ARTIFICIAL PHOTOSYNTHESIS: DIRECT PRODUCTION OF FUELS FROM SUNLIGHT

(NO BUGS, NO WIRES)

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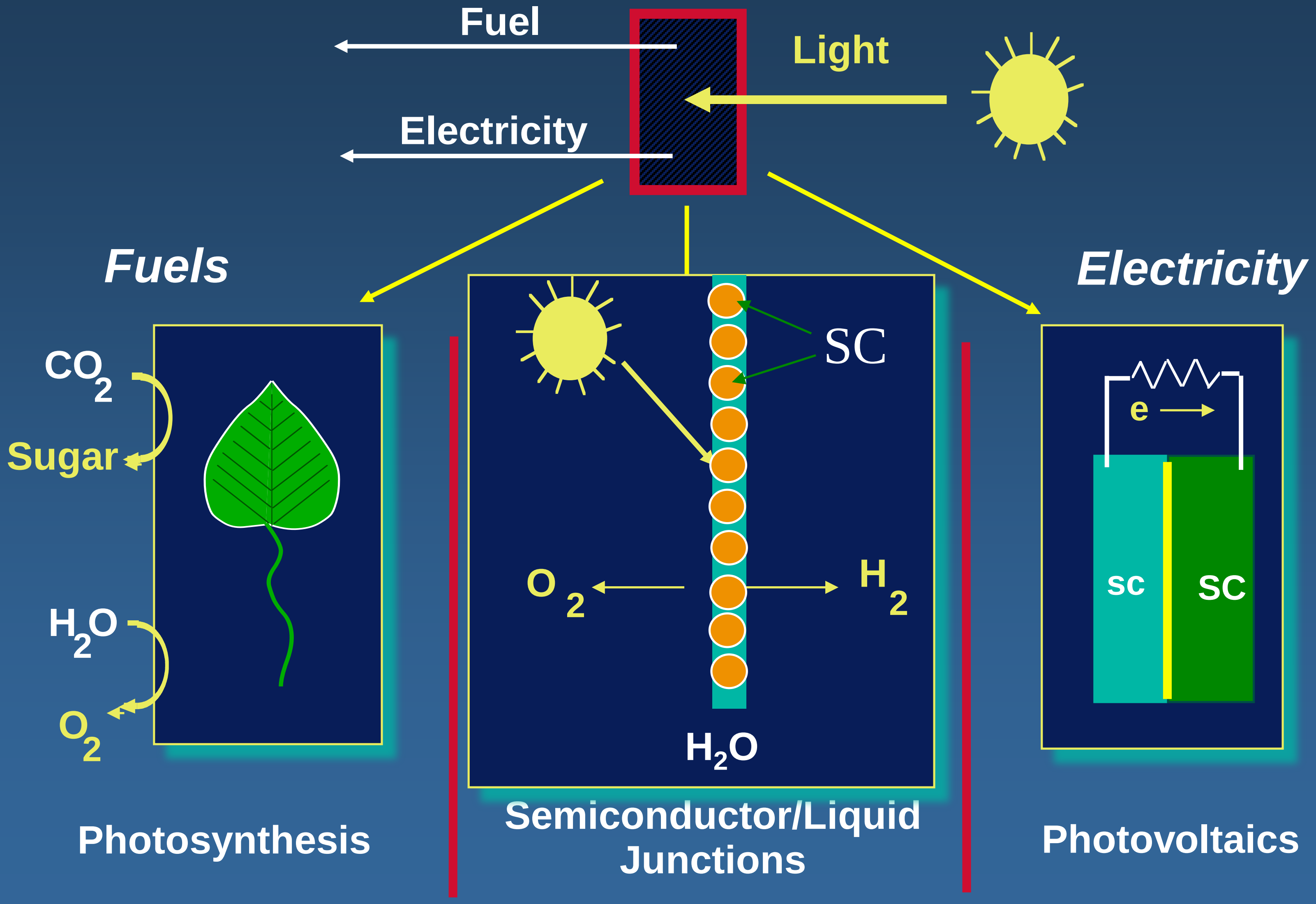
Energy Conversion Strategies



Fuel

Electricity

Light

Fuels

Electricity

CO_2

Sugar

H_2O

O_2

SC

O_2

H_2

H_2O

e →

sc

SC

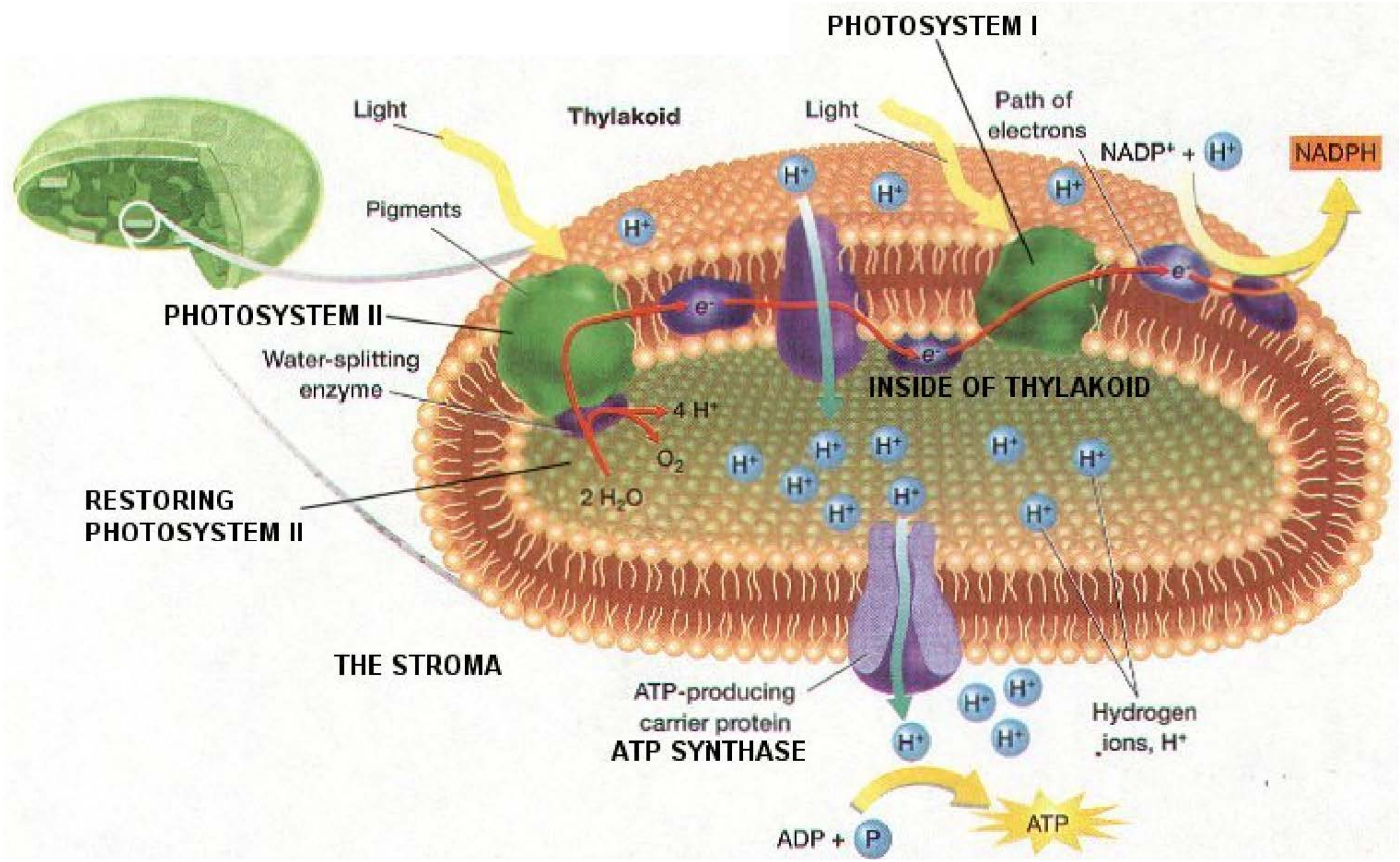
Photosynthesis

Semiconductor/Liquid Junctions

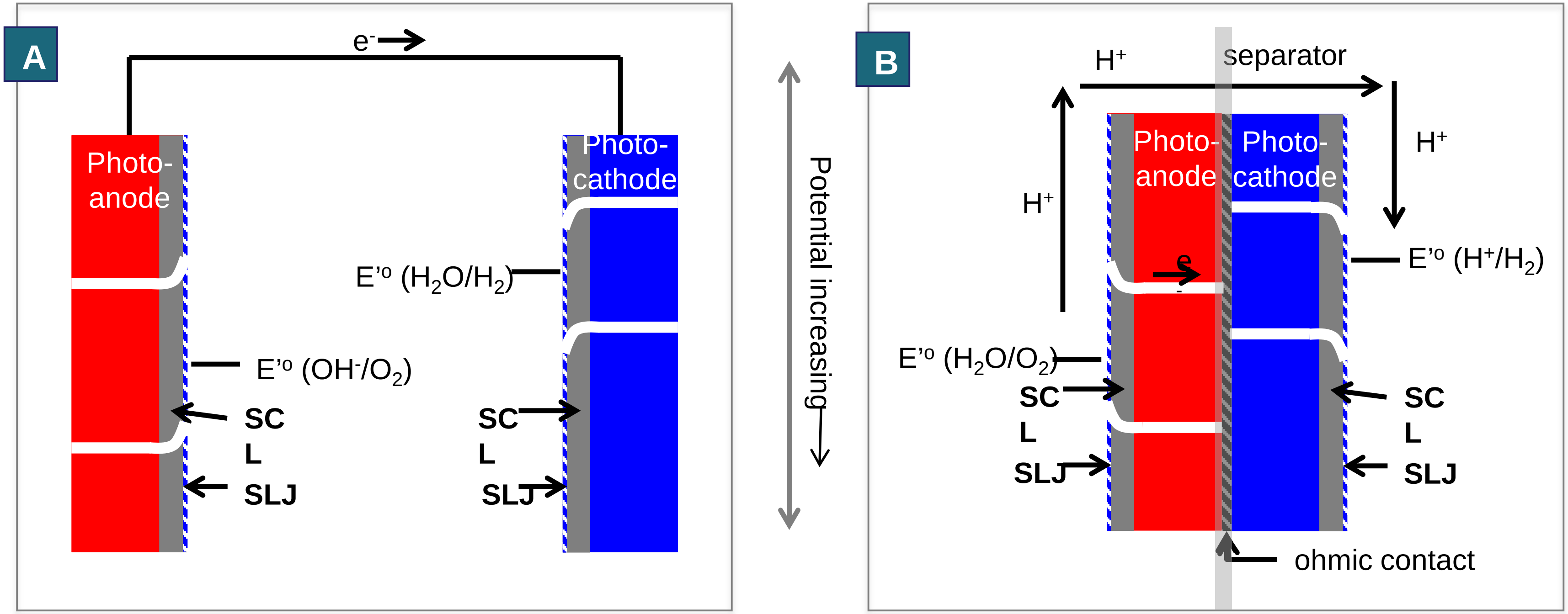
Photovoltaics

Fuel from Sunlight

Lessons from Photosynthesis



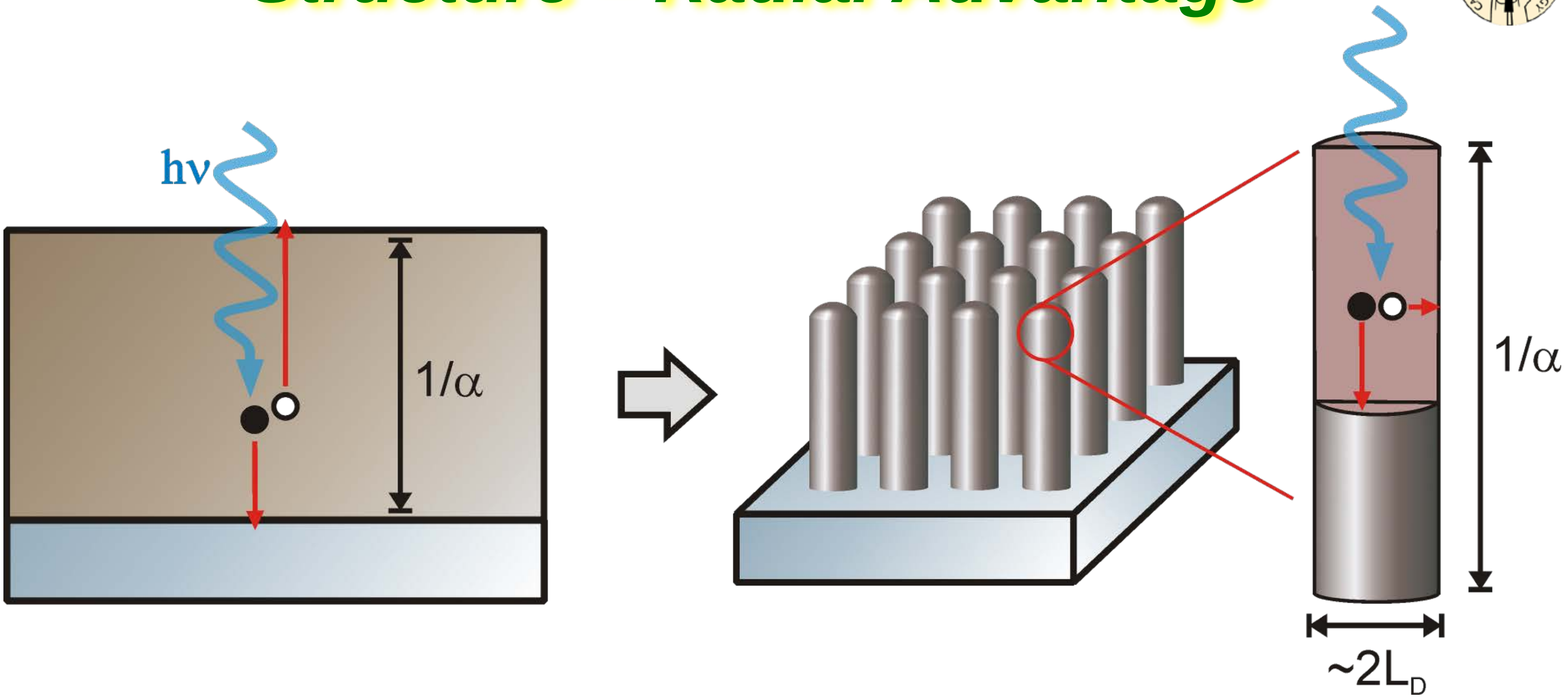
• DUAL AND TANDEM CELLS WITH SEMICONDUCTOR/LIQUID JUNCTIONS



A) Dual photoelectrodes – Each photoelectrode provides a portion of the total photovoltage produced by the system and required for splitting water.

B) Tandem photoelectrodes – The photoanode is in direct electrical contact with the photocathode. because the potential of the bottom of the conduction band of the photoelectrode is more positive than $E^o{}'(H_2O/H_2)$, so photogenerated electrons can not produce the desired fuel (in this case H_2) without some additional energy input.

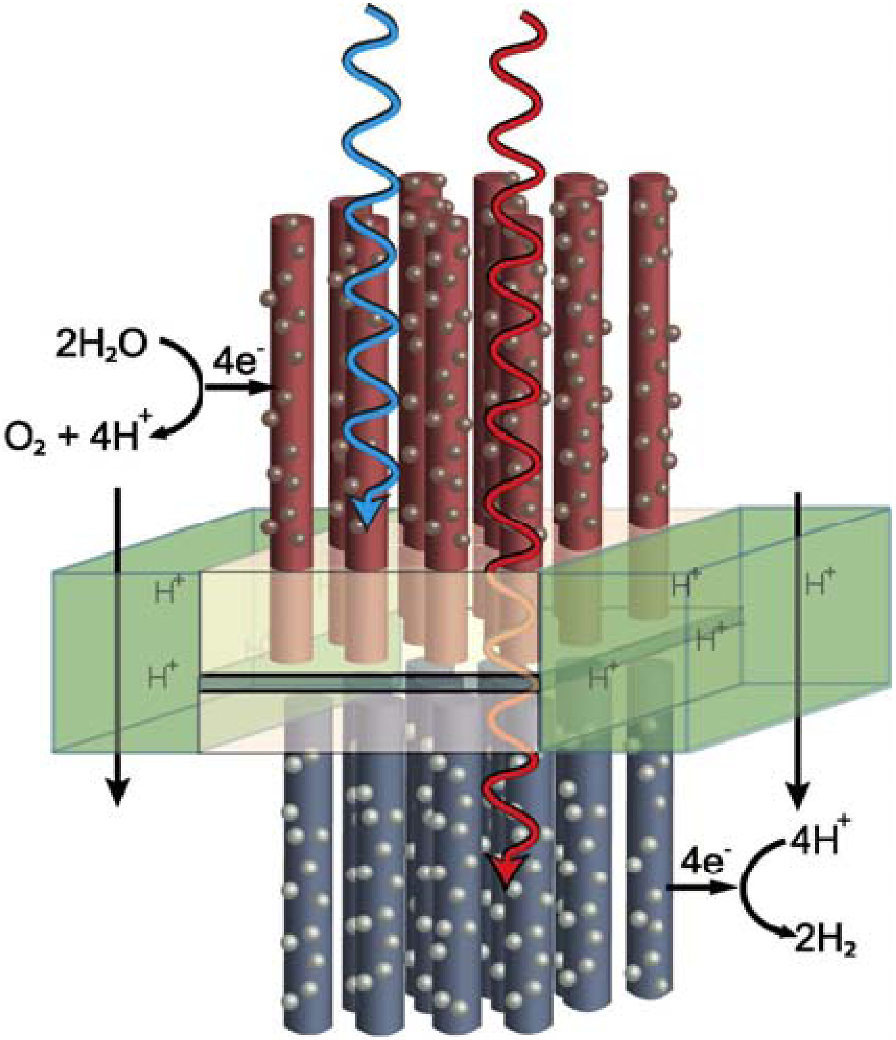
Structure – Radial Advantage



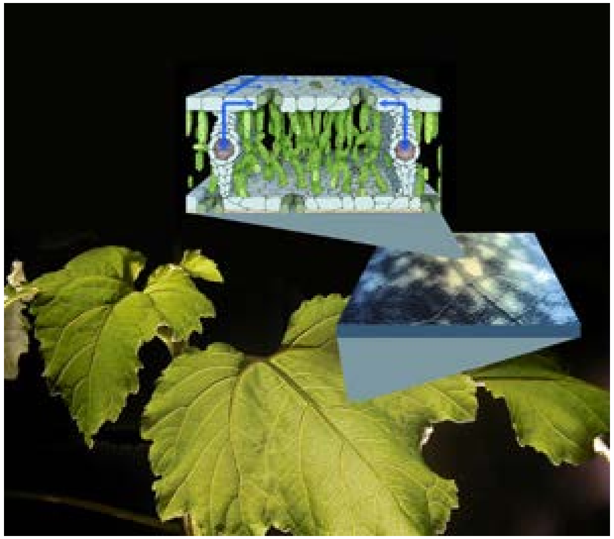
$L_D \propto$ purity $\propto$ materials cost

Impure material but high performance

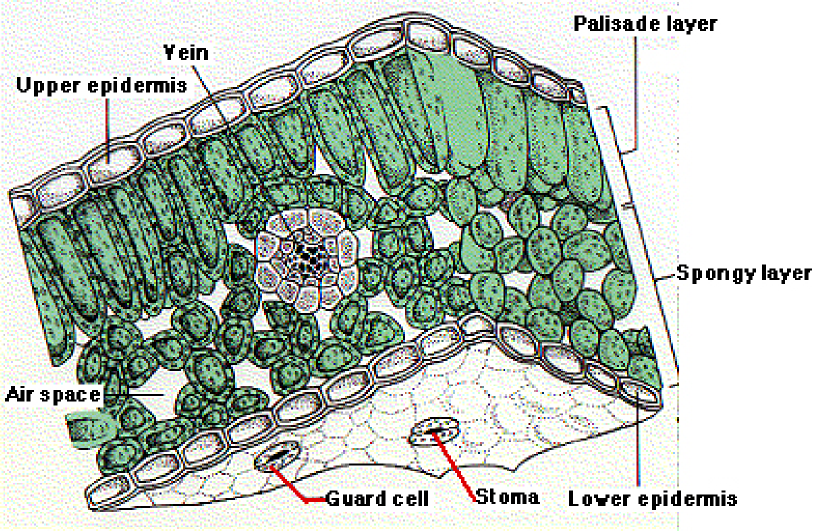
Constructing the Pieces of a Solar H_2 Fuel Generator



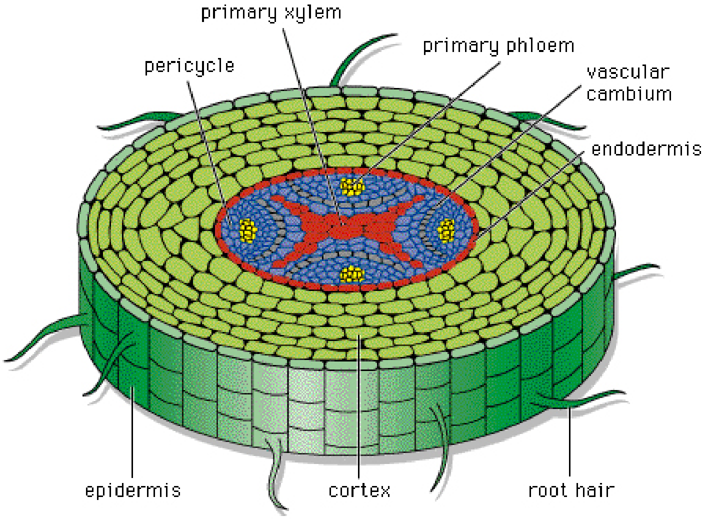
Structural Organization in Nature



Stomata



Leaf



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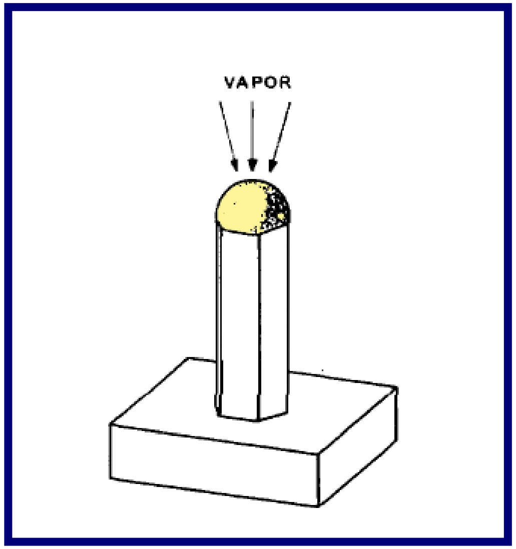
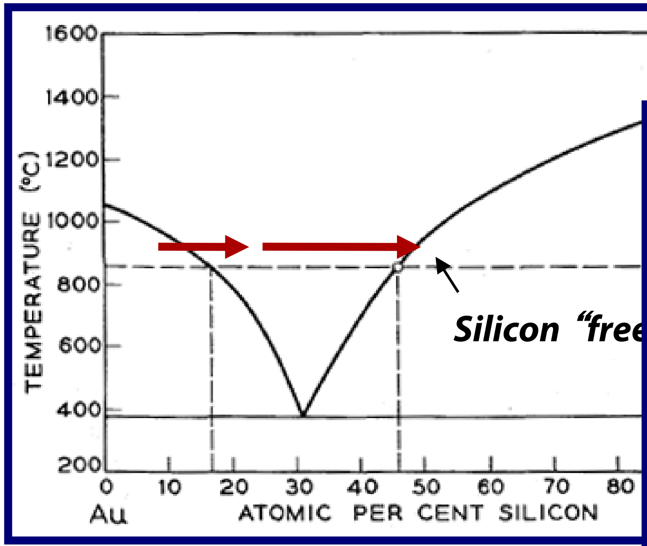
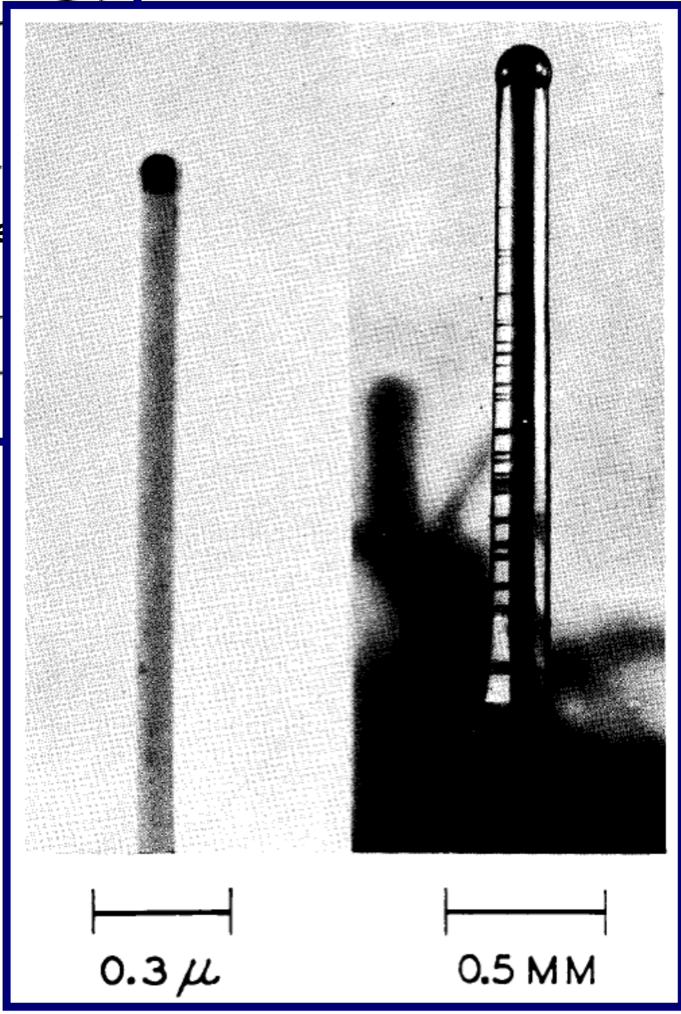
Root

Forest

Si Rods by Vapor-Liquid-Solid (VLS) Growth







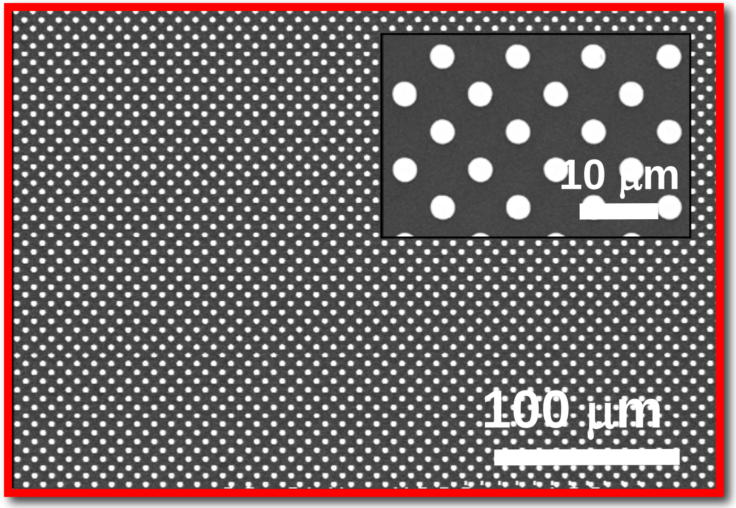
$H_2 + SiCl_4$, ~1000 C

- *Single crystals*
- *Growth direction controlled by substrate*
- *High growth rates (up to microns/s)*
- *Inexpensive gas phase precursors*

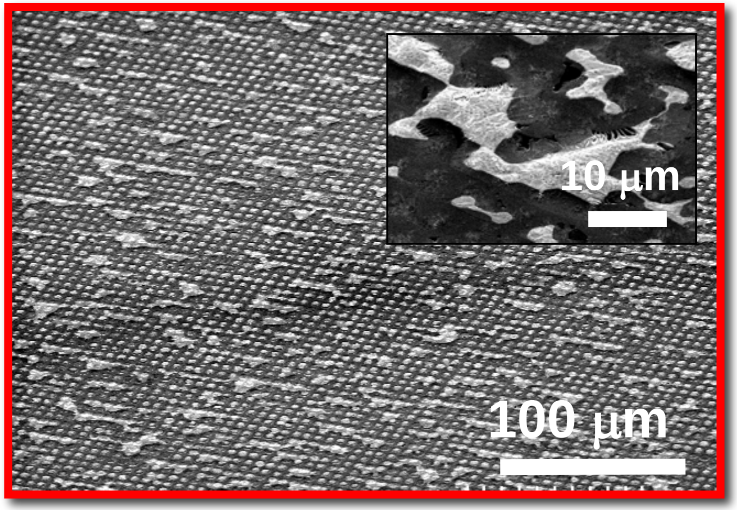
B. M. Kayes, M. A. Filler et al., *App. Phys. Lett.* **91**, 103110 (2007)
R. S. Wagner and W. C. Ellis, *App. Phys. Lett.* **4**, 89 (1964)

Oxide Buffer Layer - Pattern Fidelity

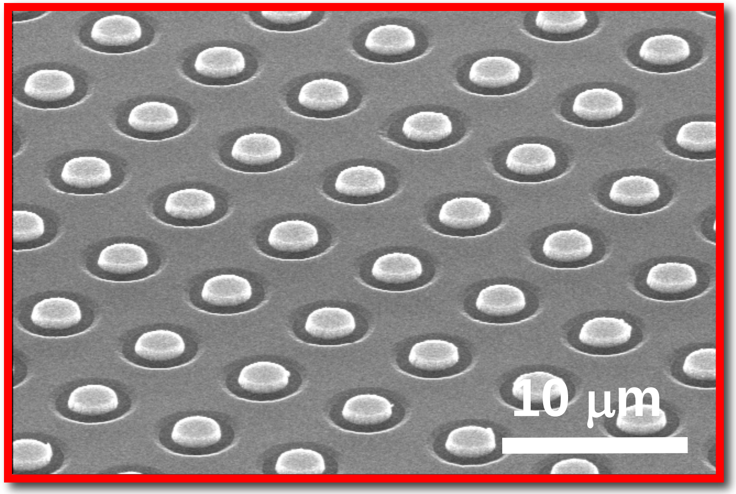
No oxide buffer layer



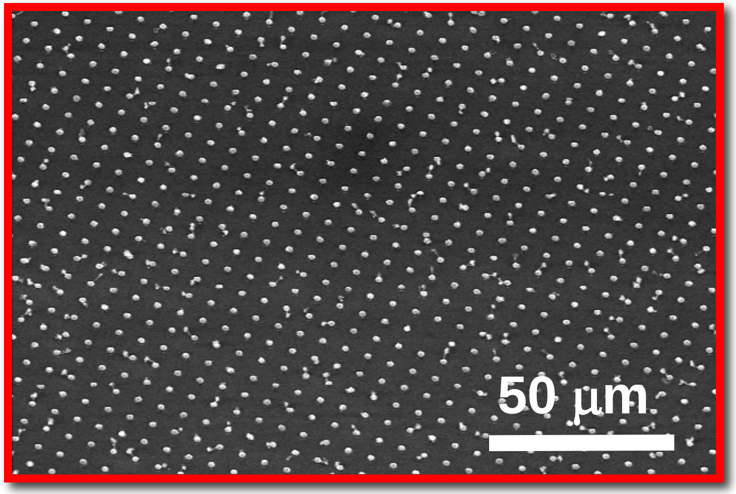
H$_2$ anneal
1000°C



Oxide buffer layer



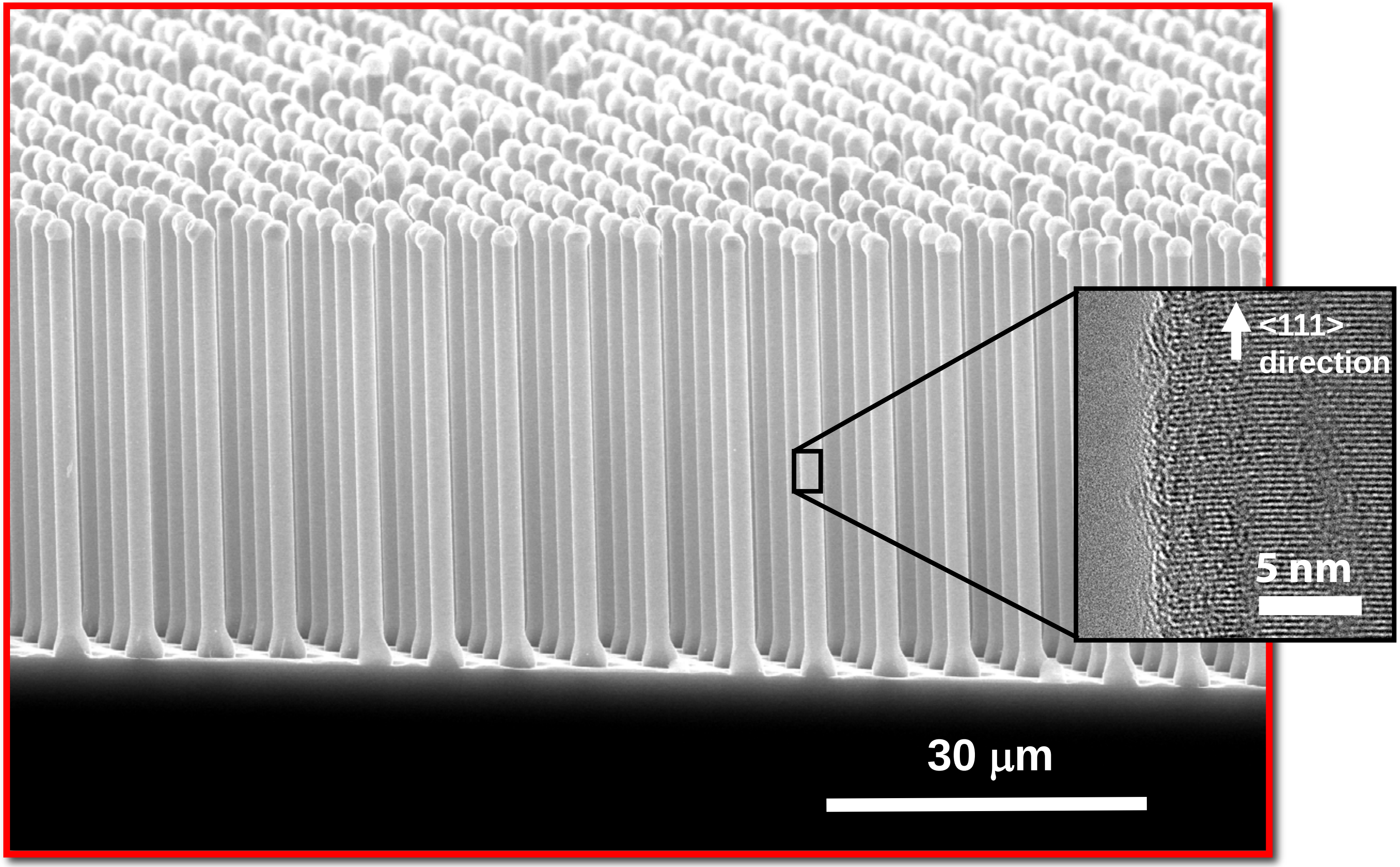
H$_2$ anneal
1000°C



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.

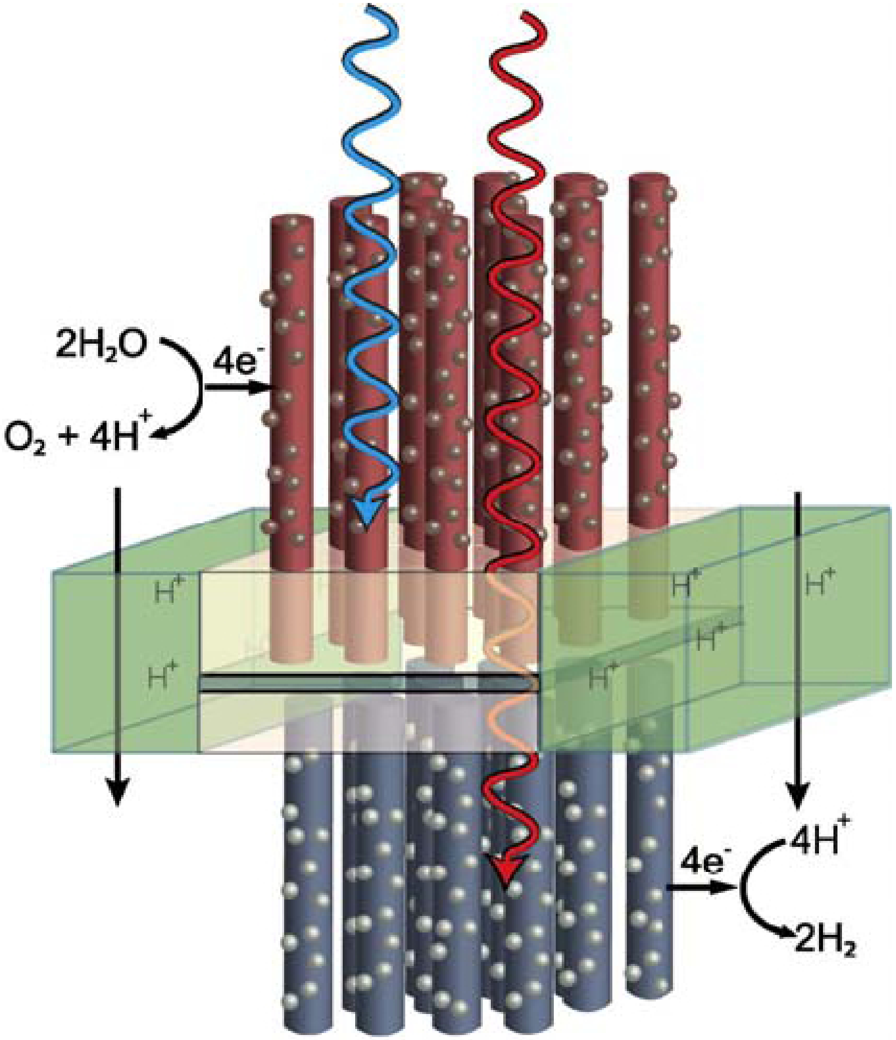
Large Area Au-Catalyzed Si Arrays



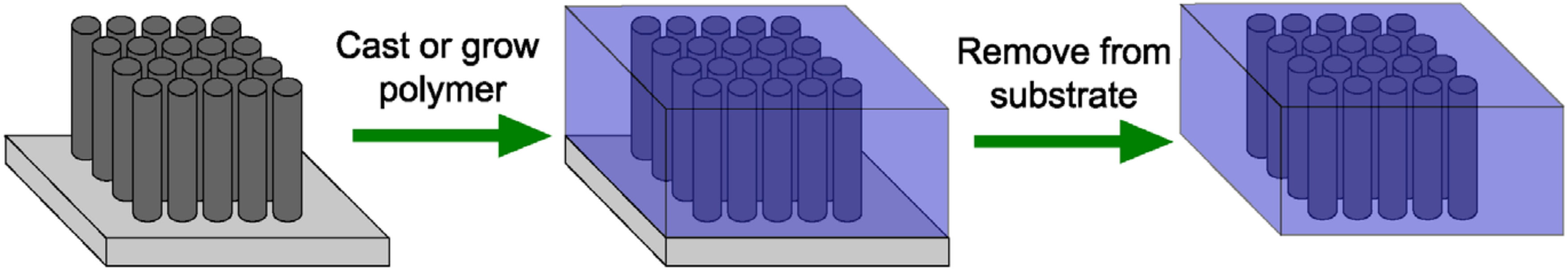
3 μm array, 500 nm Au, T_{growth} = 1000°C, P_{growth} = 760 Torr, 30 min growth, 2 mole % $SiCl_4$ in H_2

Nearly 100% vertically aligned, 75 μm length microwire arrays over areas > 1 cm^2.

Constructing the Pieces of a Solar H_2 Fuel Generator



Polymer Embedding of Si Rod Arrays

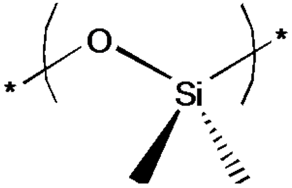


Cast or grow polymer

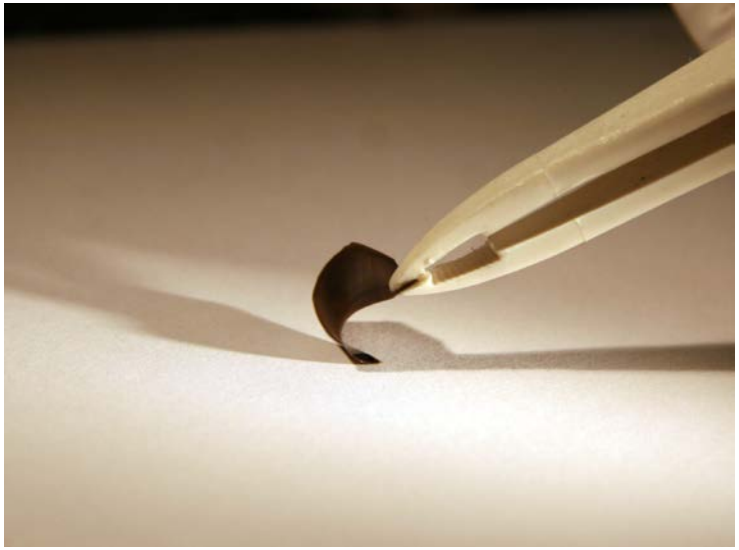
Remove from substrate

Silicon rod array on silicon substrate

Silicon rod array in polymer film

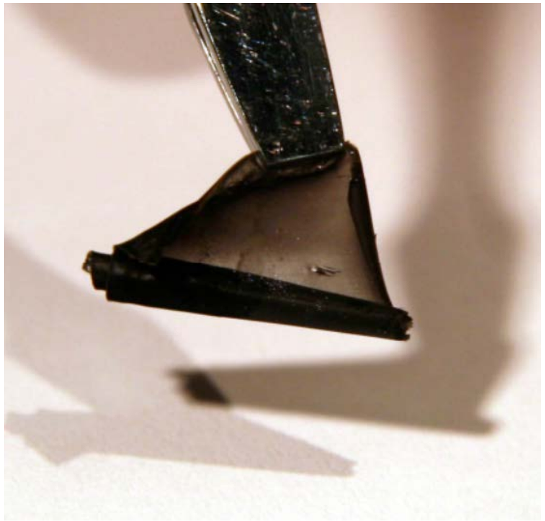


PDMS
(polydimethylsiloxane)

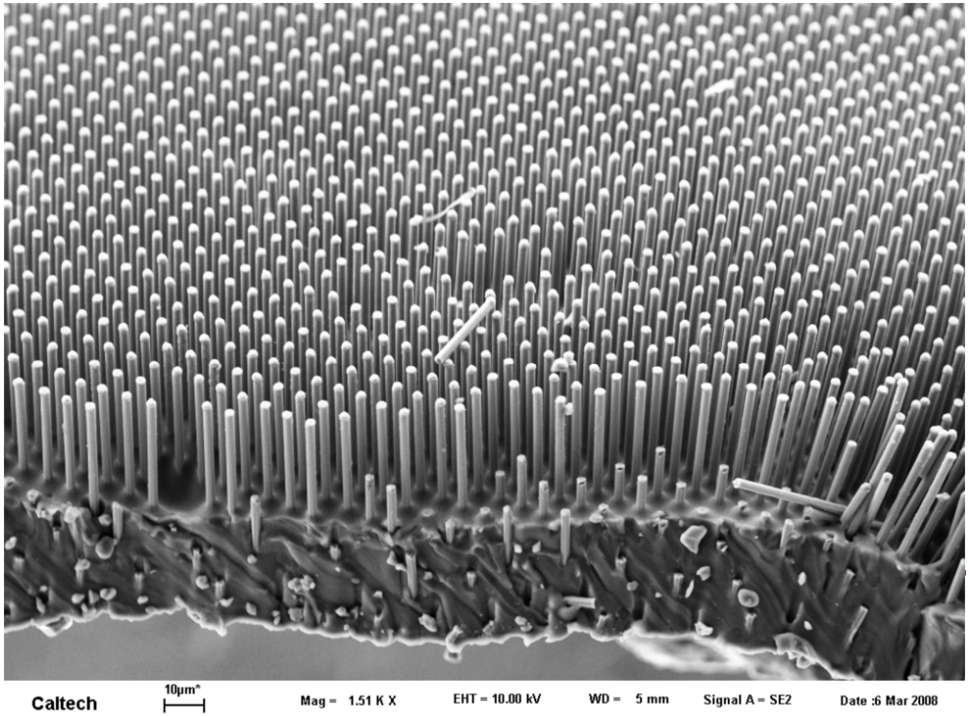


Large Area Rod Array Removal

Top-down view



Side view

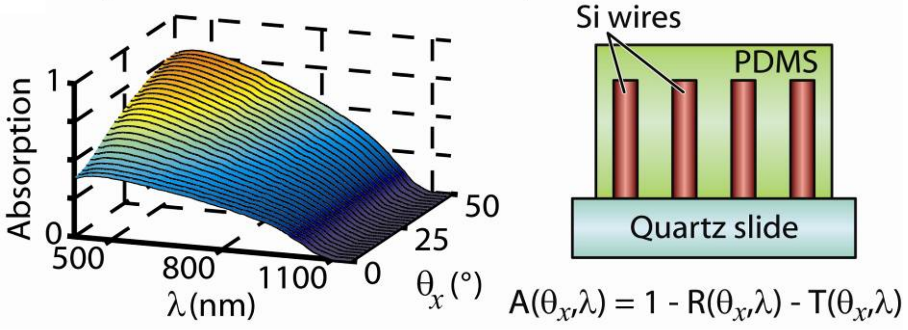


5 µm

- Large area arrays (> 1 cm^2) transferred in one piece.
- Conformal coating from top to bottom of rods

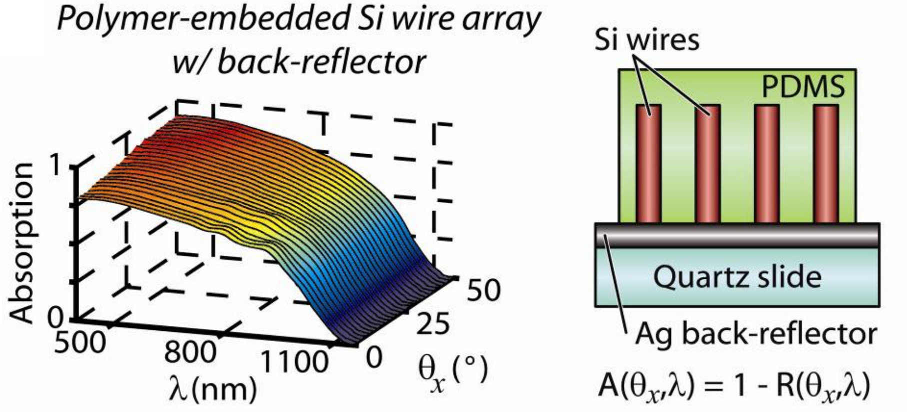
Maximizing Si wire absorption

Polymer-embedded Si wire array



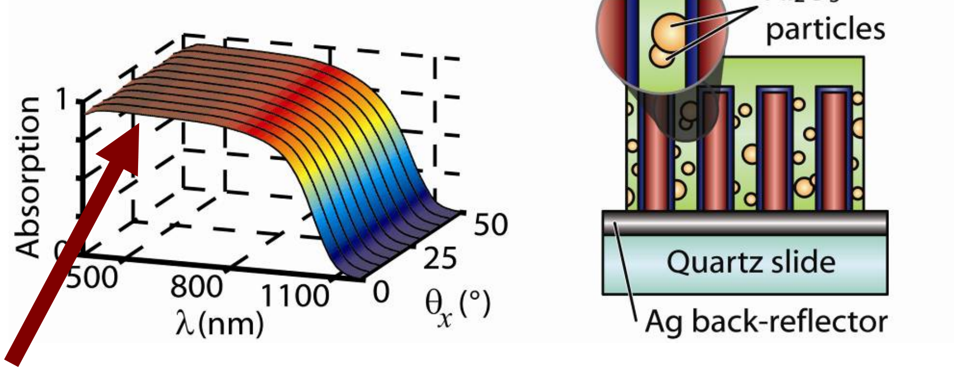
$A(\theta_x,\lambda) = 1 - R(\theta_x,\lambda) - T(\theta_x,\lambda)$

Polymer-embedded Si wire array w/ back-reflector



$A(\theta_x,\lambda) = 1 - R(\theta_x,\lambda)$

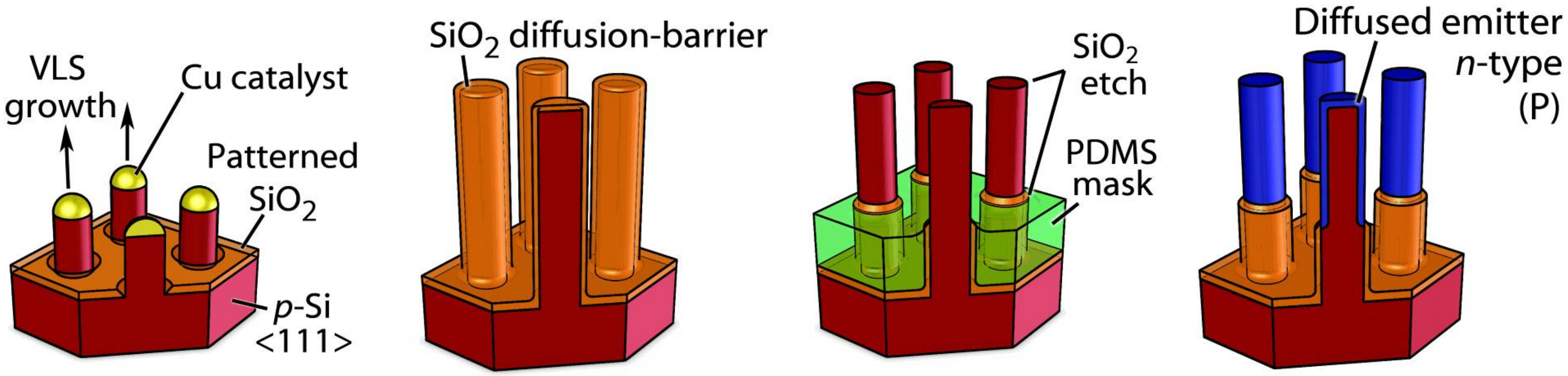
AR-coated array w/ light-scatterers and back-reflector



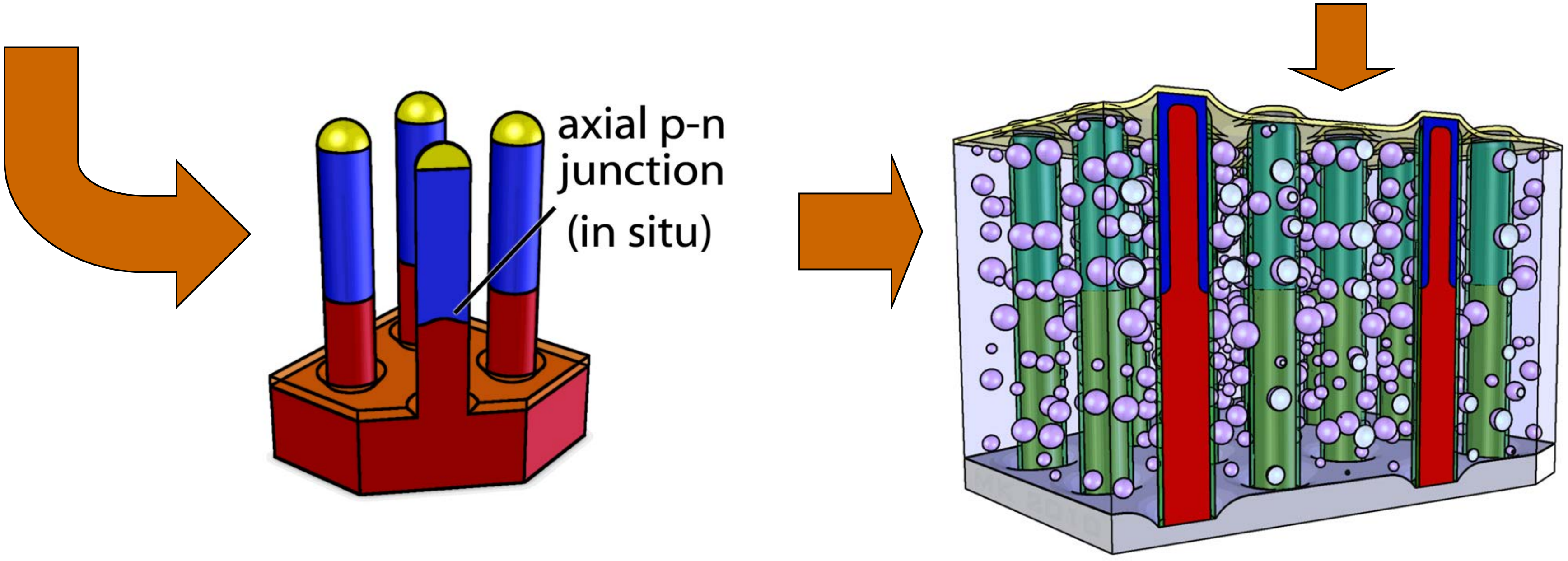
96% peak absorption

Kelzenberg, Boettcher et. al. Nat. Mater. 2010

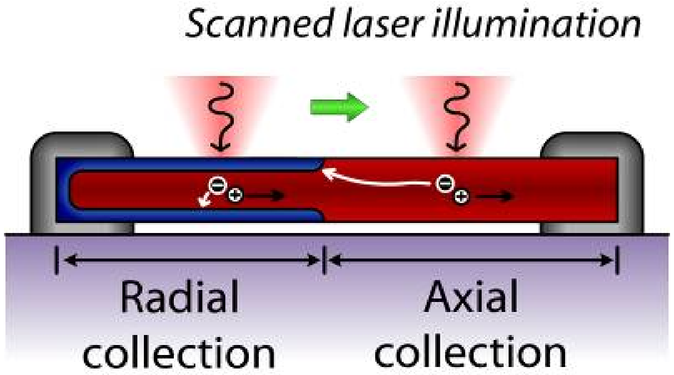
Si Microwire Solar Cell Fabrication Process

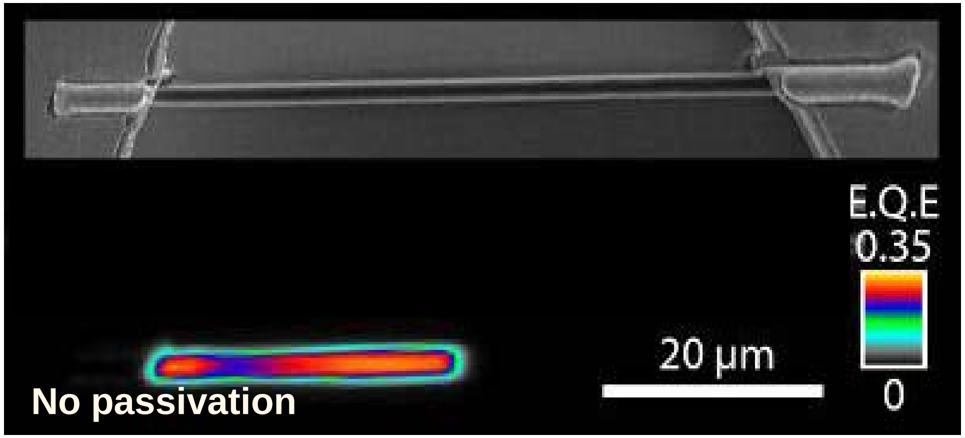


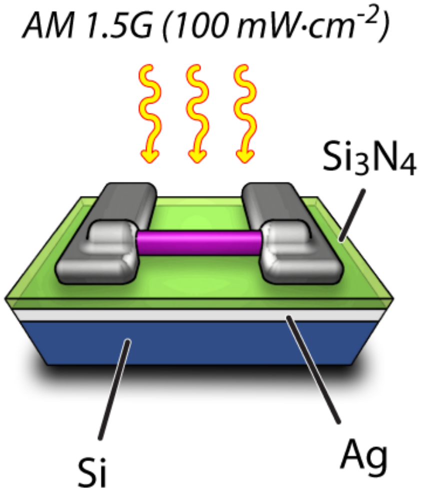
Growth **Oxidation** **Chemical processing** **Diffusion**

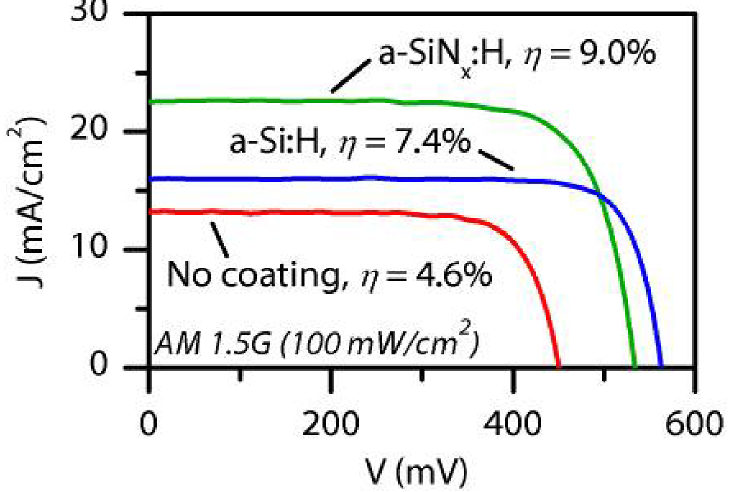


Insight from Single-Wires









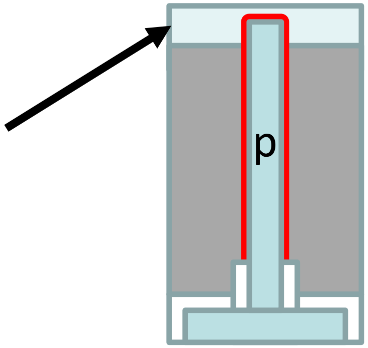
Minority carrier diffusion length >> 20 um
Confirms high quality VLS p-Si

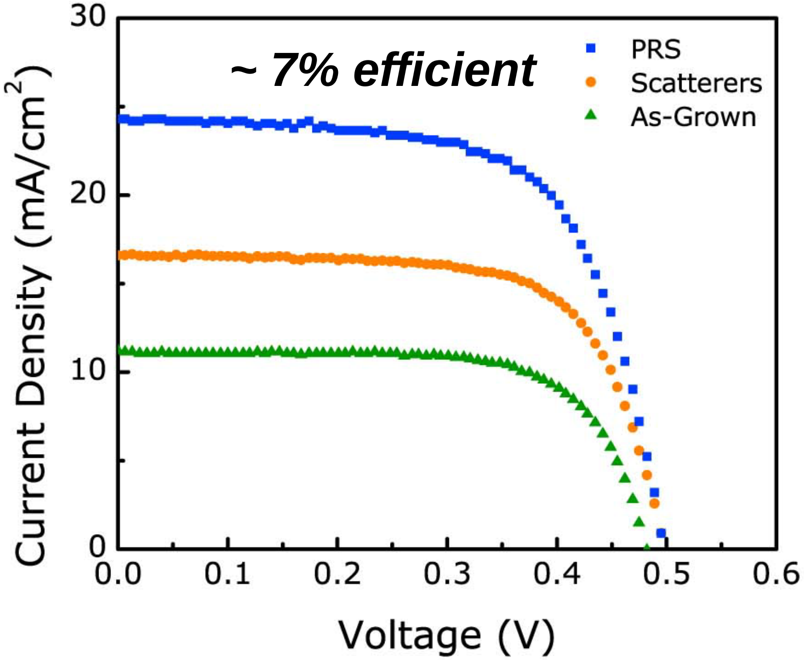
600 mV V_{OC} – competitive with commercial wafer-based Si.

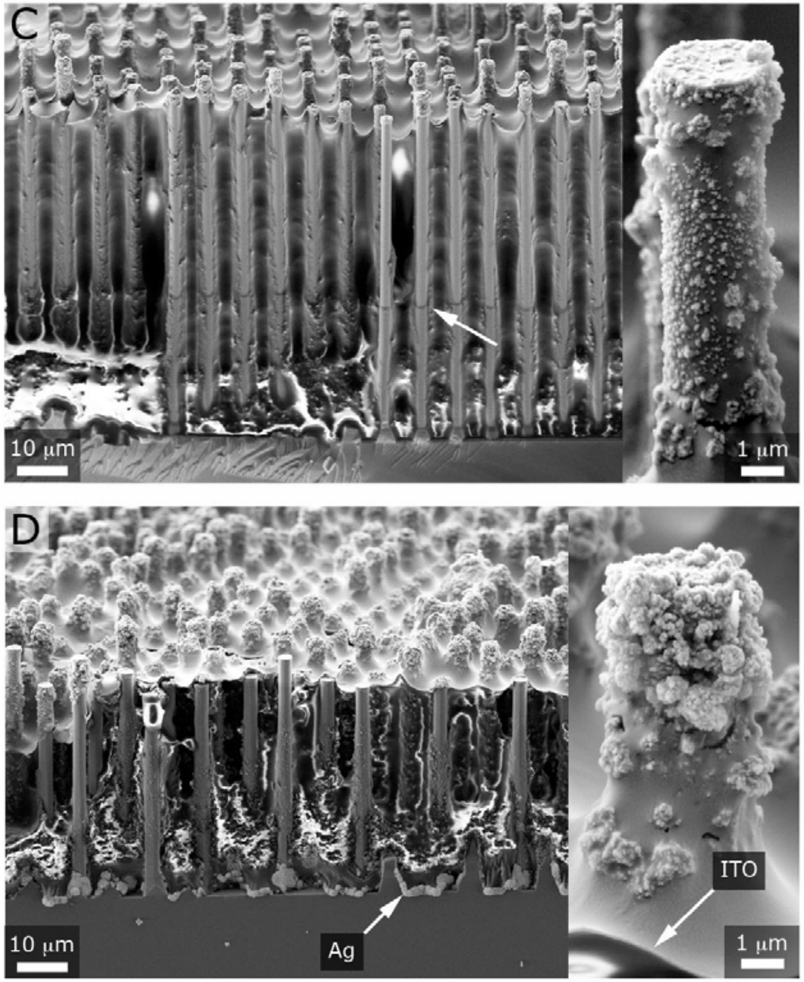
Kelzenberg, Turner-Evans, Putnam, Boettcher Energ. Env. Sci 2010.

Solid-State PV Si Microwire Arrray Devices

Add transparent top contact:

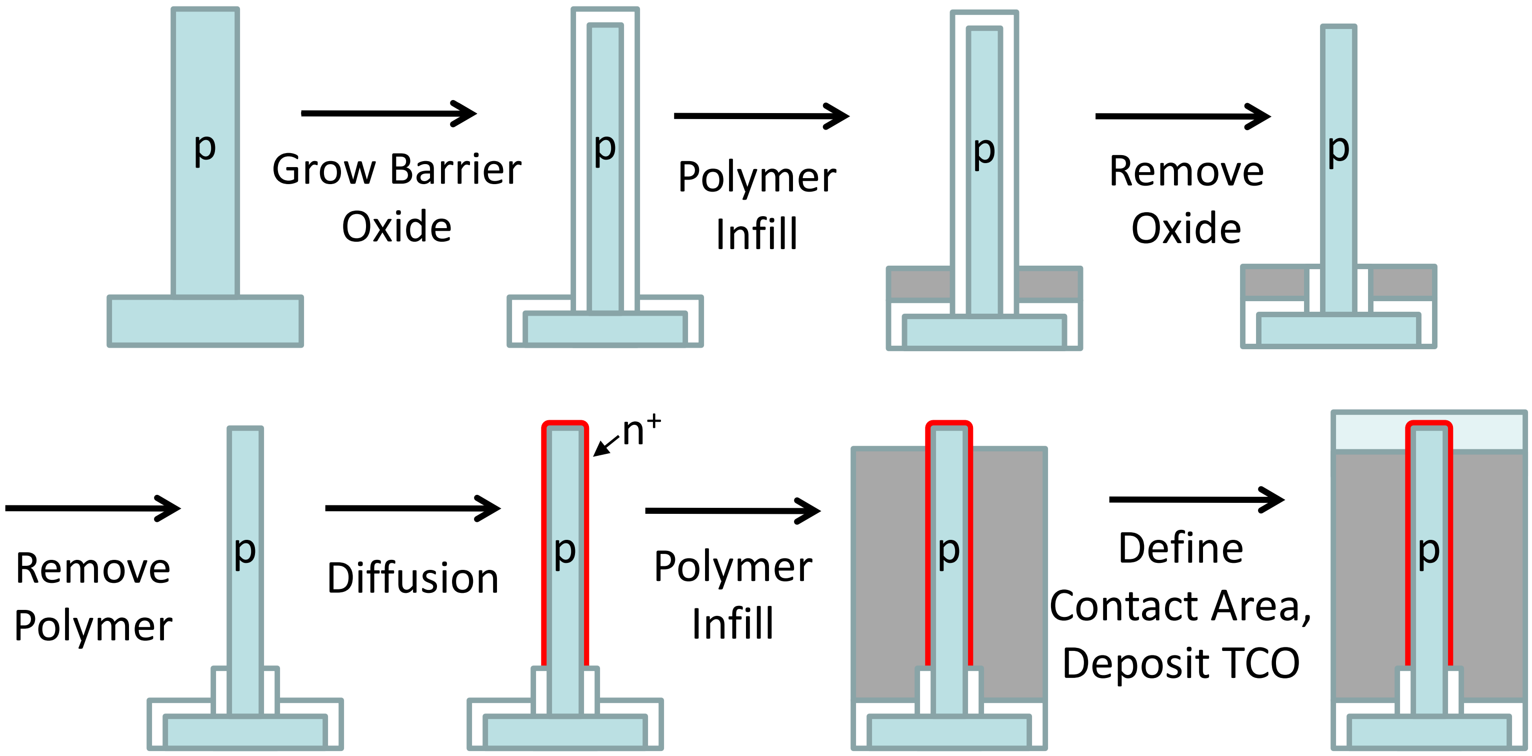



~ 7% efficient

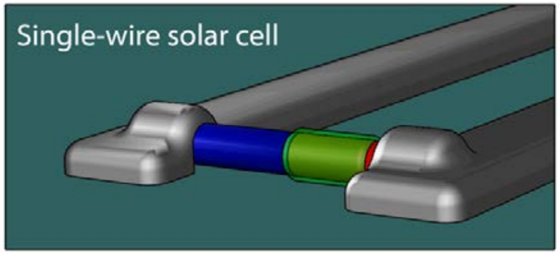


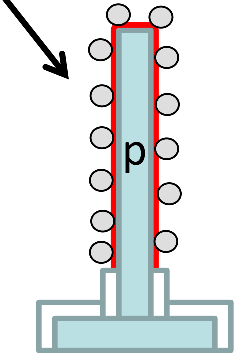
Putnam, Boettcher, Ener. Env. Sci..

Radial pn-Junction Photocathode Process



Grow Barrier Oxide → Polymer Infill → Remove Oxide → Remove Polymer → Diffusion → Polymer Infill → Define Contact Area, Deposit TCO

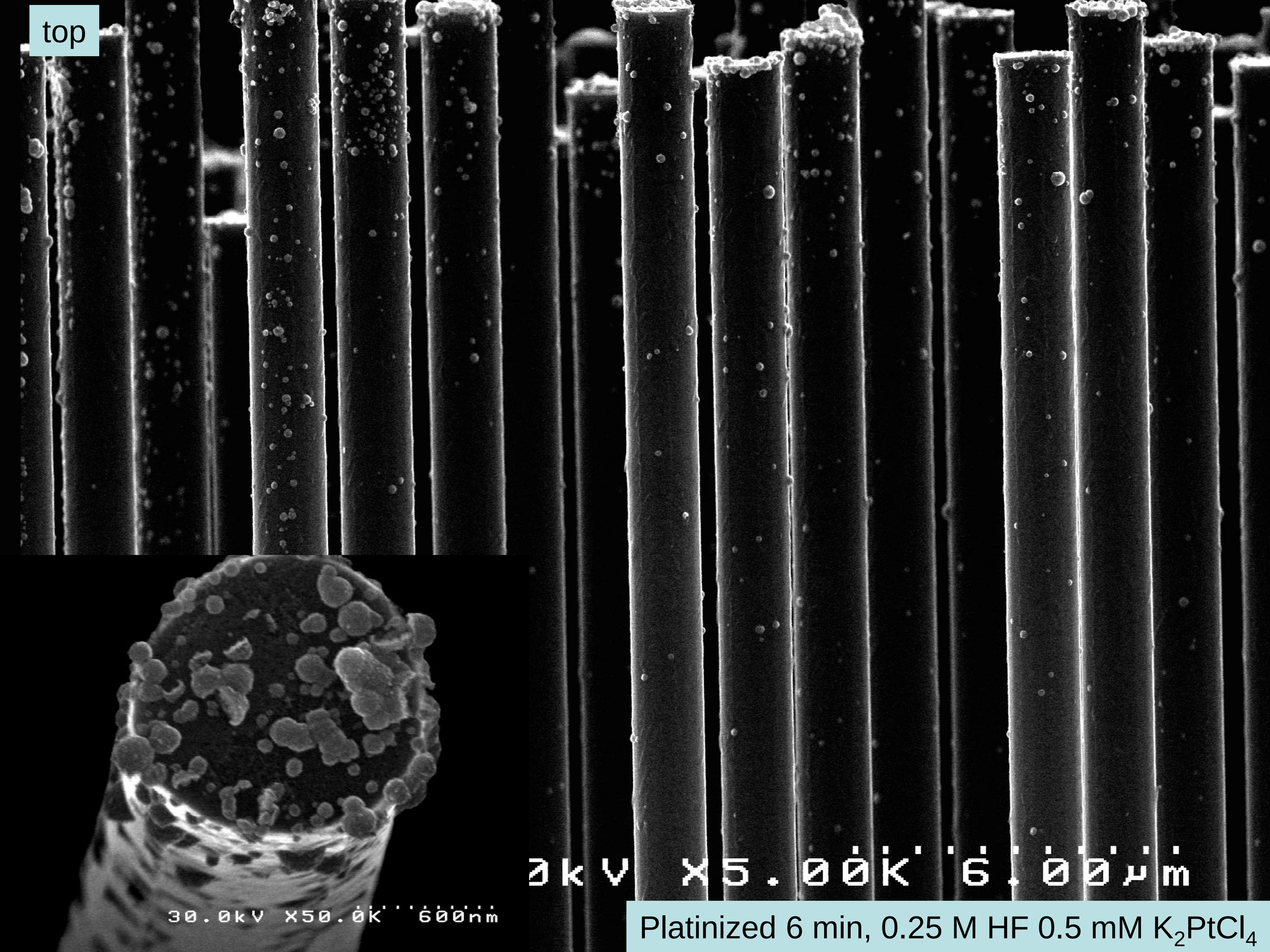




Solid-state wire-array PV

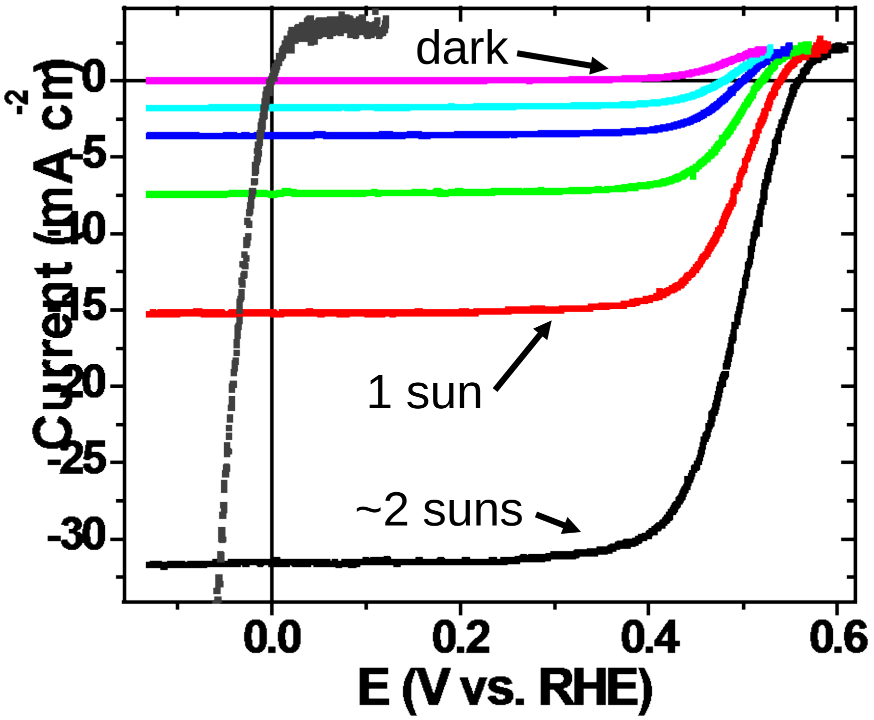
Incorporate metal catalyst for hydrogen evolution.

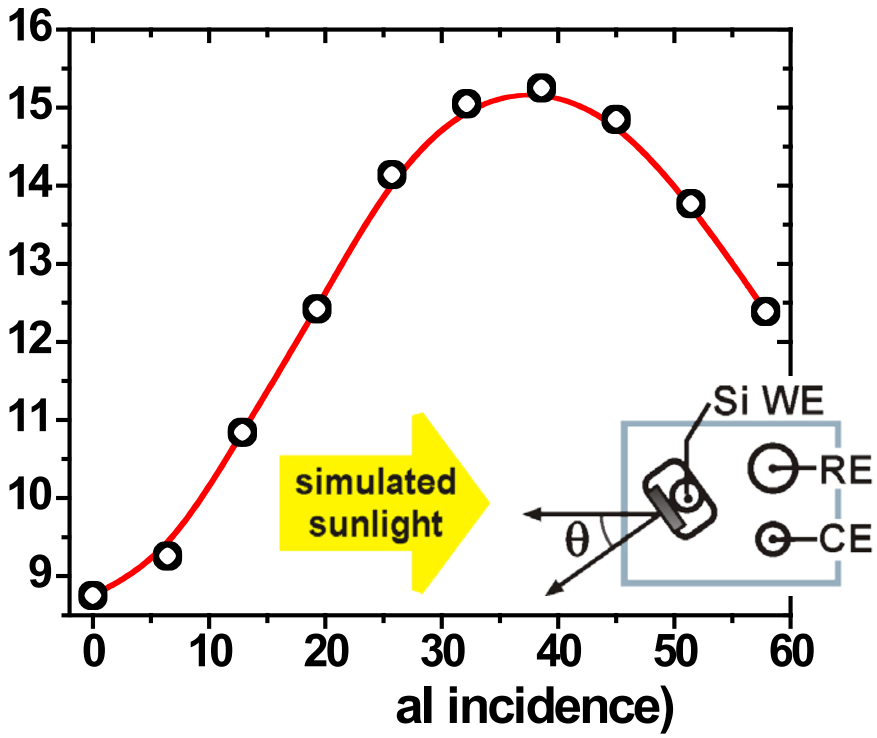
top



Platinized 6 min, 0.25 M HF 0.5 mM K_2PtCl_4

H_2 Evolution from Pt/pn-Si Rods



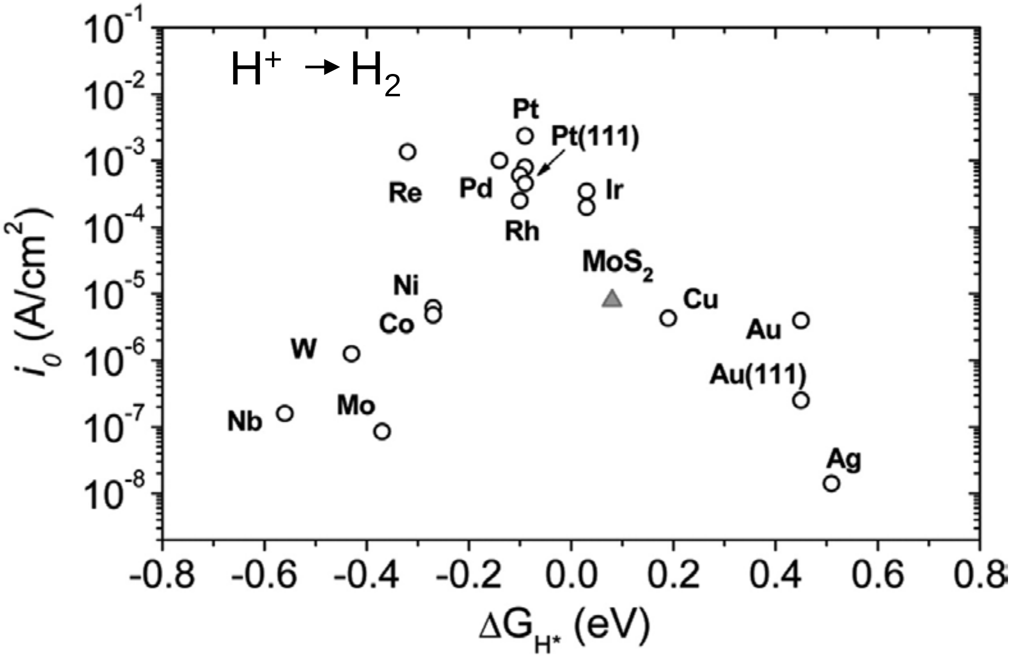


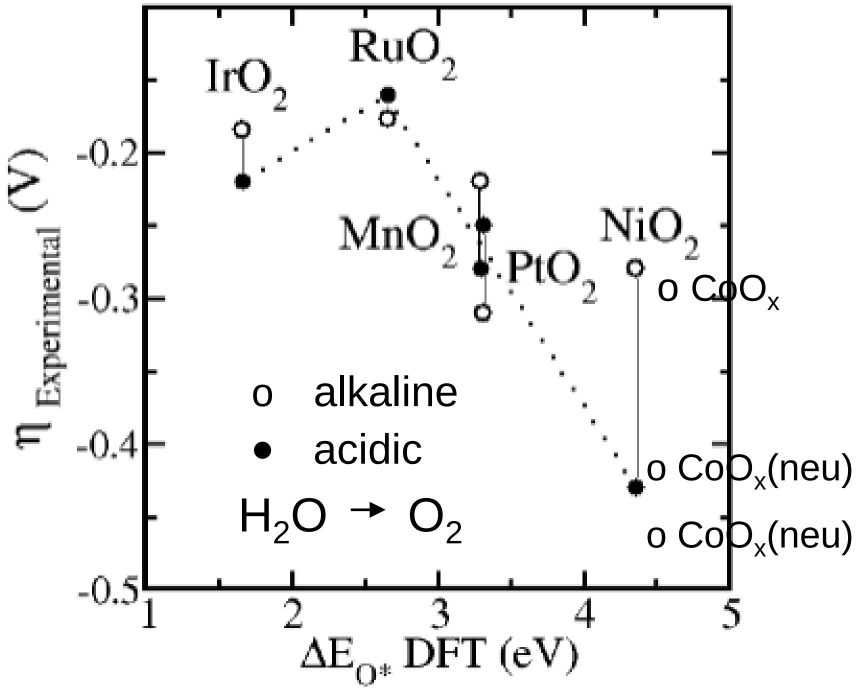
V_{OC} = 539 mV, FF = 0.71, J_{SC} = 15.3 mA cm^{-2}, η = 5.8 %

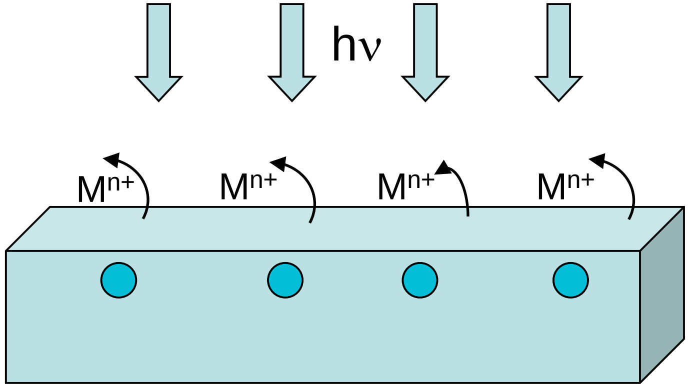
Near ideal fill factor, high V_{OC}, current low.

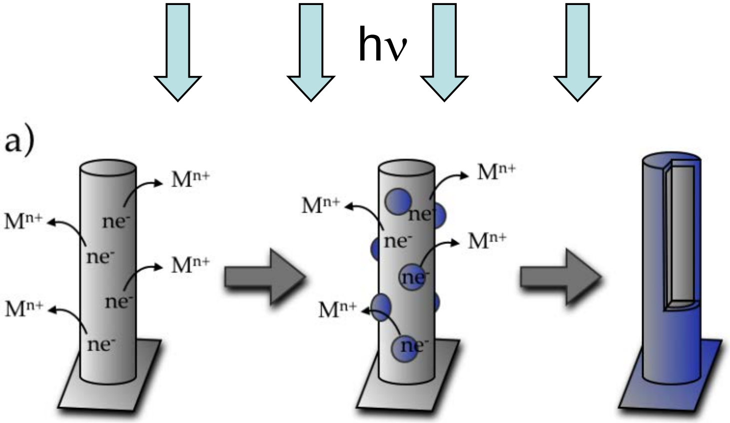
Boettcher et. al. *J. Am. Chem. Soc. 2010*

Relaxes Catalyst Activity Requirements

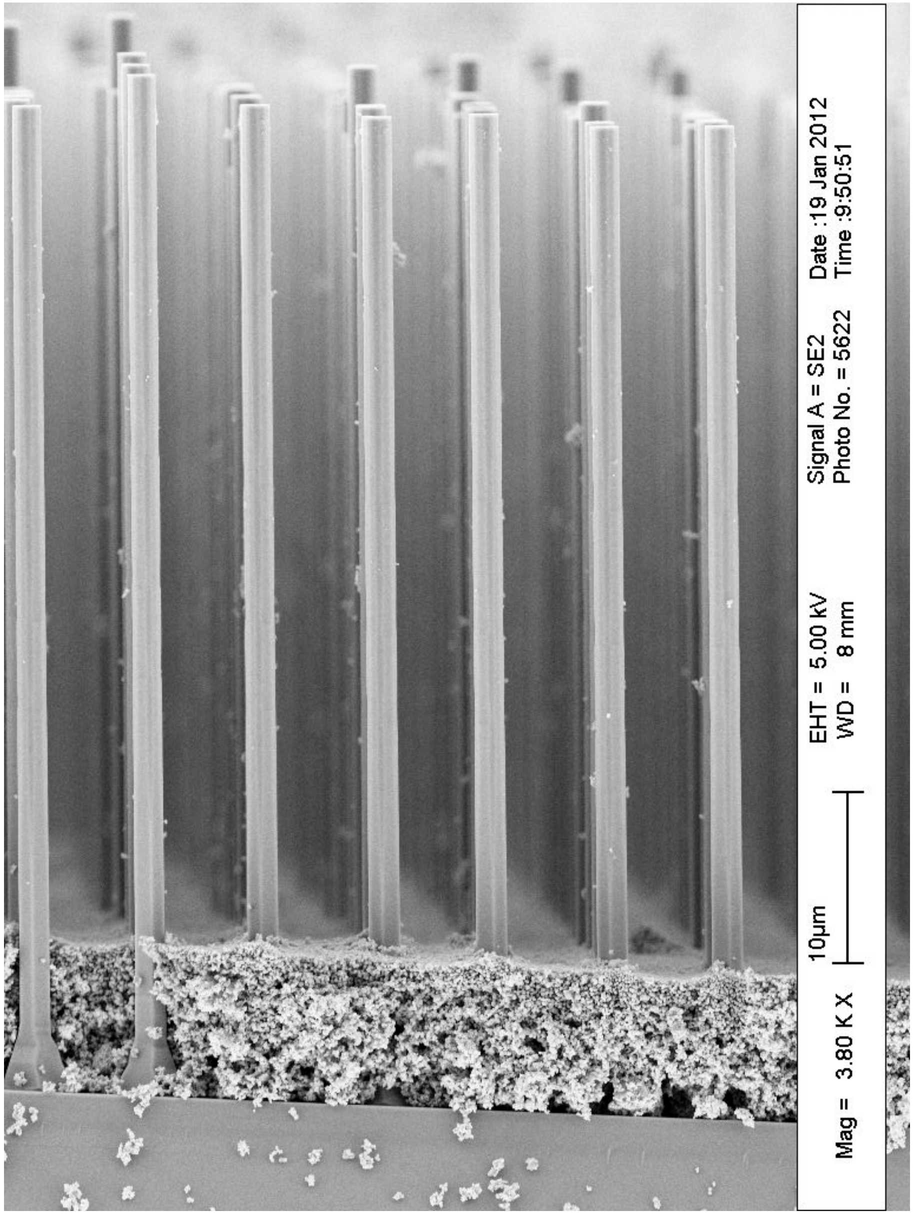




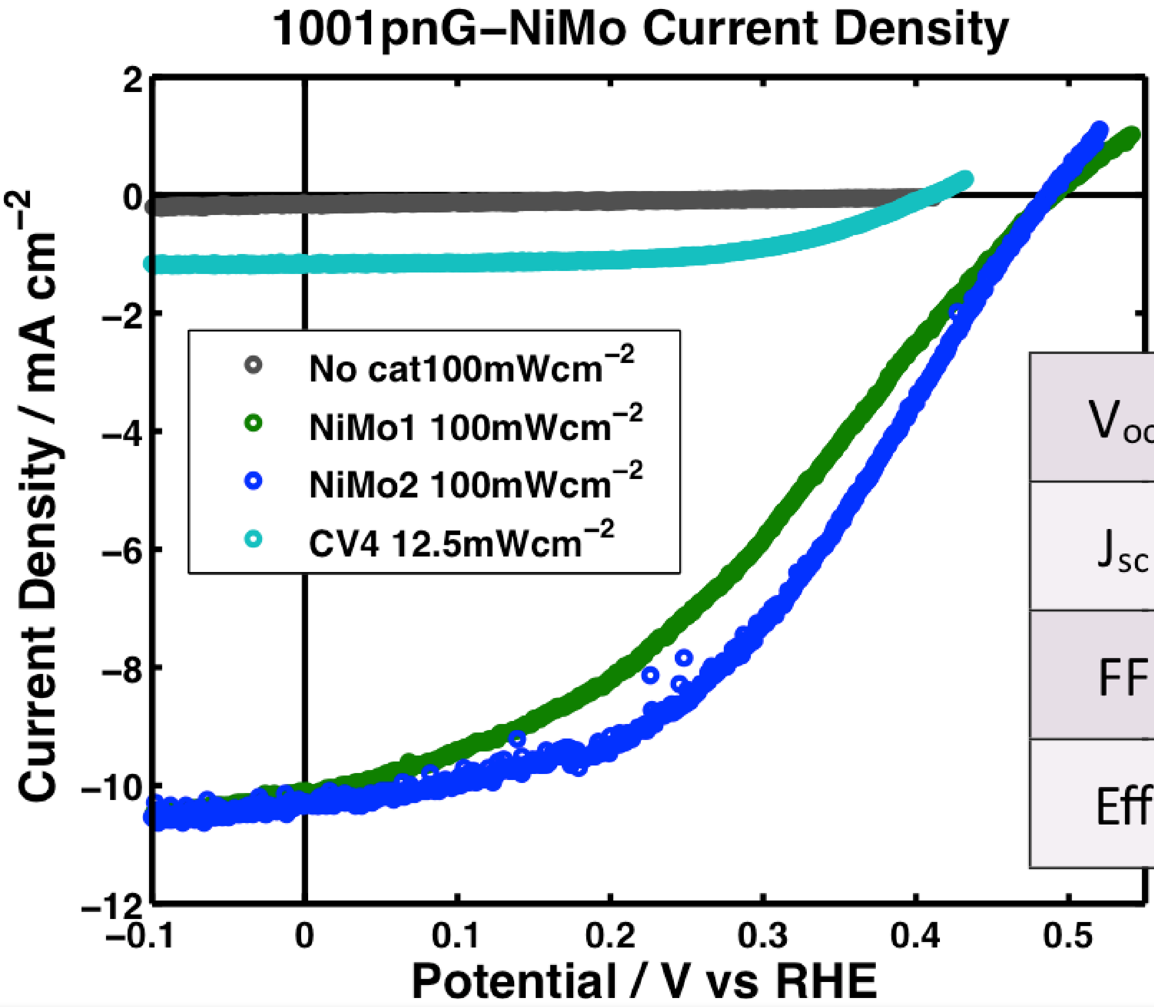




Ni-Mo HER Catalyst at Base of Si Wires

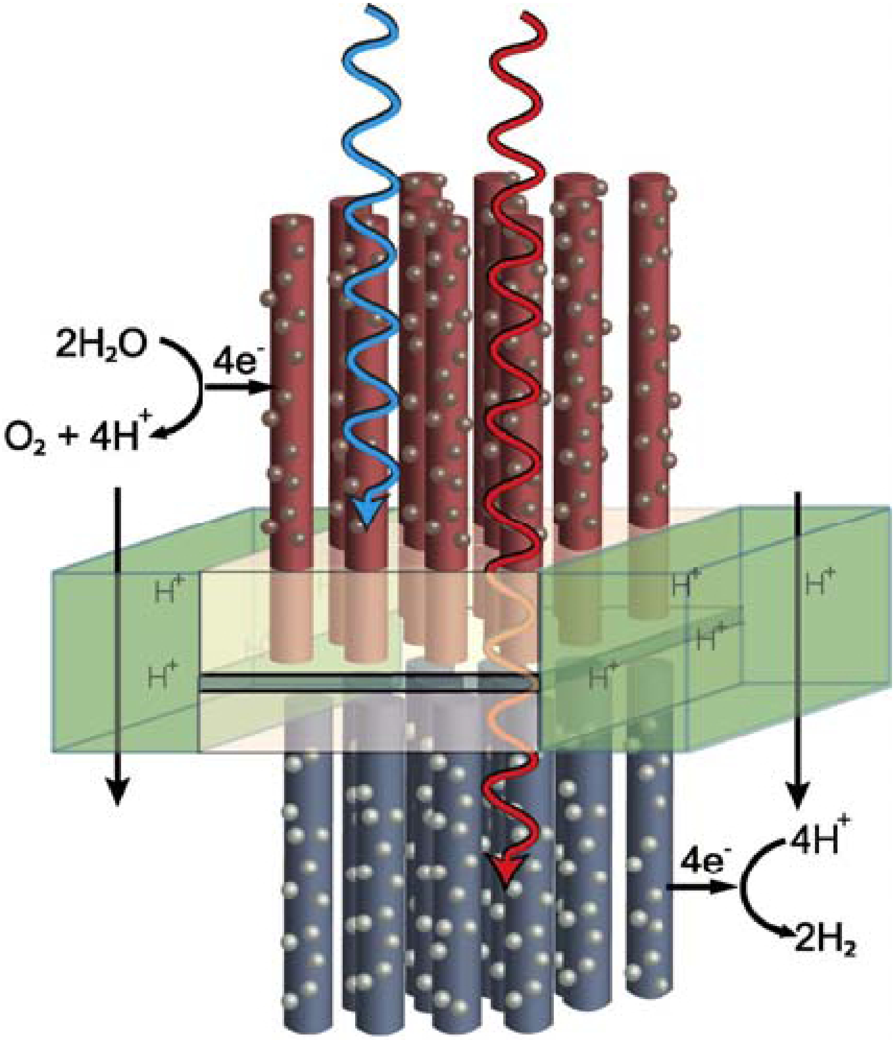


Ni-Mo on Si Microwires for H_2 Production

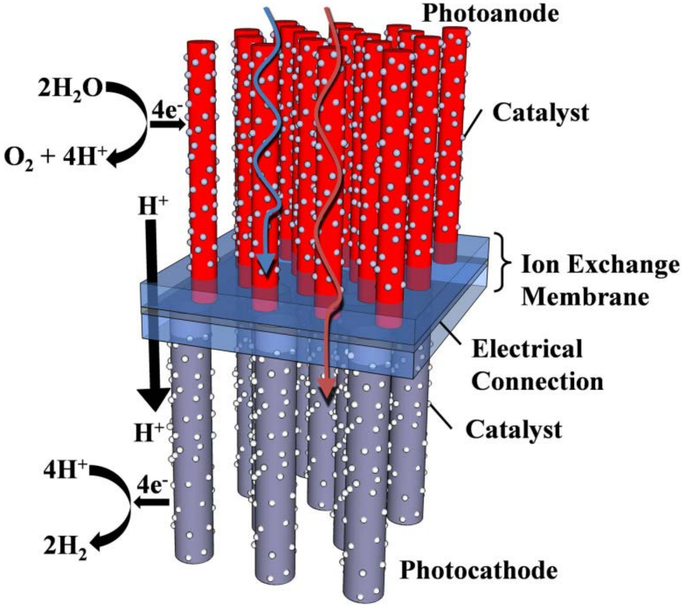


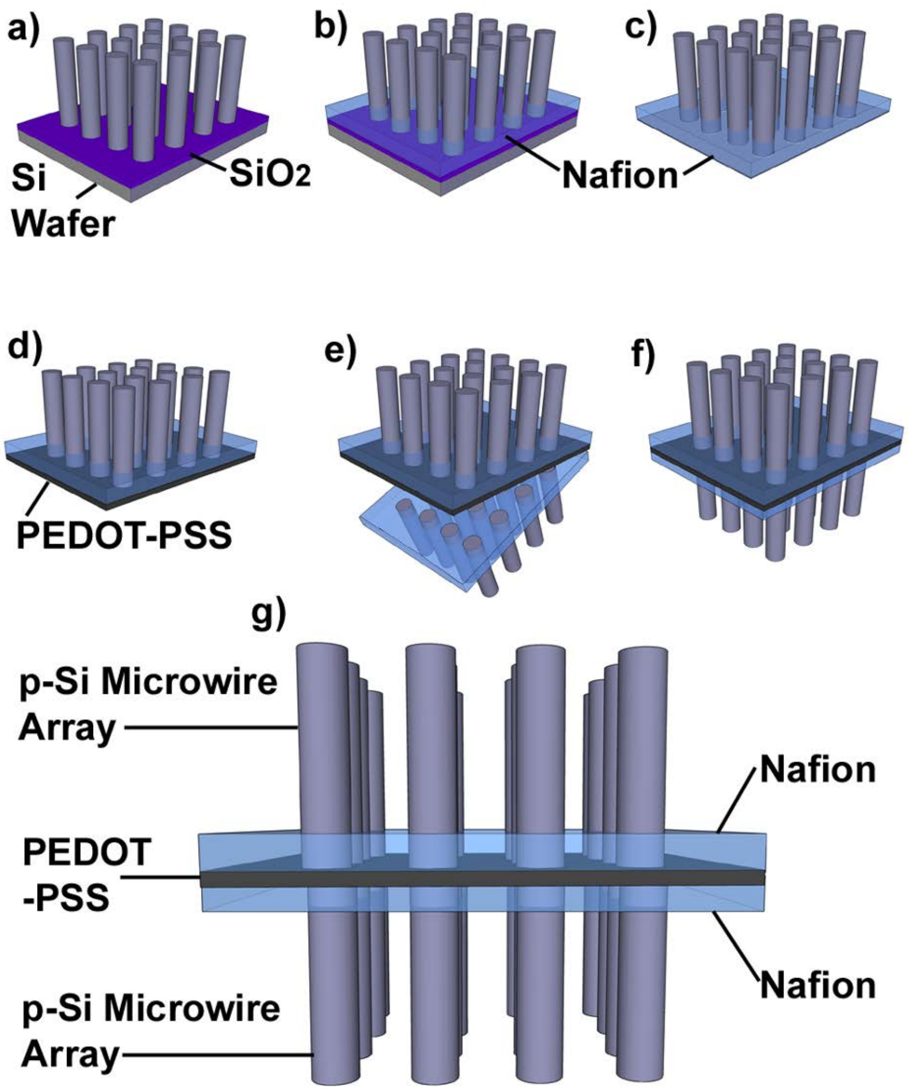
V_{oc}	0.490
J_{sc}	10.29
FF	0.45
Eff	2.2%

Constructing the Pieces of a Solar H_2 Fuel Generator



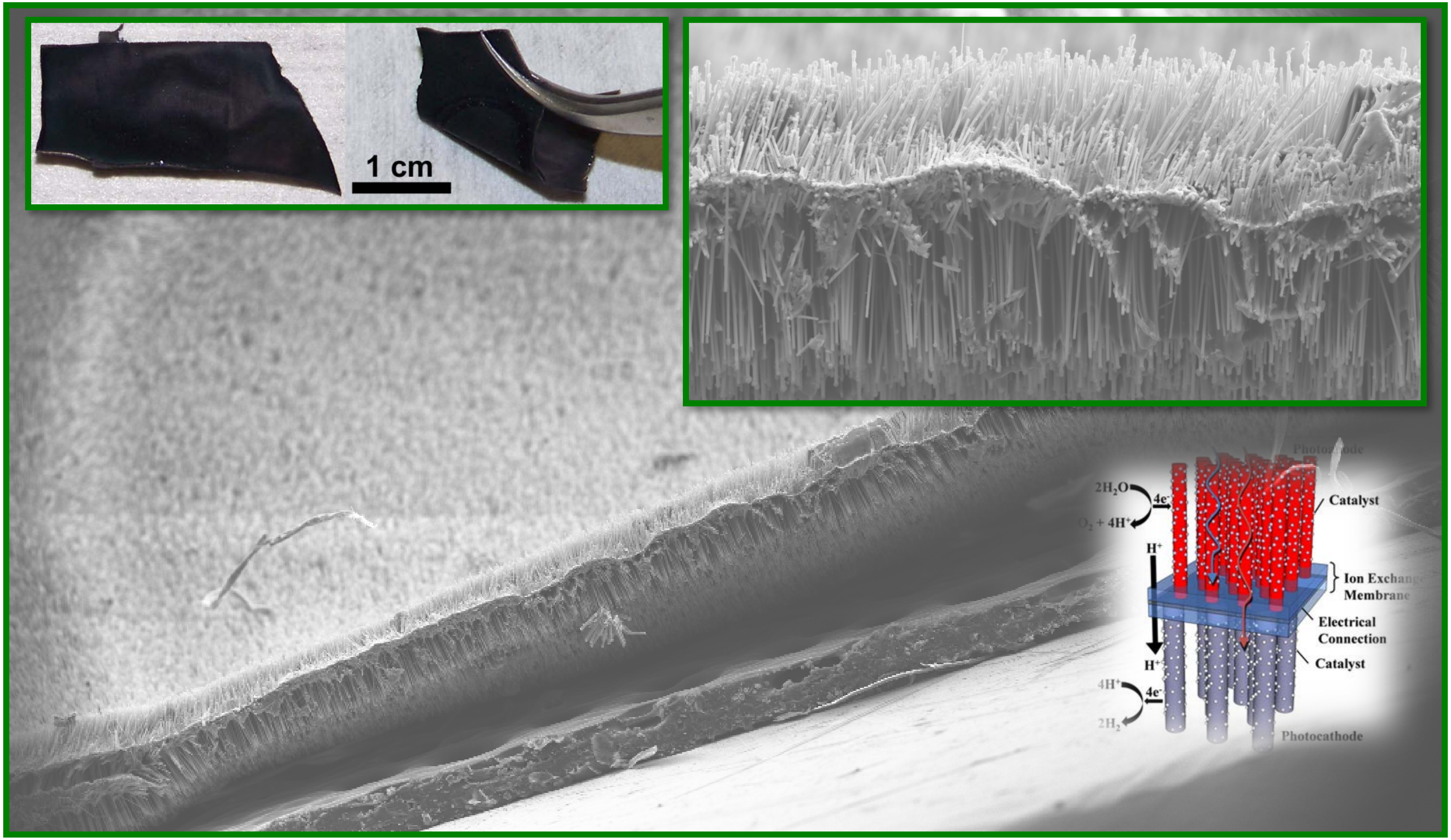
Test Membrane Fabrication





Si wire arrays on both sides and no catalyst as a first generation test membrane

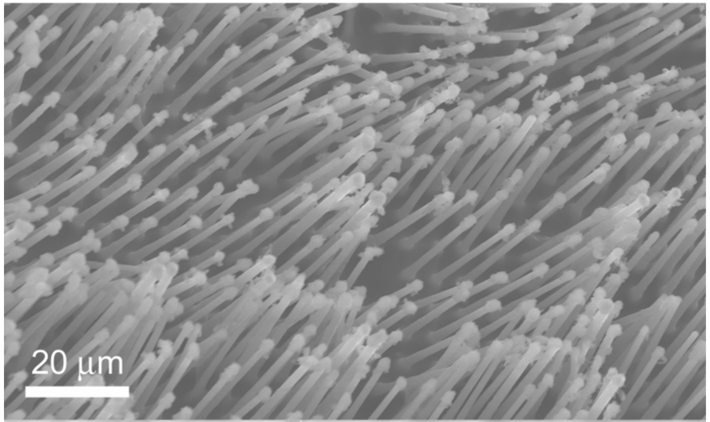
Dual Wire Array Membrane



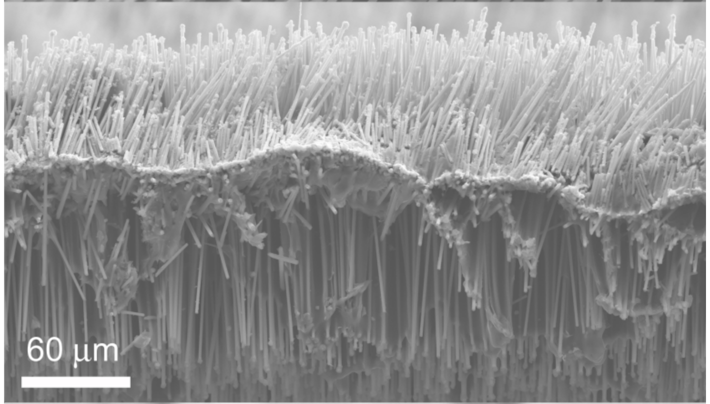
Josh Spurgeon, Lewis group, Caltech

Si Wire/Ionomer Morphology

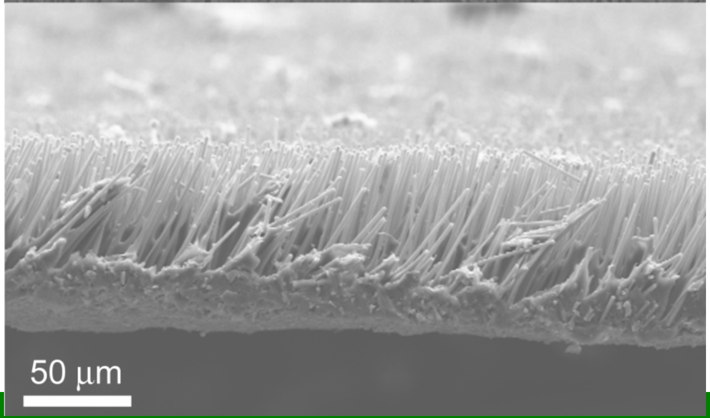
Dual (Si Wire Array/Nafion)/PEDOT-PSS



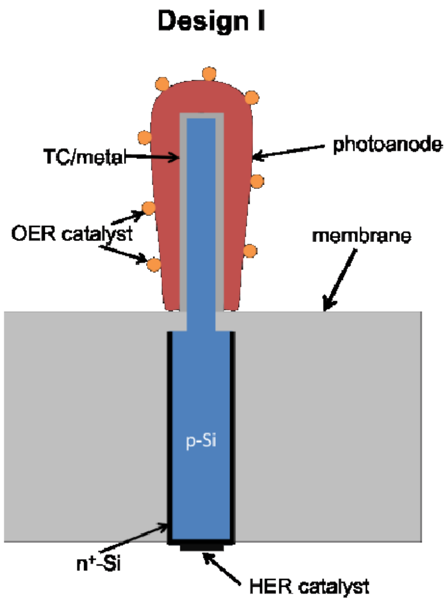
Dual (Si Wire Array/Nafion)/PEDOT-PSS

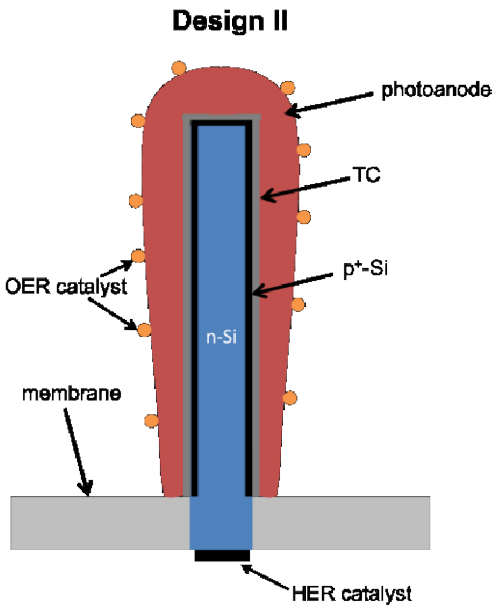


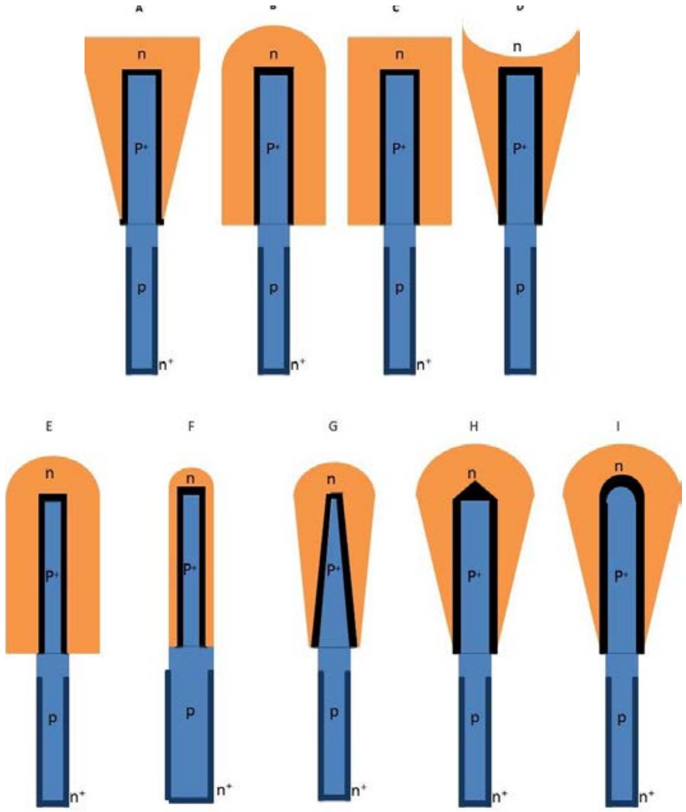
Si wire/QAPSF



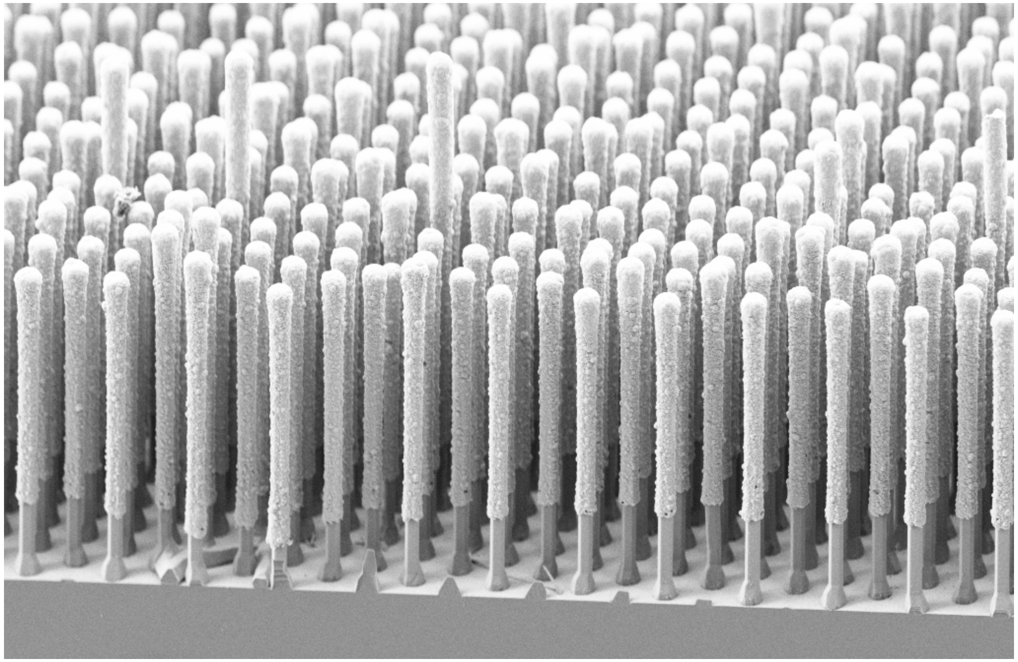
Self-Aligned Tandem Radial Junctions



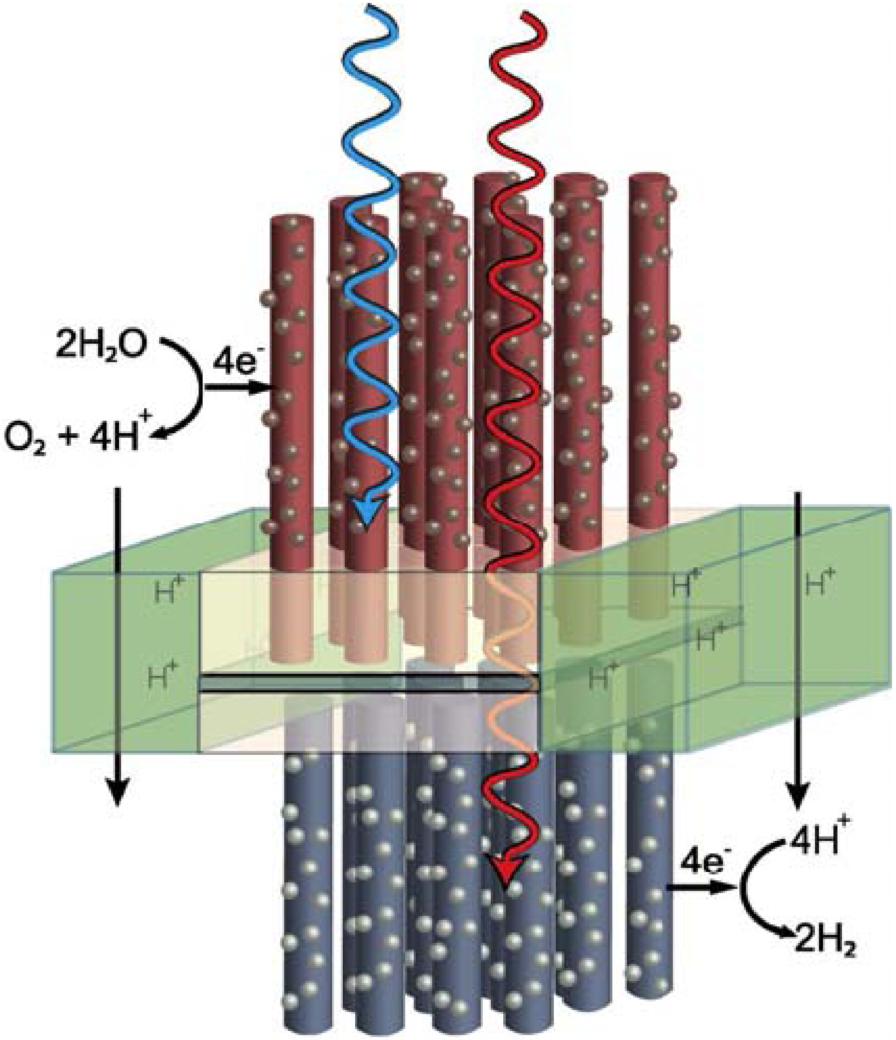




p-n$^+$ Si/ITO/WO$_3$ Tandem Radial Junctions



Constructing the Pieces of a Solar H_2 Fuel Generator



Dual Junction Nanorod Arrays

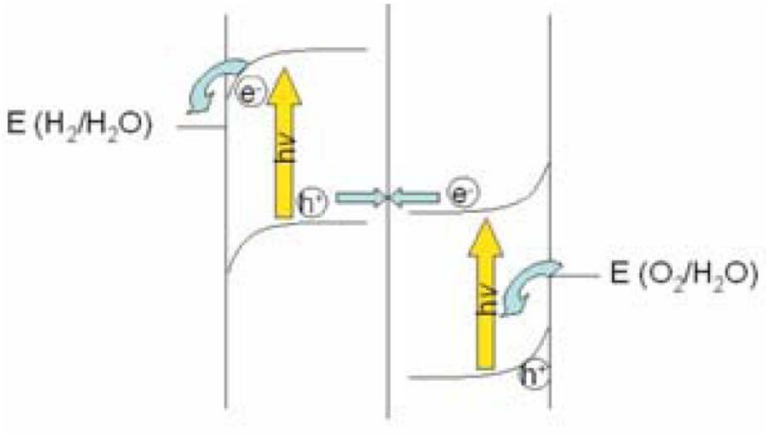
- 1.23 V needed to electrolyze water
- Requires a heterojunction or dual junction
- Single absorber: band gap of 2.0-2.6 eV that straddles the necessary potentials
- Photoanode and photocathode absorbers:

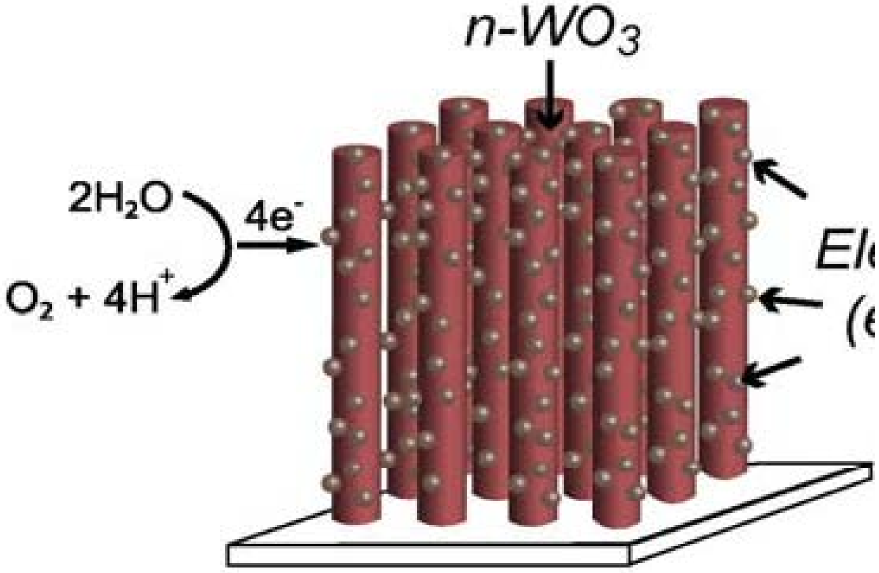
  Band gaps can better match the solar spectrum (1.1-1.4 eV)

  Allows for greater flexibility in materials design

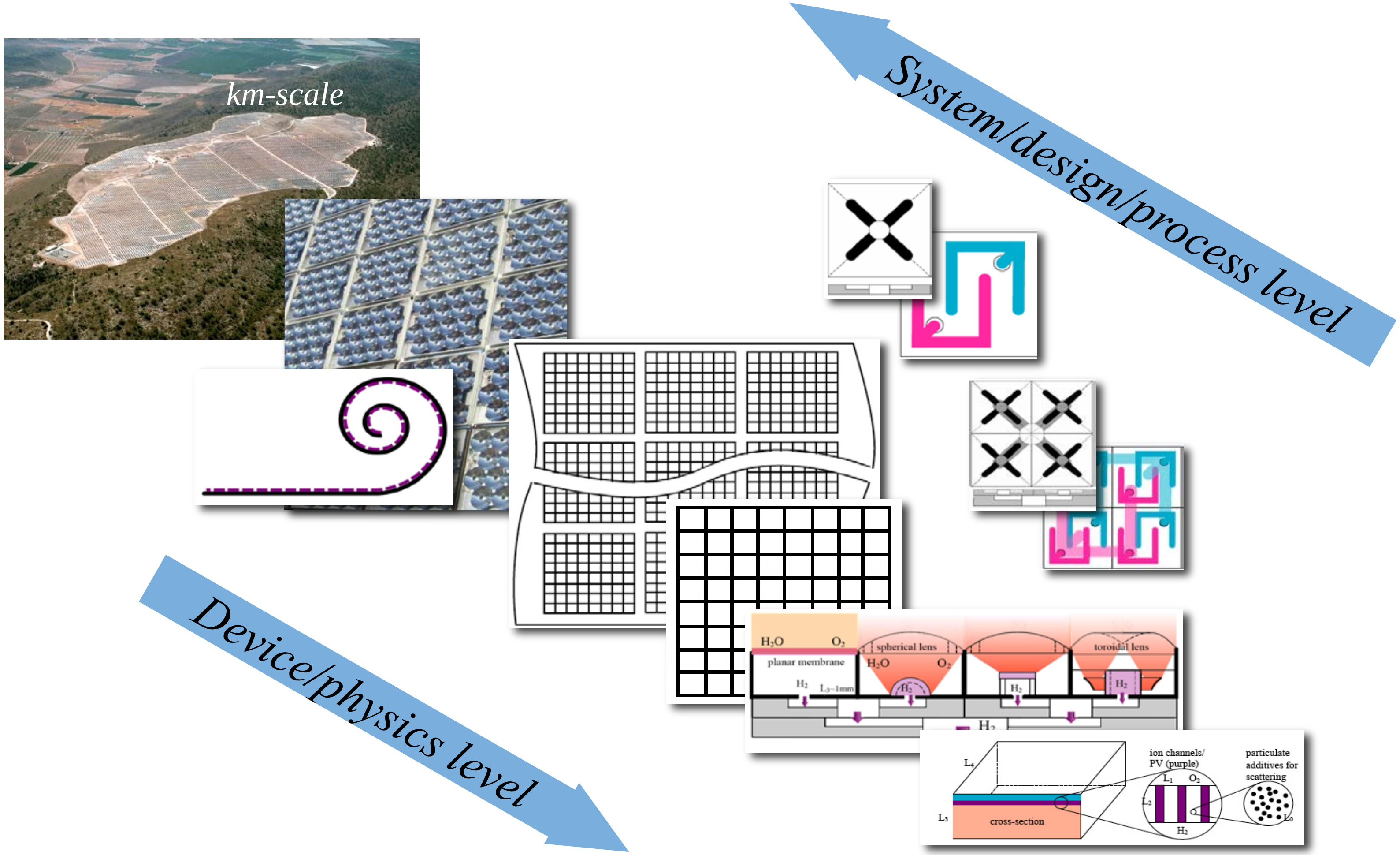
  Efficiency could approach 25%

- Optimal structure would have several light-absorbing layers absorbing different portions
- of the spectrum with an overall potential greate than 1.23 V





JCAP: DOE's Solar Fuels Energy Innovation Hub

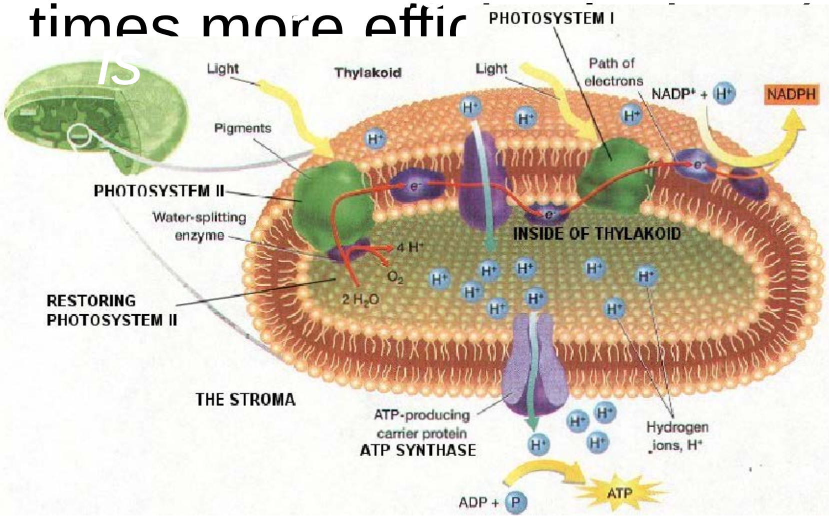


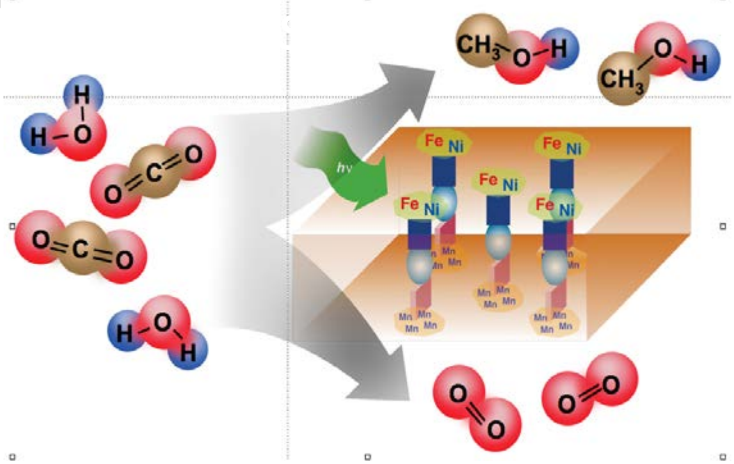
System/design/process level

Device/physics level

Mission of JCAP

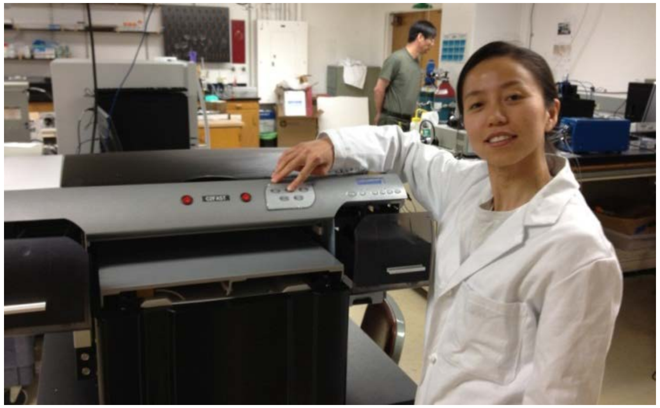
- **Melvin Calvin, 1982**: It is time to build an actual artificial photosynthetic system, to learn what works and what doesn’t work, and thereby set the stage for making it work better
- **10-year JCAP Goal**, **2010**: To demonstrate a manufacturably scalable solar fuel generator, using earth-abundant elements, that, with no wires, robustly produces fuel from the sun, 10 times more effic current) crops





Science Overview: Absorber Precursors

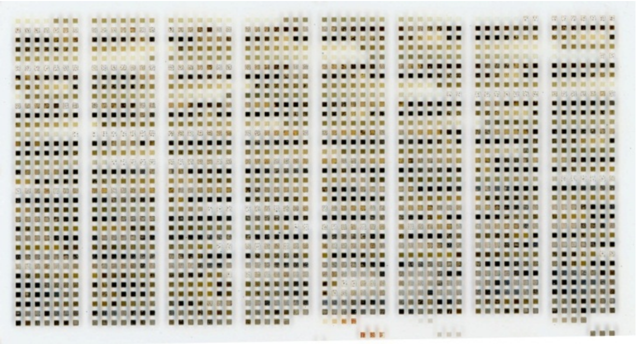
- Research Highlight – High-Throughput Experimentation (*continued*)



- **Inkjet printing (generation 2)**

- **Reactive annealing**
- Oxides, sulfides, nitrides, etc.

Co, Fe, Ti, Ni and baked: 1848 points 1mm^2



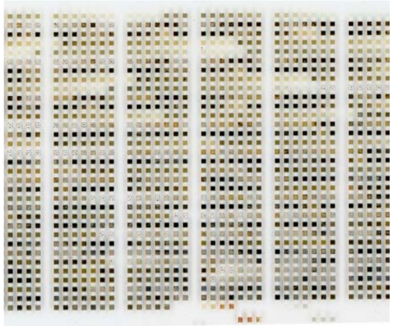
Time:
5544 samples in 7 min.!
(highest resolution
at slowest speed)

Inkjet printing methods can now produce 10^4-10^5 samples /hour for high-throughput fabrication

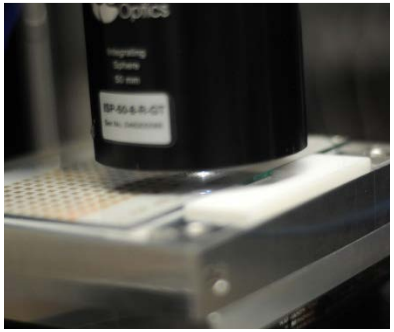
Science Overview: HTE

- **Research Highlight – Establishment of Advanced Screening Systems**

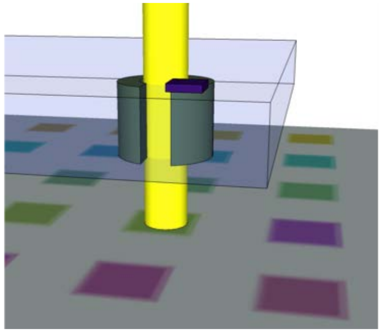
Printer Input



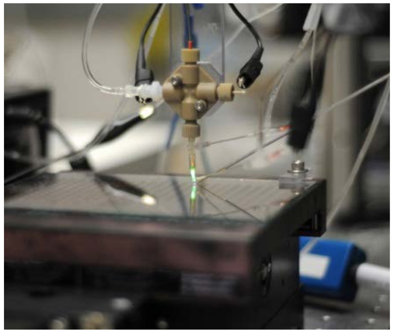
UV-Vis Absorbance



Non-aqueous IPCE

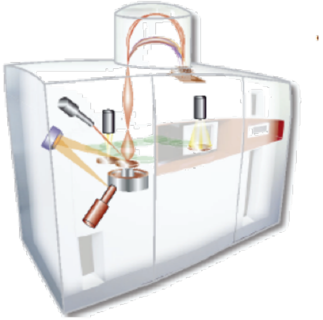


Aqueous CV



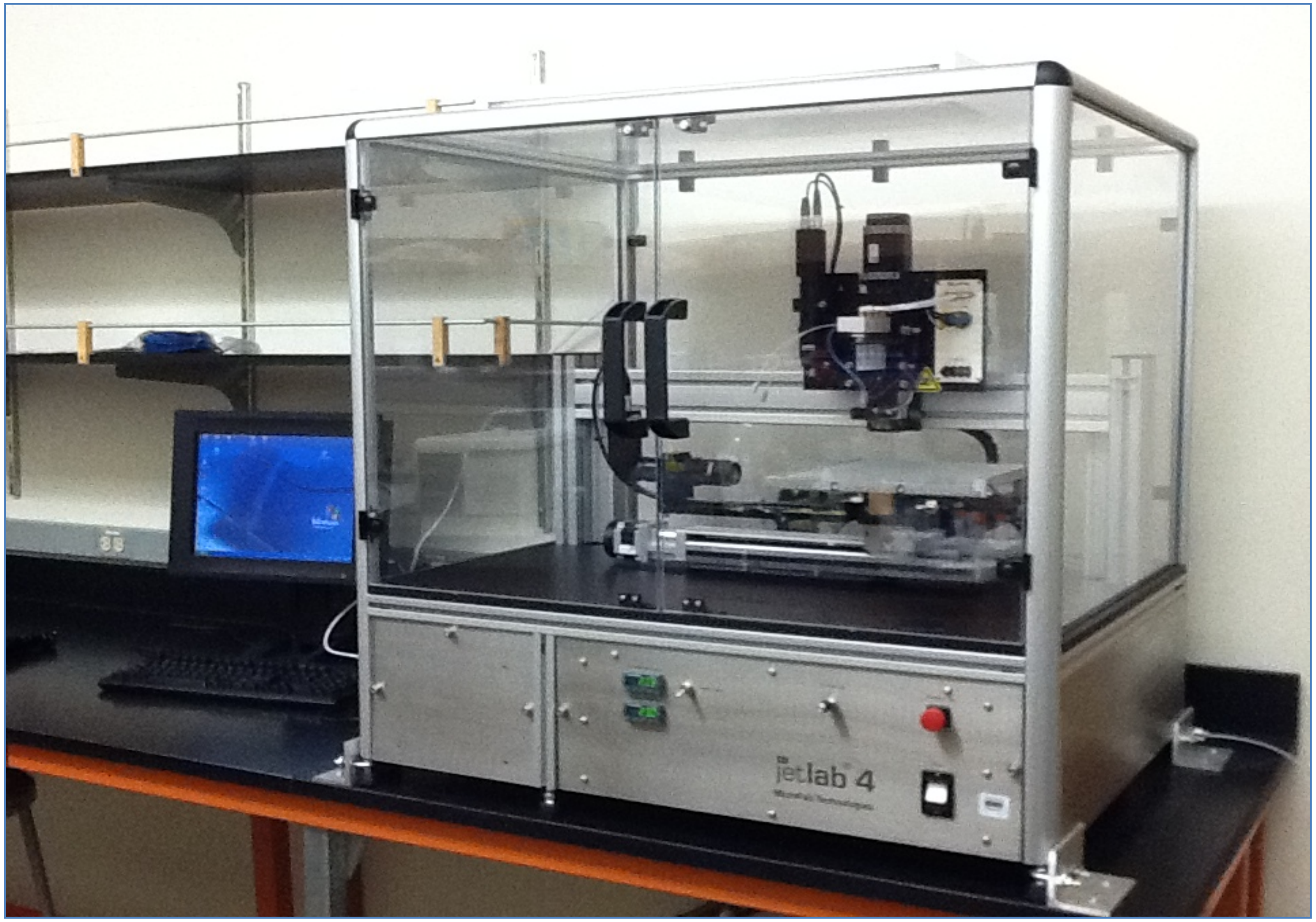
Characterization (e.g., XRD)

Characterization (e.g., XPS)



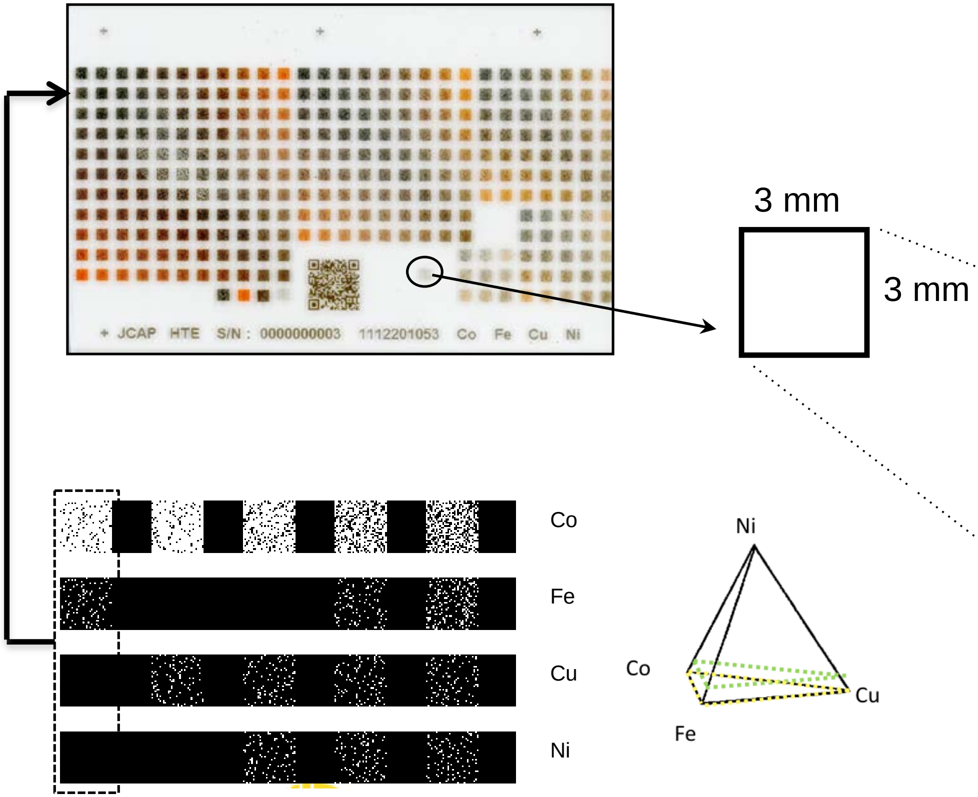
Development of World-Class Tools for High-Throughput Characterization and Analysis

MICROFAB printer

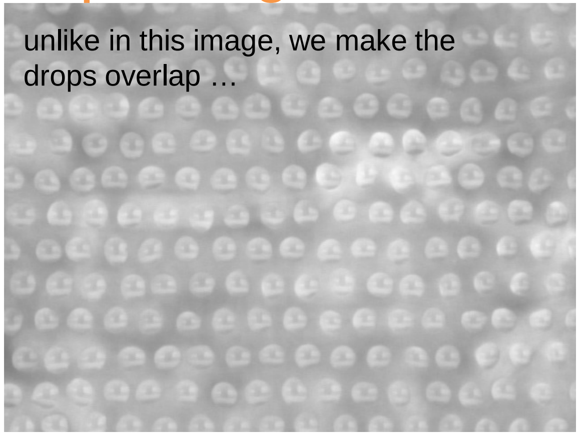


innovation no. 1 – printing methodology

- – get medium throughput
- – print 9 mm^2 spots
- – print constant volume spots



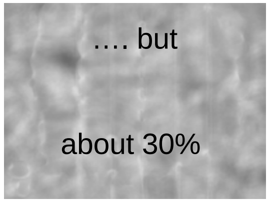
Bitmaps for 5 spots on the plate (automation routines by Marty Marcin)



unlike in this image, we make the drops overlap …

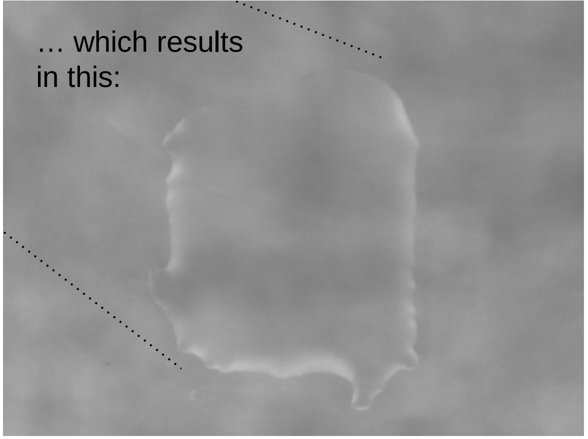
… not just a little overlap by

… or touching



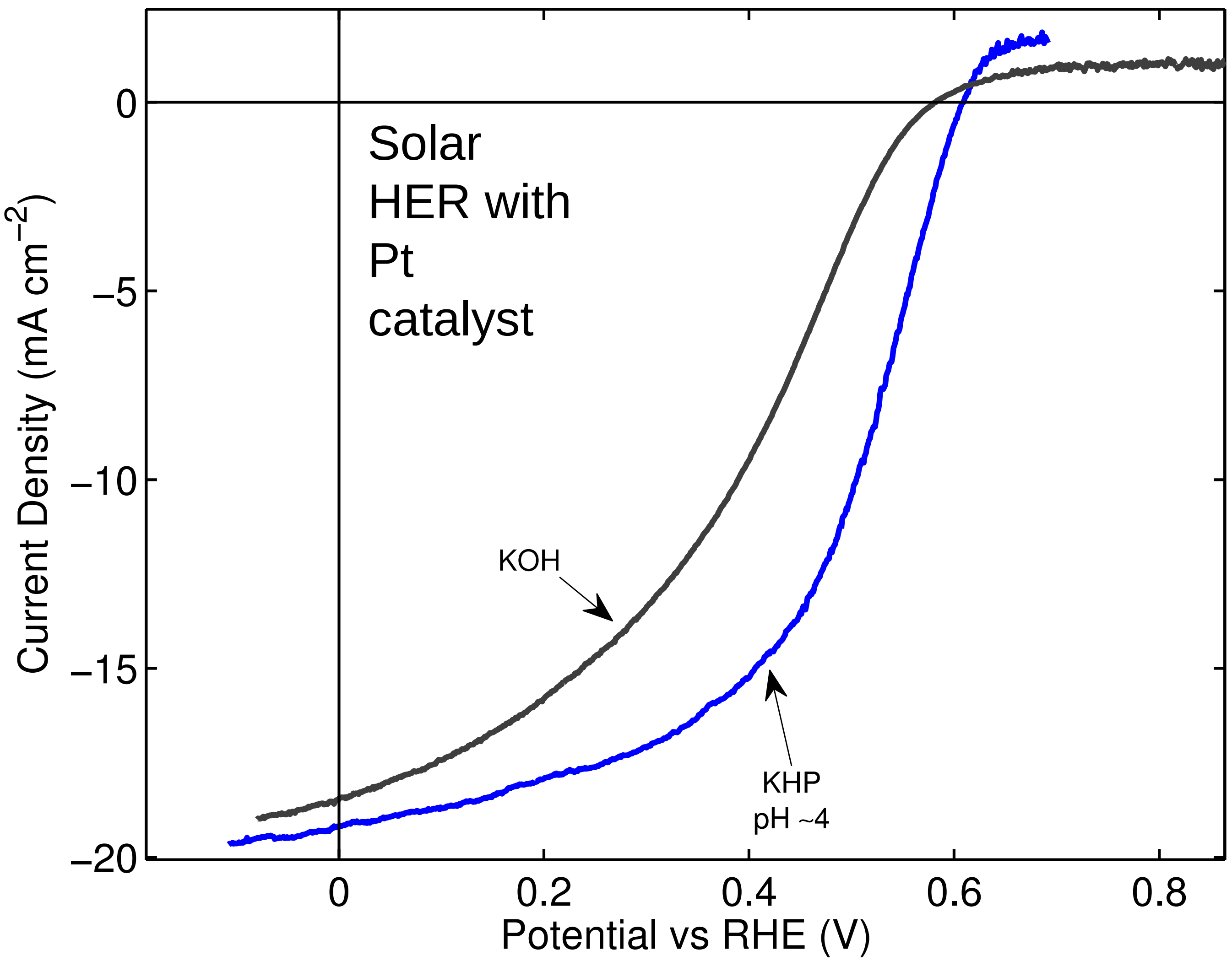
…. but

about 30%



… which results in this:

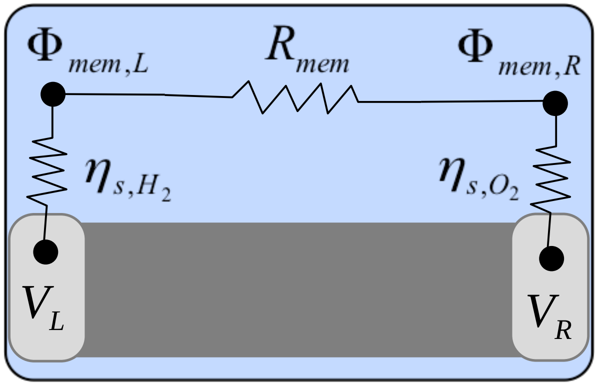
WSe_2

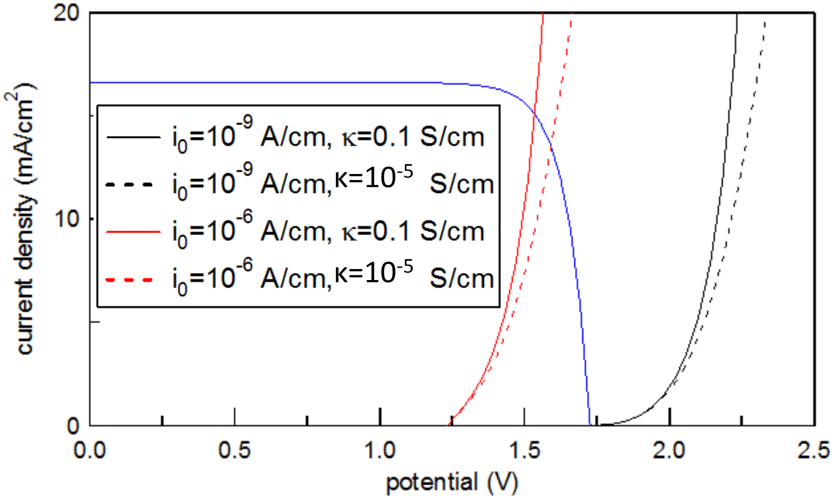


Generates H_2 at 3-5% conversion efficiency in acid or base!

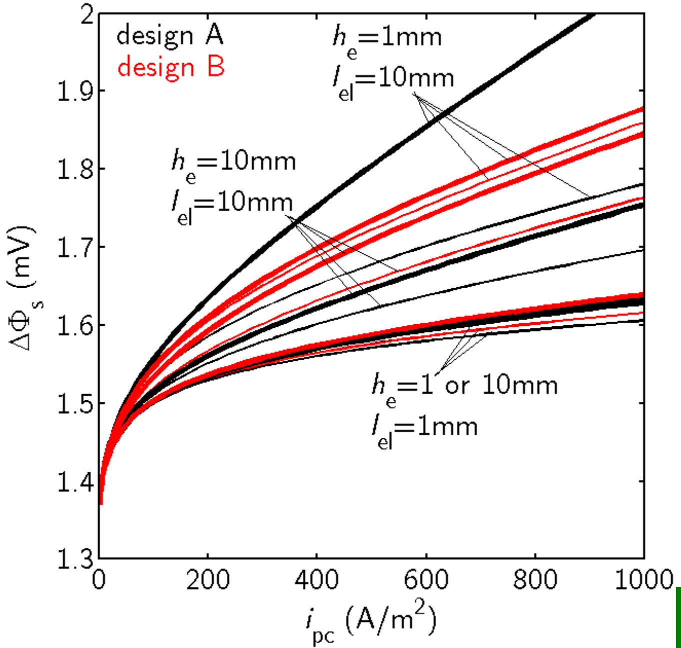
Identifying design requirements through device simulation

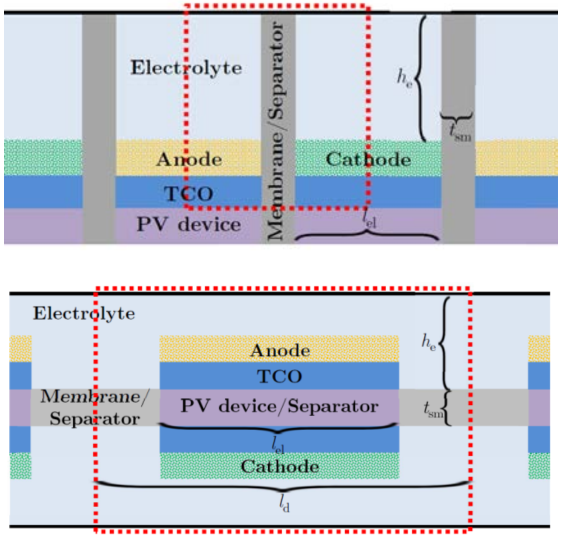
Sensitivity analysis determines acceptable range of membrane conductivity



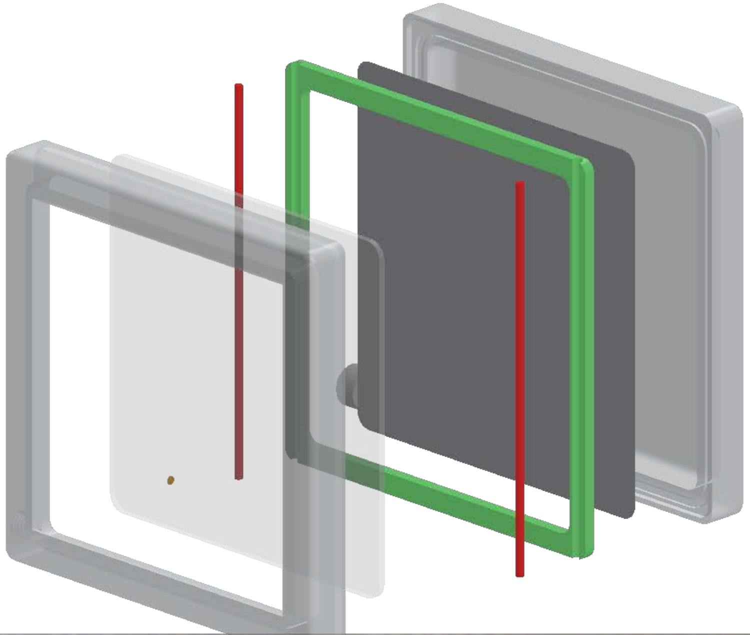


Comparison and optimization of proposed device architectures





Absorber-in-Membrane Design

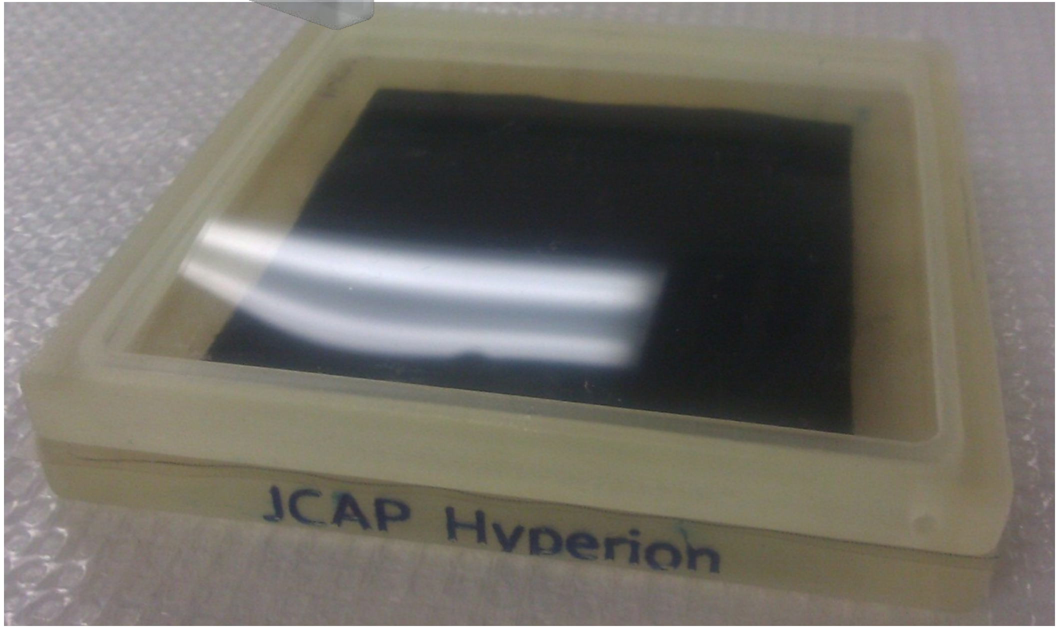


Membrane: H_2-reduced or metal doped $SrTiO_3$ dispersed in Nafion. $SrTiO_3$ on H_2 side metallized with thin Pt film.

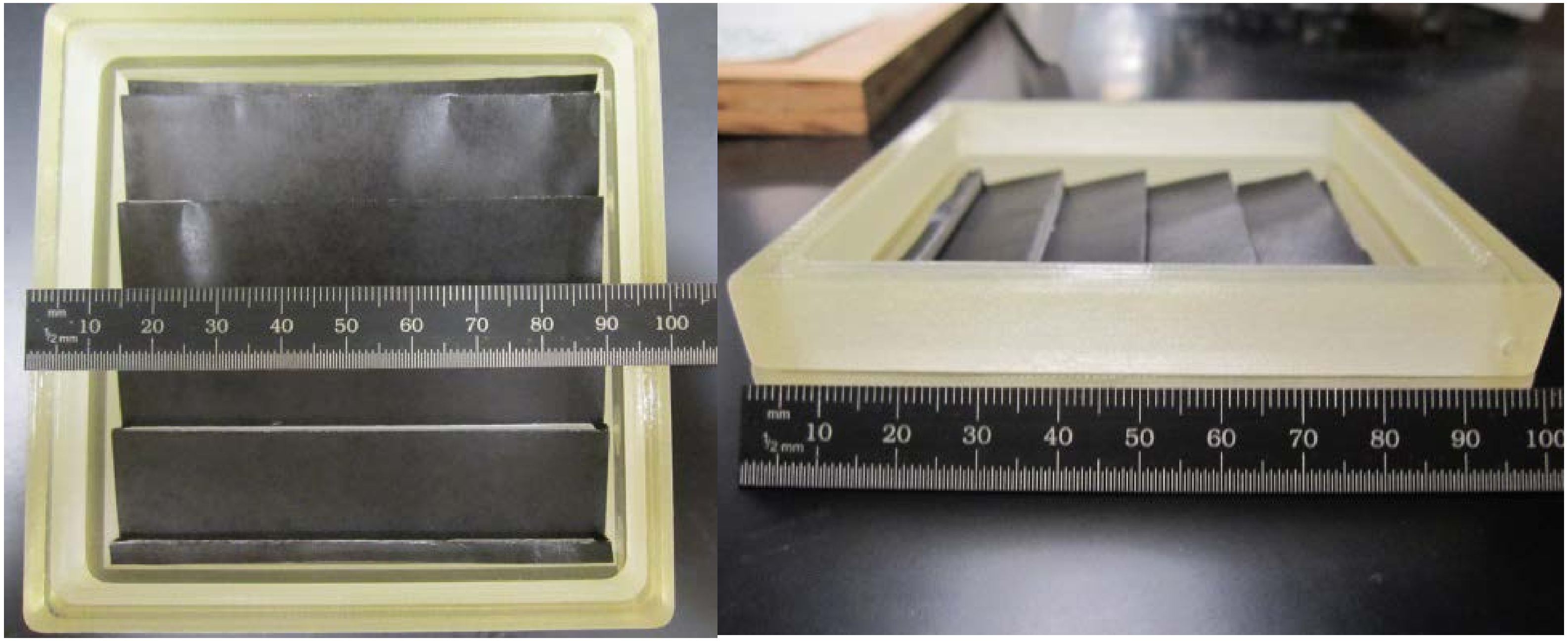
Based on (for example): “Photoelectrolysis of water in cells with $SrTiO_3$ anodes” J. G. Mavroides, J. A. Kafalas, and D. F. Kolesar, *Appl. Phys. Lett.*, **28**, 241 (1976).

Absorber-in-membrane chassis with commercial MEA (left).

JCAP-prepared H_2-reduced $SrTiO_3$-Nafion membrane (below).



- Top and side view of the shared square chassis of the absorber-in-membrane and the PV-based prototype (PV-based interior shown)
- Ruler indicates the prototypes housed in this chassis will be 10x10cm



Top (shown left) and side (shown right) view of the PV-based prototype measured with a ruler

Foresightful Energy Analysis

- **We are like tenant farmers chopping down the fence around our house for fuel when we should be using Nature's inexhaustible sources of energy — sun, wind and tide. ...**

- “Sunshine is spread out thin and so is electricity. Perhaps they are the same, but we will take that up later. Now the trick was, you see, to concentrate the juice and liberate it as you needed it. The old-fashioned way inaugurated by Jove, of letting it off in a clap of thunder, is dangerous, disconcerting and wasteful. It doesn’t fetch up anywhere. My task was to subdivide the current and use it in a great number of little lights, and to do this I had to store it. And we haven’t really found out how to store it yet and let it off real easy-like and cheap. Why, we have just begun to commence to get ready to find out about electricity. This scheme of combustion to get power makes me sick to think of–it is so wasteful. It is just the old, foolish Prometheus idea, and the father of Prometheus was a baboon.”

Foresightful Energy Analysis

- **I'd put my money on the sun and solar energy. What a source of power!**
- **I hope we don't have to wait until oil and coal run out before we tackle that..**

Foresightful Energy Analysis

- **I'd put my money on the sun and solar energy. What a source of power!**
- **I hope we don't have to wait until oil and coal run out before we tackle that..**

- **Thomas A. Edison, 1931**

Acknowledgments