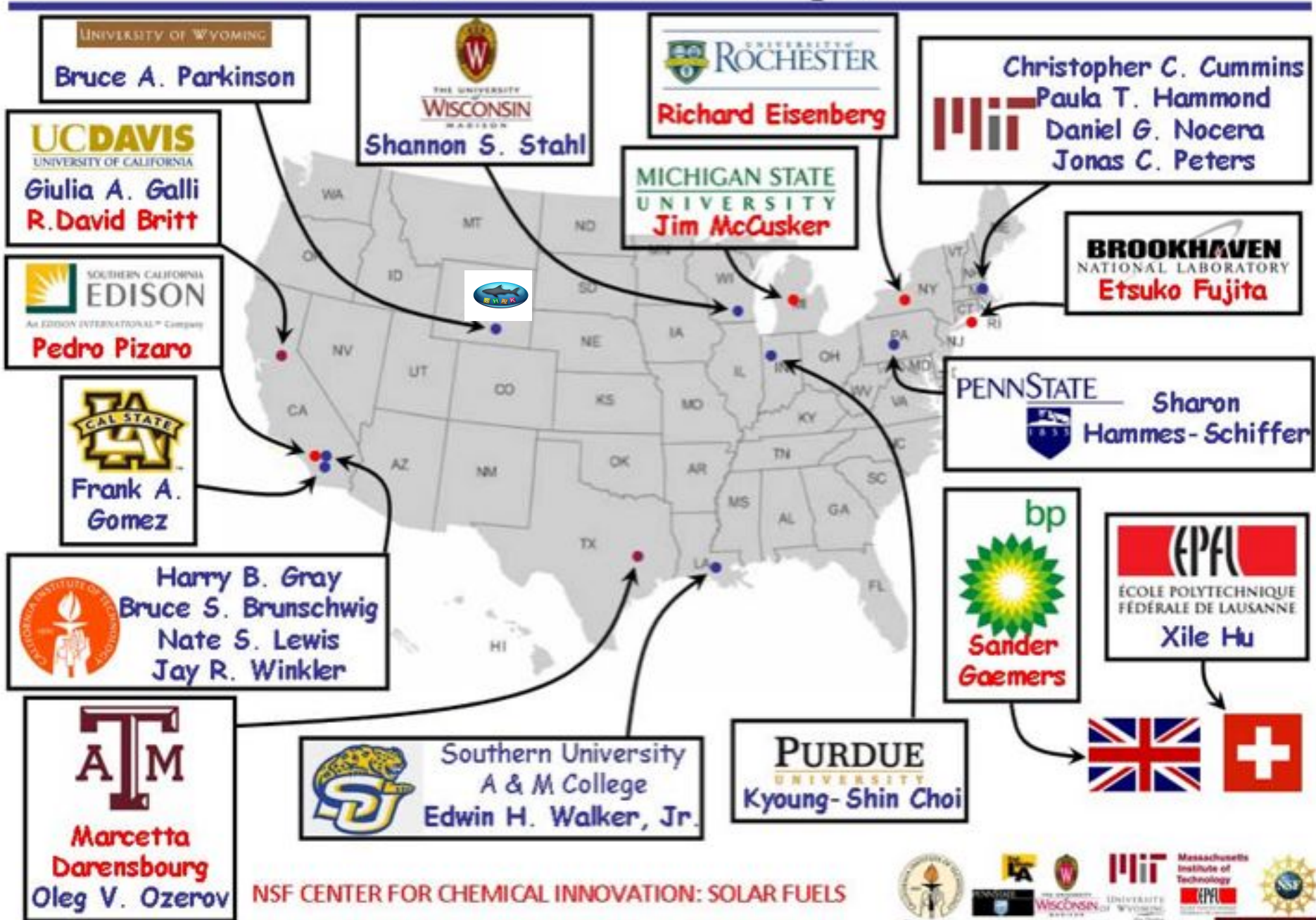
The photocurrent activities of ternary metal oxide combinations were investigated using SHArK (Solar Hydrogen Activity Research Kit) with a pipette-based (rather than inkjet printer-based) method. 5x5 grids with 10 different combinations of Co, Al and Fe oxides as well as internal standards ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> for n-type photoactivity and CuO for p-type) were prepared using metal precursor concentrations of .35 M and .025 M and 5  $\mu$ L drops, and scanned with applied biases of + 0.5V and - 0.5V. Preparations of varying drop sizes (7, 5, 3, and 1  $\mu$ L) of Fe, Cu, and Co oxides were also scanned. Photocurrent responses for the standards increased 2 and 3-fold after decreasing the metal precursor concentrations from .35 M to .025 M (.1 to .2  $\mu$ A for Fe and 1.4 to 4.7  $\mu$ A for Cu) with demonstration of greater p-type activity than n-type at both concentrations. Instead, Co showed a 95% decrease in p-type activity from .35 M to .025 M (40% of Cu activity to 2%). The drop size evaluation favored 5  $\mu$ L drops and showed more pronounced p-type Co activity at .35 M consistent with a promising p-type photocatalyst. Funding provided by a donation to Professor Wamser from the Silicon Chemical Corporation.

# Introduction

A simple pipette method is being developed for the SHArK outreach project (<http://www.thesharkproject.org/>) which will target young scientists in high schools and undergraduate colleges. The goal of SHArK (“dedicated to splitting water with sunlight”) is to screen for stable, inexpensive, efficient, earth-abundant metal oxide semiconductors capable of splitting water into H<sub>2</sub> and O<sub>2</sub> using sunlight. The H<sub>2</sub> produced can be stored and used for transportation or “solar” energy at night. SHArK provides young people a unique opportunity to participate in real-time scientific research, working collaboratively via SHArK’s wide distributed research network. SHArK engages/encourages very much needed future researchers to take an active role in solving the global energy and climate change problems. SHArK is the outreach arm of Professor Bruce Parkinson’s solar water splitting research group (University of Wyoming, [http://www.uwyo.edu/parkinson/Parkinson\\_Research\\_Group/Home.html](http://www.uwyo.edu/parkinson/Parkinson_Research_Group/Home.html)) and is also part of the NSF-funded “Powering the Planet” project (<http://www.ccisolar.caltech.edu/>).



# NSF CCI Solar Program



NSF CENTER FOR CHEMICAL INNOVATION: SOLAR FUELS

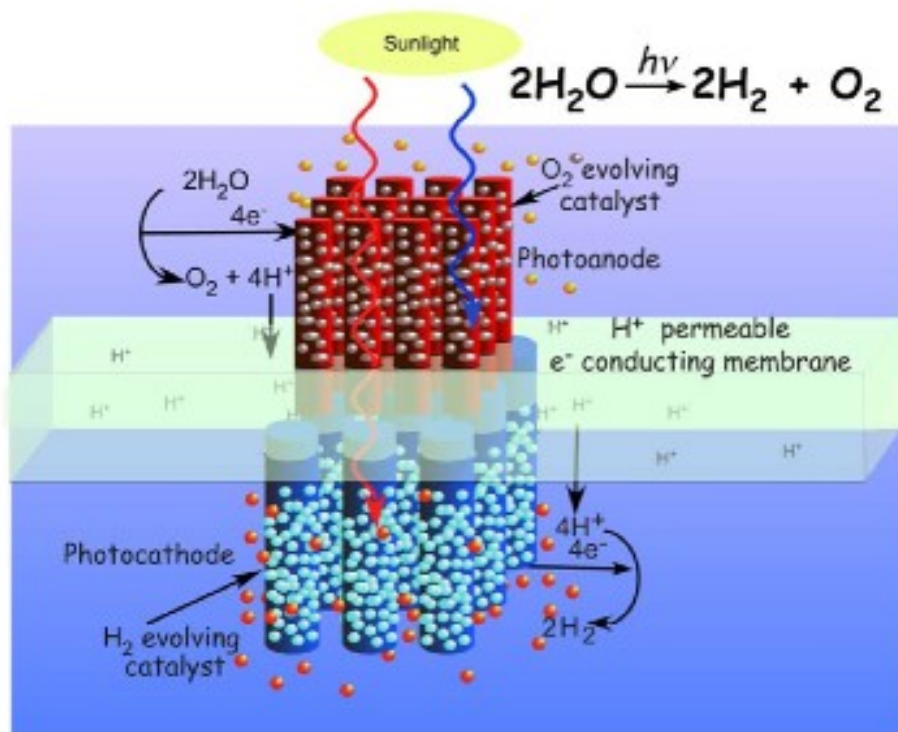




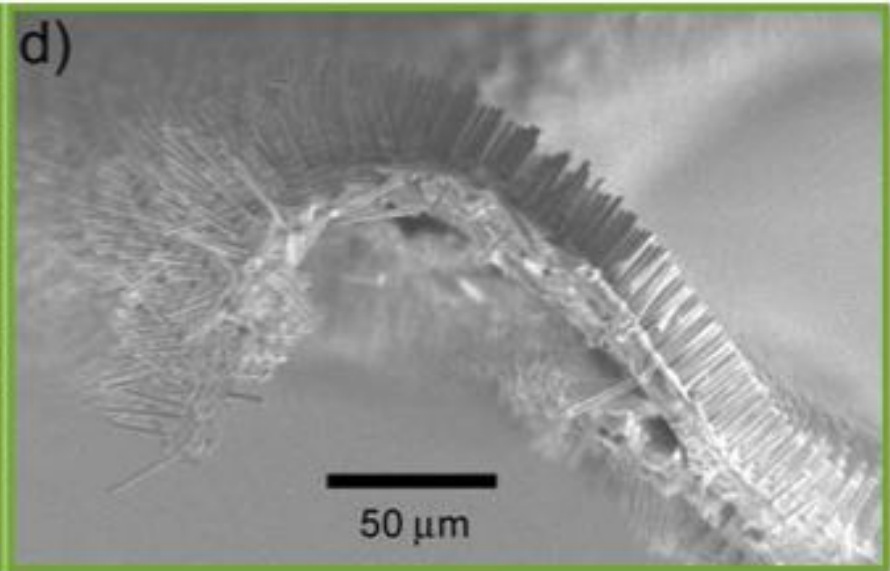
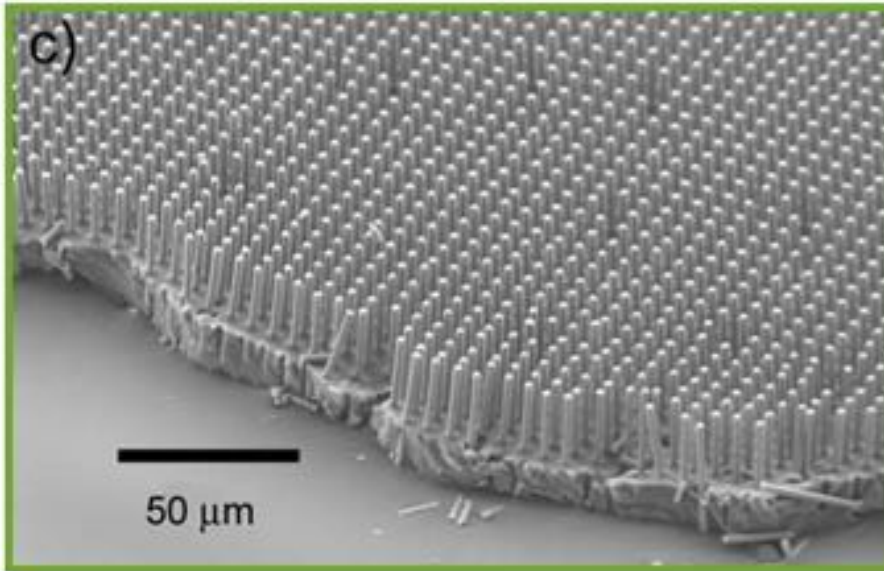


# Powering the Planet

## 3 Component Photoelectrochemical Water Splitting Model



- **membrane**-supported assembly that captures sunlight and efficiently creates separated electrons and holes having sufficient chemical potential to drive the water-splitting reactions
- **four-electron catalyst** for water **oxidation to  $\text{O}_2$**  at the photoanode
- **two-electron catalyst** to facilitate **reduction of water to  $\text{H}_2$**  at the photocathode



## Solar Carpet



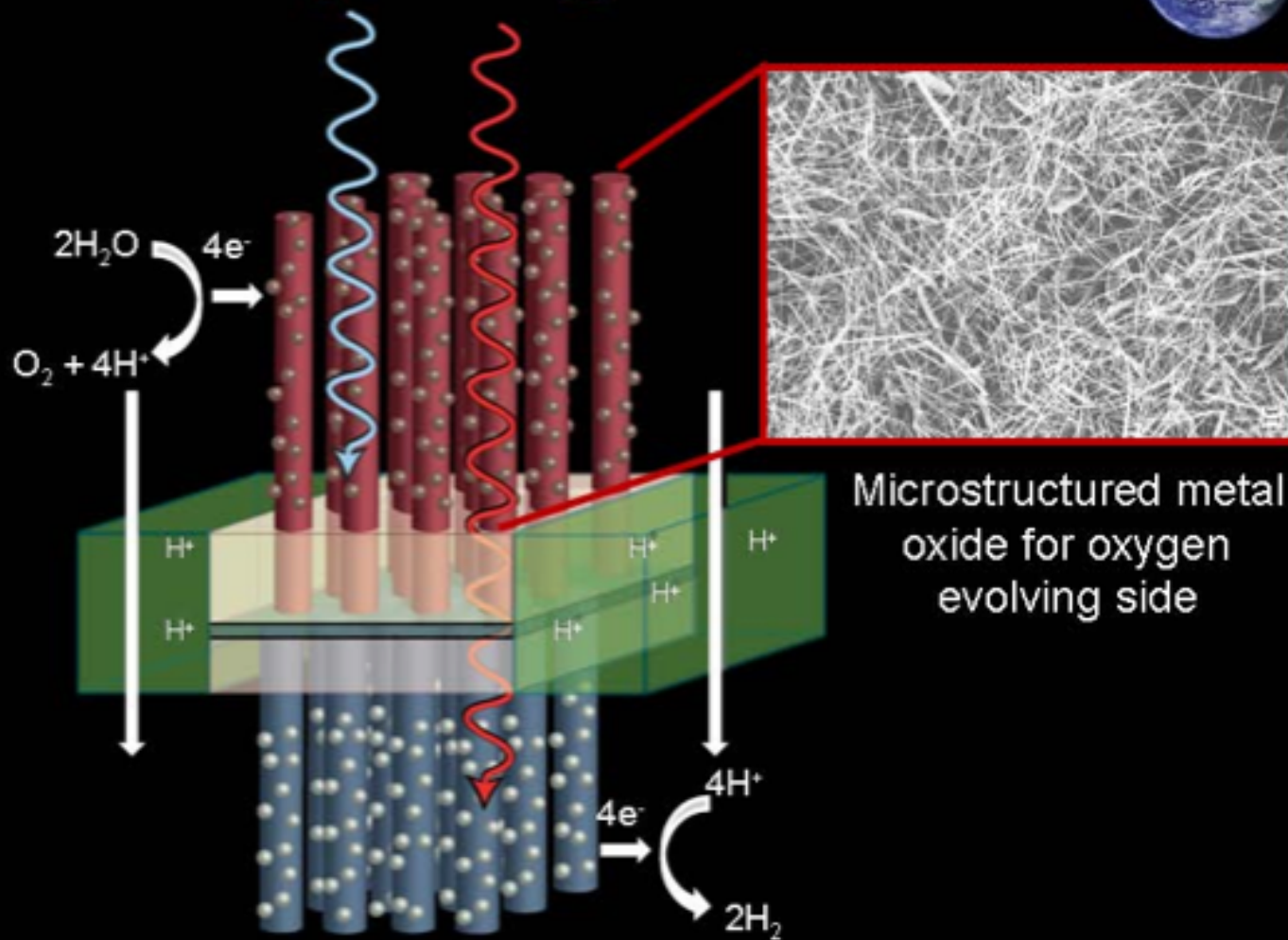
Josh Spurgeon, Brendan Kayes, Kate Plass,  
Shannon Boettcher, Nate Lewis



Harry Gray, Watson Lecture, 2/18/2009



# Solar Water-Splitting Membrane





# Nanostructured Cobalt Oxide Clusters in Mesoporous Silica as Efficient Oxygen-Evolving Catalysts

(Feng Jiao, Heinz Frei; Angewandte Chemie, 2009, 121:10 ,1873-76)

- Cobalt oxide nanocrystals can effectively be used to split water molecules, one of the half reactions critical to an artificial photosynthesis system for producing liquid fuels from sunlight.
- “The yield for clusters of cobalt oxide ( $\text{Co}_3\text{O}_4$ ) nano-sized crystals was about 1,600 times higher than for micron-sized particles,” said Frei, “and the turnover frequency (speed) was about 1,140 oxygen molecules per second per cluster, which is commensurate with solar flux at ground level (approximately 1,000 Watts per square meter).”
- Frei and Jiao used mesoporous silica as their scaffold, growing their cobalt nanocrystals within the naturally parallel nano-scale channels of the silica via a technique known as “wet impregnation”.

<http://newscenter.lbl.gov/press-releases/2009/03/10/turning-sunlight-into-liquid-fuels-berkeley-lab-researchers-create-a-nano-sized-photocatalyst-for-artificial-photosynthesis/>  
[http://pbd.lbl.gov/PBD\\_web\\_site/web\\_site/html/about/people/frei.html](http://pbd.lbl.gov/PBD_web_site/web_site/html/about/people/frei.html)

# MIT group's progress on catalyst for oxygen-evolving side

Tutorial Review

Chem. Soc. Rev., 2009, 38, 109 - 114, DOI: 10.1039/b802885k

## Cobalt–phosphate oxygen-evolving compound

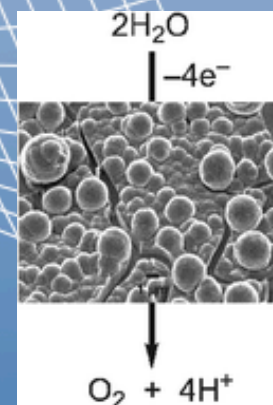
Matthew W. Kanan, Yogesh Surendranath and Daniel G. Nocera

The utilization of solar energy on a large scale requires efficient storage. Solar-to-fuels has the capacity to meet large scale storage needs as demonstrated by natural photosynthesis. This process uses sunlight to rearrange the bonds of water to furnish  $O_2$  and an  $H_2$ -equivalent. We present a tutorial review of our efforts to develop an **amorphous cobalt–phosphate catalyst that oxidizes water to  $O_2$** . The use of earth-abundant materials, operation in water at neutral pH, and the formation of the catalyst in situ captures functional elements of the oxygen evolving complex of Photosystem II.

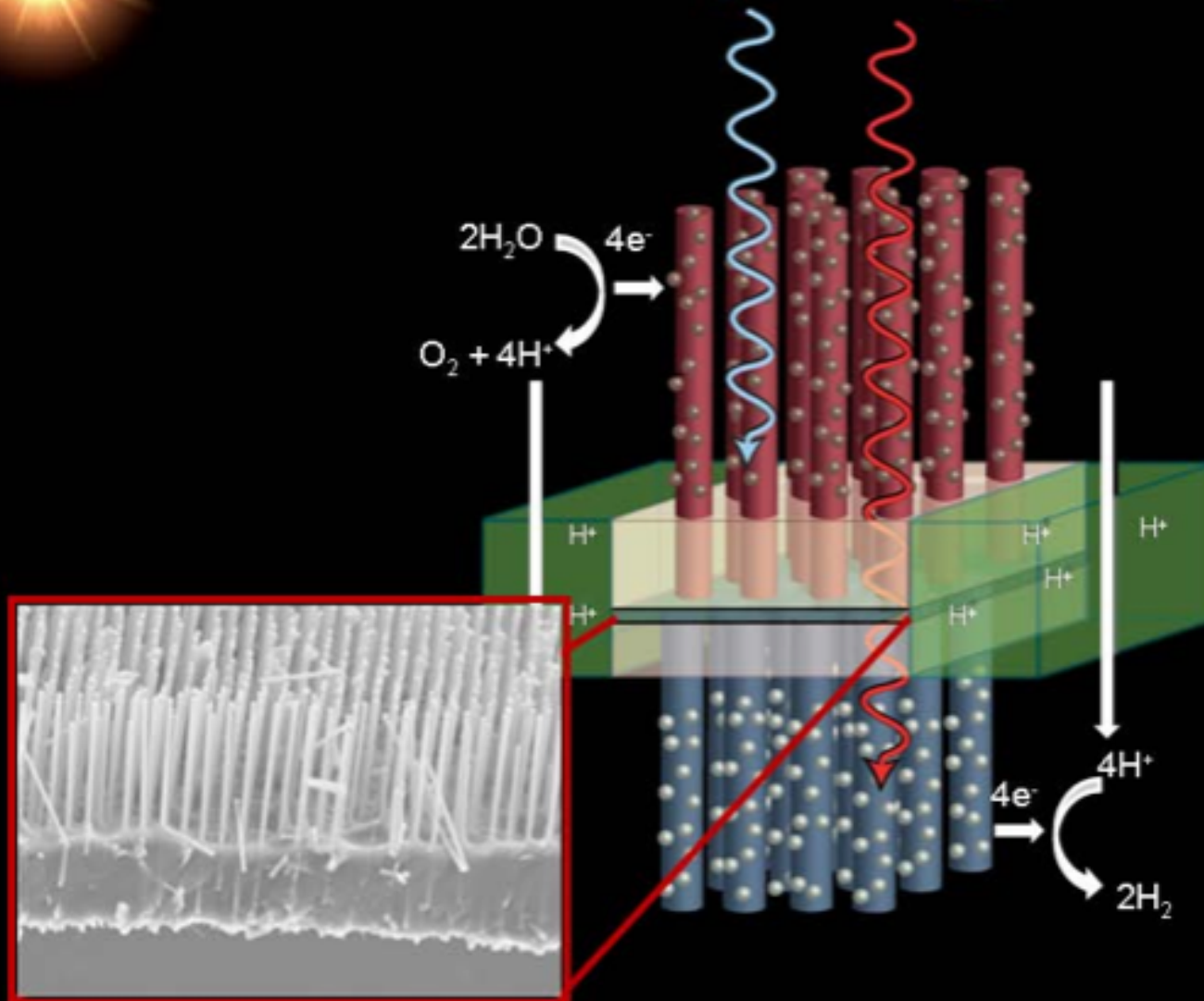
<http://www.technologyreview.com/Energy/21155/page1/>

<http://web.mit.edu/newsoffice/2008/oxygen-0731.html>

- runs on electricity from outlet
- still needs development work on photoanode material



# Solar Water-Splitting Membrane

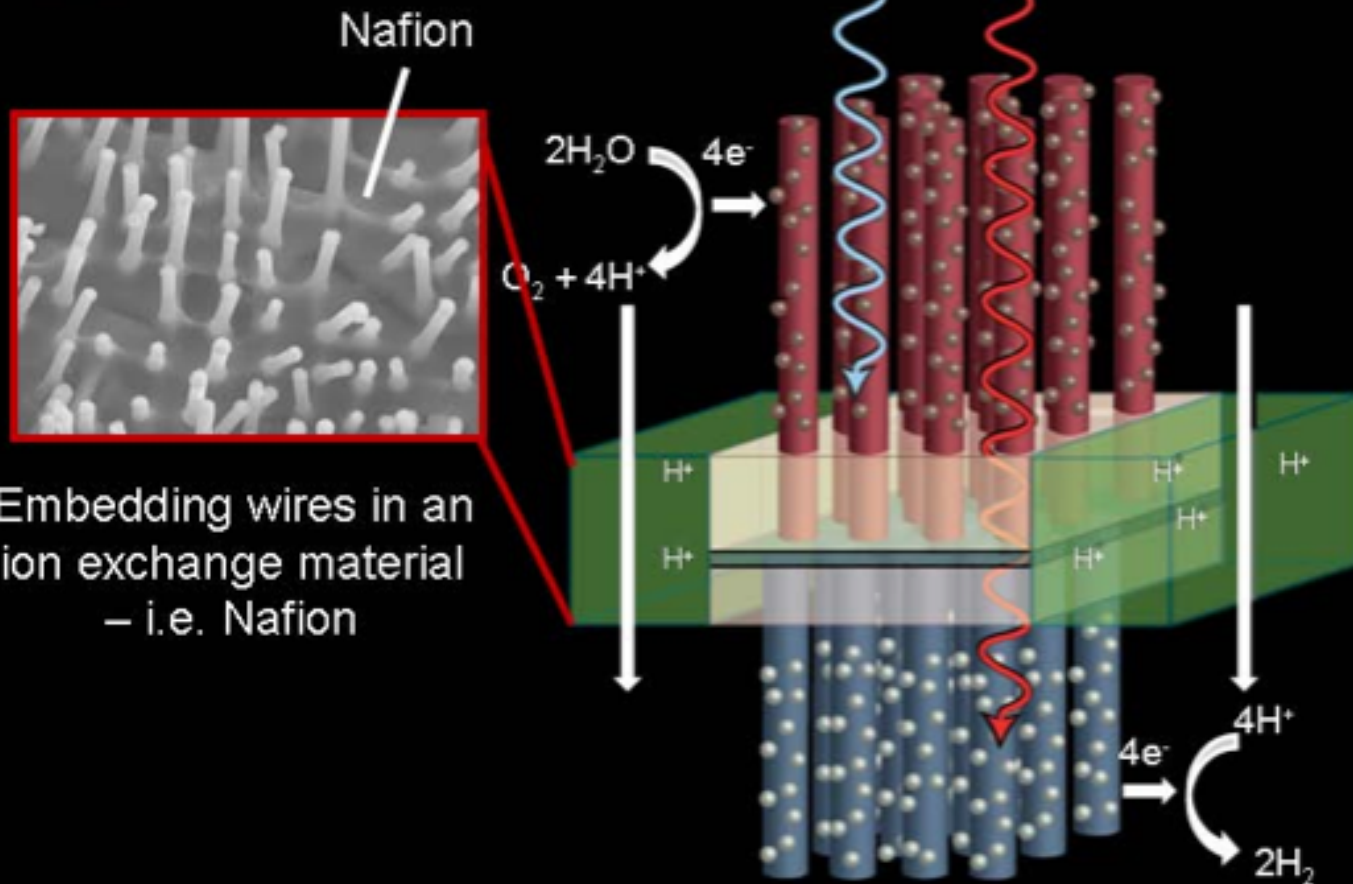


p-Si wire array embedded in transparent, structurally support film

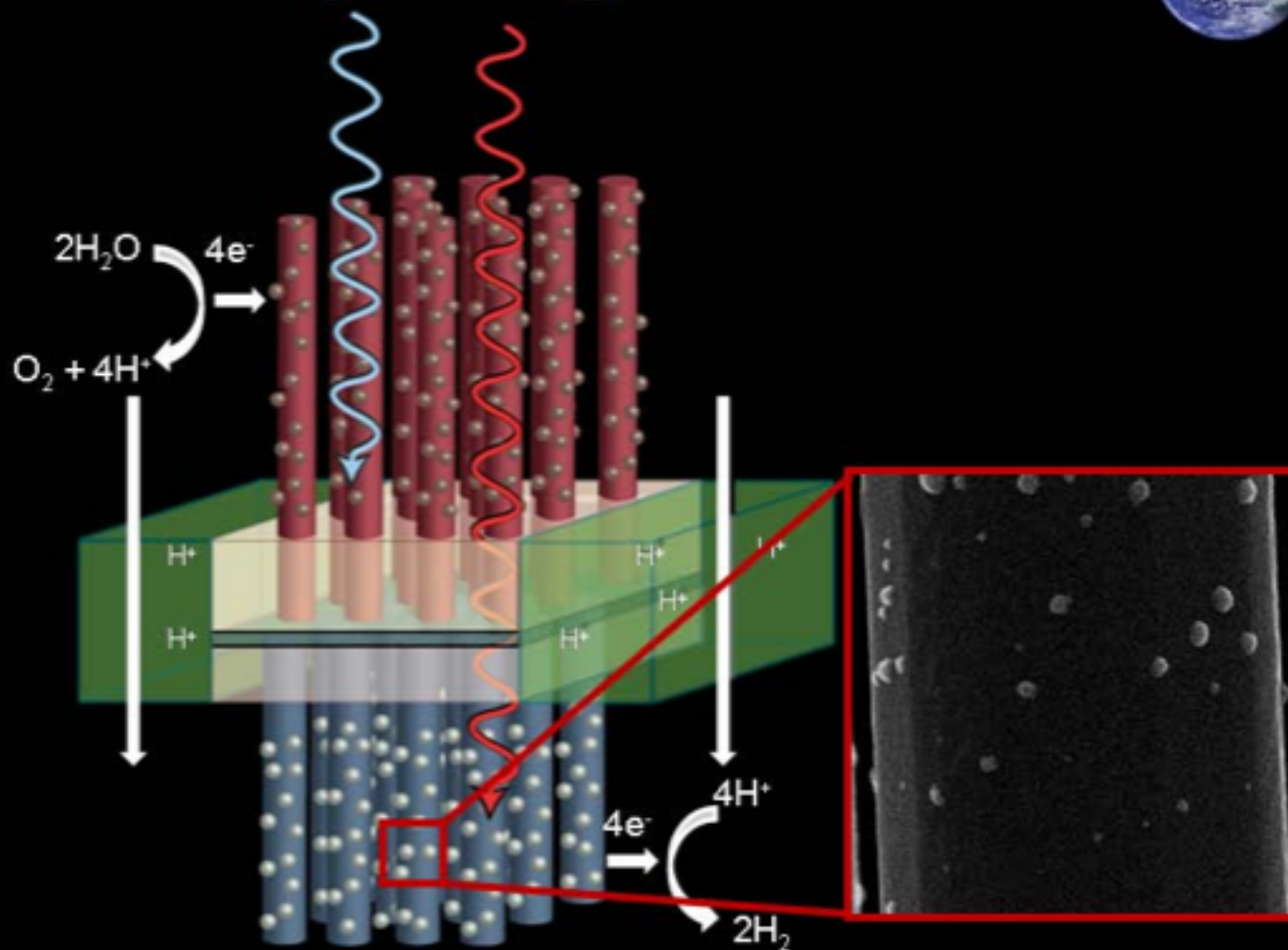




# Solar Water-Splitting Membrane

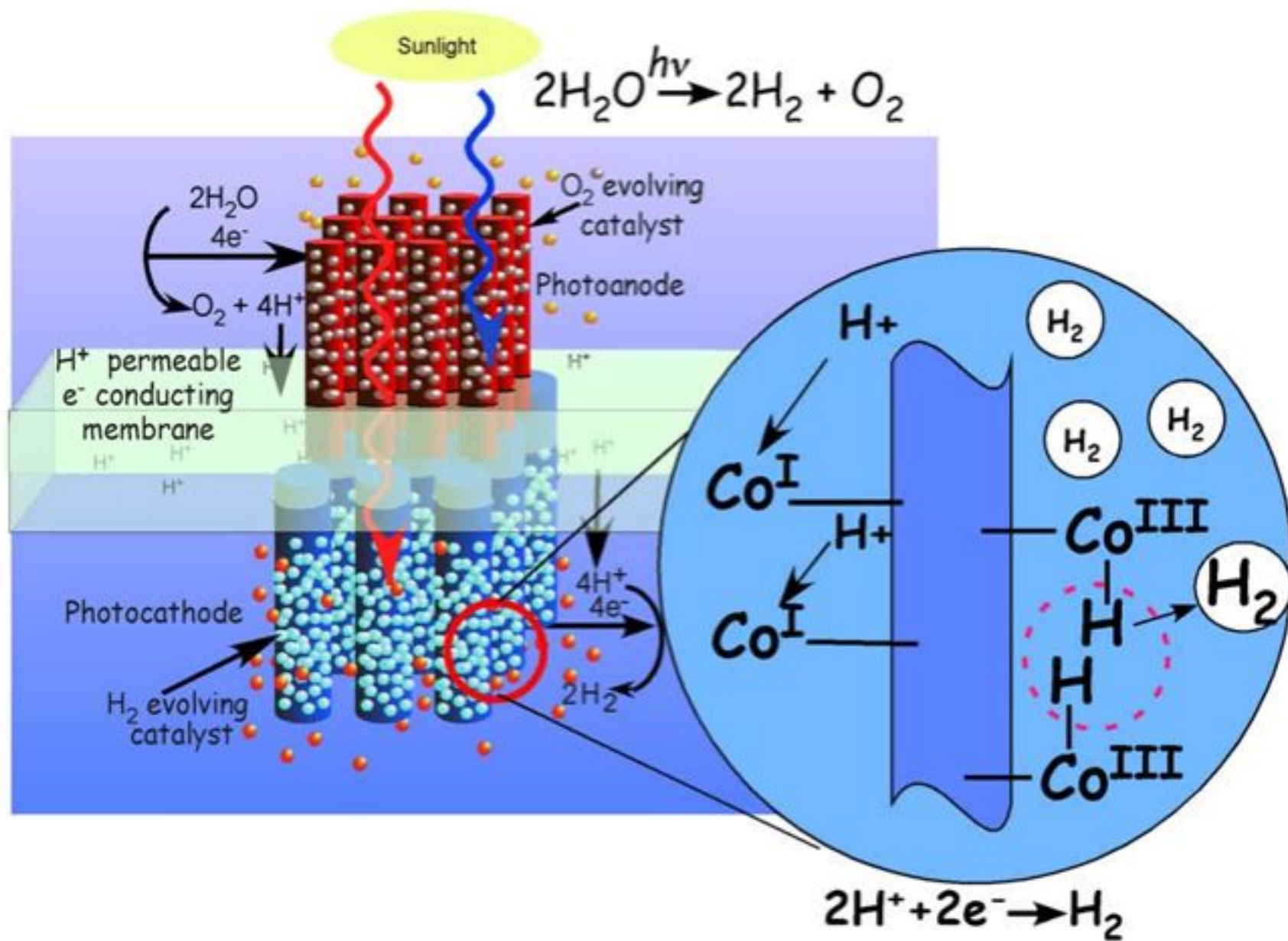


# Solar Water-Splitting Membrane



Wires decorated with catalyst  
(Pt, Ni, molecular catalyst)



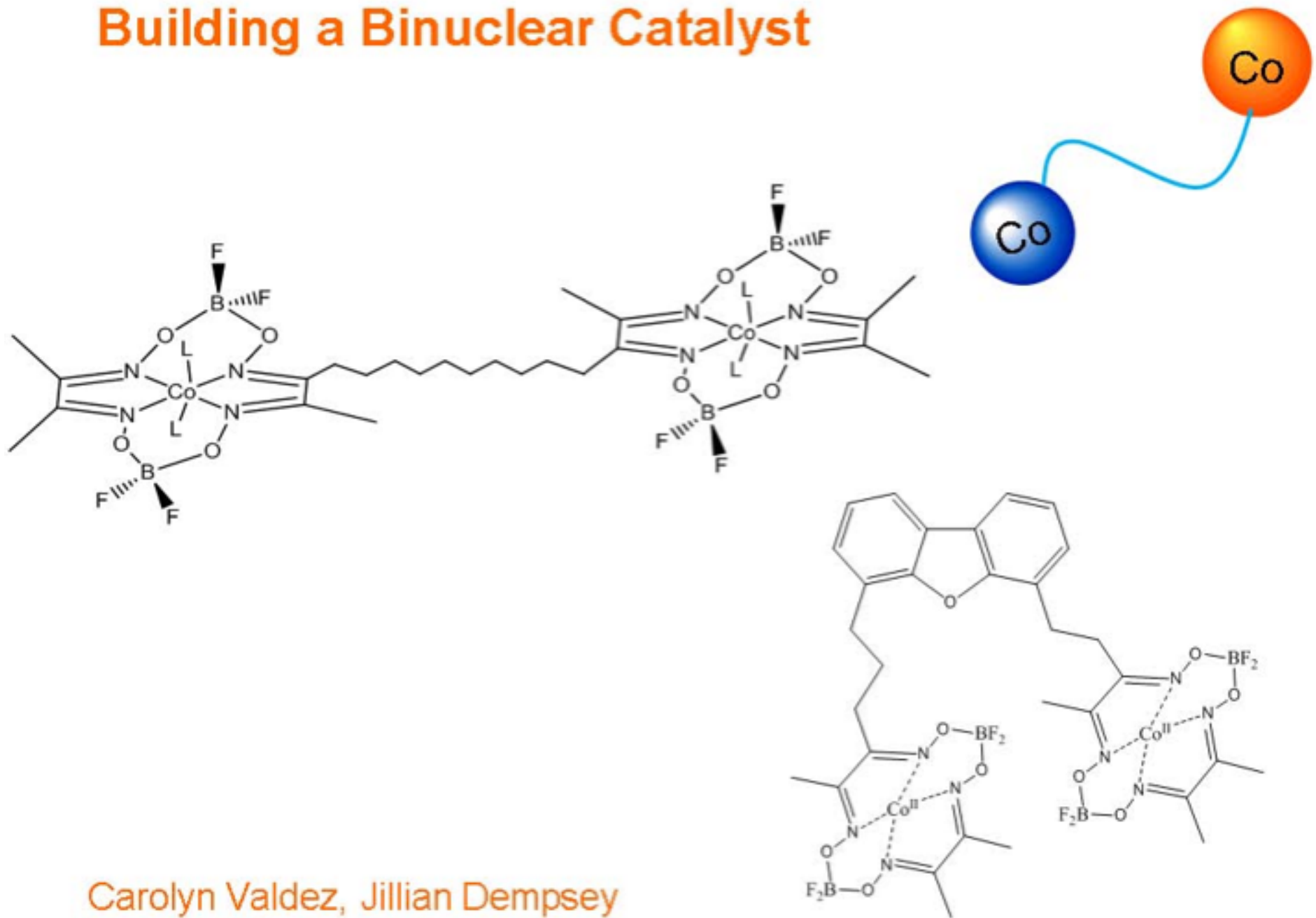


Carolyn Valdez, Jillian Dempsey

Harry Gray, Watson Lecture, 2/18/2009



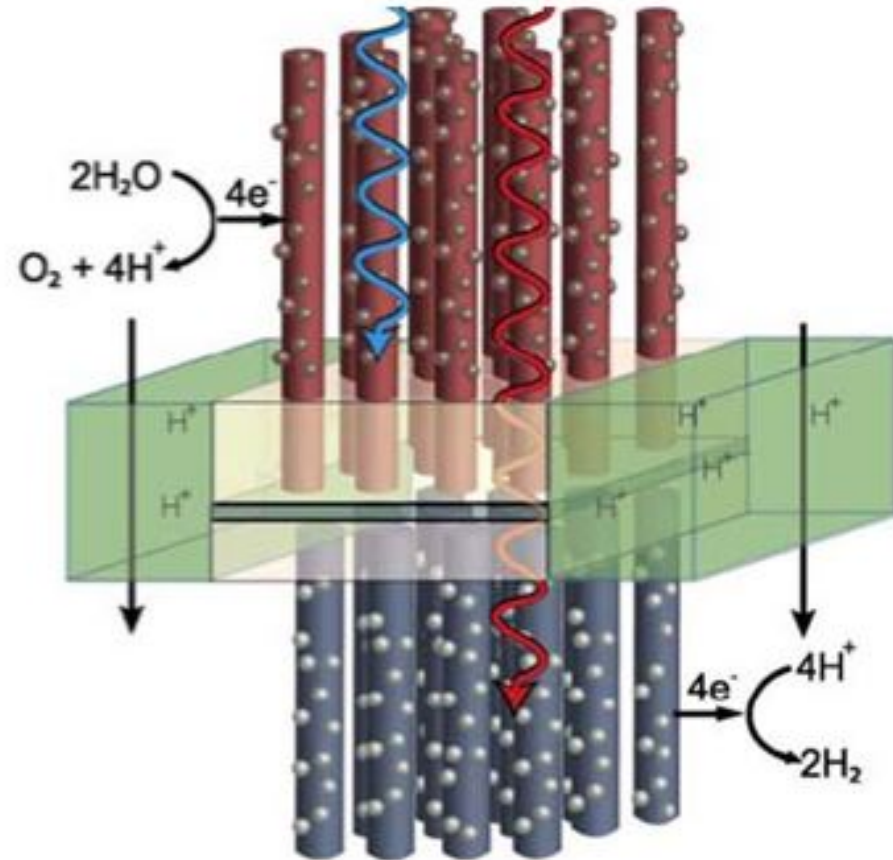
# Building a Binuclear Catalyst



Carolyn Valdez, Jillian Dempsey

Harry Gray, Watson Lecture, 2/18/2009

# Challenge: Water Oxidation!!



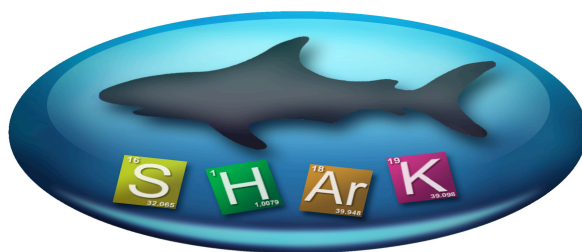
Powering the Planet



Harry Gray, Watson Lecture, 2/18/2009

# Metal Oxides Can Meet All the Criteria

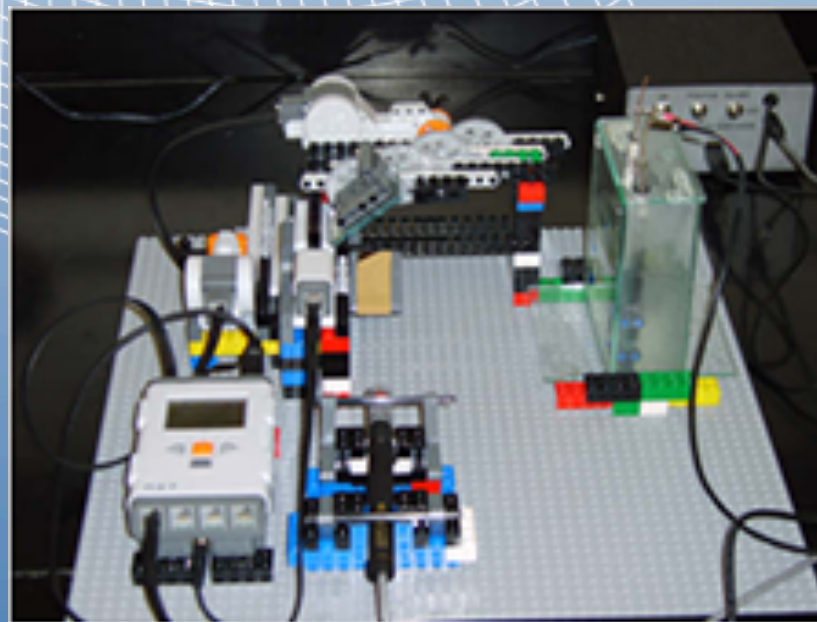
- 60 elemental metal oxides
- For ternary > 200,000
- For quaternary > 10,000,000



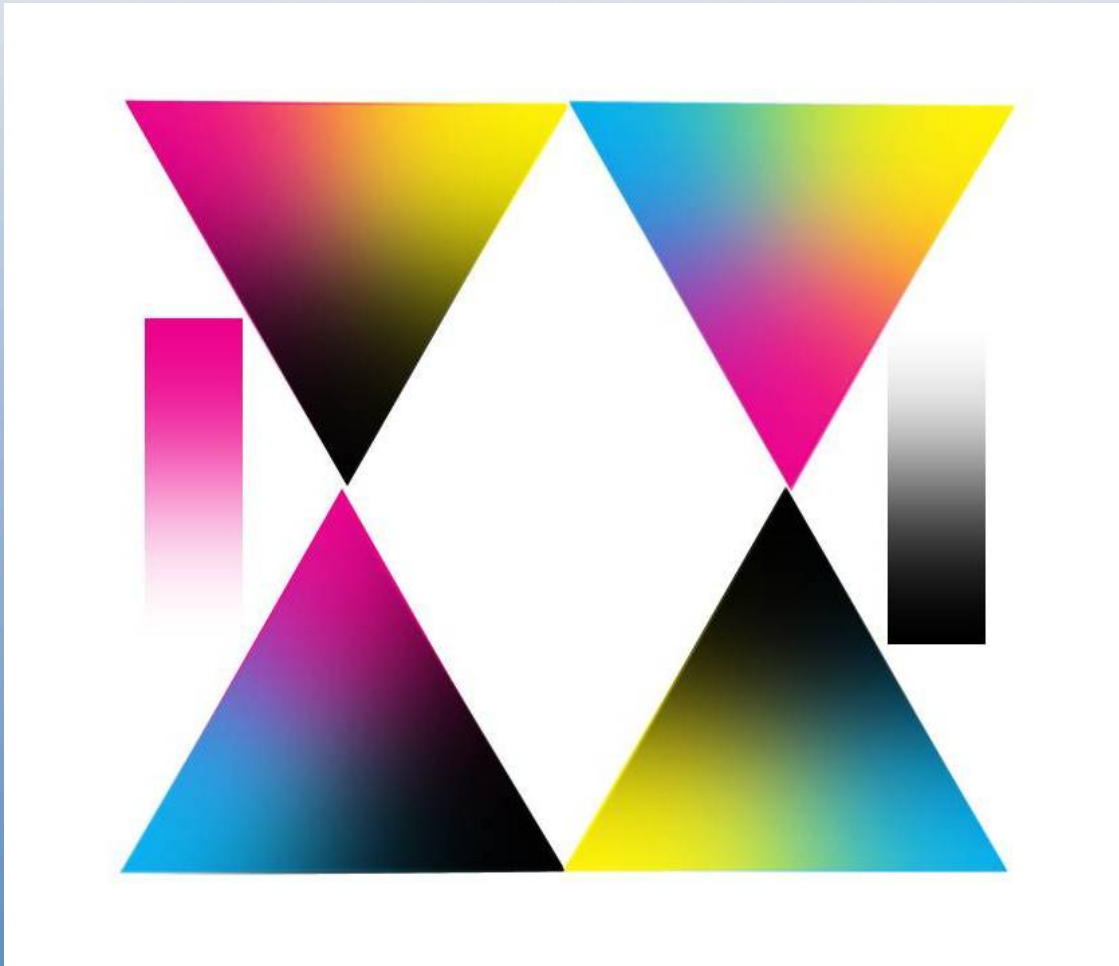


# A SHArK Project Kit

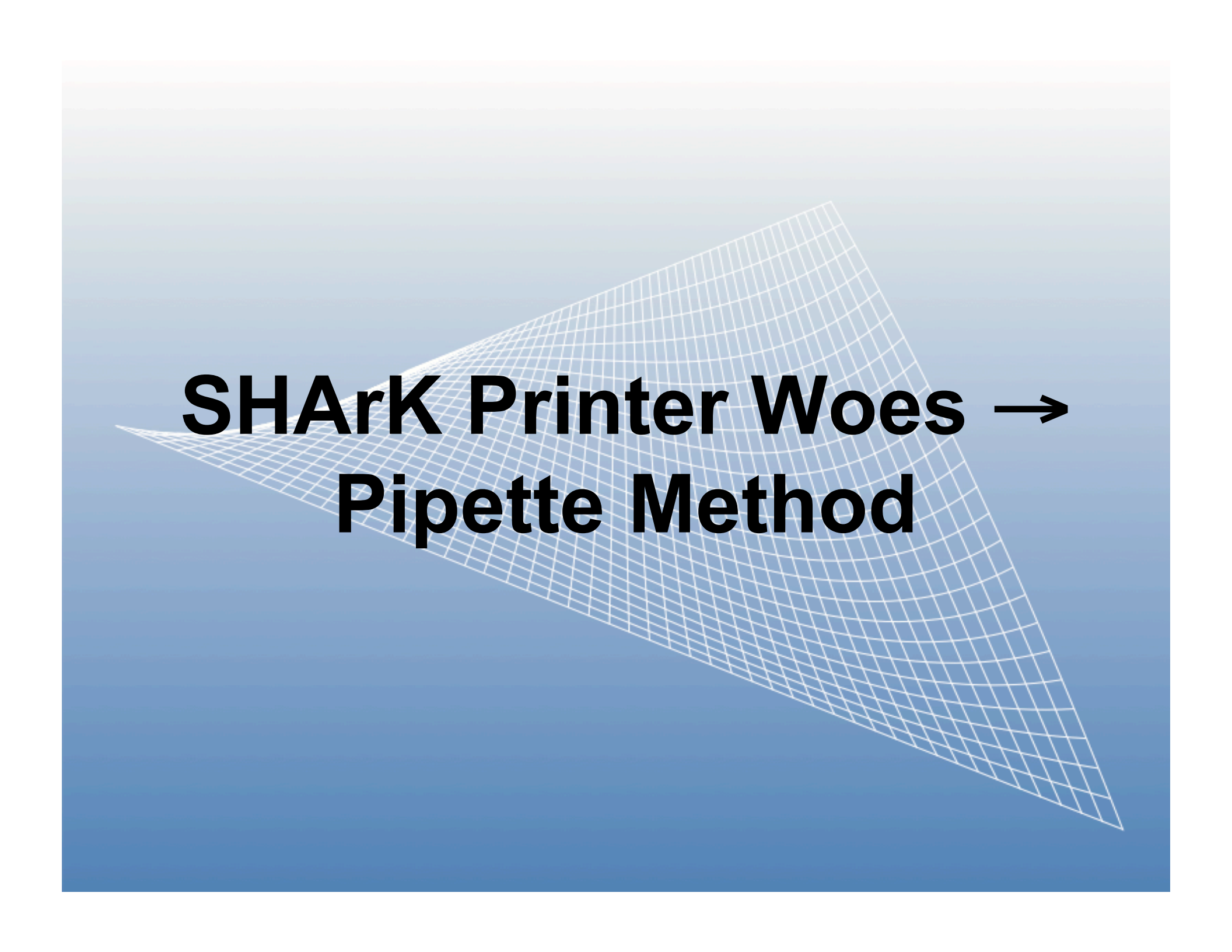
- LEGO Mindstorms® Kits
- Extra LEGOs® Parts
- Commercial Inkjet Printer
- Pipettes
- Commercial Green Laser Pointer
- Data Acquisition Box
- Conductive Glass Substrates
- Etched Glass Electrochemical Cell
- Alligator clips, Copper wire, and Graphite (counter-electrode)
- Laser Safety Goggles
- Software installed from website



# Printing Template for HP D5460



- **Black- Fe**
  - n-type standard
  - positive bias
- **Magenta- Cu**
  - p-type standard
  - negative bias
- **Cyan**
- **Yellow**



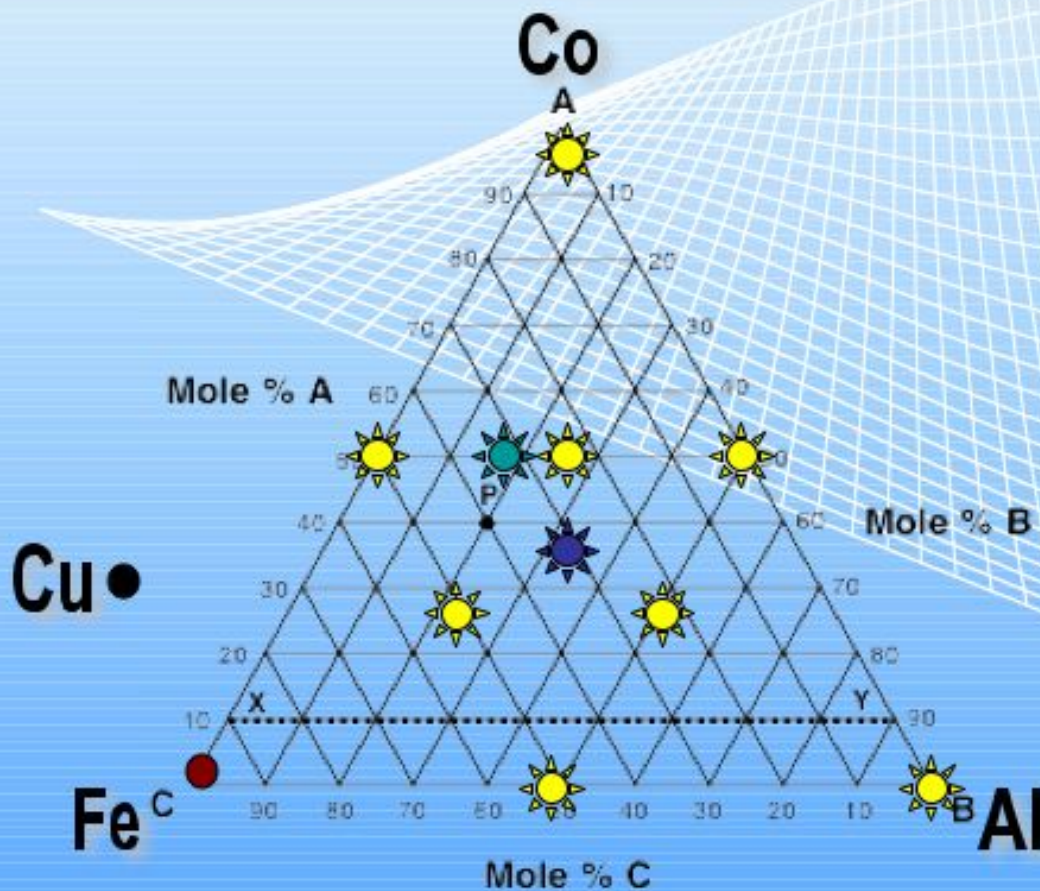
**SHArK Printer Woes →  
Pipette Method**



# SHArK Pipette Method

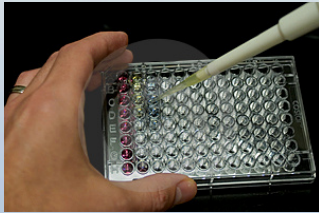
- **Glass substrate-** fluorine-doped tin oxide (FTO) coating
- **Metal precursors-** aqueous .35 M and .025 M metal nitrate solutions
  - 500 °C overnight to convert to metal oxides
- 10 different ternary metal nitrate combinations mixed in well plate
- 5  $\mu\text{L}$  drops pipetted onto conductive side of substrate in a 5x5 grid pattern which includes the internal standards

# SHArK Pipette Method Ternary Map (Co-Al-Fe)



- In addition to the standards (●, ●), **10 points** are selected on the ternary map to determine the combinations to be placed on the 5x5 grid.
- At the apex of the triangle is 100% Co, lower right corner is 100% Al, lower left corner is 100% Fe, center of triangle★ is equimolar mixture of Co-Al-Fe.

# SHArK Pipette Method



## Co-Al-Fe

Fe	Fe	Cu	Cu	1:1:1
Co	Co	Al*	Al*	1:1:1
1:1:0	1:1:0	1:0:1	1:0:1	0:1:1
2:1:1	2:1:1	1:2:1	1:2:1	0:1:1
1:1:2	1:1:2	3:1:2	Cu	Fe

Laser Calibration Card



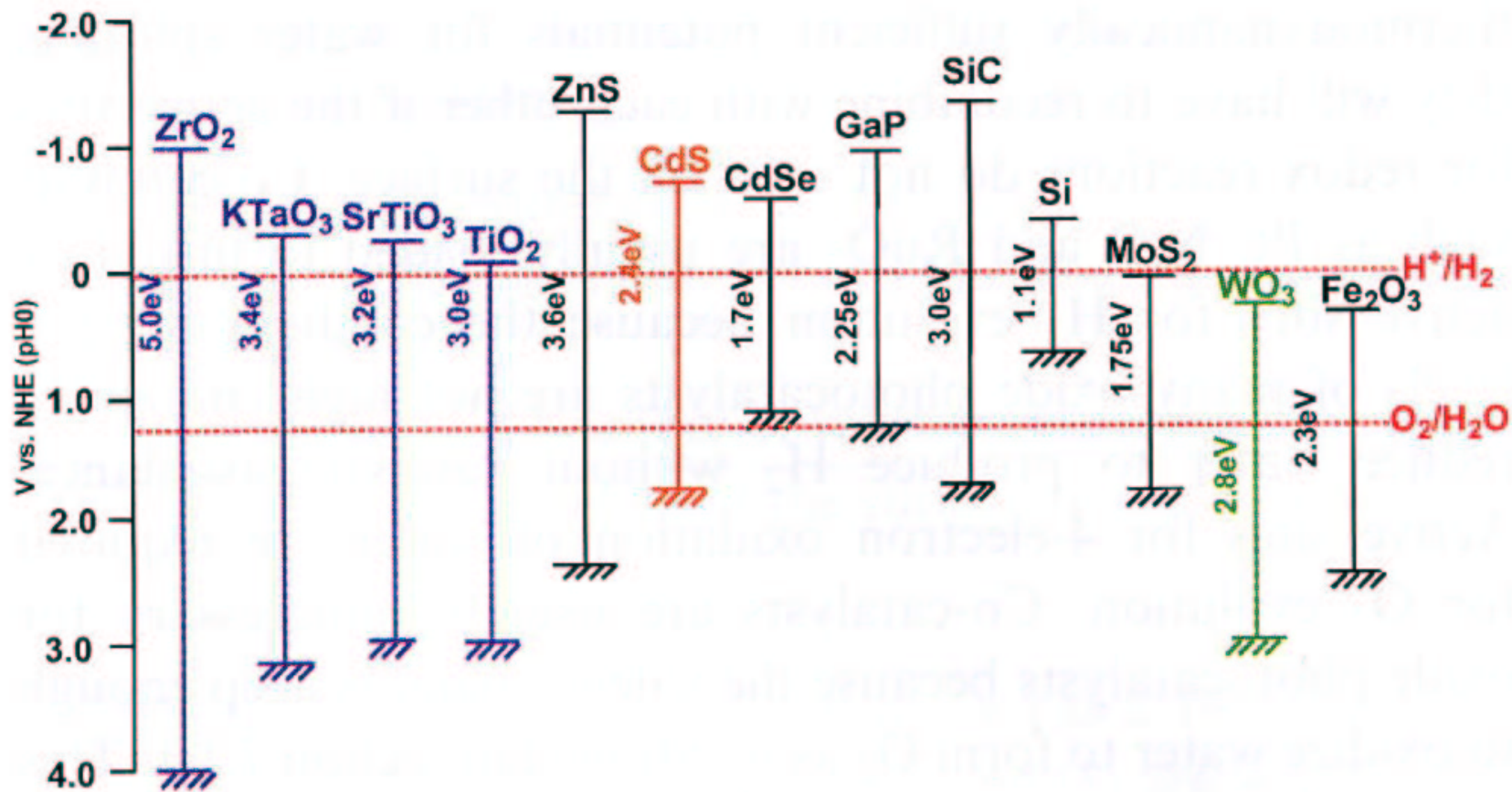
\*Al drops are colorless.



# Metal Oxides- Potential Role in Photoelectrode

- **Structural** (Ti, W, Zr, Ta, Si, Mo, Nb, Hf, In, Sn, Ga, Y, Sc)
- **Light absorbing** (Fe, Cr, V, Co, Mn, Ni, Cu, and some rare earths such as Ce)
- **Catalytic** (Ru, Rh, Pd, Pt, Ir, Os, Re, Ni)
- **Ionic charge compensators** (Ca, Sr, Ba, Mg, Zn, Cd, Li, Na, K, Rb, Cs)
- **Avoid toxic metals** (Pb, Tl, Cd, Hg)

# Semiconductor Redox Levels



From Professor Carl Wamser

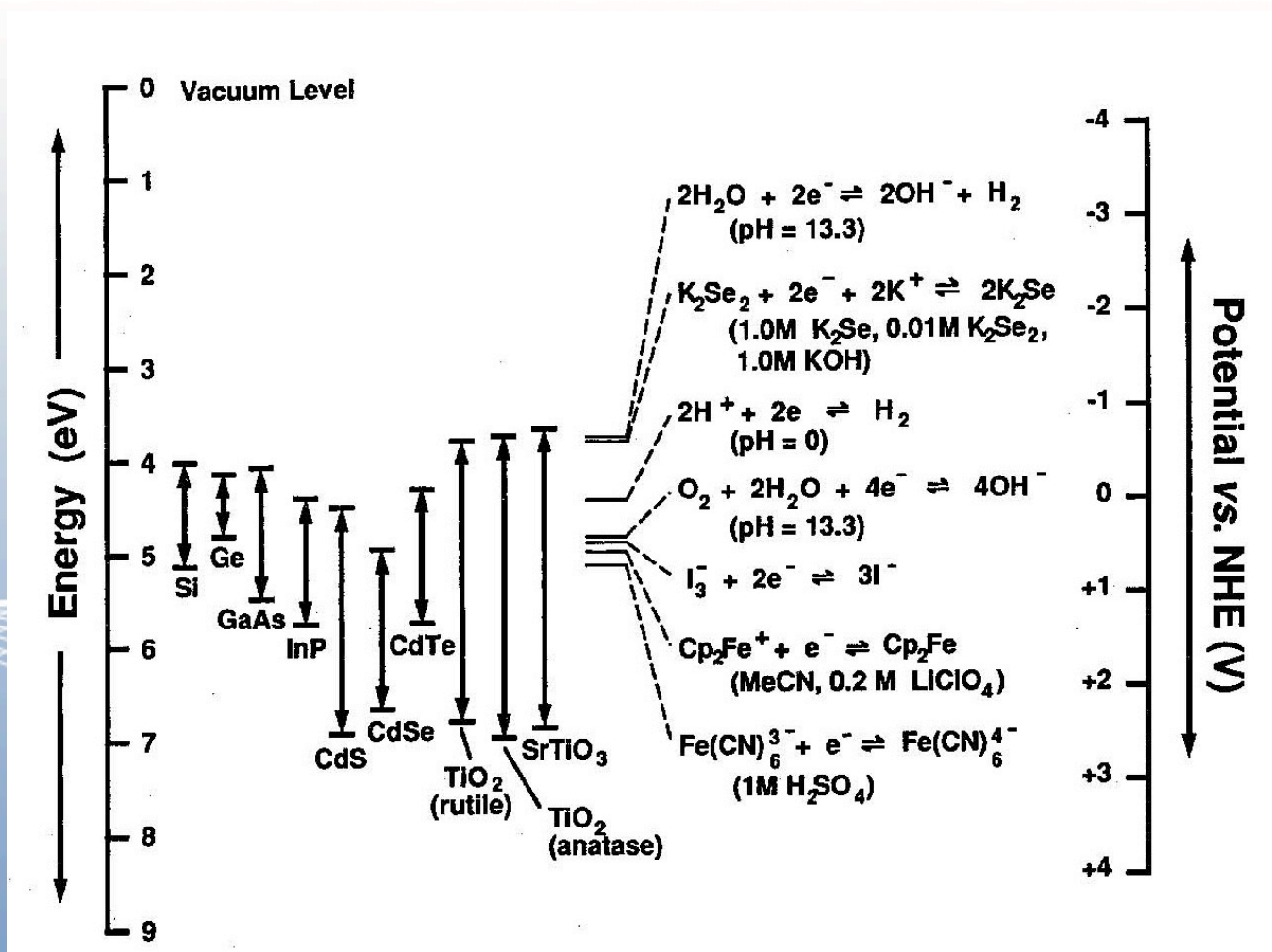


Figure 13. The positions of the conduction and valence band edges of various semiconductors and the redox potentials of selected solutions. The semiconductor conduction band edge positions are determined from electron affinity measurements, and are referenced against the vacuum level (45, 56, 81). The solution redox potentials are measured against the NHE in V (78, 82) and can be converted to energies (eV) by multiplying by  $q$ . The electrochemical potential of the normal hydrogen electrode (NHE) is taken to be 4.43 eV below the vacuum level (80). It should be noted that the band edge positions of TiO<sub>2</sub> and SrTiO<sub>3</sub> depend on the pH of the contacting solution. The positions illustrated here are for these semiconductors when in contact with solutions of pH = 13.3 (56, 82). The potentials for the reduction of H<sub>2</sub>O to H<sub>2</sub>(g), and for the oxidation of H<sub>2</sub>O to O<sub>2</sub>(g), are also given for pH = 13.3. From the figure, it is obvious that TiO<sub>2</sub> (rutile) cannot reduce water, while TiO<sub>2</sub> (anatase) and SrTiO<sub>3</sub> can split water to H<sub>2</sub>(g) and O<sub>2</sub>(g) under standard conditions.

- Fine structure is important.
- TiO<sub>2</sub>(rutile) cannot reduce H<sub>2</sub>O.
- TiO<sub>2</sub>(anatase) can split H<sub>2</sub>O to H<sub>2</sub> and O<sub>2</sub>.



# Metal Oxides- Potential Role in Photoelectrode

- Ideally, would like semiconductor with band gap between 1.1 and 1.7 eV (near IR) to optimize solar absorption and minimize waste heat from photoexcitation. However, such semiconductors tend to easily corrode and are not stable in a photoelectrochemical cell.
  - Solar: 1 to 3 eV
  - Si: 1.1 eV
  - TiO<sub>2</sub>: 3.03 eV for rutile and 3.18 for anatase
- “Structural” metal oxide components which are stable chemically typically have large band gaps and need to be paired with a “light absorbing” component.

# Scanning Basics

- $\alpha\text{-Fe}_2\text{O}_3$  is **n-type standard** (photoanode,  $\text{O}_2$  production)
  - “Lights up” with **positive bias**
- **CuO** is **p-type standard** (photocathode,  $\text{H}_2$  production)
  - “Lights up” with **negative bias**
- Metal oxide arrays are scanned for solar water splitting potential using the Lego® Laser Scanning Station ( $\lambda = 532$  nm, green).
  - Material with photocurrent response at least 2 times higher than either of the standards is considered promising.

# Distributed SHArK Network

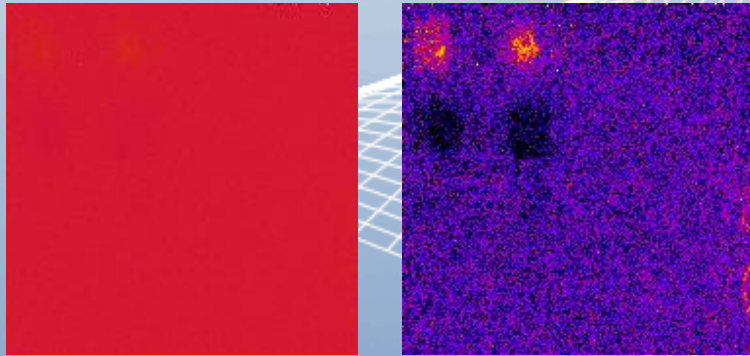


- SHArK sites exist all over the U.S., as well as one in Germany.
- Networking and collaboration mediated by the SHArK website (<http://www.thesharkproject.org/>).
- Data from experiments are posted online and accessible to all in the network.
- Easy sharing and collaboration via online SHArK forums and blogs.

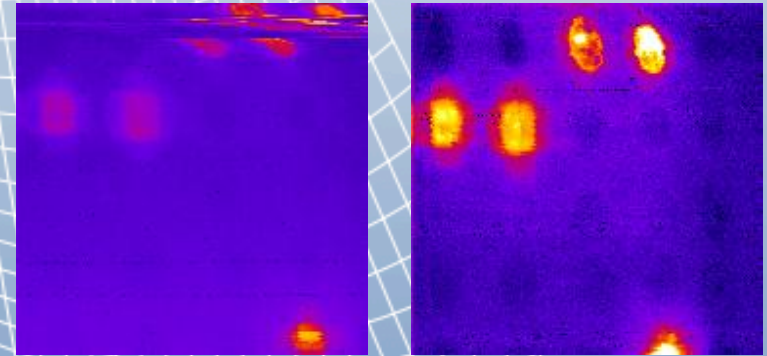


# Early Mistakes with 1st Plate Scanned .35 M Co-Al-Fe

## Positive Bias



## Negative Bias



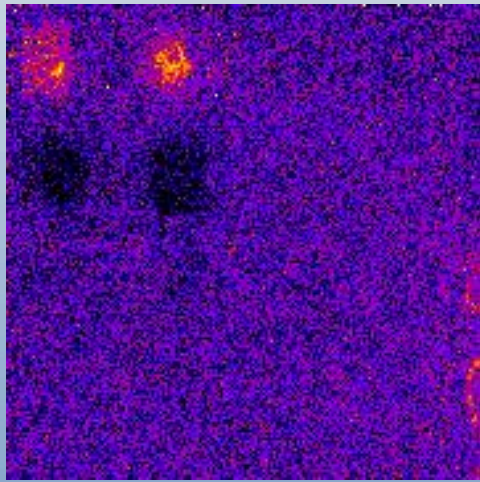
- Learning to use the brightness and contrast controls
- Don't delete a "botched" scan! You never know...

Fe	Fe	Cu	Cu	1:1:1
Co	Co	Al	Al	1:1:1
1:1:0	1:1:0	1:0:1	1:0:1	0:1:1
2:1:1	2:1:1	1:2:1	1:2:1	0:1:1
1:1:2	1:1:2	3:1:2	Cu	Fe

- Need to fill the cell high enough to prevent distortion from surface refraction

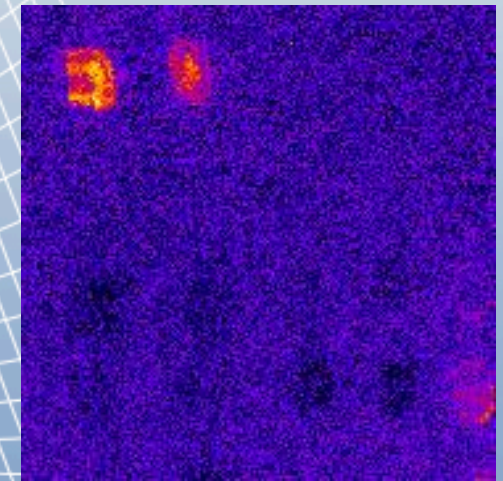
# Photocurrent Images: Co-Al-Fe

Bias = +0.5V, Electrolyte: 0.1 M NaOH



**.35 M** metal precursor,  
5  $\mu\text{L}$  drops on 5x5 grid  
Fe: +0.1  $\mu\text{A}$   
Co: -.03  $\mu\text{A}$

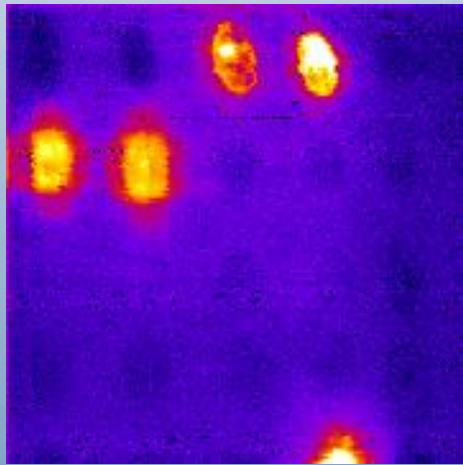
Fe	Fe	Cu	Cu	1:1:1
Co	Co	Al	Al	1:1:1
1:1:0	1:1:0	1:0:1	1:0:1	0:1:1
2:1:1	2:1:1	1:2:1	1:2:1	0:1:1
1:1:2	1:1:2	3:1:2	Cu	Fe



**.025 M** metal precursor,  
5  $\mu\text{L}$  drops on 5x5 grid  
Fe: +0.2  $\mu\text{A}$   
Co: negligible

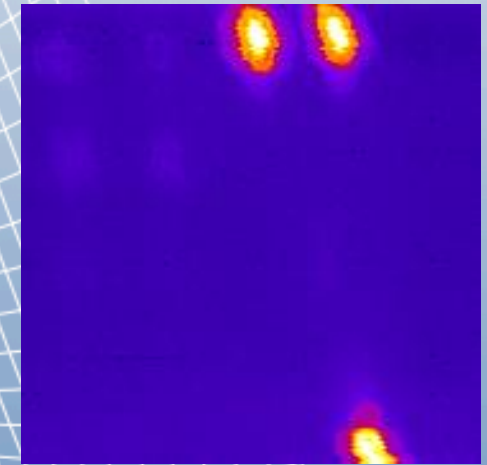
# Photocurrent Images: Co-Al-Fe

Bias = -0.5V, Electrolyte: 0.1 M NaOH



**.35 M** metal precursor,  
5  $\mu\text{L}$  drops on 5x5 grid  
Cu: +1.4  $\mu\text{A}$   
Co: +0.6  $\mu\text{A}$  (40% of Cu)

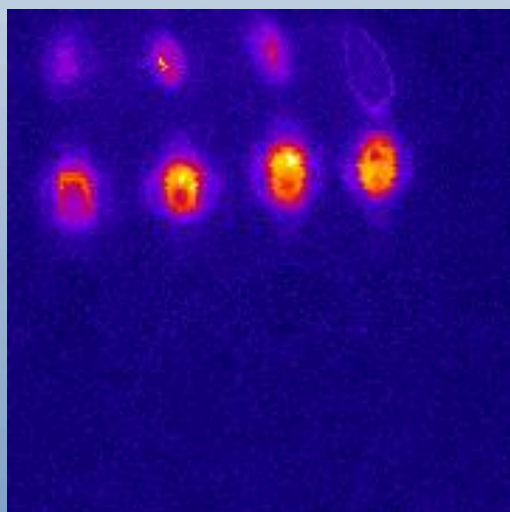
Fe	Fe	Cu	Cu	1:1:1
Co	Co	Al	Al	1:1:1
1:1:0	1:1:0	1:0:1	1:0:1	0:1:1
2:1:1	2:1:1	1:2:1	1:2:1	0:1:1
1:1:2	1:1:2	3:1:2	Cu	Fe



**.025 M** metal precursor,  
5  $\mu\text{L}$  drops on 5x5 grid  
Cu: +4.7  $\mu\text{A}$   
Co: +0.1  $\mu\text{A}$  (2% of Cu)

# Photocurrent Images: Fe-Cu-Co

Electrolyte: 0.1 M NaOH



**Bias = +0.5V**

<b>Fe-A</b> a	<b>Fe-A</b> b	<b>Fe-A</b> c	<b>Fe-A</b> d	<b>Co-B</b> a
<b>Fe-B</b> a	<b>Fe-B</b> b	<b>Fe-B</b> c	<b>Fe-B</b> d	<b>Co-B</b> b
<b>Cu-A</b> a	<b>Cu-A</b> b	<b>Cu-A</b> c	<b>Cu-A</b> d	<b>Co-B</b> c
<b>Cu-B</b> a	<b>Cu-B</b> b	<b>Cu-B</b> c	<b>Cu-B</b> d	<b>Co-B</b> d
<b>Co-A</b> a	<b>Co-A</b> b	<b>Co-A</b> c	<b>Co-A</b> d	

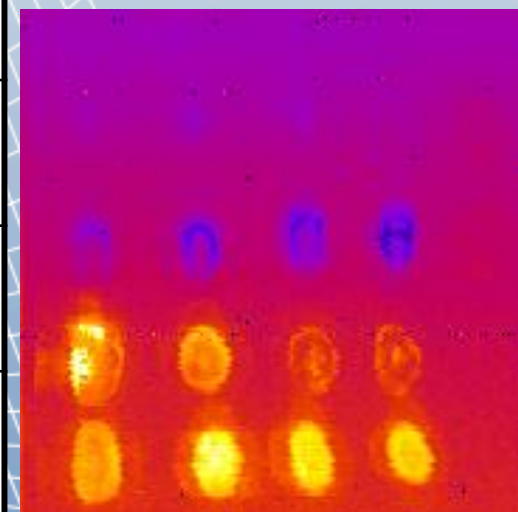
**Concentration**

A = .35 M metal precursor

B = .025 M metal precursor

**Drop Size**

a = 7  $\mu$ L, b = 5  $\mu$ L, c = 3  $\mu$ L, d = 1  $\mu$ L



**Bias = -0.5V**



# Drop Size Variation and Photocurrent Response

## Positive Bias

Metal Oxide Concentration	Drop Size ( $\mu\text{L}$ )	*Photocurrent ( $\mu\text{A}$ )
.35M Fe	7	.25
.35M Fe	<b>5</b>	.38 to <b>.76</b>
.35M Fe	<b>3</b>	<b>.49</b>
.35M Fe	1	.05 to .09
.025M Fe	7	.34 to .70
.025M Fe	<b>5</b>	.59 to <b>1.30</b>
.025M Fe	<b>3</b>	.71 to <b>1.33</b>
.025M Fe	1	.61 to .97

## Negative Bias

Metal Oxide Concentration	Drop Size ( $\mu\text{L}$ )	*Photocurrent ( $\mu\text{A}$ )
.35 Cu	7,5,3,1	**
.025 Cu	7	.4 to <b>1.4</b>
.025 Cu	<b>5</b>	<b>.5</b>
.025 Cu	3	.2
.025 Cu	1	.2
.35 Co	7	.6
.35 Co	<b>5</b>	<b>1.3</b>
.35 Co	3	1.0
.35 Co	1	.9
.025 Co	7,5,3,1	negligible

\*\* .35 Cu drops- photocurrent responses near or slightly below background

\*Measurements taken in central "hot" zones when possible. Ranges given for more inhomogeneous drops. Averaged over pixel area of 12 (180 x 180 scan array) and background subtracted.

# Drop Size Variation and Photocurrent Response

- Overall, 5  $\mu\text{L}$  is good drop size.
  - Good photocurrent response.
  - Not so large that it “runs into” adjacent drops.
- .35 M Cu drop series showed near background or slightly below background activity.
  - ? Too thick- photogenerated carriers recombine before reaching conducting surface.
  - noise, possible contamination
- .35 M Co drop series- greater photocurrent response for the the 5  $\mu\text{L}$  drop in this series than on the earlier .35 M Co-Al-Fe plate scan.
  - Possibly secondary to difference in sample prep and fine structure of drops.
  - Pronounced p-type Co activity at .35 M consistent with a promising p-type photocatalyst.
- Discrepancies may be further investigated by looking into the fine microscopic differences between the .35 M Cu and .35 M Co drops on the different plates.

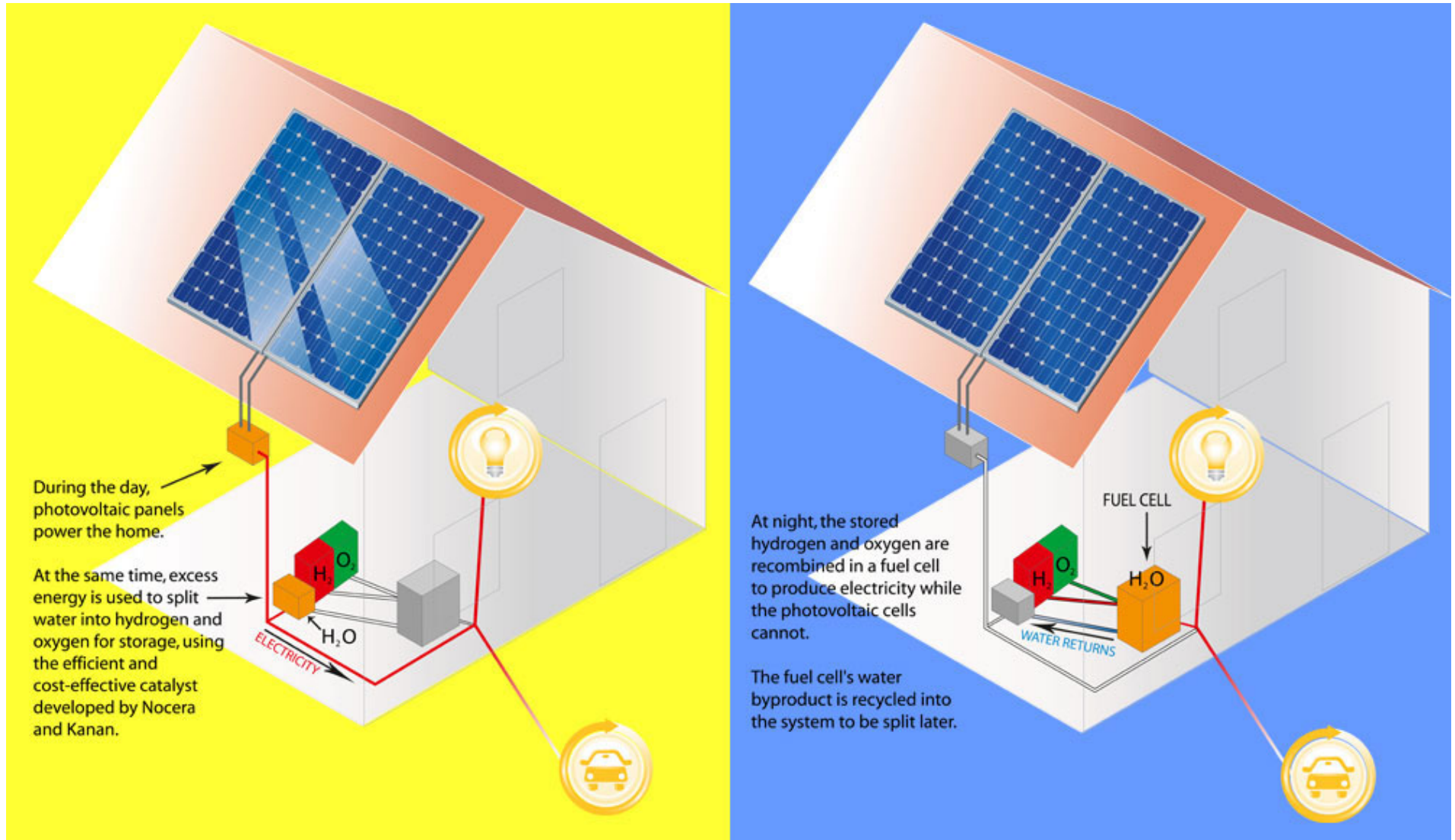
# Discussion

- Photocurrent responses for the standards increased 2 and 3-fold after decreasing the metal precursor concentrations from .35 M to .025 M (.1 to .2  $\mu\text{A}$  for Fe and 1.4 to 4.7  $\mu\text{A}$  for Cu) with demonstration of greater p-type activity than n-type at both concentrations.
- Instead, Co showed a 95% decrease in p-type activity from .35 M to .025 M (40% of Cu activity to 2%).
- Drop size evaluation favored 5  $\mu\text{L}$  drops and showed more pronounced p-type Co activity at .35 M consistent with a promising p-type photocatalyst.
- Inhomogeneities exist within individual drops
  - Thickness variation across drops due to surface tension
  - Concentration variations within drops
  - Mixture of oxide states [e.g. Cobalt oxide- Co (II) oxide ( $\text{CoO}$ ), Co (III) oxide ( $\text{Co}_2\text{O}_3$ ), Co (II, III) oxide ( $\text{Co}_3\text{O}_4$ )]
  - Heterogeneous fine particle structure details

# What's Next?

- Recommend scanning **both** .35 M and .025 M preps using 5  $\mu$ L drops.
- Examine fine structure of droplets (optical microscopy, SEM, XRD).
- Investigate nano-particle methods of preparation such as sol-gel chemistry and/or wet impregnation<sup>9</sup>. Would require both different prep and scanning systems.
  - Enhanced surface area associated with nano-scale has potential of significantly increasing photocatalytic efficiency.
- Continue studying other metal oxide combinations- particularly, Co-based ones. In addition to p-type ( $H_2$ -evolving) photocatalytic potential demonstrated here, others<sup>9,10</sup> have found Co to be a promising base as an n-type ( $O_2$ -evolving) photocatalyst.
- Try different substrate preps to look at surface tension effects.
- Continue outreach efforts that engage young students and researchers around the world in a concerted effort to solve the global energy and climate change problems.





<http://web.mit.edu/newsoffice/2008/oxygen-0731.html>

Daniel Nocera and Matthew Kanan, MIT

# References

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