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Thursday, March 10, 2016

### Chemistry of Hello: Lithium Ion Batteries

*Challenges and Opportunities for Personal Electronics Applications*

**Dee Strand**, Chief Scientific Officer, Wildcat Discovery Technologies

**Mark Jones**, Executive External Strategy and Communications Fellow, Dow Chemical



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**Tierra Range**, 2015 Chem Champs Runner Up and Student, Centenary College of Louisiana

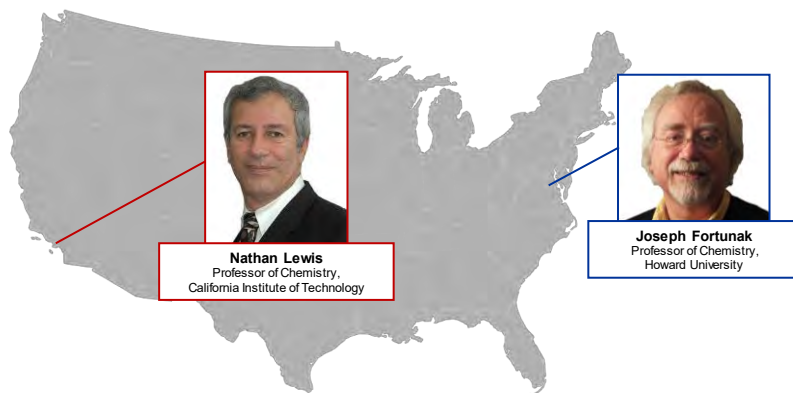
**Chris McCarthy**, Social Media & Multimedia Manager, American Chemical Society

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## **Artificial Photosynthesis: Making Fuels Directly from Sunlight**



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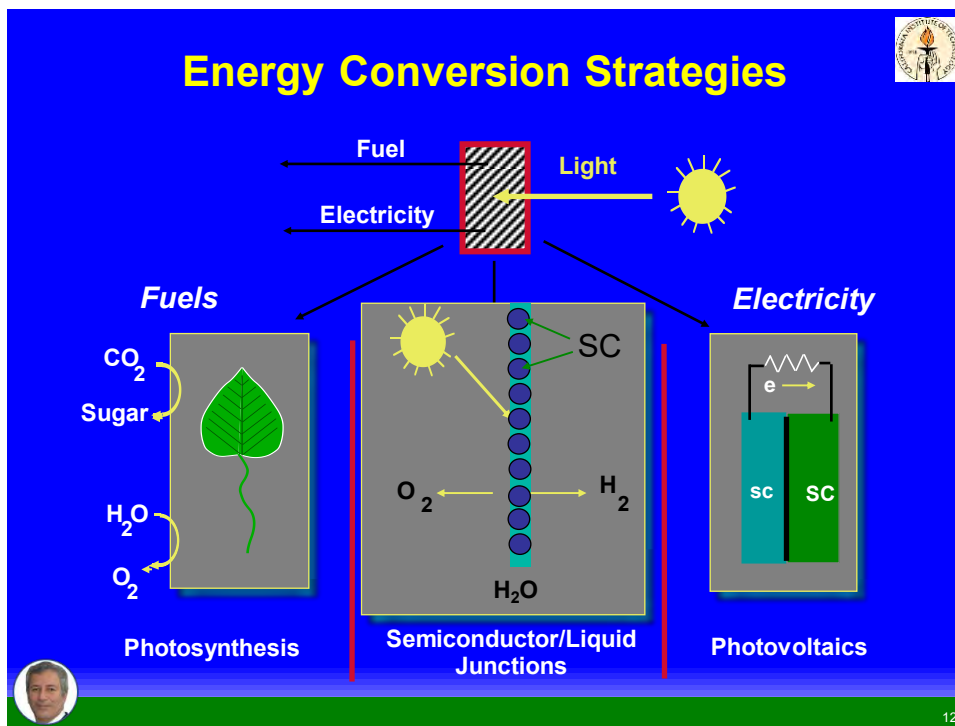
NSF CCI, DOE BES, AFOSR, Moore Foundation



## **“Artificial Photosynthesis: Direct Production of Fuels from Sunlight”**

Nathan S. Lewis  
 Division of Chemistry and Chemical Engineering  
 California Institute of Technology

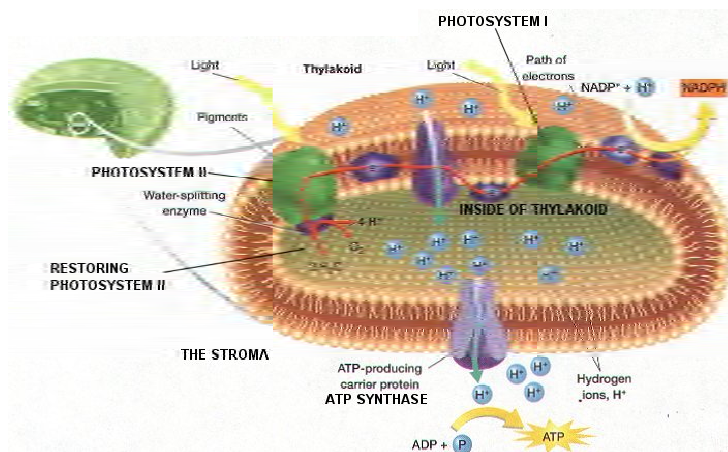
11



## Fuel from Sunlight

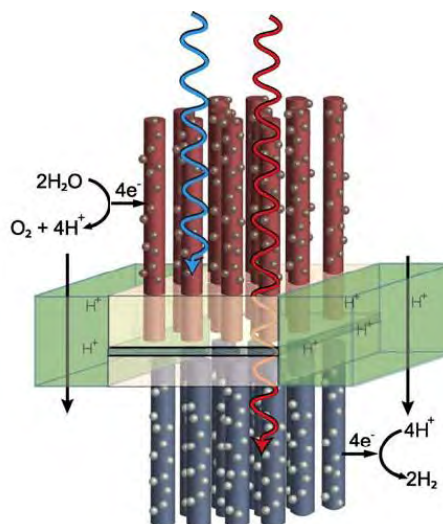


## Lessons from Photosynthesis



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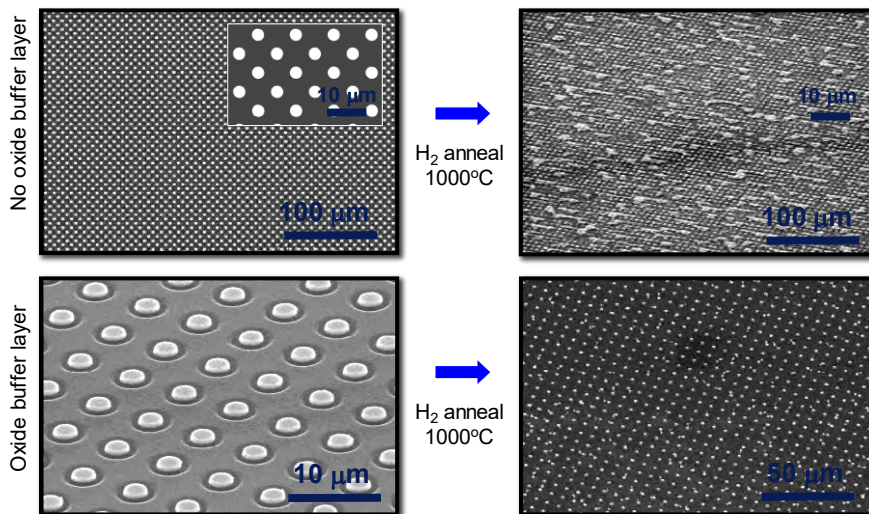
## Constructing the Pieces of a Solar H<sub>2</sub> Fuel Generator



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## Oxide Buffer Layer - Pattern Fidelity



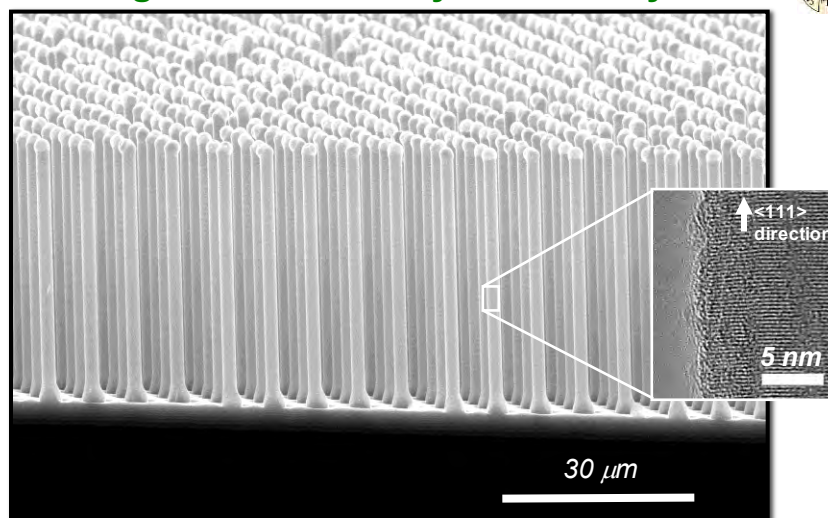
3  $\mu\text{m}$  array, 500 nm Au,  $T_{\text{growth}} = 1000^\circ\text{C}$ ,  $P_{\text{growth}} = 760$  Torr



An oxide buffer layer is critical for maintaining pattern fidelity during growth.

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## Large Area Au-Catalyzed Si Arrays



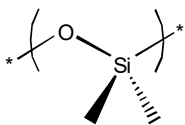
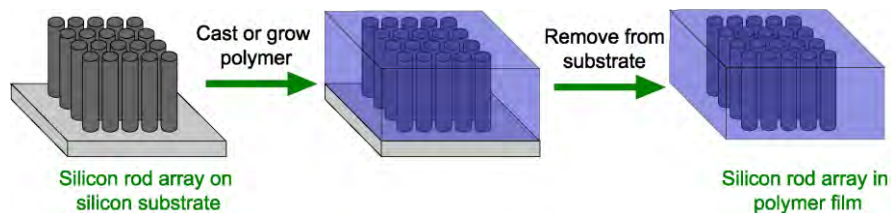
3  $\mu\text{m}$  array, 500 nm Au,  $T_{\text{growth}} = 1000^\circ\text{C}$ ,  $P_{\text{growth}} = 760$  Torr, 30 min growth, 2 mole % SiCl<sub>4</sub> in H<sub>2</sub>



Nearly 100% vertically aligned, 75  $\mu\text{m}$  length microwire arrays over areas > 1 cm<sup>2</sup>.

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## Polymer Embedding of Si Rod Arrays

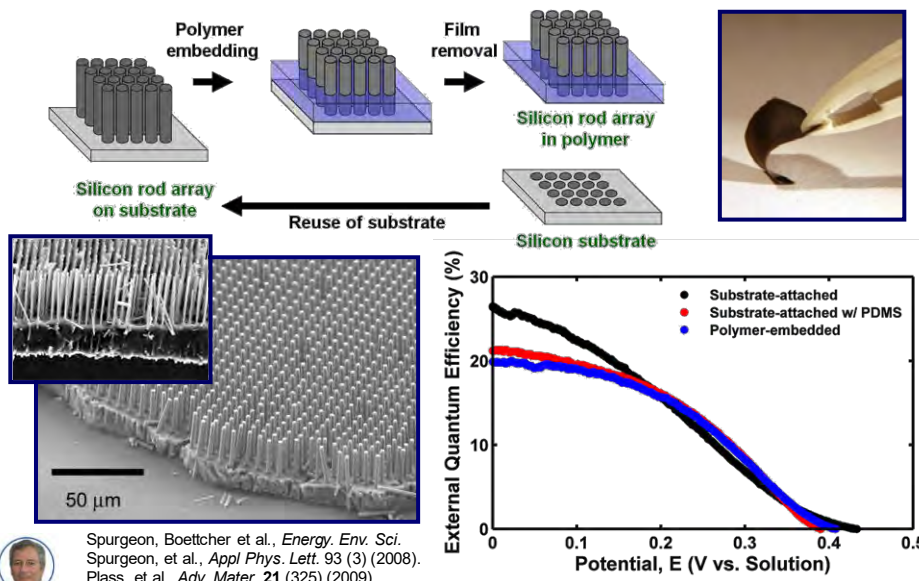


PDMS  
(polydimethylsiloxane)

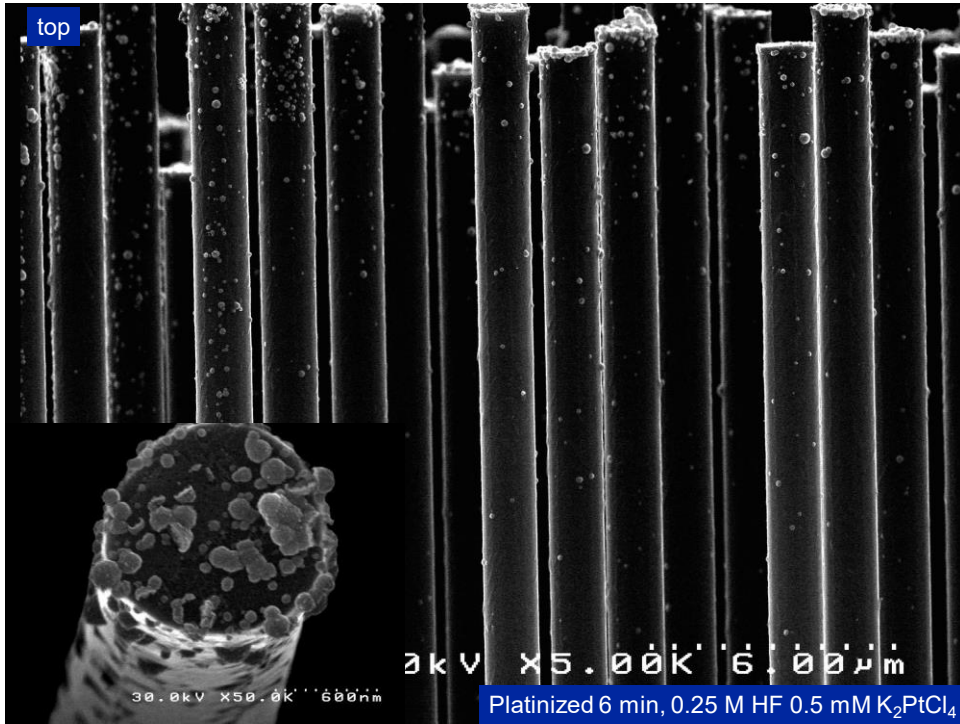


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## Polymer Embedding and Wafer Reuse

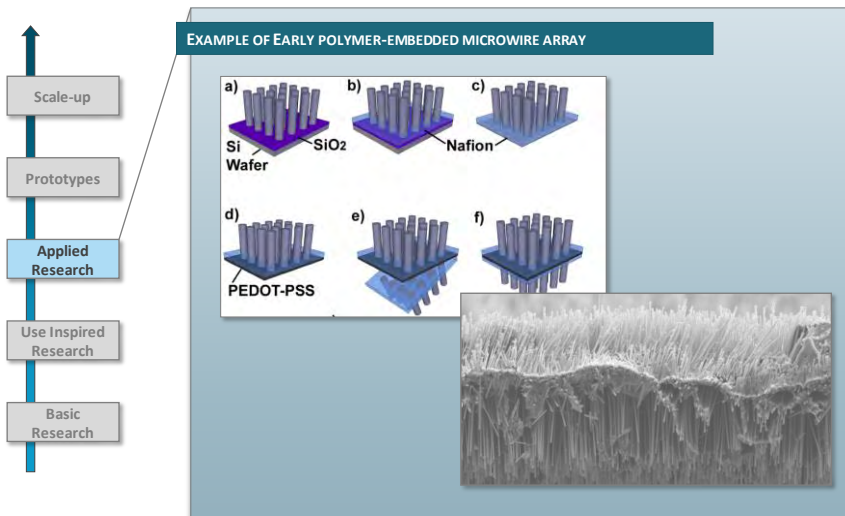


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## Integrated Architectures

### Accomplishments and Future Direction



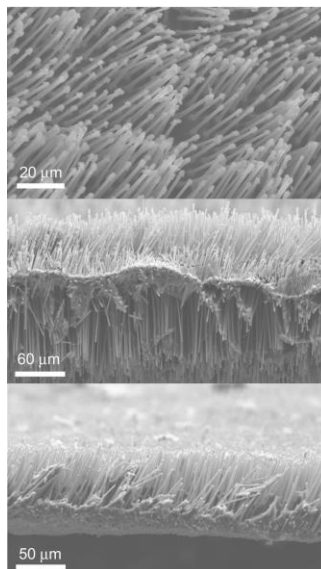
## Si Wire/Ionomer Morphology



Dual (Si Wire Array/Nafion)/PEDOT-PSS

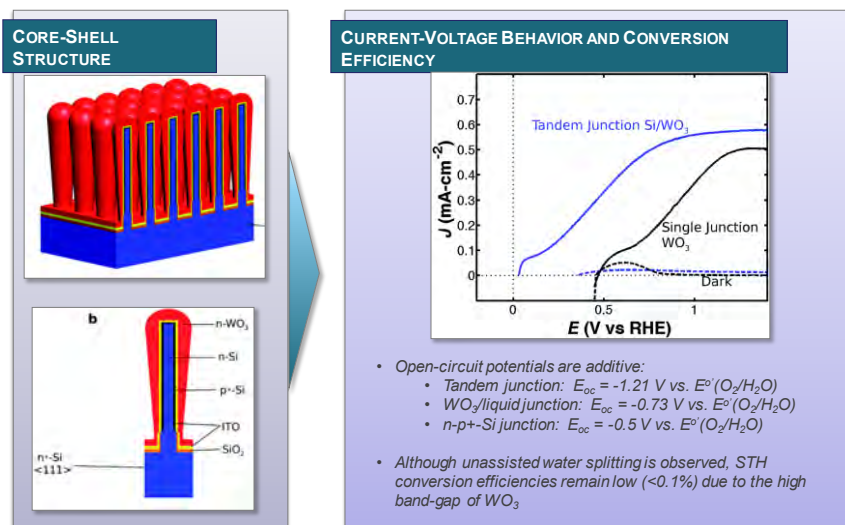
Dual (Si Wire Array/Nafion)/PEDOT-PSS

Si wire/QAPSF



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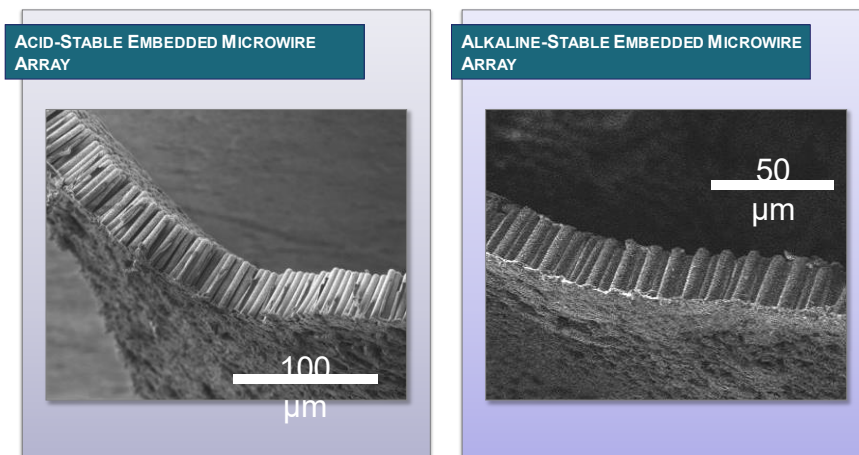
## Development of a microwire architecture capable of solar-driven water splitting



Matthew M. Shaner, Katherine T. Fountaine, Shane Ardo, Rob H. Cordan, Harry A. Atwater, Nathan S. Lewis  
*Energy Environ. Sci.* 2014, 7, 779-790. (10.1039/c3ee43048k)

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## Core-Shell Tandem Junction Microwire Arrays

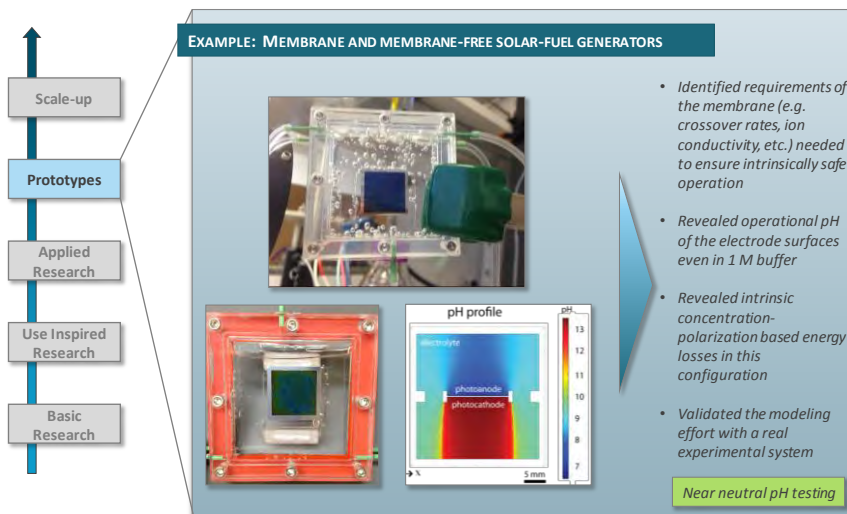


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## Integrated Prototyping Approach in JCAP (cont.)



JCAP's research prototypes are fully integrated systems



Jin, J.; Walczak, K.; Singh, M. R.; Karp, C.; Lewis, N. S.; Xiang, C., "An Integrated Membrane-free Solar-Fuel Generator with Solar-to-Hydrogen Conversion Efficiency of 3.2% and product Cross-over" *Energ Env Sci*, 2014

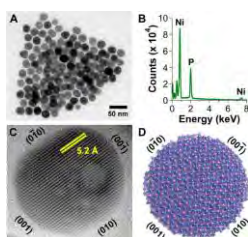
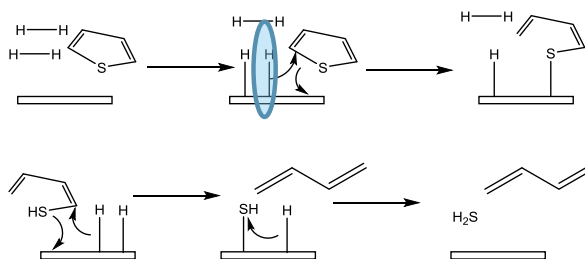
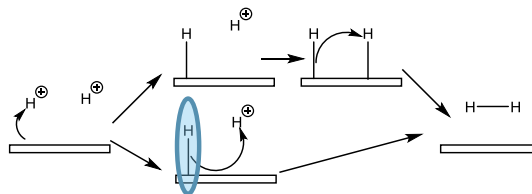
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## The HER-HDS Hypothesis

### Acid-Stable, Earth-Abundant HER Electrocatalysts



- MoS<sub>2</sub> is also an HDS catalyst.
- HER and HDS share key hydridic intermediates.
- HDS may be a predictor for HER
- Ni<sub>2</sub>P was the first target.

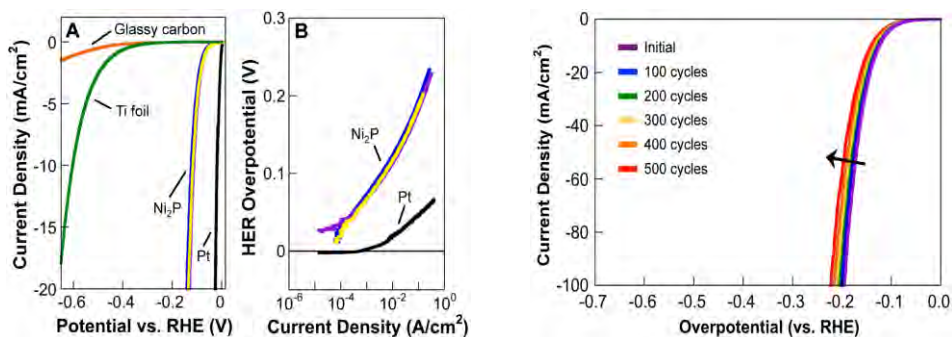


*J. Am. Chem. Soc.*, 2013, 135 (25), pp 9267–9270



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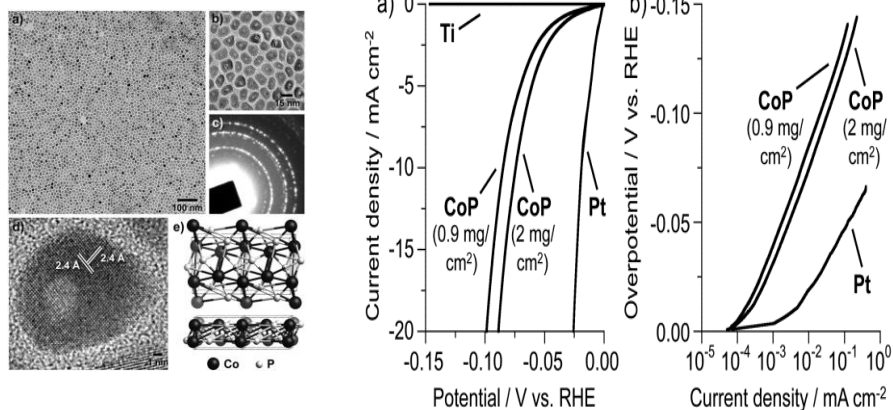
## Ni<sub>2</sub>P HER in 1 M H<sub>2</sub>SO<sub>4</sub>; 120 mV overpotential at 10 mA/cm<sup>2</sup>



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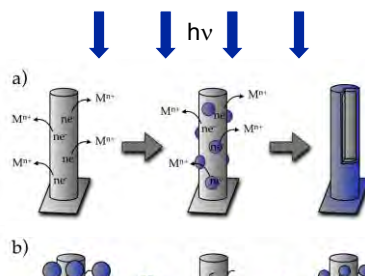
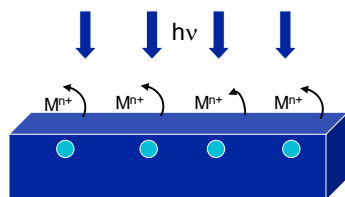
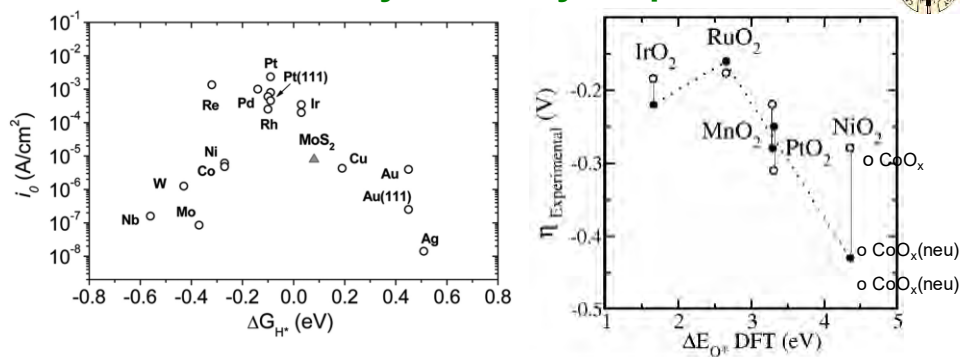


## CoP HER IN 1 M H<sub>2</sub>SO<sub>4</sub>; 85 mV OVERPOTENTIAL AT 10 mA/CM<sup>2</sup>



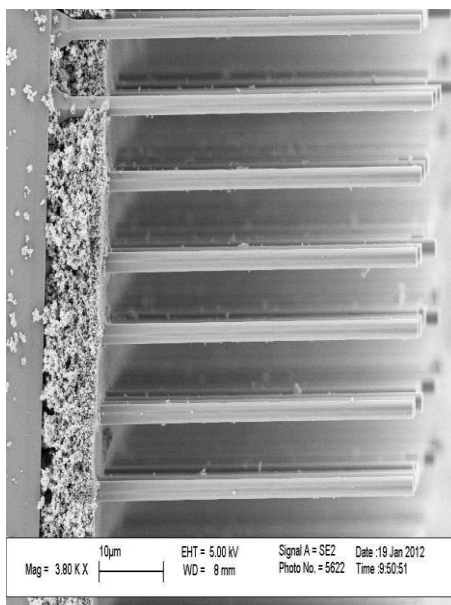
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## Relaxes Catalyst Activity Requirements



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## Ni-Mo HER Catalyst at Base of Si Wires

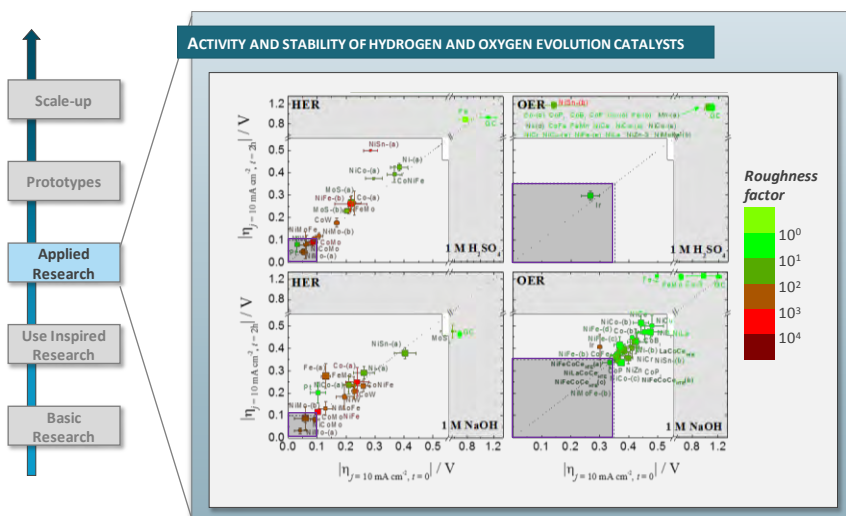


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## Performance Benchmarking of Electrocatalysts in JCAP



JCAP's benchmarking facility allows for consistent performance evaluation of catalysts



Charles C. L. McCrory, Suho Jung, Jonas C. Peters, and Thomas F. Jaramillo "Benchmarking Heterogeneous Catalysts for the Oxygen Evolution Reaction" *J. Am. Chem. Soc.* **2013**, *135*, 16977-16987. (DOI: [10.1021/ja407115p](https://doi.org/10.1021/ja407115p))

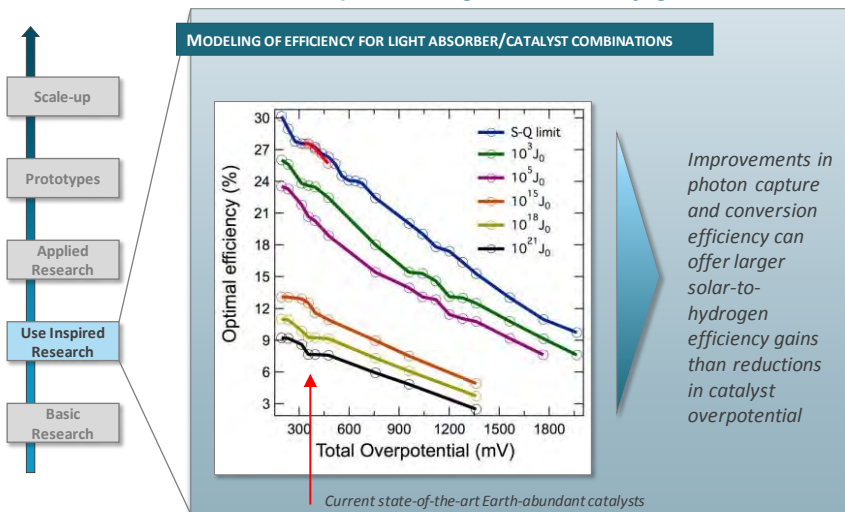
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## Sensitivity analysis of Solar-Fuel Generators



Simulations indicate that photoelectrode improvements provide the greatest efficiency gains



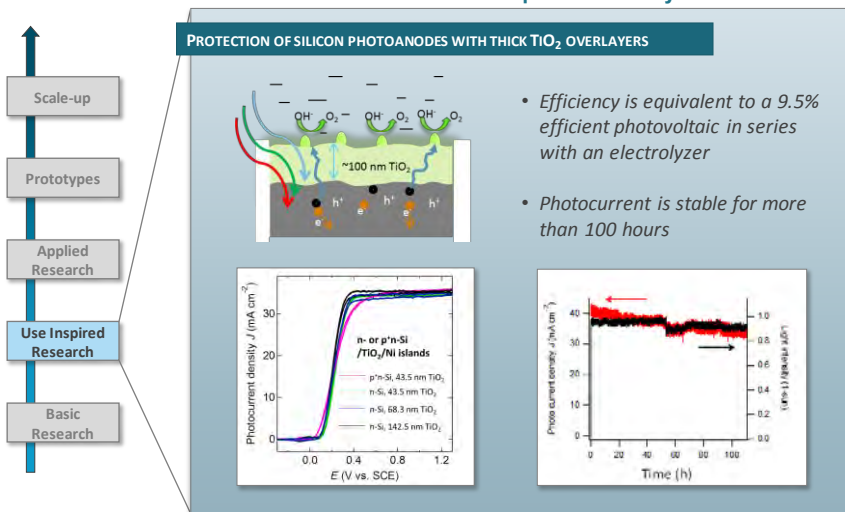
Chengxiang, Xiang, Katie Chen, and Nathan Lewis, *Energy Env. Sci.*, 2015.

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## Development of Alkaline stable photoanodes (cont.)



Protection of unstable photoanodes with thick  $\text{TiO}_2$  overlayers offers another path to stability



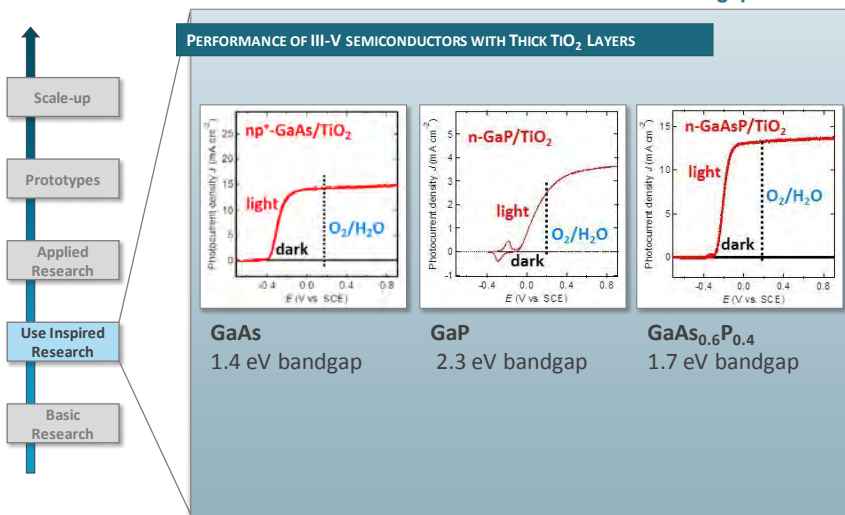
Shu Hu, Matthew Shaner, Joseph Beardlee, Michael Lichterman, Bruce S. Brunschwig, and Nathan S. Lewis "Quantitative, Sustained, Efficient Solar-Driven Oxidation of  $\text{H}_2\text{O}$  to  $\text{O}_2(\text{g})$  Using Thin Ni Electrocatalytic Films on  $\text{TiO}_2$ -Coated Si, GaAs, and GaP Semiconductor Photoanodes" 2014, *Science*

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## Development of Alkaline stable photoanodes (cont.)



Thick  $\text{TiO}_2$  overlayers are also compatible with III-V semiconductors that have near ideal band gaps

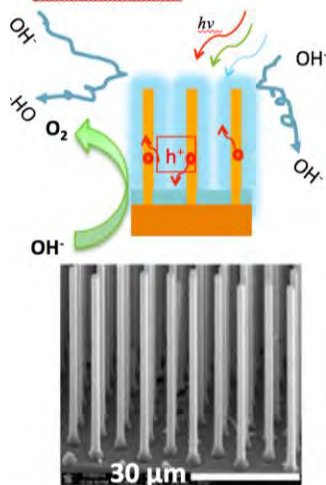


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## Wire-shape photoanodes stabilized by atomic layer deposited $\text{TiO}_2$



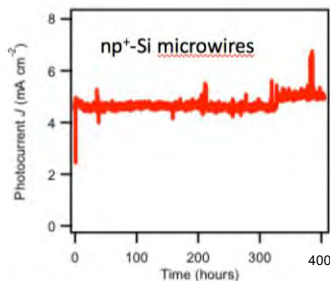
**Schematic and SEM image of GaAs or Si wire/ $\text{TiO}_2$ / $\text{NiO}_x$  photoelectrodes**



**PEC performance and stability**

in 1 M KOH

Stability: >400 hours  
FF remains the same.

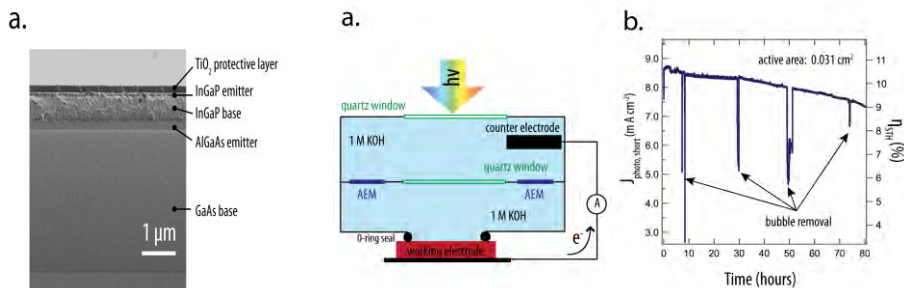


M. Shaner et al., *Energy Env Sci*, 2014.



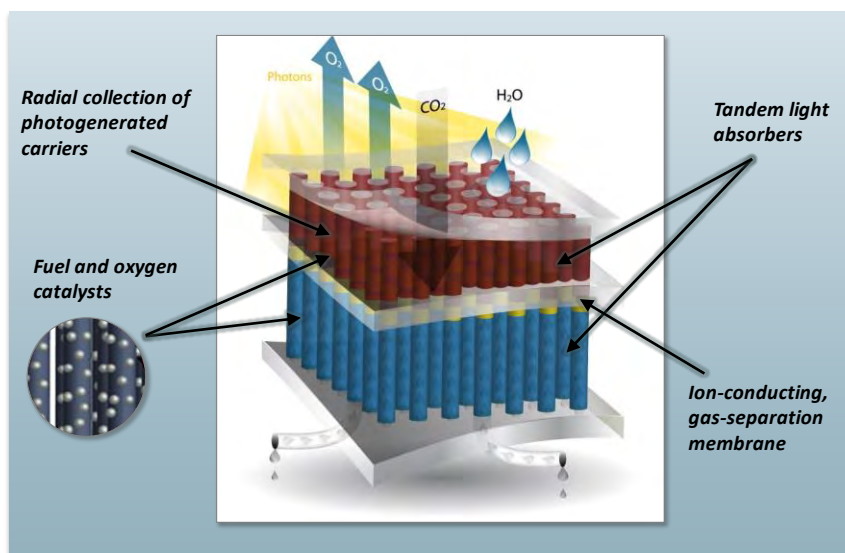
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## An Intrinsically Safe, 10% Efficient Solar-to-Hydrogen System with TiO<sub>2</sub>-Stabilized III-V Tandem and Ni-Mo/NiO<sub>x</sub> Electrocatalysts



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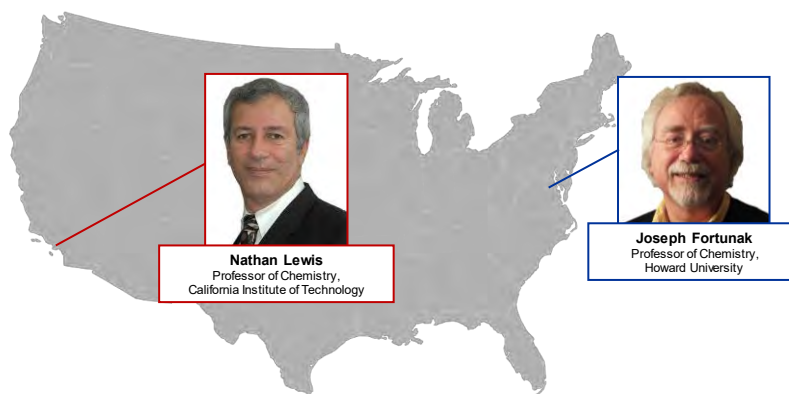
## Blueprint for an Integrated Solar-Fuel Generator



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## *Artificial Photosynthesis: Making Fuels Directly from Sunlight*



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**Tierra Range**, 2015 Chem Champs Runner Up and Student, Centenary College of Louisiana

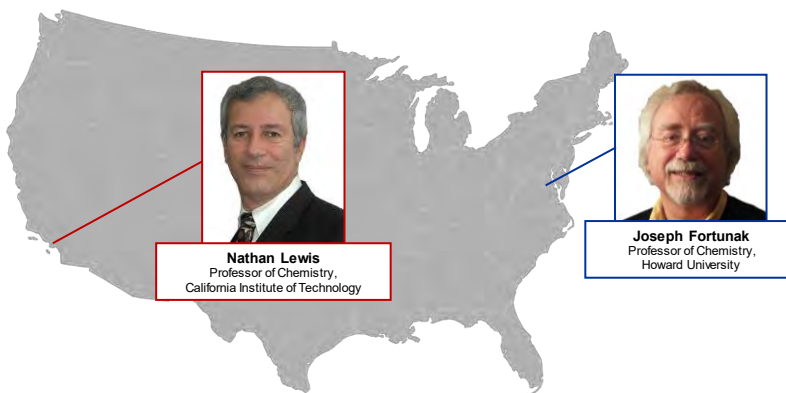
**Chris McCarthy**, Social Media & Multimedia Manager, American Chemical Society

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## Artificial Photosynthesis: Making Fuels Directly from Sunlight



**Nathan Lewis**  
Professor of Chemistry,  
California Institute of Technology



**Joseph Fortunak**  
Professor of Chemistry,  
Howard University

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Assistant Professor  
Dept. of Chemical and Physical Sciences  
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