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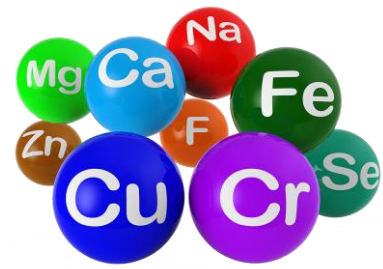

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Fan of the Week

Lindsey A. Welch, Ph.D.
Assistant Professor
Dept. of Chemical and Physical Sciences
Cedar Crest College

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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

Thursday, March 24, 2016

Chemistry Champs: Soaking in Solar Energy

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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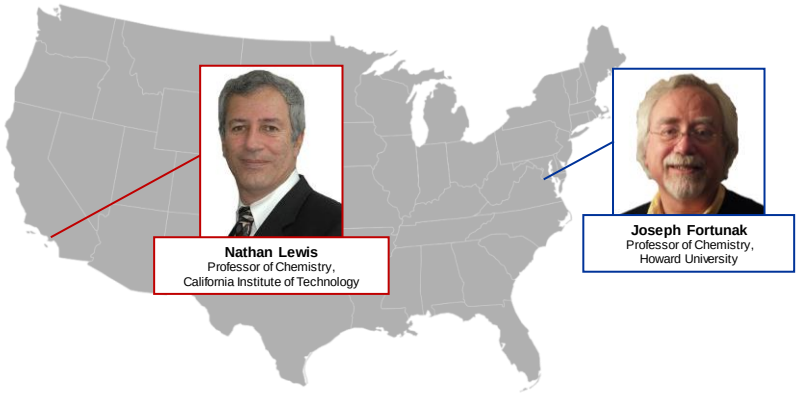
Artificial Photosynthesis:
Making Fuels Directly from Sunlight



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JCAP
JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

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

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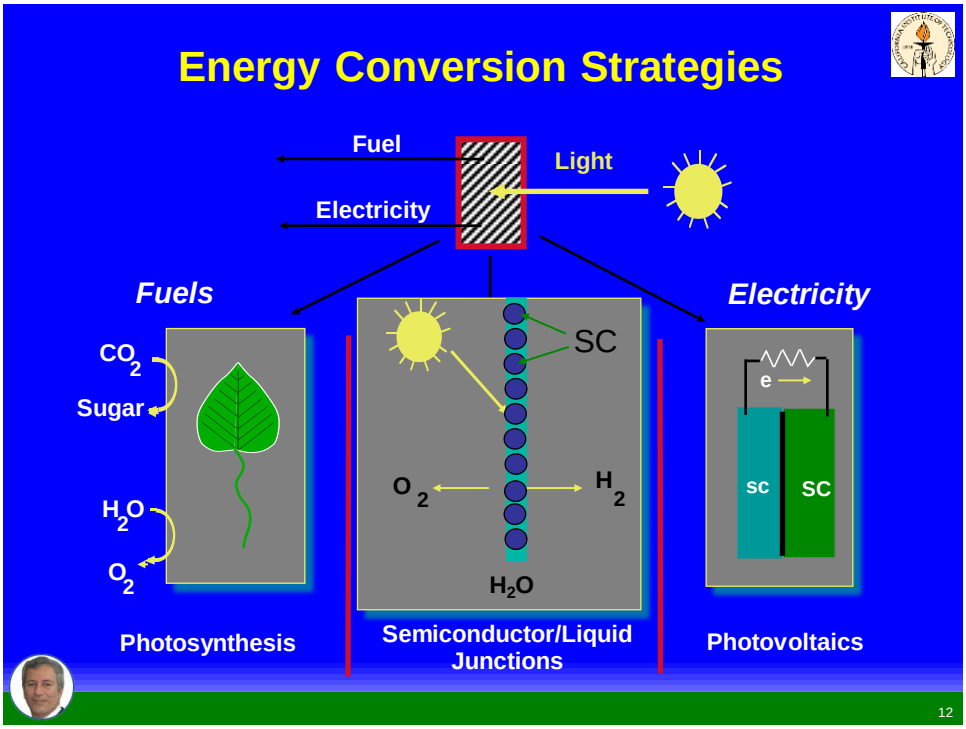
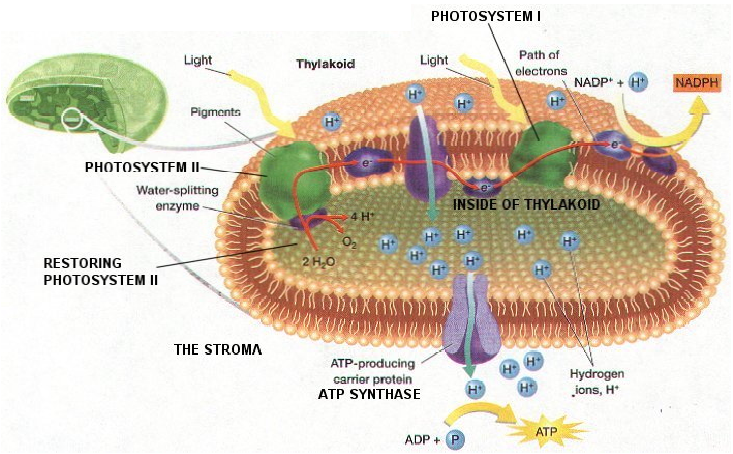
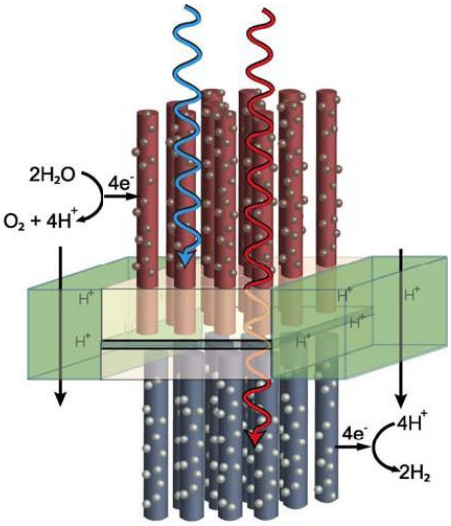


Fuel from Sunlight

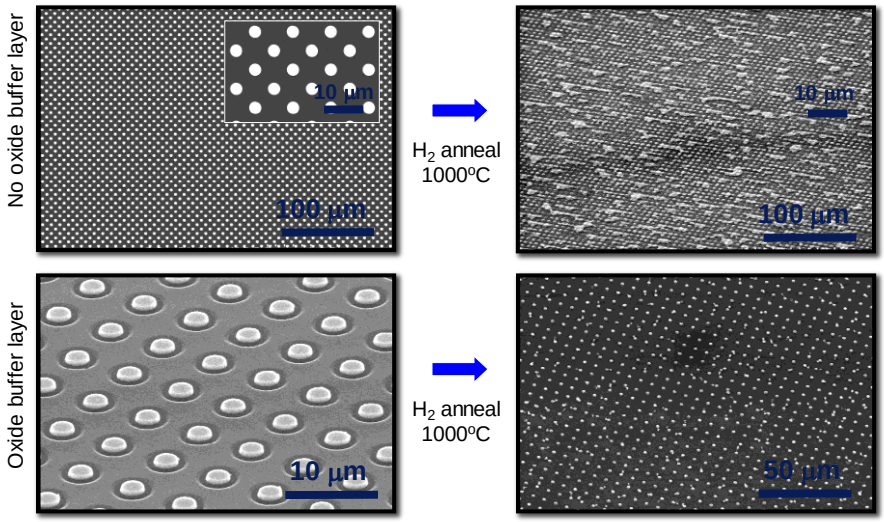
Lessons from Photosynthesis



Constructing the Pieces of a Solar H_2 Fuel Generator



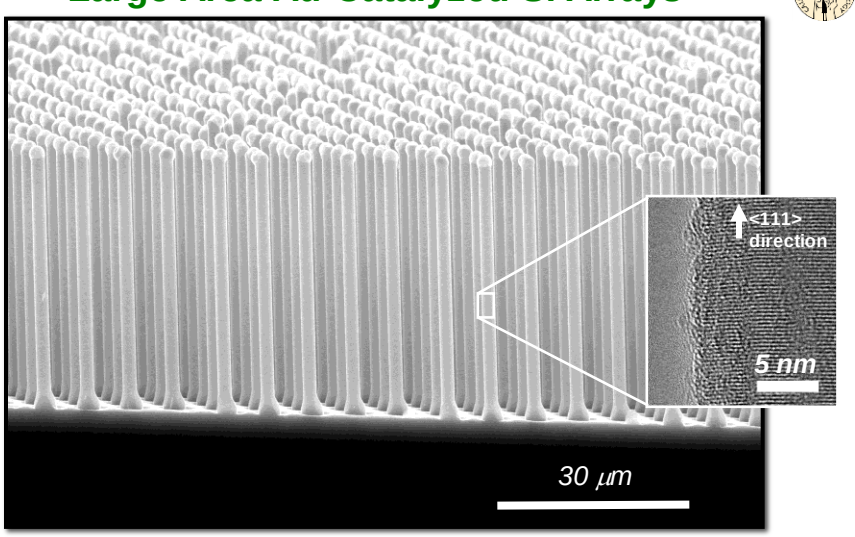
Oxide Buffer Layer - Pattern Fidelity



3 µm array, 500 nm Au, T_{growth} = 1000°C, P_{growth} = 760 Torr

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

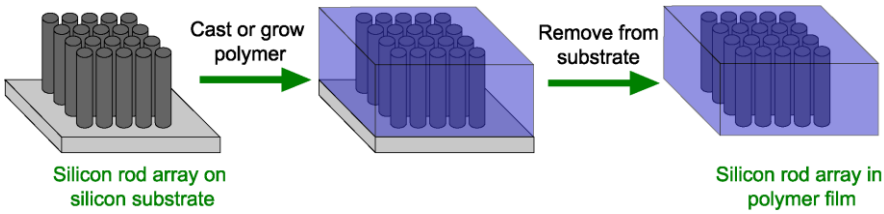
Large Area Au-Catalyzed Si Arrays

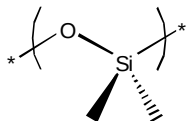


3 µm array, 500 nm Au, T_{growth} = 1000°C, P_{growth} = 760 Torr, 30 min growth, 2 mole % $SiCl_4$ in H_2

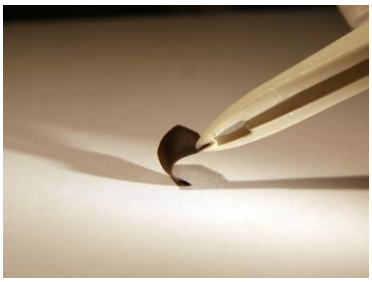
Nearly 100% vertically aligned, 75 µm length microwire arrays over areas > 1 cm².

Polymer Embedding of Si Rod Arrays

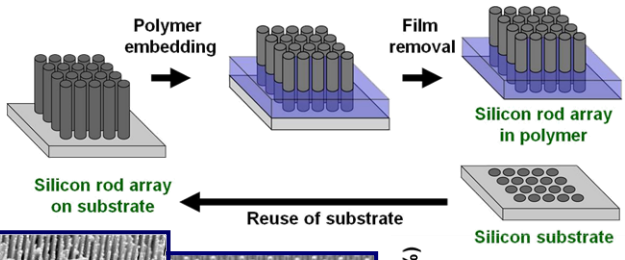


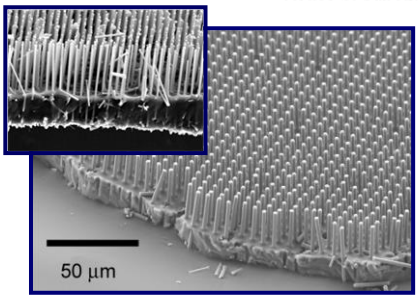


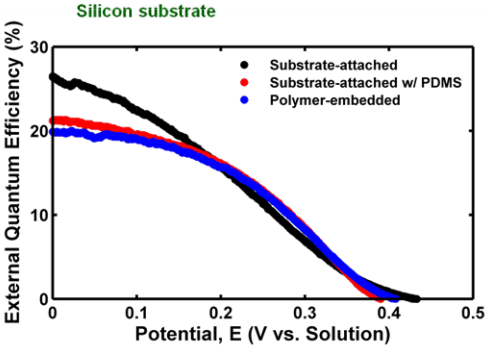
PDMS
(polydimethylsiloxane)



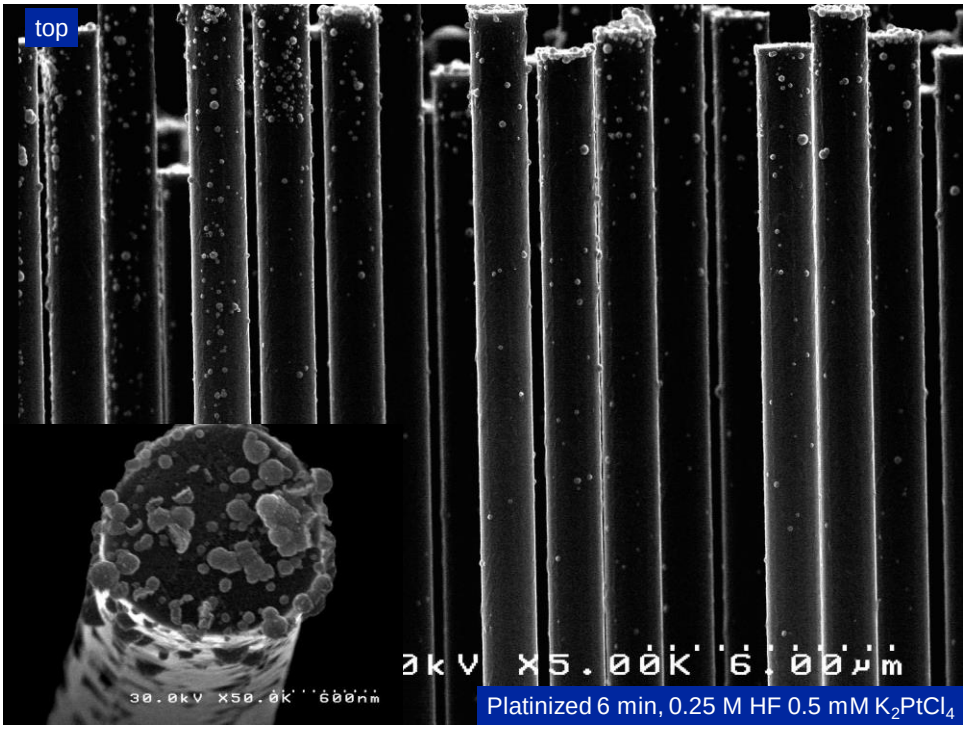
Polymer Embedding and Wafer Reuse







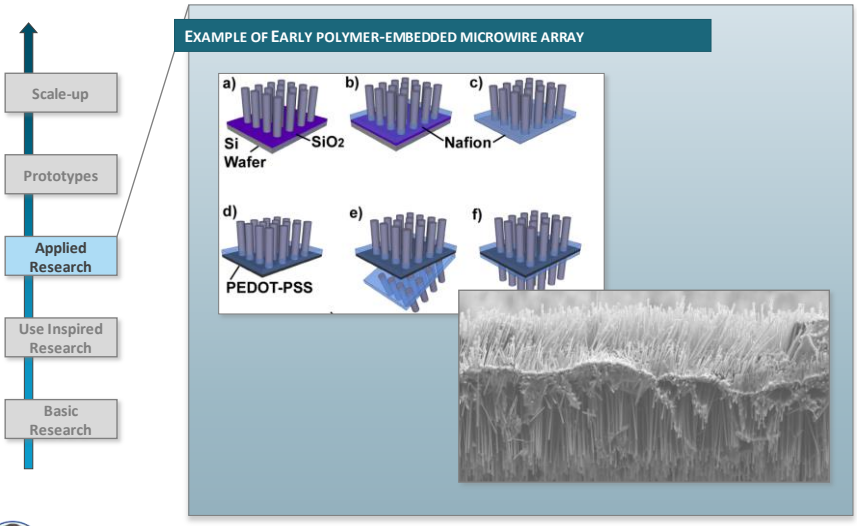
Spurgeon, Boettcher et al., *Energy. Env. Sci.*
Spurgeon, et al., *Appl Phys. Lett.* 93 (3) (2008).
Plass, et al., *Adv. Mater.* **21** (325) (2009).



Platinized 6 min, 0.25 M HF 0.5 mM K_2PtCl_4

Integrated Architectures

Accomplishments and Future Direction

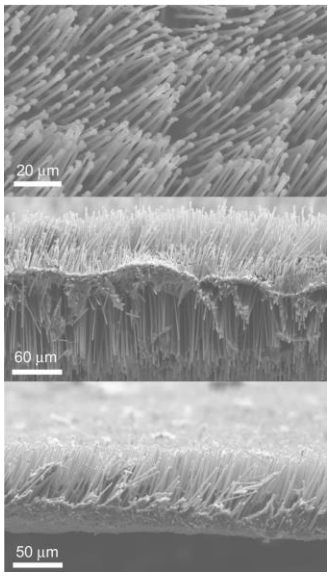


Si Wire/Ionomer Morphology

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

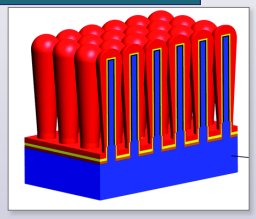
Dual (Si Wire Array/Nafion)/PEDOT-PSS

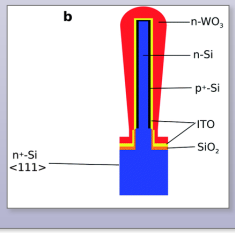
Si wire/QAPSF



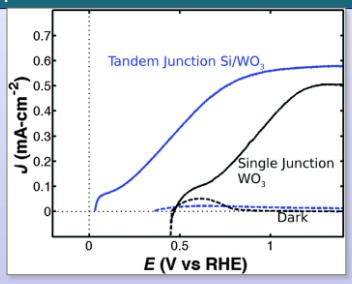
Development of a microwire architecture capable of solar-driven water splitting

CORE-SHELL STRUCTURE





CURRENT-VOLTAGE BEHAVIOR AND CONVERSION EFFICIENCY

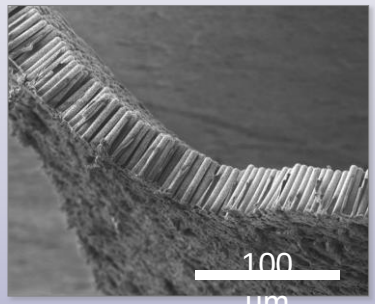


- *Open-circuit potentials are additive:*
  - *Tandem junction: E_{oc} = -1.21 V vs. $E^o(O_2/H_2O)$*
  - *WO_3/liquid junction: E_{oc} = -0.73 V vs. $E^o(O_2/H_2O)$*
  - *n-p+-Si junction: E_{oc} = -0.5 V vs. $E^o(O_2/H_2O)$*
- *Although unassisted water splitting is observed, STH conversion efficiencies remain low (<0.1%) due to the high band-gap of WO_3*

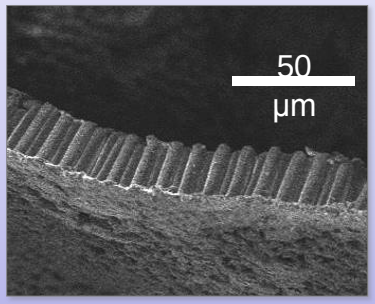
Matthew M. Shaner, Katherine T. Fountaine, Shane Ardo, Rob H. Cordian, Harry A. Atwater, Nathan S. Lewis
Energy Environ. Sci. **2014**, *7*, 779-790. (10.1039/c3ee43048k)

Core-Shell Tandem Junction Microwire Arrays

ACID-STABLE EMBEDDED MICROWIRE ARRAY



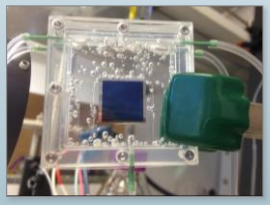
ALKALINE-STABLE EMBEDDED MICROWIRE ARRAY

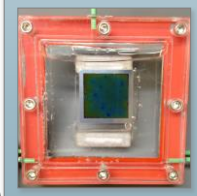


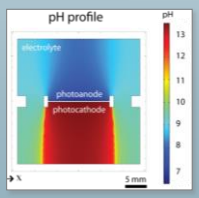
Integrated Prototyping Approach in JCAP (cont.)

JCAP's research prototypes are fully integrated systems

EXAMPLE: MEMBRANE AND MEMBRANE-FREE SOLAR-FUEL GENERATORS







- *Identified requirements of the membrane (e.g. crossover rates, ion conductivity, etc.) needed to ensure intrinsically safe operation*
- *Revealed operational pH of the electrode surfaces even in 1 M buffer*
- *Revealed intrinsic concentration-polarization based energy losses in this configuration*
- *Validated the modeling effort with a real experimental system*

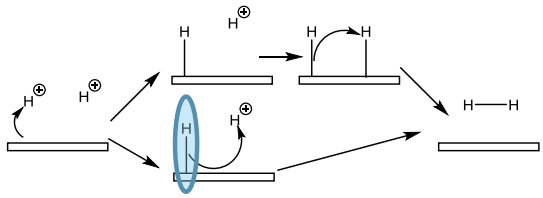
Near neutral pH testing

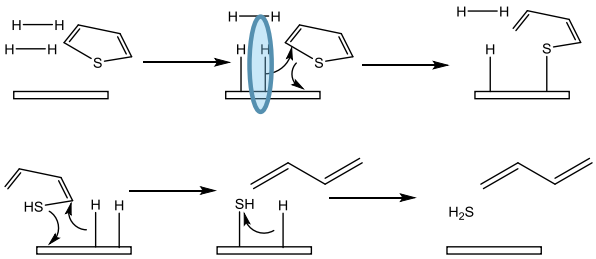
Jin, J.; Walczak, K.; Singh, M. R.; Karp, C.; Lewis, N. S.; Xiang, C., "An Integrated Membrane-free Solar-Fuel Generator with Solar-to-Hydrogen Conversion Efficiency of 3.2% and product Cross-over"*Energ Env Sci*, **2014**

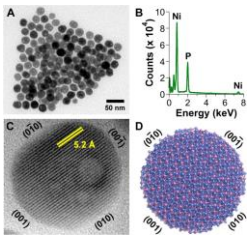
The HER-HDS Hypothesis

Acid-Stable, Earth-Abundant HER Electrocatalysts

- MoS_2 is also an HDS catalyst.
- HER and HDS share key hydridic intermediates.
- HDS may be a predictor for HER
- Ni_2P was the first target.

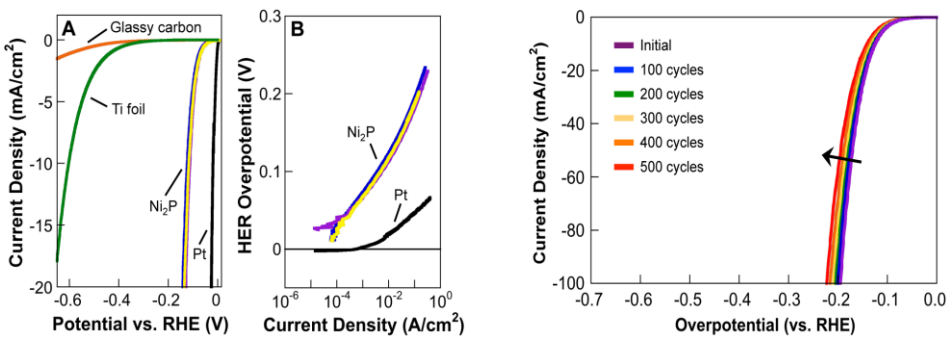




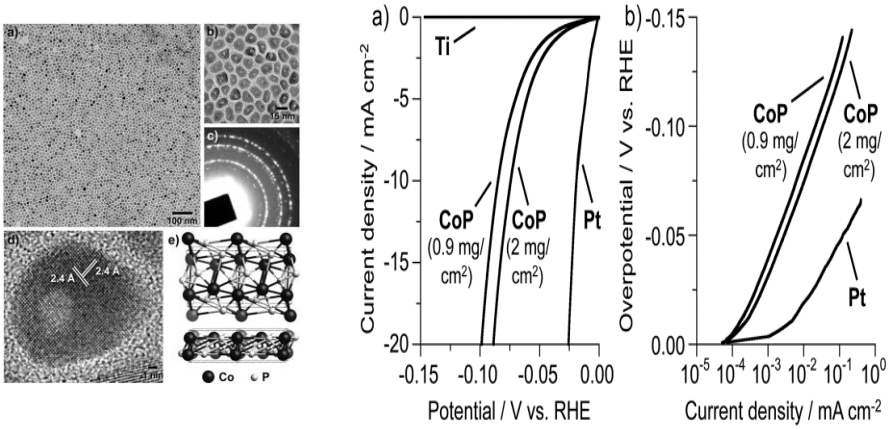


J. Am. Chem. Soc., **2013**, *135* (25), pp 9267–9270

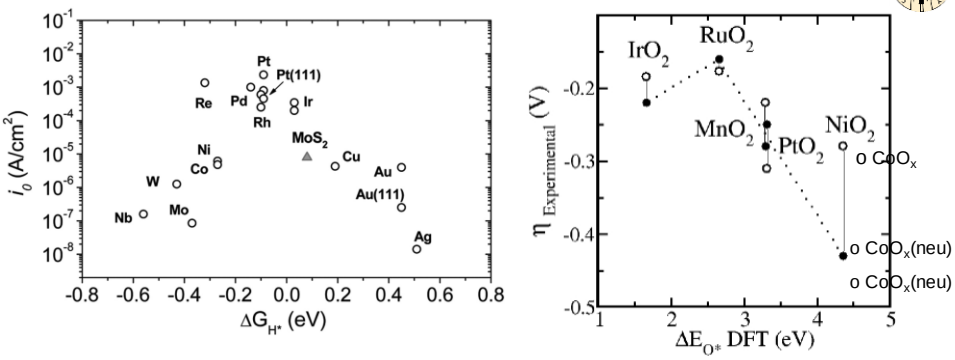
Ni_2P HER in 1 M H_2SO_4; 120 mV overpotential at 10 mA/cm^2

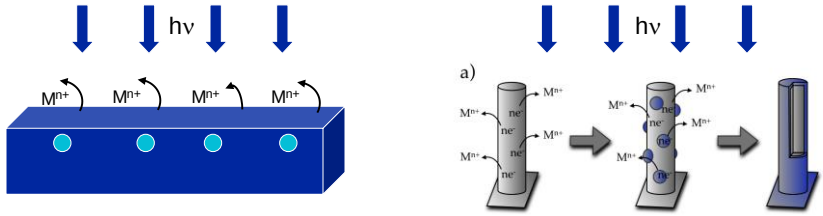


CoP HER in 1 M H_2SO_4; 85 mV overpotential at 10 mA/cm^2

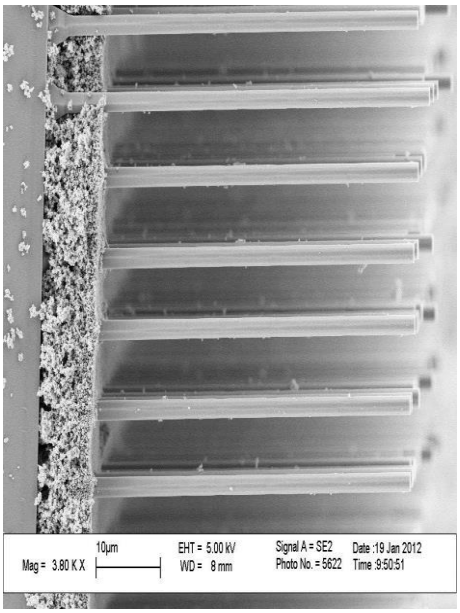


Relaxes Catalyst Activity Requirements



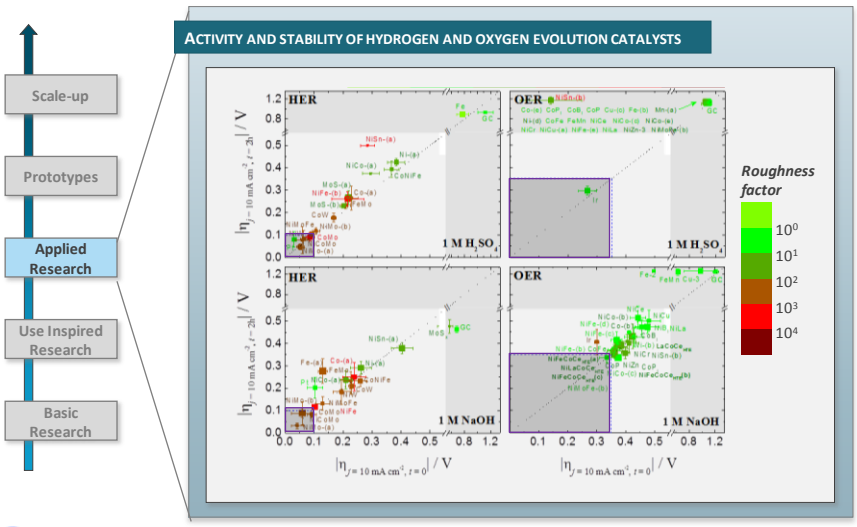


Ni-Mo HER Catalyst at Base of Si Wires



Performance Benchmarking of Electrocatalysts in JCAP

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



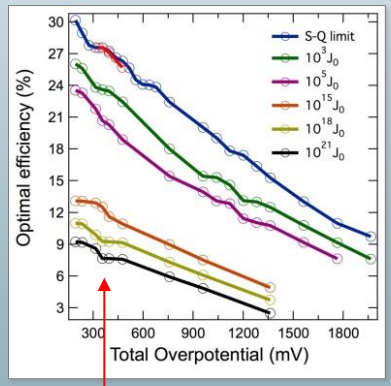
Charles C. L. McCrory, Suho Jung, Jonas C. Peters, and Thomas F. Jaramillo "Benchmarking Heterogeneous Catalysts for the Oxygen Evolution Reaction" *J. Am. Chem. Soc.* **2013**, *135*, 16977-16987. (DOI: 10.1021/ja407115p)

Sensitivity analysis of Solar-Fuel Generators

Simulations indicate that photoelectrode improvements provide the greatest efficiency gains

Scale-up
Prototypes
Applied Research
Use Inspired Research
Basic Research

MODELING OF EFFICIENCY FOR LIGHT ABSORBER/CATALYST COMBINATIONS



Current state-of-the-art Earth-abundant catalysts

Improvements in photon capture and conversion efficiency can offer larger solar-to-hydrogen efficiency gains than reductions in catalyst overpotential

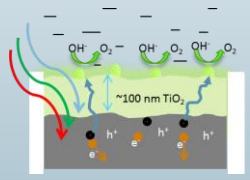
Chengxiang, Xiang, Katie Chen, and Nathan Lewis, *Energy Env. Sci.*, **2015**.

Development of Alkaline stable photoanodes (cont.)

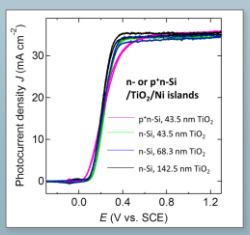
Protection of unstable photoanodes with thick TiO_2 overlayers offers another path to stability

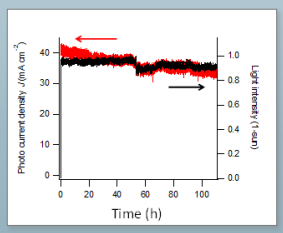
Scale-up
Prototypes
Applied Research
Use Inspired Research
Basic Research

PROTECTION OF SILICON PHOTOANODES WITH THICK TiO_2 OVERLAYERS



- *Efficiency is equivalent to a 9.5% efficient photovoltaic in series with an electrolyzer*
- *Photocurrent is stable for more than 100 hours*

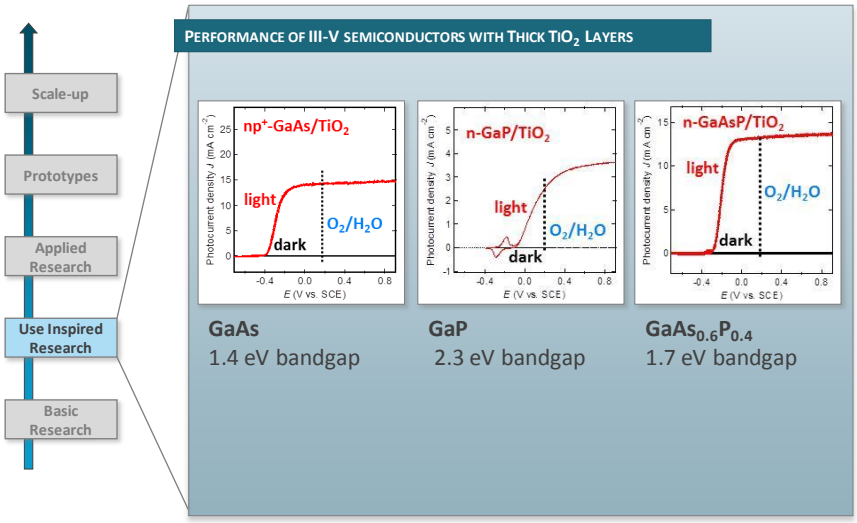




Shu Hu, Matthew Shaner, Joseph Beardslee, Michael Lichterman, Bruce S. Brunschwig, and Nathan S. Lewis "Quantitative, Sustained, Efficient Solar-Driven Oxidation of H_2O to O_2(g) Using Thin Ni Electrocatalytic Films on TiO_2-Coated Si, GaAs, and GaP Semiconductor Photoanodes" **2014**, *Science*

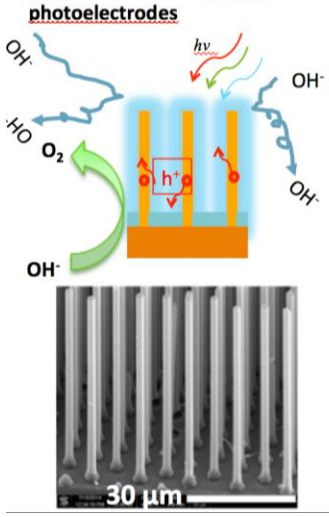
Development of Alkaline stable photoanodes (cont.)

Thick TiO_2 overlayers are also compatible with III-V semiconductors that have near ideal band gaps



Wire-shape photoanodes stabilized by atomic layer deposited TiO_2

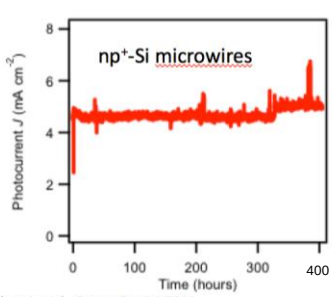
Schematic and SEM image of GaAs or Si wire/TiO_2/NiOx photoelectrodes



PEC performance and stability

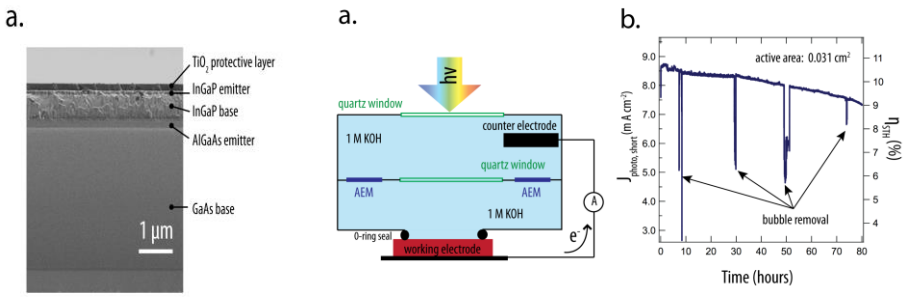
in 1 M KOH

Stability: >400 hours
FF remains the same.

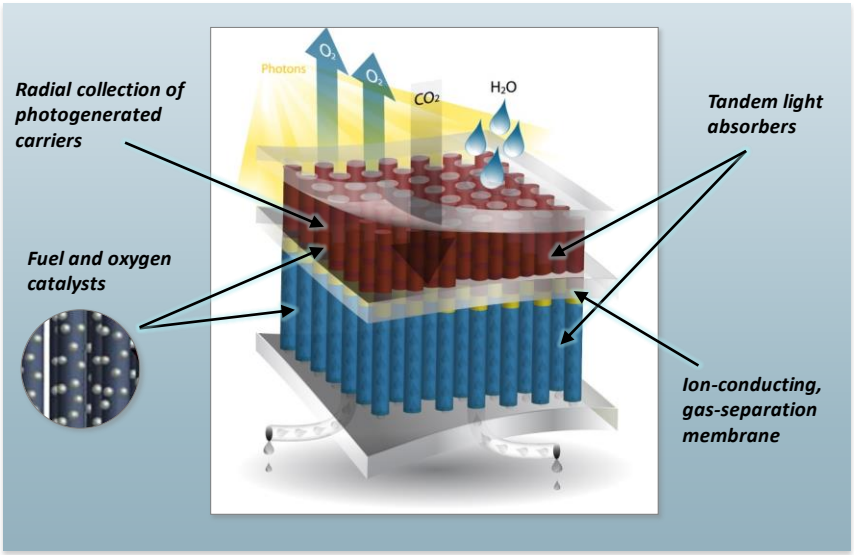


M. Shaner et al., *Energy Env Sci.* 2014.

An Intrinsically Safe, 10% Efficient Solar-to-Hydrogen System with TiO_2-Stabilized III-V Tandem and Ni-Mo/NiO_x Electrocatalysts



Blueprint for an Integrated Solar-Fuel Generator



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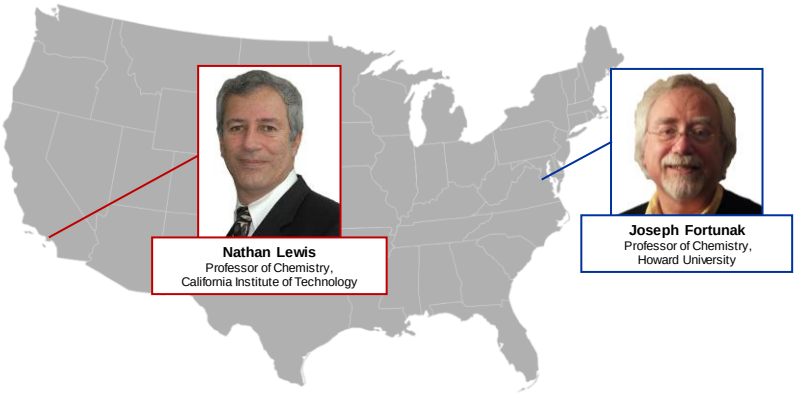

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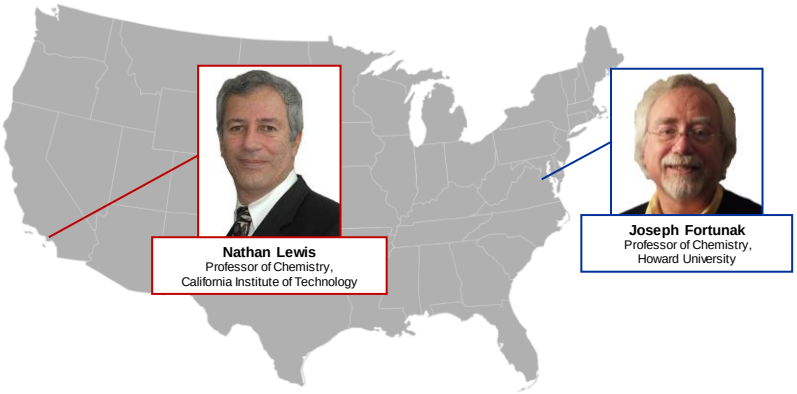

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