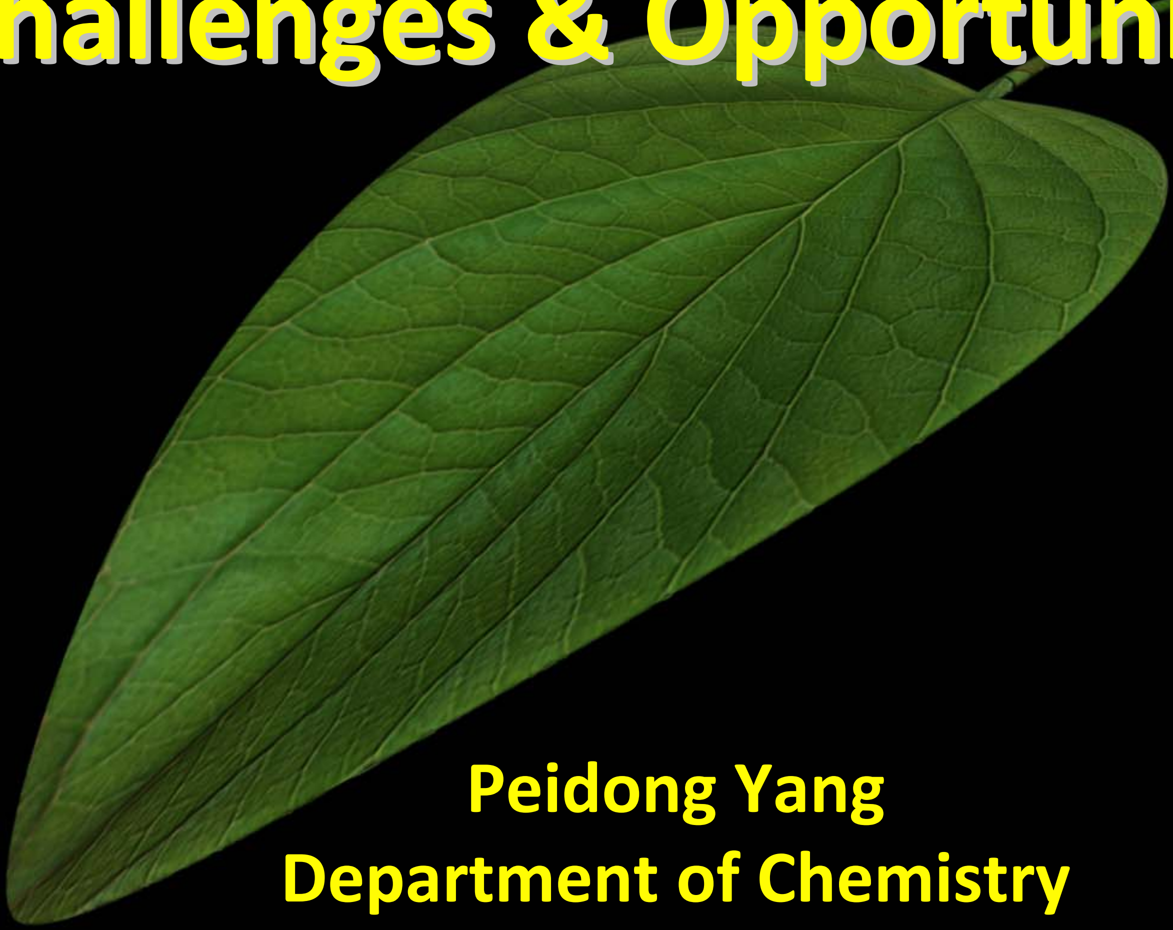
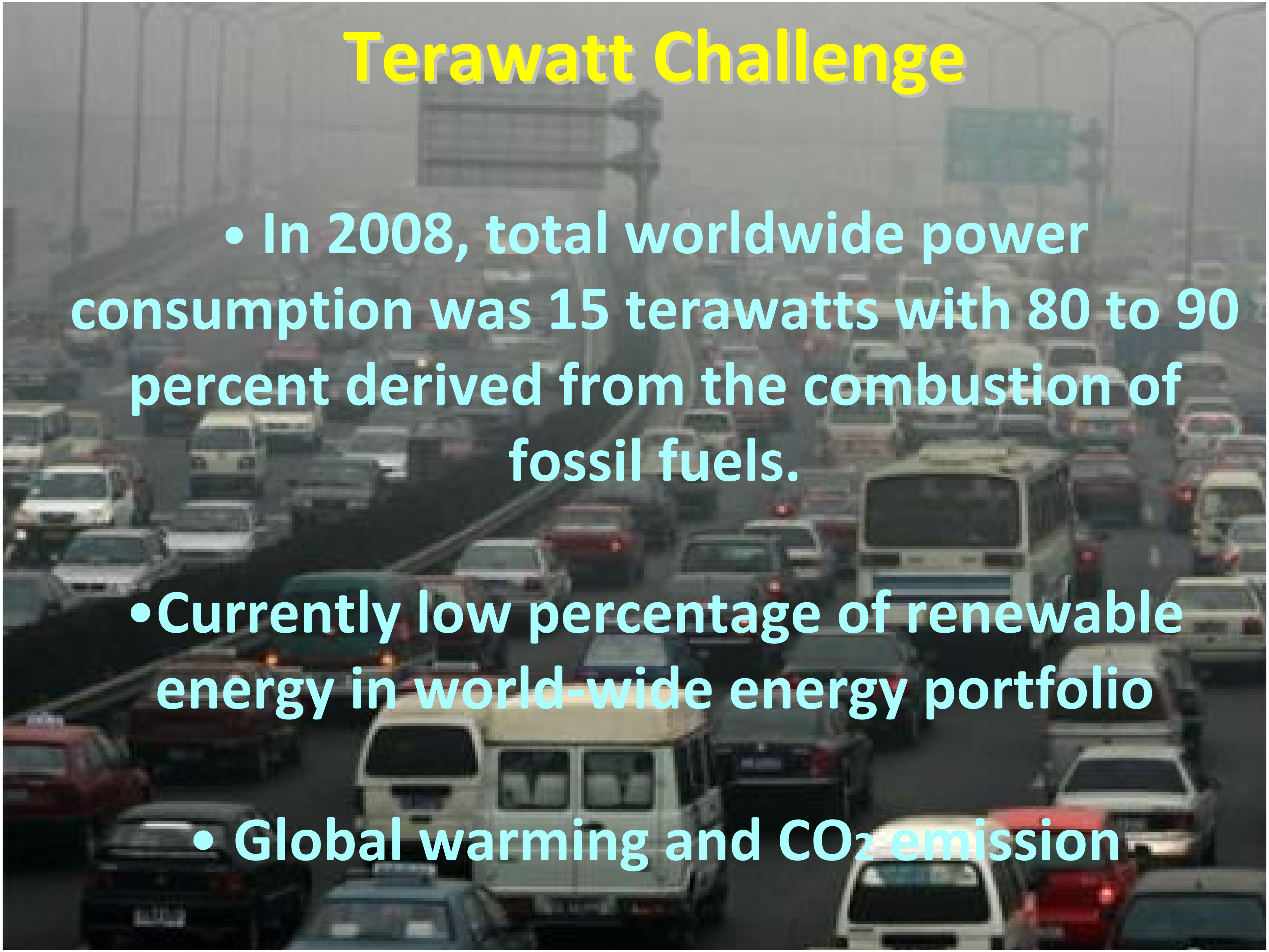
Artificial Photosynthesis

Challenges & Opportunities



Peidong Yang
Department of Chemistry
University of California, Berkeley

Terawatt Challenge



- In 2008, total worldwide power consumption was 15 terawatts with 80 to 90 percent derived from the combustion of fossil fuels.

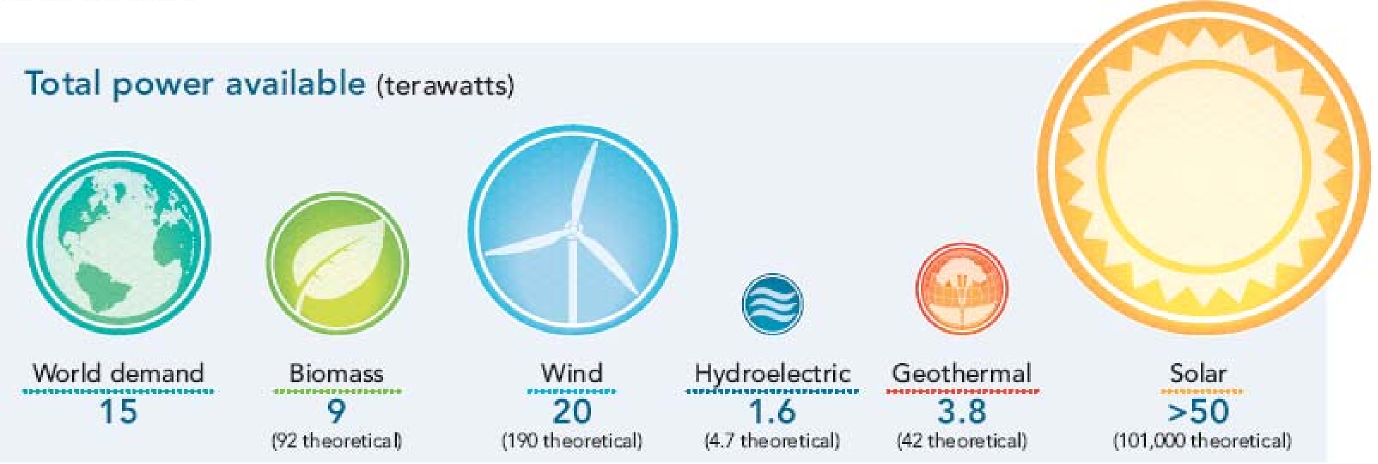
- Currently low percentage of renewable energy in world-wide energy portfolio

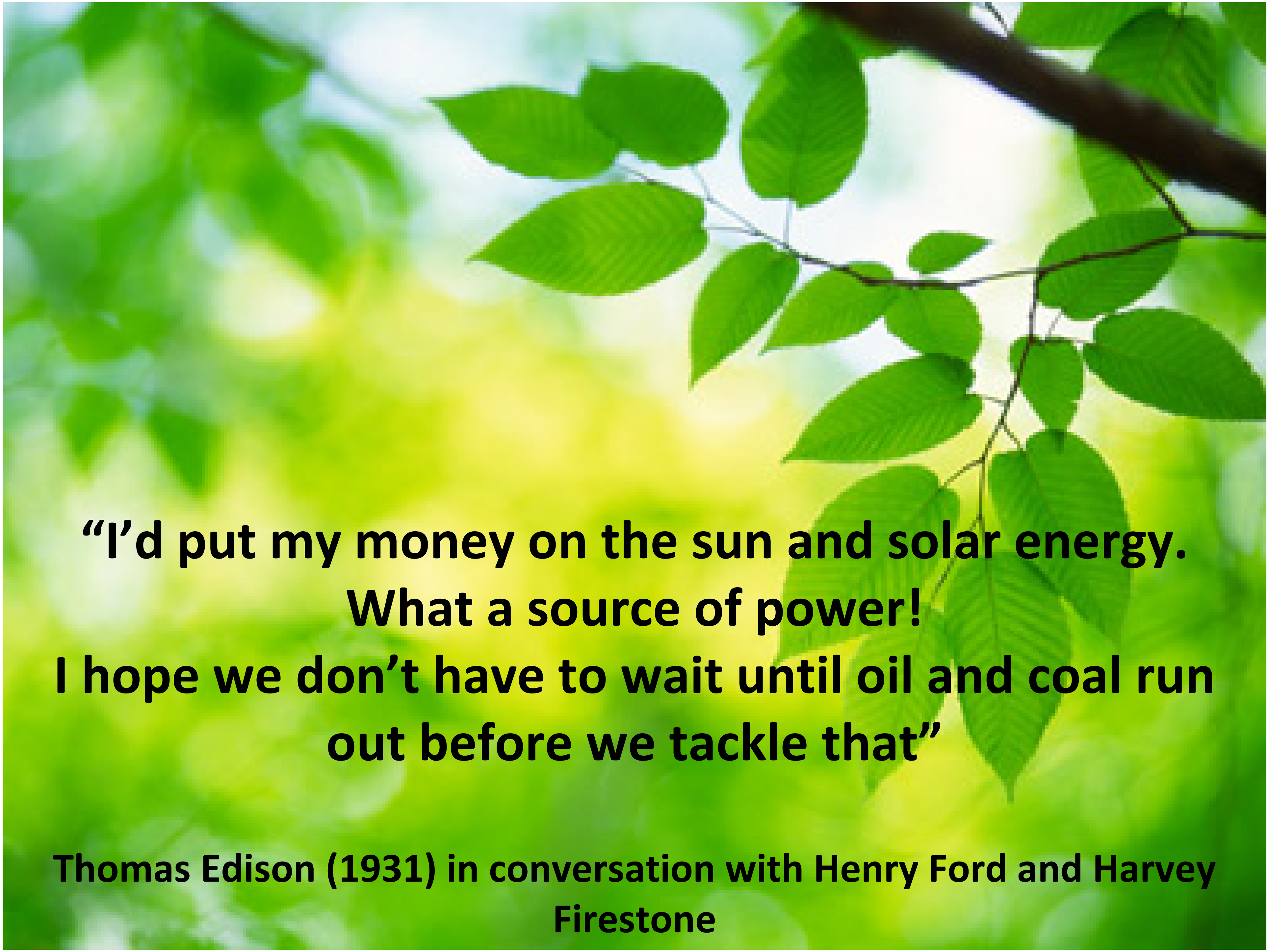
- Global warming and CO_2 emission

Terawatt Challenge: Solar

- Total Solar Energy: 165,000 TW of sunlight hit the earth.

- Renewable & Sustainable.

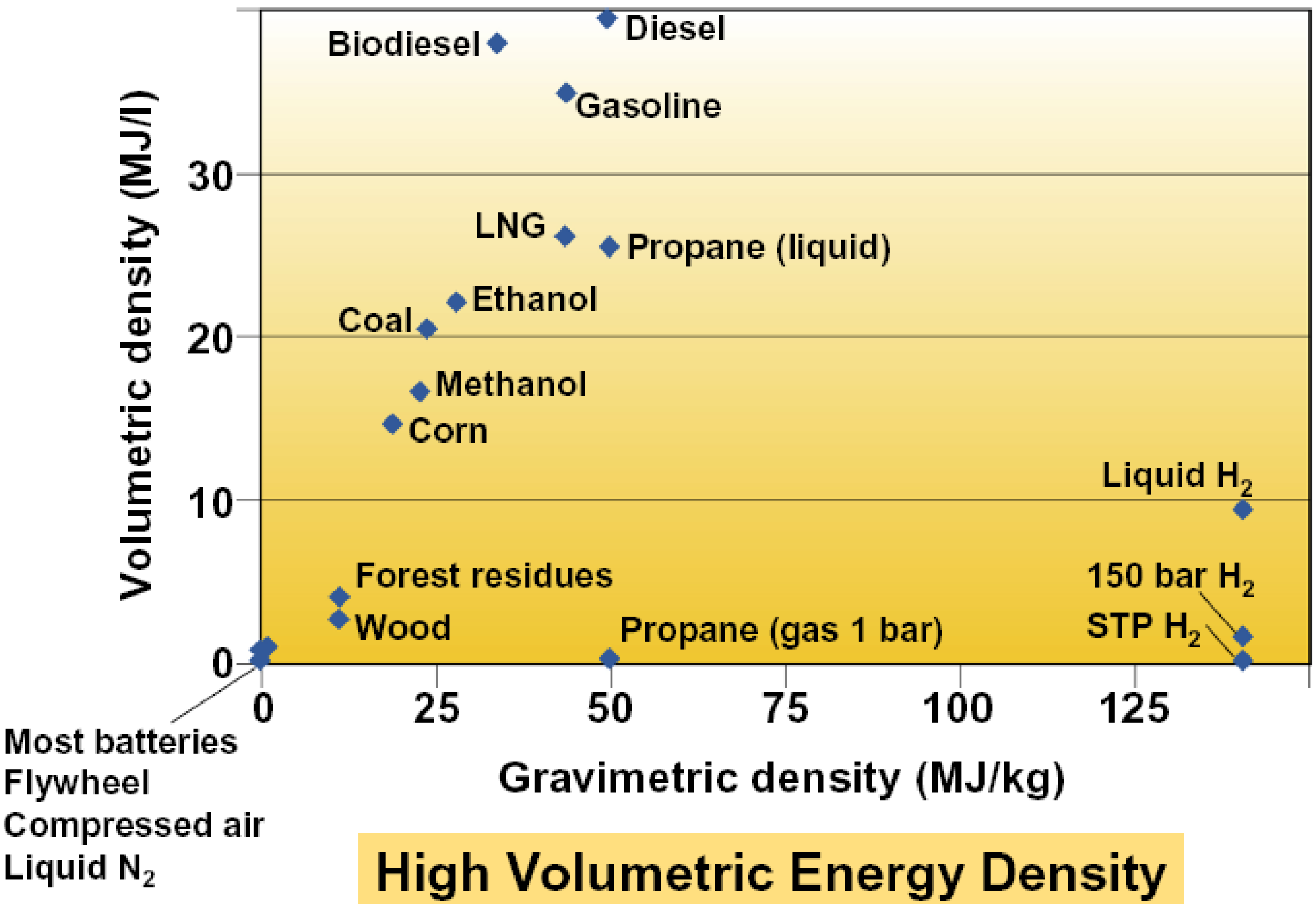




**“I’d put my money on the sun and solar energy.
What a source of power!
I hope we don’t have to wait until oil and coal run out before we tackle that”**

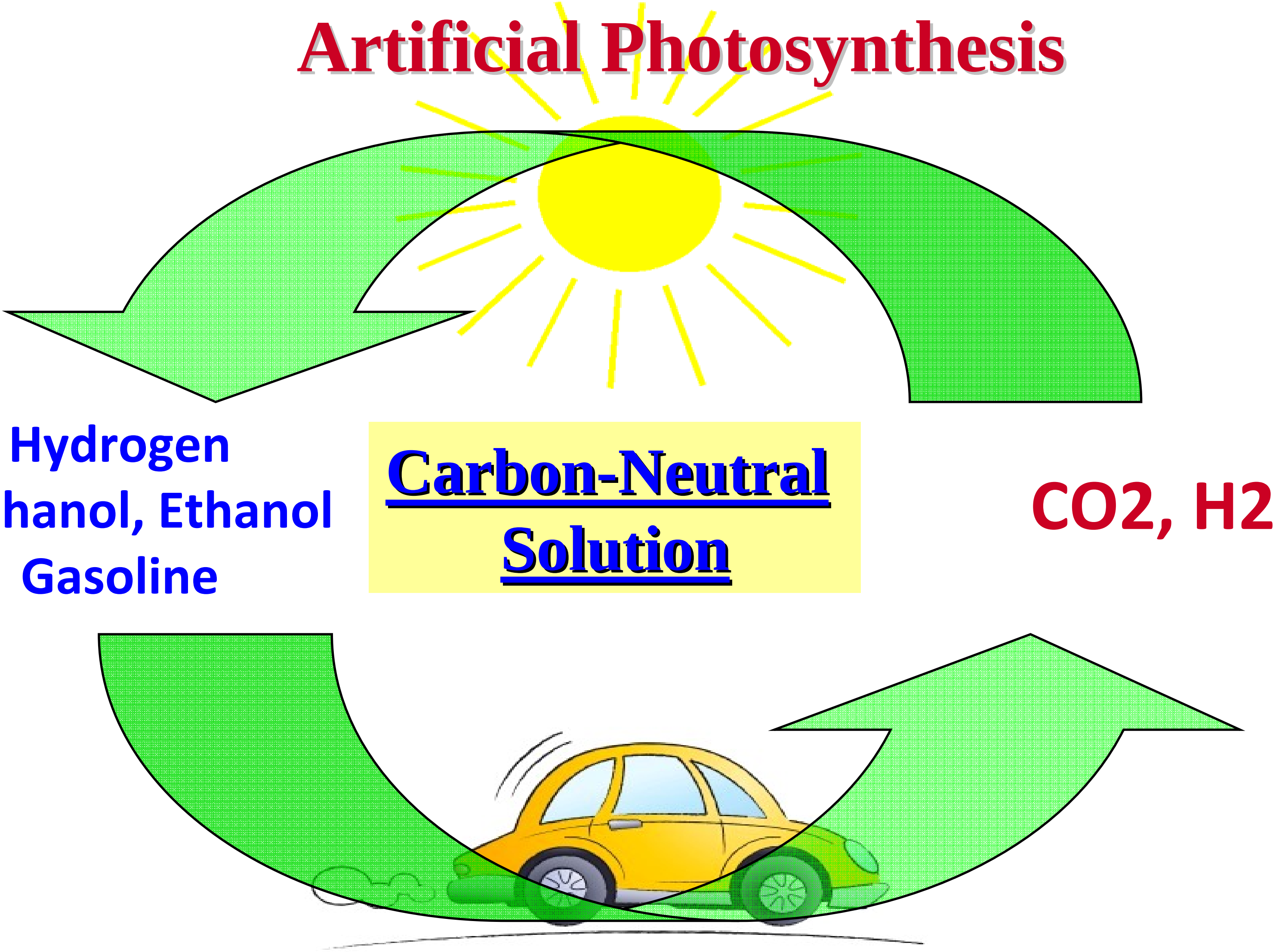
Thomas Edison (1931) in conversation with Henry Ford and Harvey Firestone

Energy Density & Storage



High Volumetric Energy Density

Harvesting Solar Energy: Solar to fuel



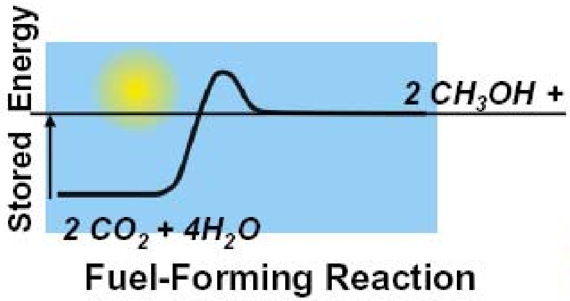
Artificial Photosynthesis

Hydrogen
Methanol, Ethanol
Gasoline

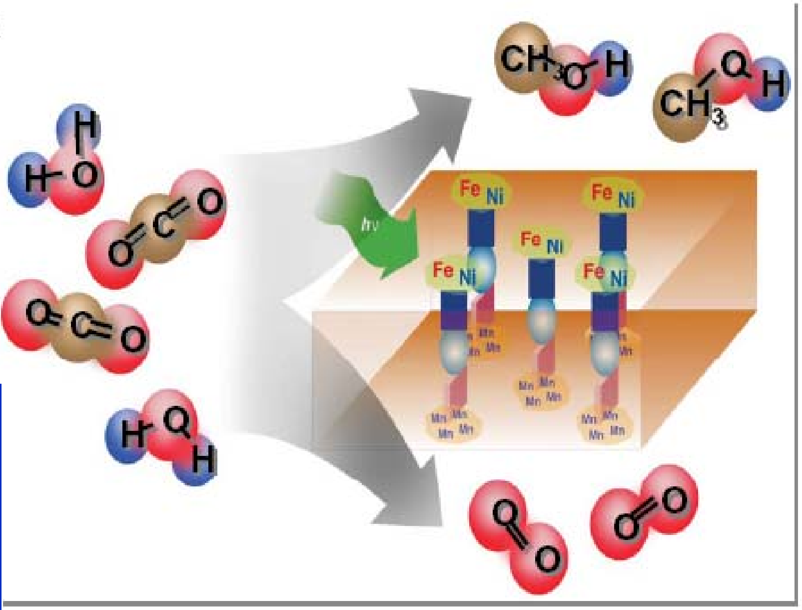
Carbon-Neutral Solution

CO2, H2O

Some Endergonic Fuel Generation Reactions



$2\ CO_2 + 4\ H_2O \longrightarrow 2\ CH_3OH + 3\ O_2$

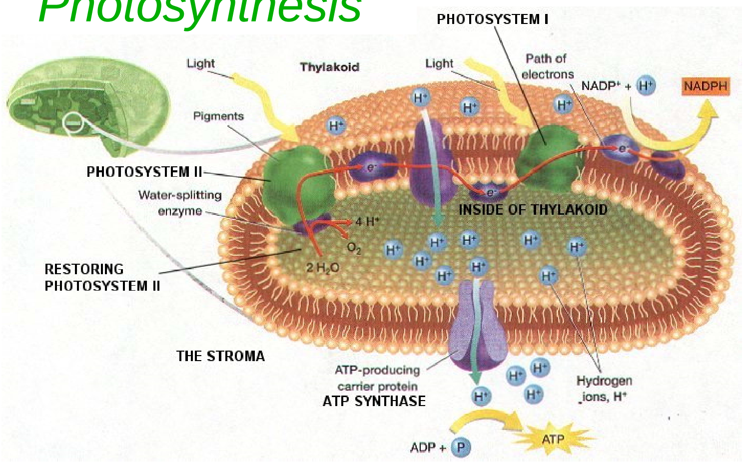


Reaction			ΔG° (kJ mol^{-1})	n	ΔE° (eV)	λmax (nm)
H_2O	→	$H_2 + ½\ O_2$	237	2	1.23	611
$CO_2 + H_2O$	→	$HCOOH + ½\ O_2$	270	2	1.40	564
$CO_2 + H_2O$	→	$HCHO + O_2$	519	4	1.34	579
$CO_2 + 2H_2O$	→	$CH_3OH + 3/2\ O_2$	702	6	1.21	617
$CO_2 + 2H_2O$	→	$CH_4 + 2O_2$	818	8	1.06	667
$CO_2 + H_2O$	→	$1/6\ C_6H_{12}O_6(s) + O_2$	480	4	1.24	608
$N_2 + 3H_2O$	→	$2NH_3 + 3/2\ O_2$	679	6	1.17	629

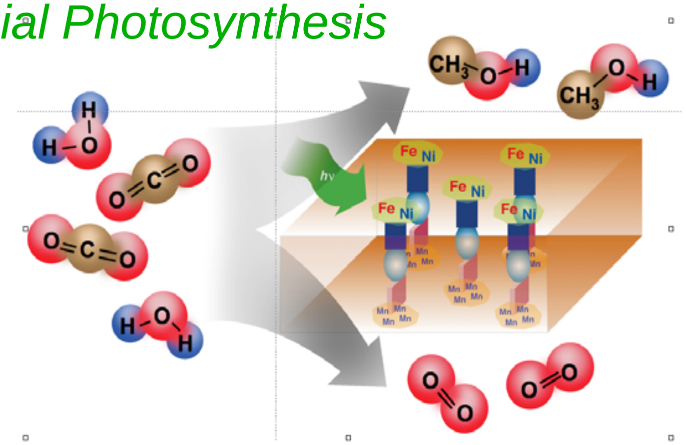
DOE Energy Innovation Hub: Solar to Fuels

- **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 efficiently than (current) crops

Photosynthesis



Artificial Photosynthesis



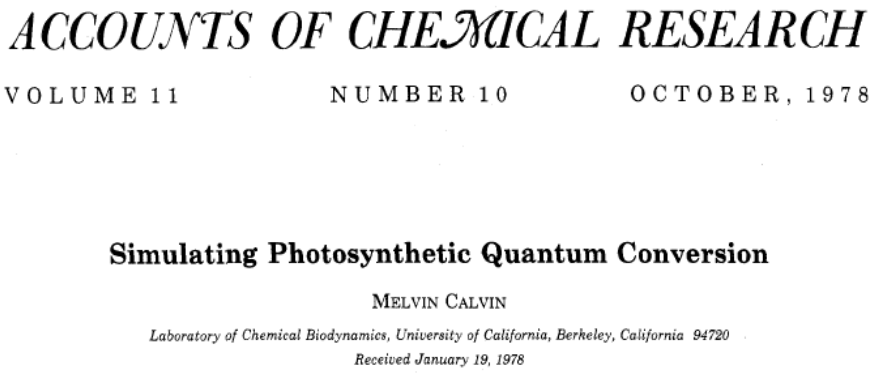
JCAP
JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

DOE $120 Million
Energy Hub
PI: Nate Lewis (Caltech)
Peidong Yang (LBNL)

"…they're developing a way to turn sunlight and water into fuel for our cars. …"
President Obama's State of the Union remarks
Jan. 2011

A Nobel Challenge

- Melvin Calvin：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.



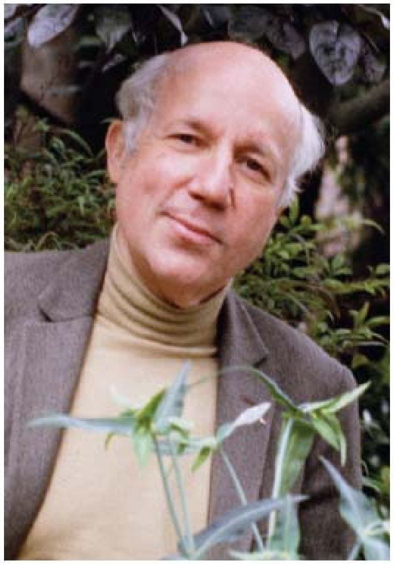
ACCOUNTS OF CHEMICAL RESEARCH

VOLUME 11 NUMBER 10 OCTOBER, 1978

Simulating Photosynthetic Quantum Conversion

MELVIN CALVIN

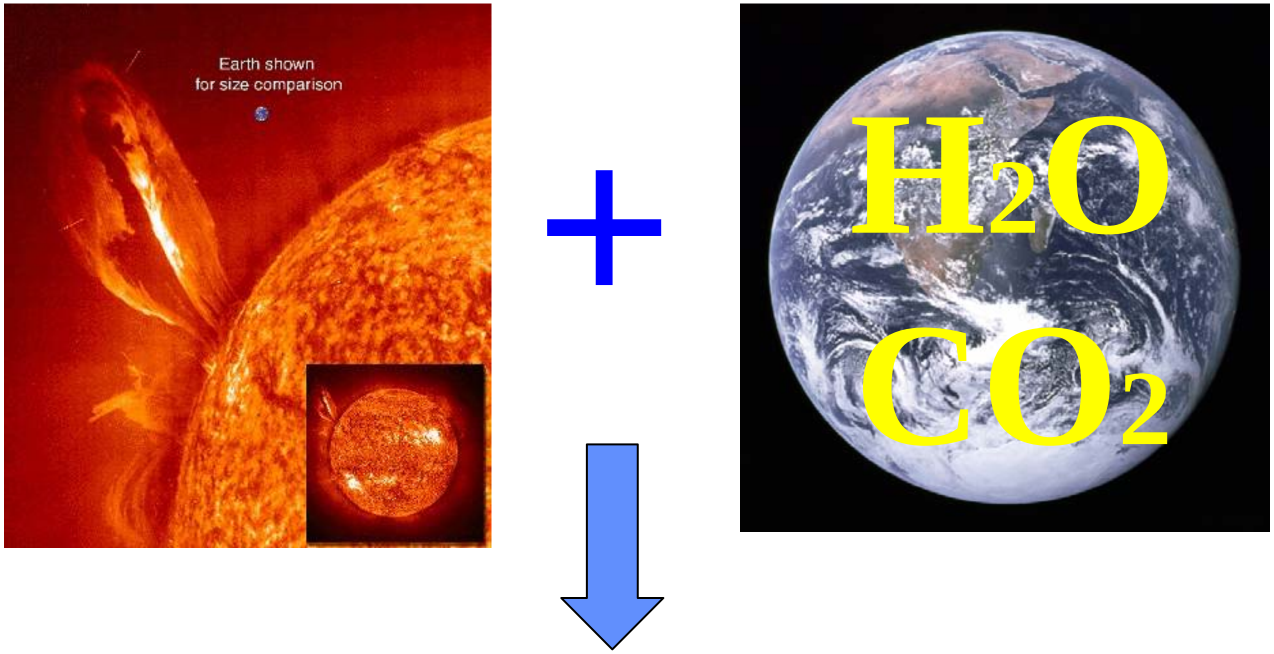
Laboratory of Chemical Biodynamics, University of California, Berkeley, California 94720
Received January 19, 1978



1961, Nobel prize in chemistry

So, why is this so difficult?

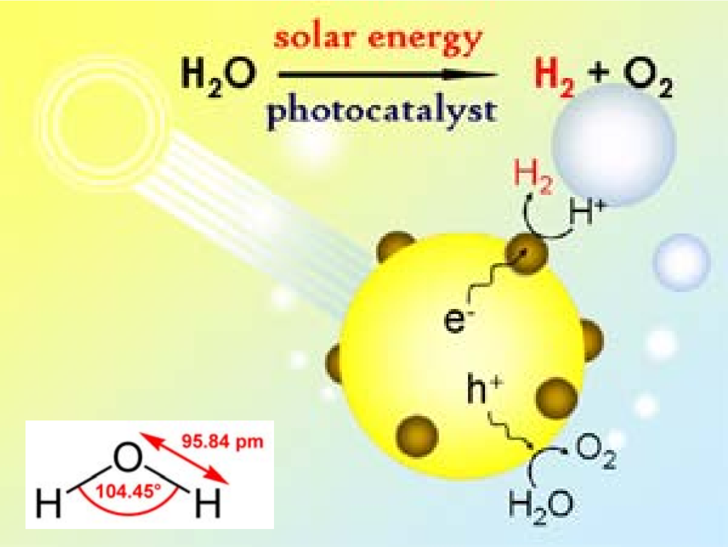
Sustainable and Renewable: Solar Fuel

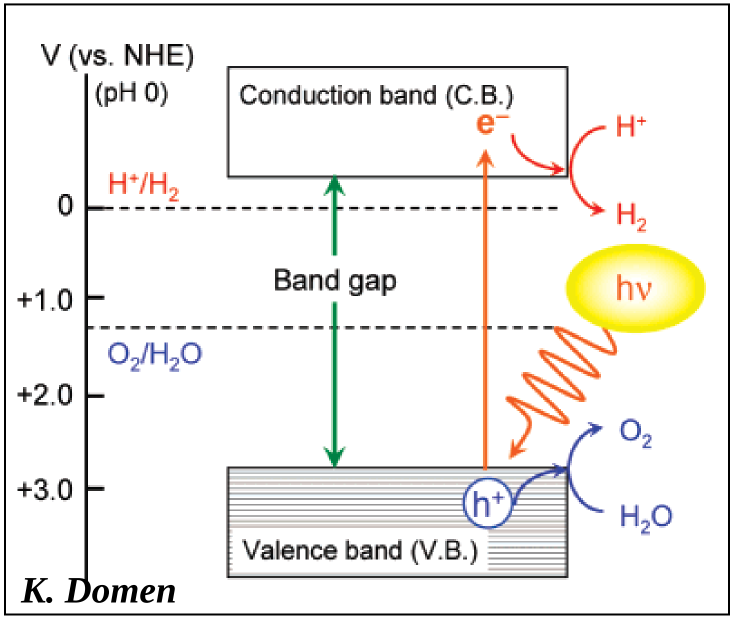


Hydrogen; Methanol…

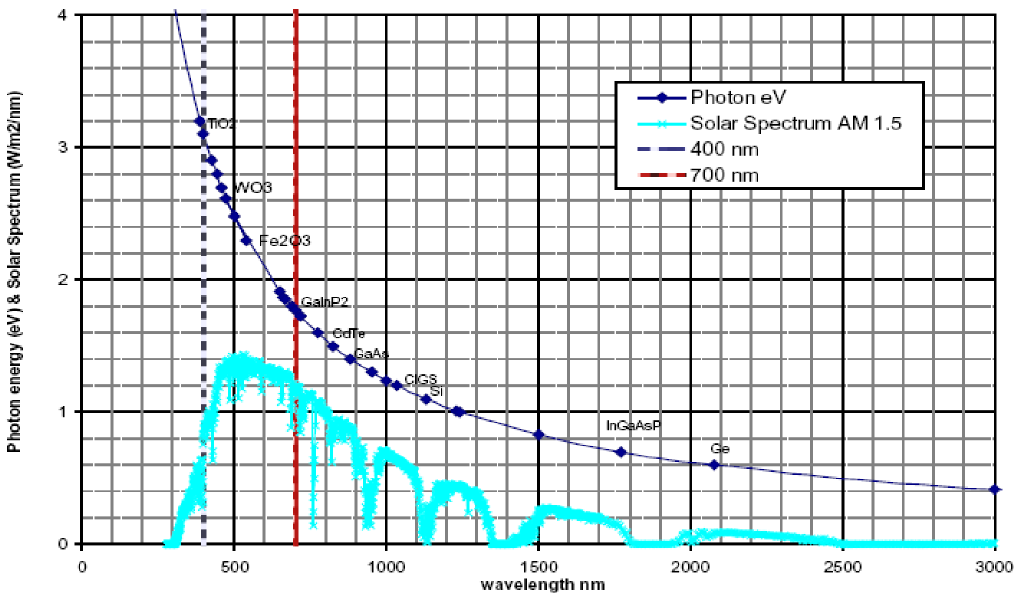
*Require the invention of new photoactive materials that accomplish the combined tasks of **light harvesting, charge separation, and compartmentalized chemical transformations**.*

Grand challenges for solar water splitting





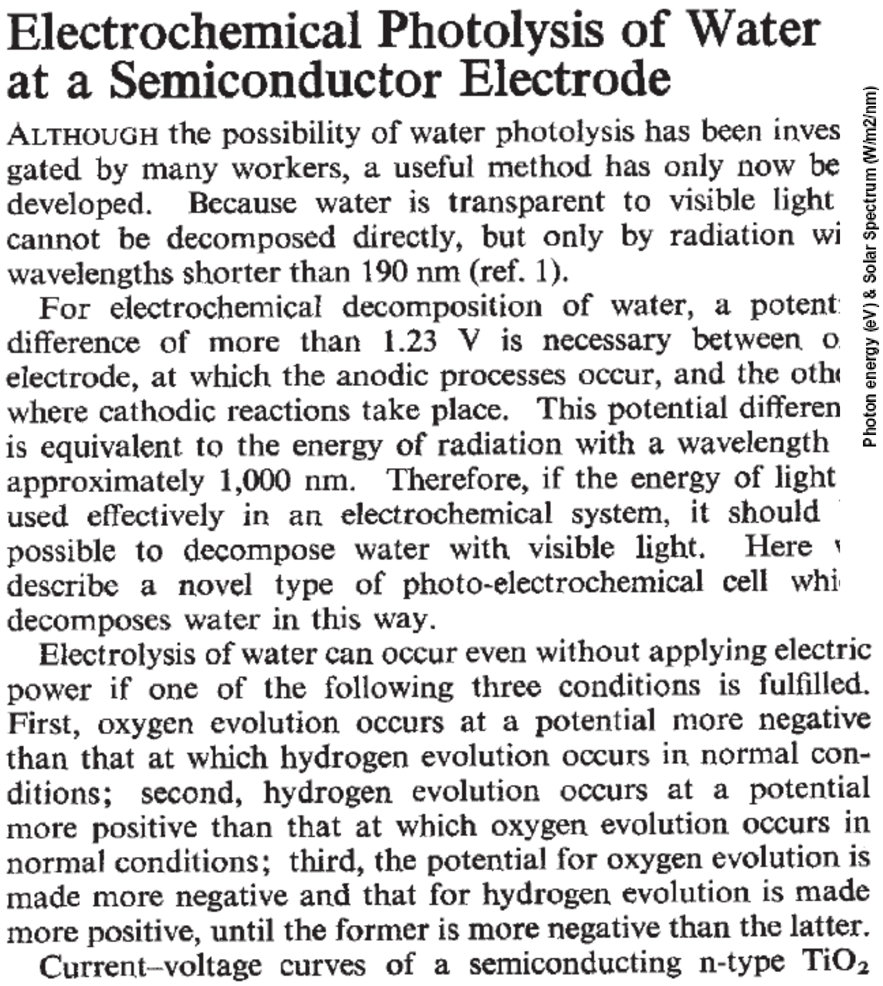
K. Domen



Required Photocatalyst Parameters:

1. Bandgap in the visible
2. Correct CBM and VBM
3. Fast charge transfer across interface
4. Resistance to photocorrosion
5. Low-cost, abundant elements

First work on TiO2 water splitting



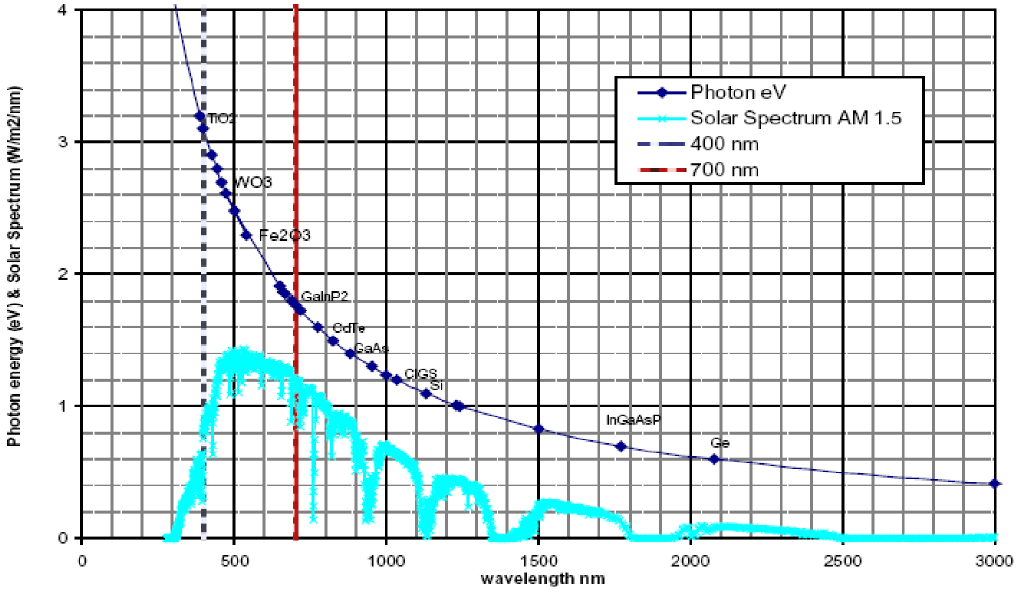
Electrochemical Photolysis of Water at a Semiconductor Electrode

ALTHOUGH the possibility of water photolysis has been inves gated by many workers, a useful method has only now be developed. Because water is transparent to visible light cannot be decomposed directly, but only by radiation wi wavelengths shorter than 190 nm (ref. 1).

For electrochemical decomposition of water, a potent difference of more than 1.23 V is necessary between o electrode, at which the anodic processes occur, and the oth where cathodic reactions take place. This potential differen is equivalent to the energy of radiation with a wavelength approximately 1,000 nm. Therefore, if the energy of light used effectively in an electrochemical system, it should possible to decompose water with visible light. Here describe a novel type of photo-electrochemical cell whi decomposes water in this way.

Electrolysis of water can occur even without applying electric power if one of the following three conditions is fulfilled. First, oxygen evolution occurs at a potential more negative than that at which hydrogen evolution occurs in normal conditions; second, hydrogen evolution occurs at a potential more positive than that at which oxygen evolution occurs in normal conditions; third, the potential for oxygen evolution is made more negative and that for hydrogen evolution is made more positive, until the former is more negative than the latter.

Current–voltage curves of a semiconducting n-type TiO_2



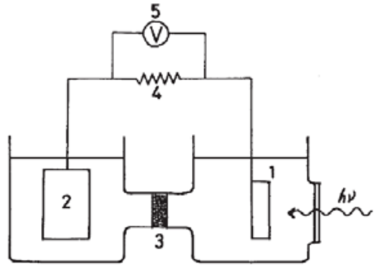


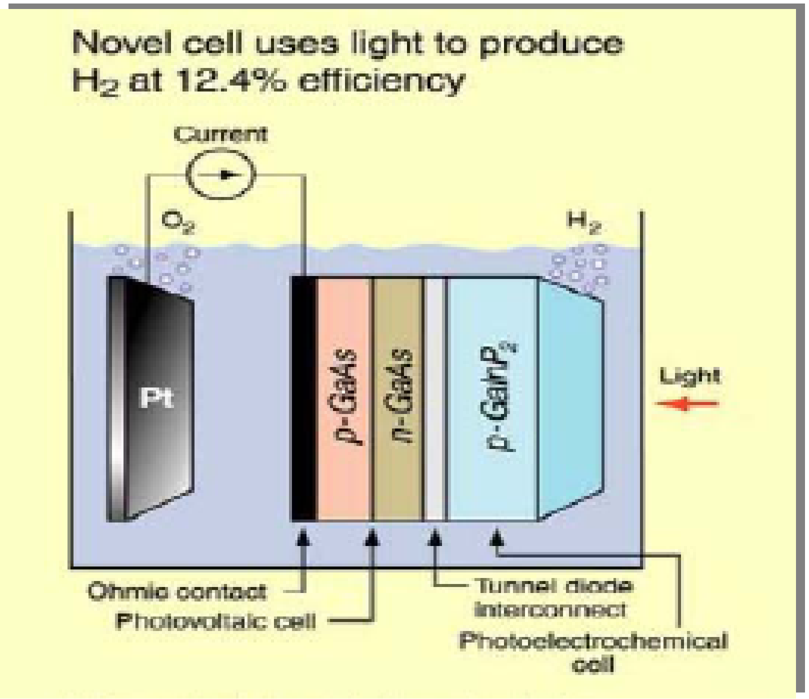
Fig. 2 Electrochemical cell in which the TiO_2 electrode is connected with a platinum electrode (see text). The surface area of the platinum black electrode used was approximately 30 cm^2.

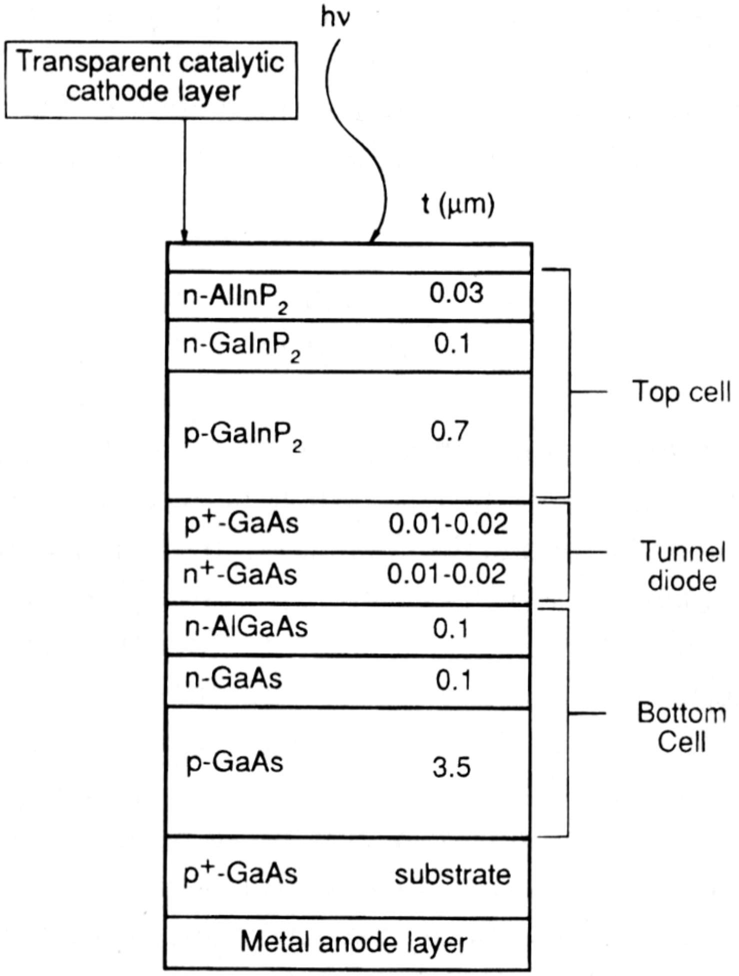
A. Fujishiam, K. Honda, Nature, 1972, 238, 38

Using multi-junctions

Photo-electrochemical Device

O. Khaselev, J. Turner, *Science* 280, 425 (1998)

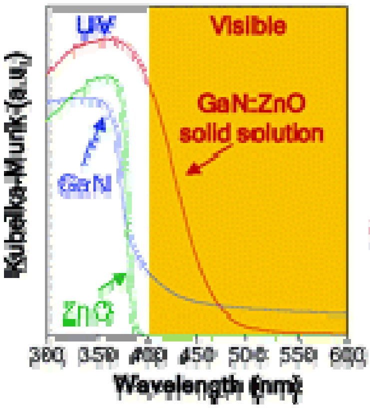




efficient but expensive

> 11% efficient water splitting

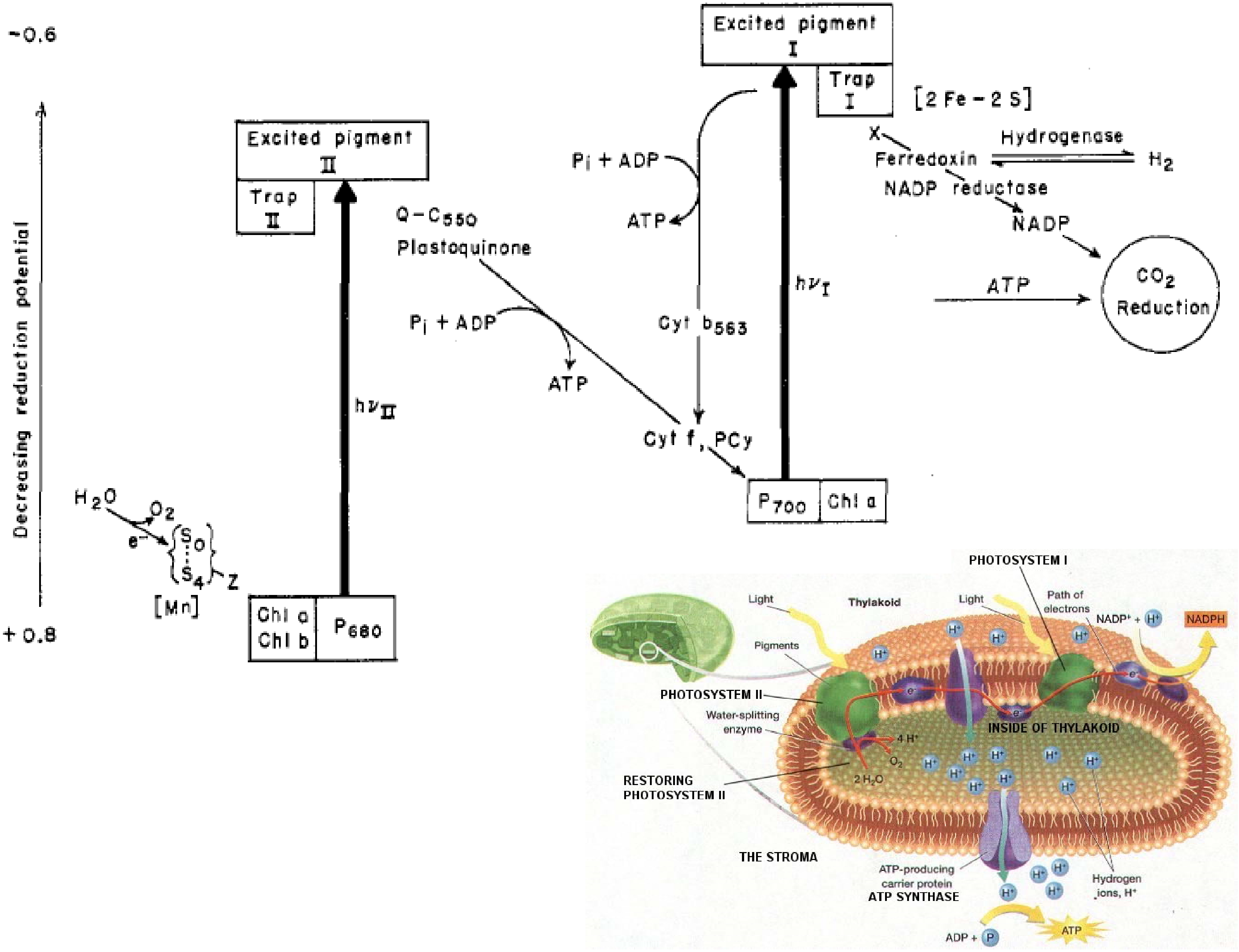
Single Bandgap semiconductor for water splitting



Q.Y 2.5% at 430 nm

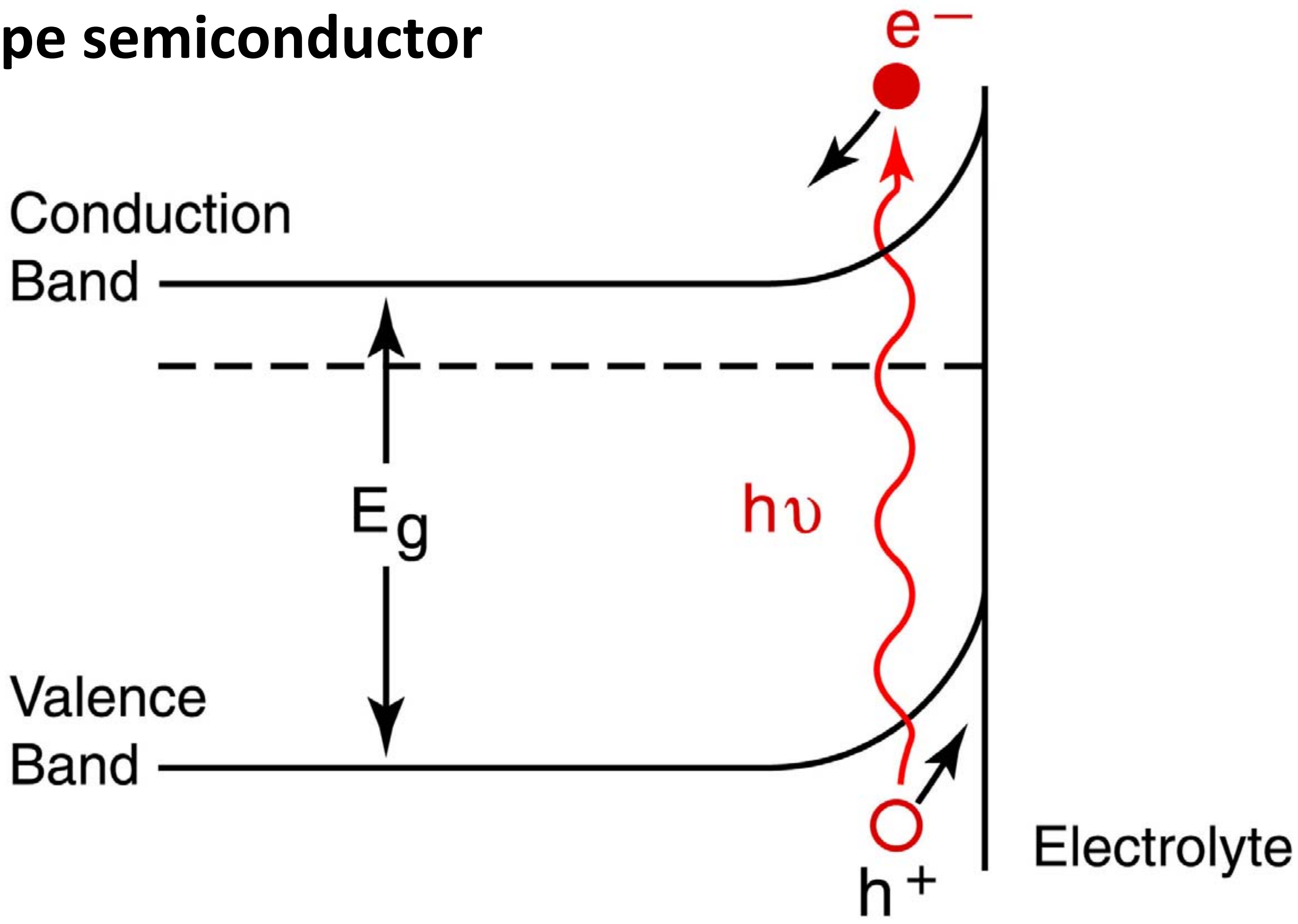
GaNZnO Alloy

Single bandgap semiconductor particles for overall water splitting with visible light
K. Domen, Nature ***440****, 295 (2006); Angew. Chem. Int. Ed.* ***45****, 7806 (2006)*

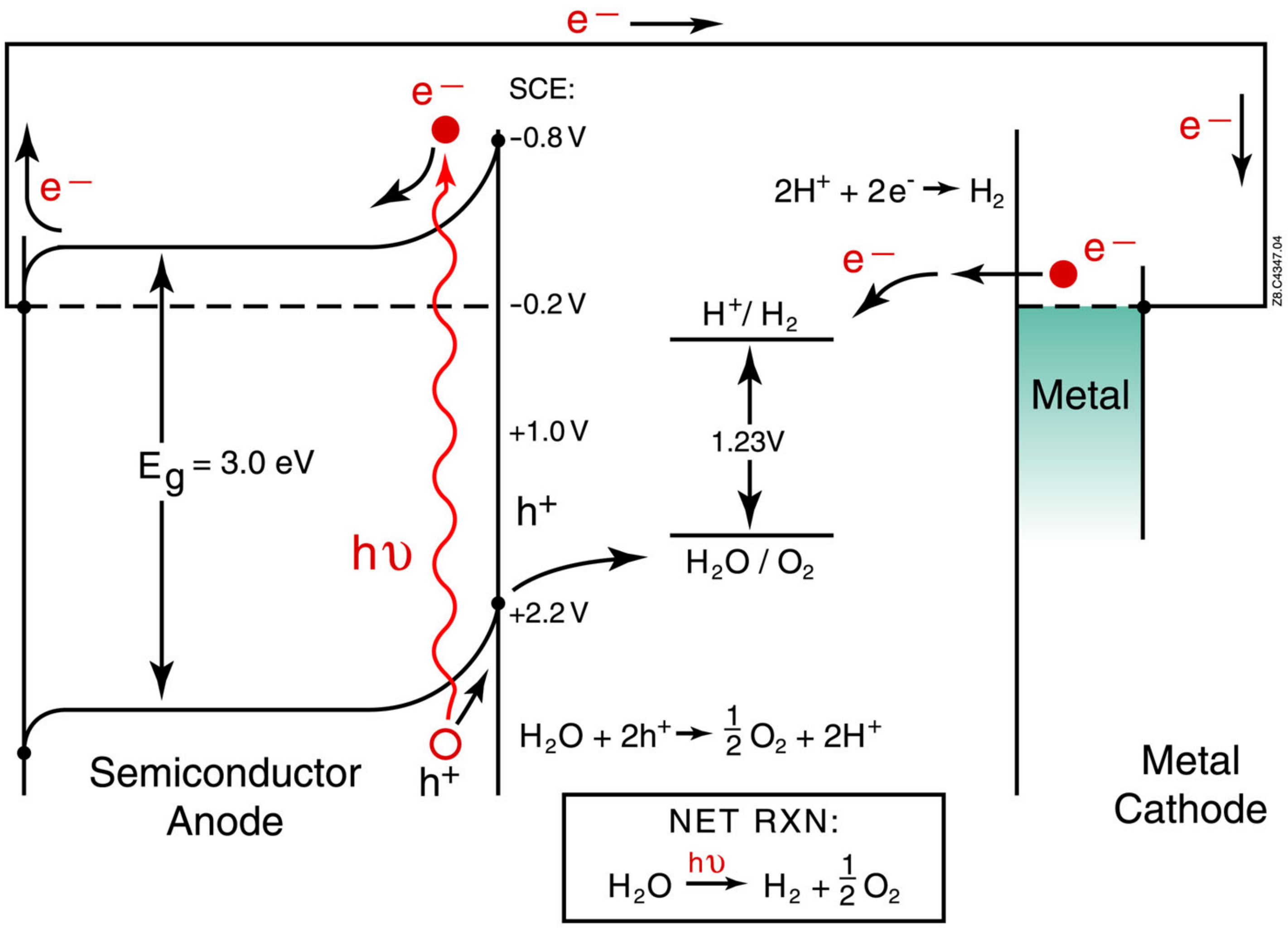

-0.6
+0.8
Decreasing reduction potential
Excited pigment II
Trap II
Chl a
Chl b
P680
hν II
H2O
O2
e⁻
S0
S4
Z
[Mn]
Q-C550
Plastoquinone
Pi + ADP
ATP
Cyt f, PCy
Cyt b563
Pi + ADP
ATP
Excited pigment I
Trap I
hν I
P700
Chl a
[2 Fe - 2 S]
X
Ferredoxin
Hydrogenase
H2
NADP reductase
NADP
ATP
CO2 Reduction
PHOTOSYSTEM I
Light
Thylakoid
Light
Path of electrons
NADP⁺ + H⁺
NADPH
Pigments
H⁺
PHOTOSYSTEM II
e⁻
Water-splitting enzyme
4 H⁺
O2
2 H2O
INSIDE OF THYLAKOID
RESTORING PHOTOSYSTEM II
THE STROMA
ATP-producing carrier protein
ATP SYNTHASE
Hydrogen ions, H⁺
ADP + P
ATP

Semiconductor Electrolyte Interface

n-type semiconductor



Solar Water Splitting with single bandgap light absorber



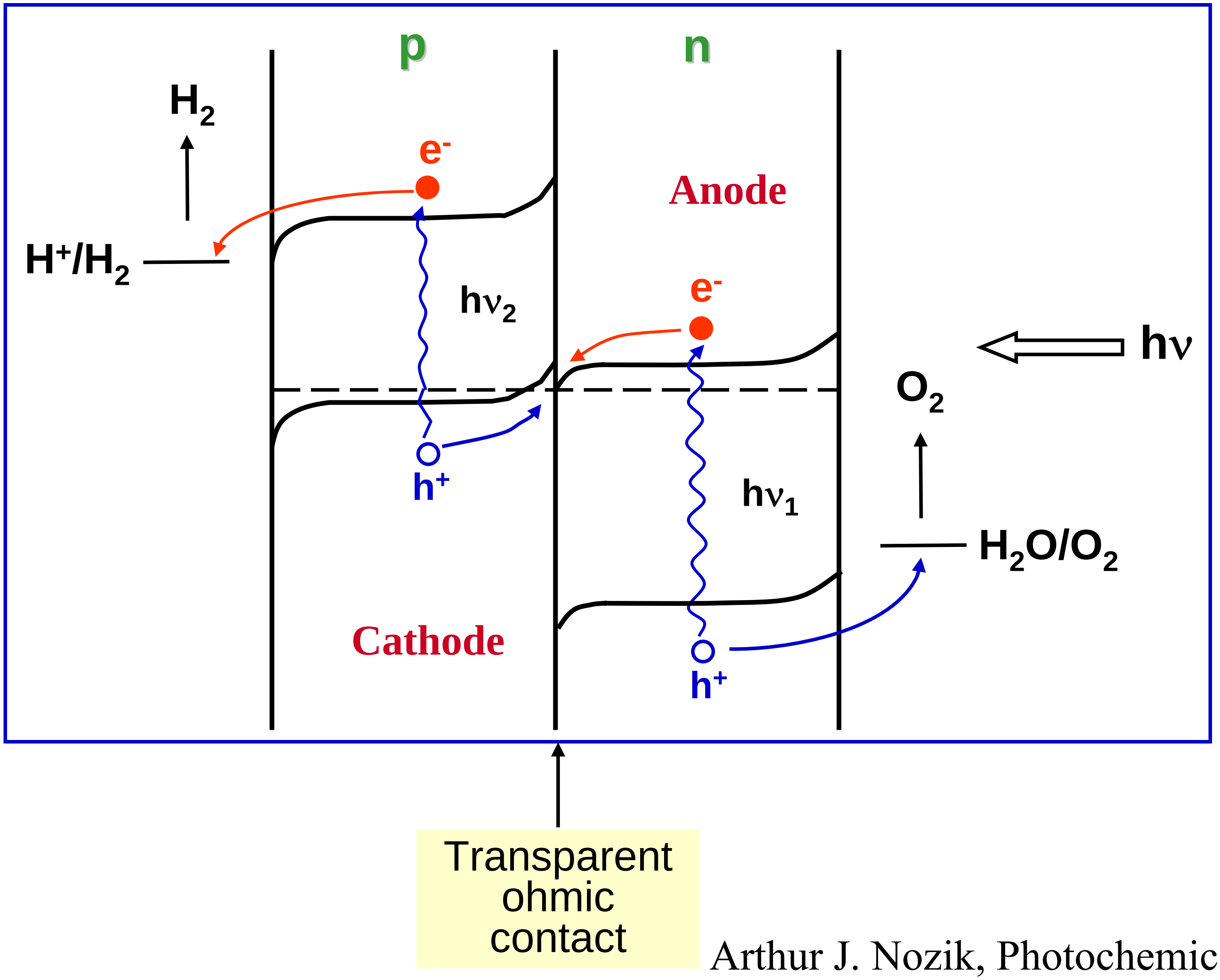
$2H^+ + 2e^- \rightarrow H_2$

$H_2O + 2h^+ \rightarrow \frac{1}{2}O_2 + 2H^+$

NET RXN:

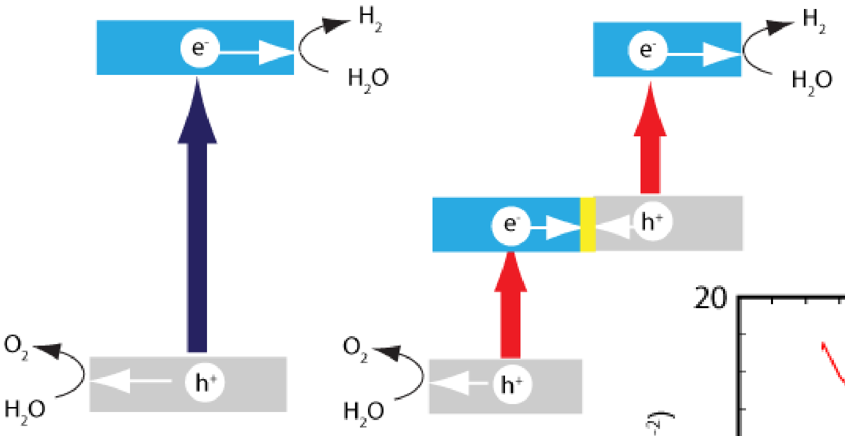
$H_2O \xrightarrow{h\upsilon} H_2 + \frac{1}{2}O_2$

Photoelectrochemical diodes: Dual Bandgap Concept

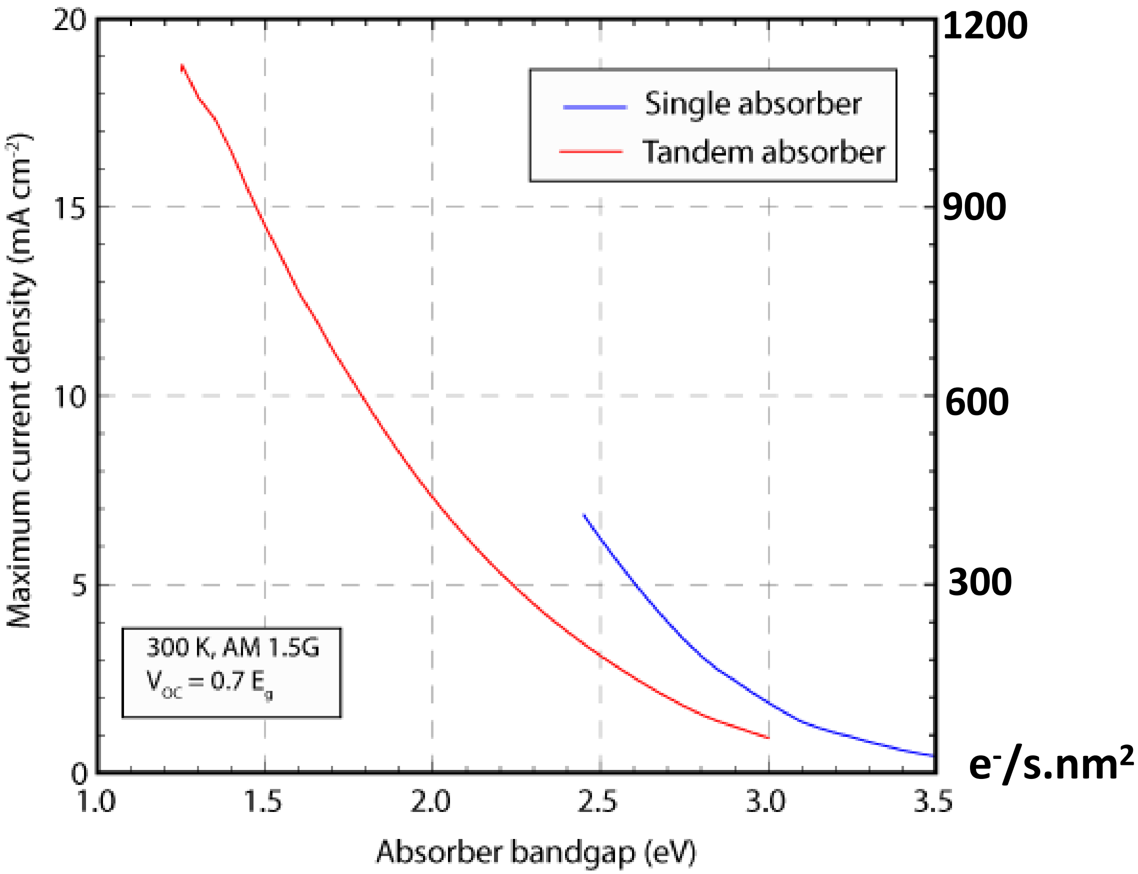


Arthur J. Nozik, Photochemical Diodes, Applied Physics Letters 30, 567-569 (1977).

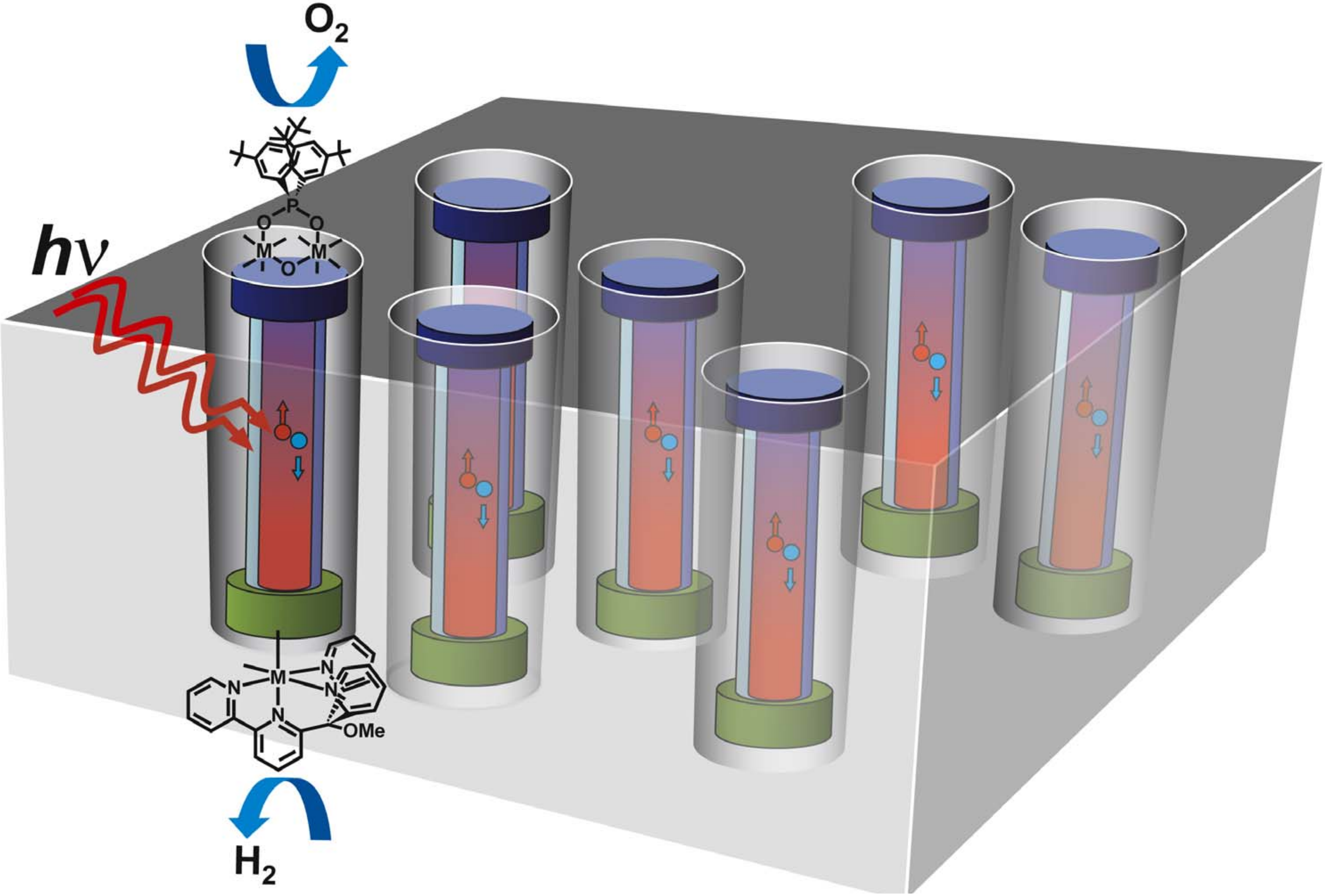
Designing dual-bandgap light absorber



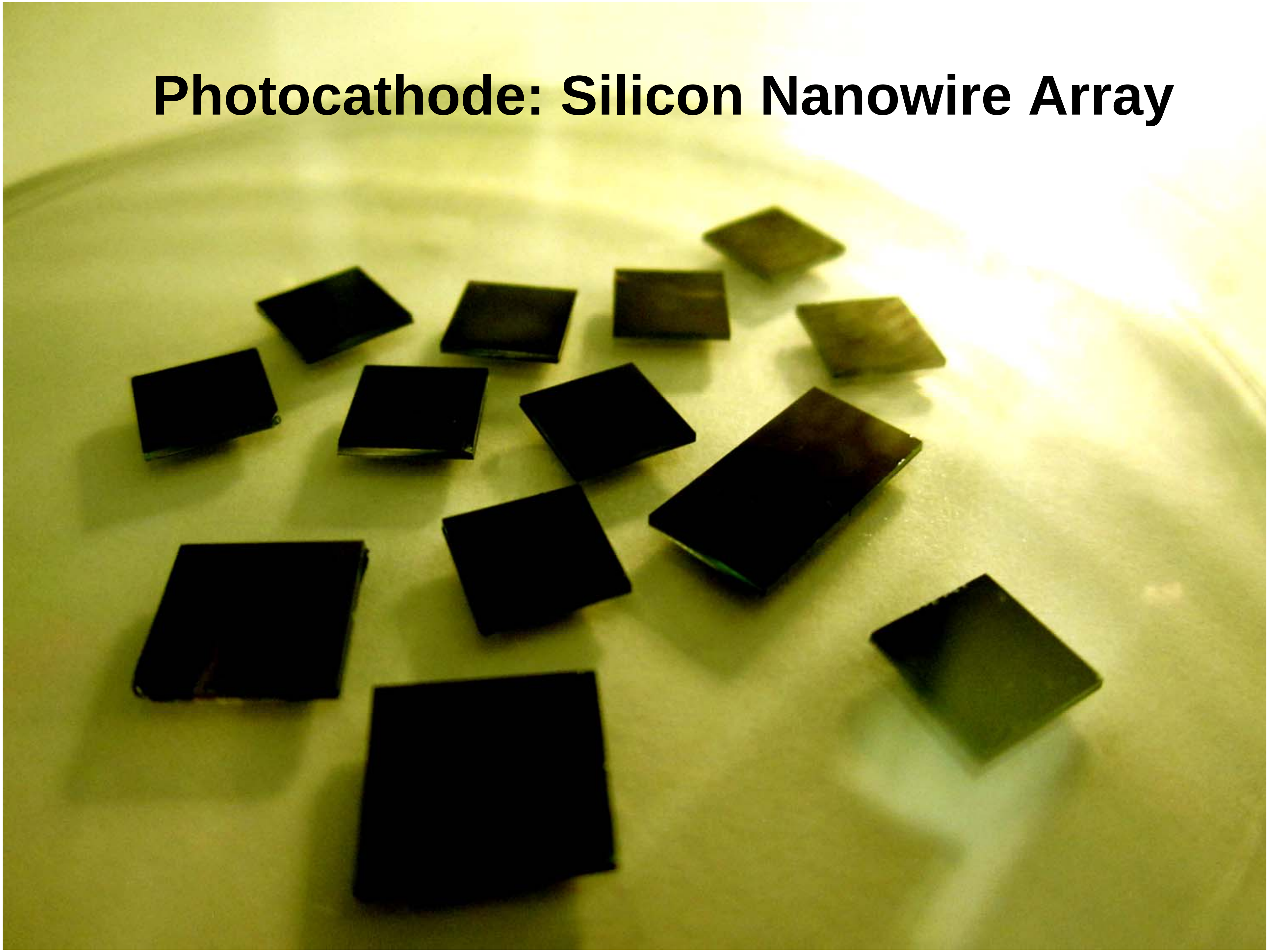
Spectrally splitting two-photon systems, Voltage & Current density needs



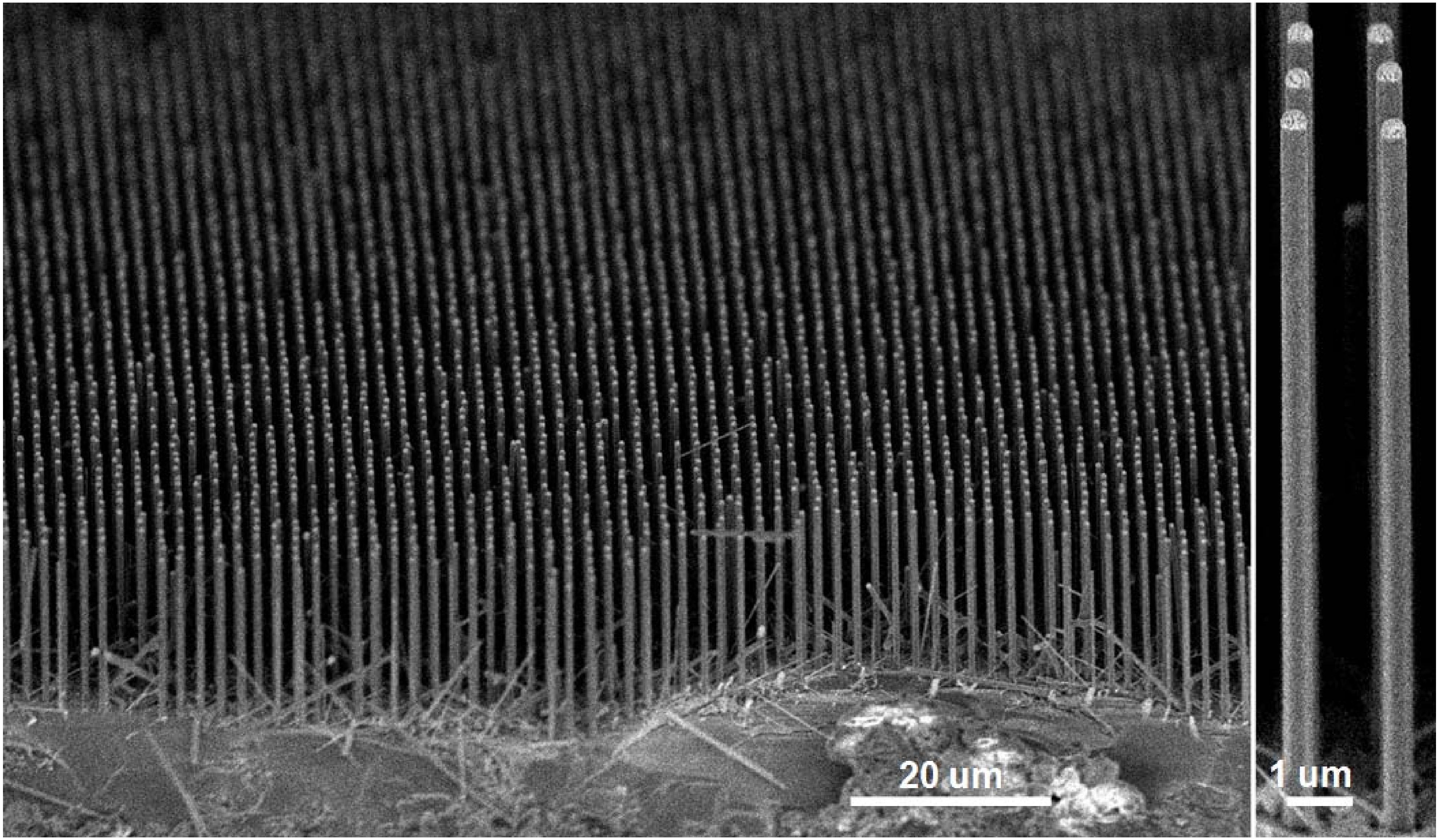
Solar-Fuels Generators



Photocathode: Silicon Nanowire Array

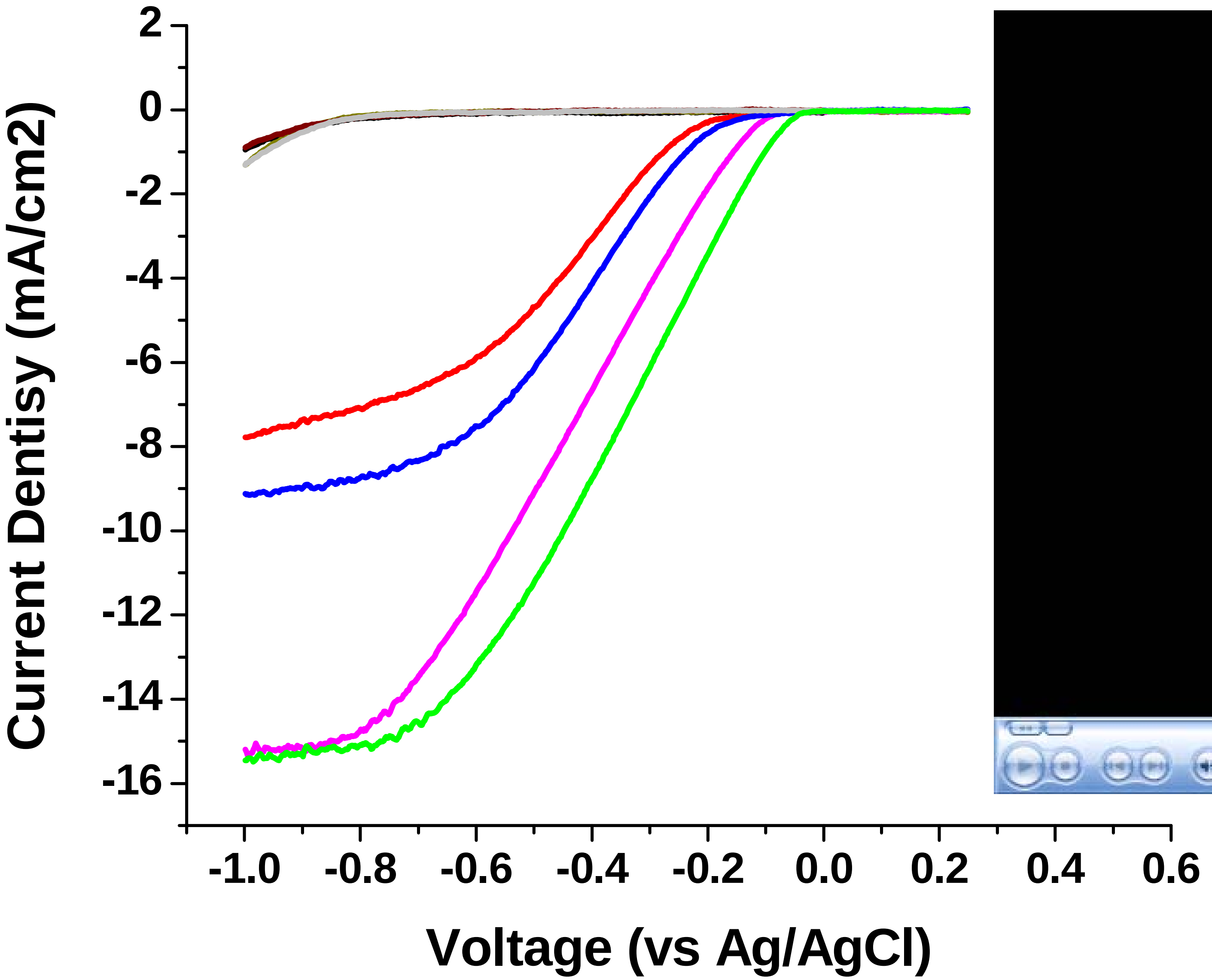


Si wire array as photocathode



H. Jeong et al. 2009

Photocathode: Silicon nanowire array



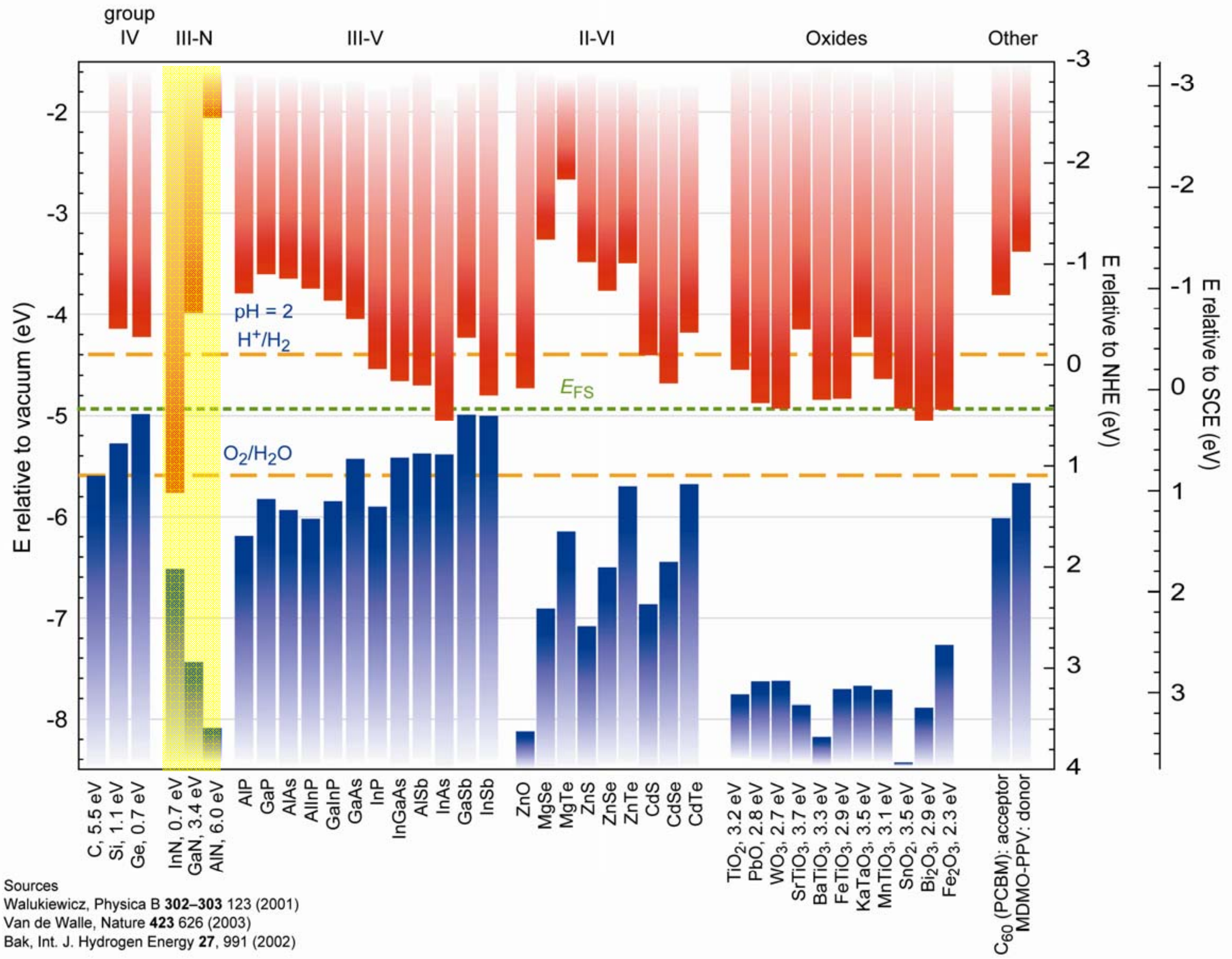
Y. Hwang et al. 2010

Photocurrent from the Anode Materials

	Light I_{input}	$I_{current}$(mA/cm^2)
TiO_2[1]	UV only	N/A
doped- TiO_2[2]	Simulated AM 1.5 100 mW/cm^2	0.85 mA/cm^2
Si-doped Fe_2O_3[3]	Simulated AM 1.5 100 mW/cm^2	2.3 mA/cm^2
$(Ga_{1-x}Zn_x)(N_{1-x}O_x)$[4]	Respond up to 450-500 nm	N/A
KTaO3[5]	UV only	N/A

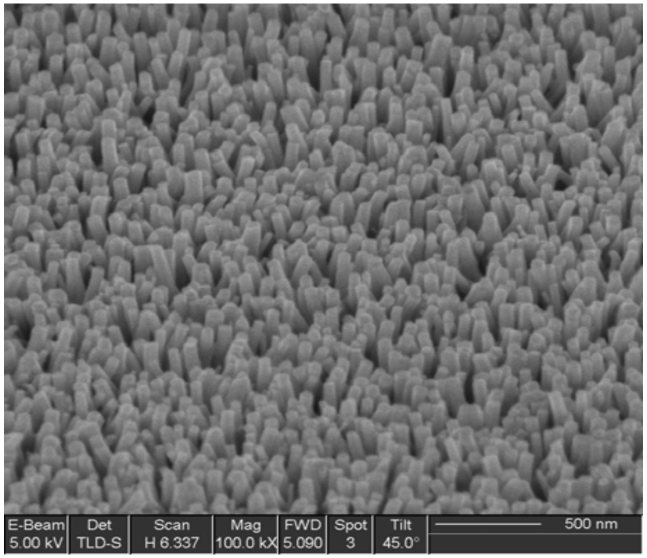
1). Fujishima A, Honda K. Nature 1972;238:37–8.; 2) J. K. Park, S. Kim, A. J. Bard. *Nano. Lett.* **2006,** *6*, 24. 3) A. Kay, I. Cesar, M. Grätzel, *J. Am. Chem. Soc.* **2006,** *128*, 15717; 4) K. Maeda *et al*, *Nature*. **2006,** *440*, 295; 5). Kato H, Asakura K, Kudo A. J Am Chem Soc 2003;125:3082–9.

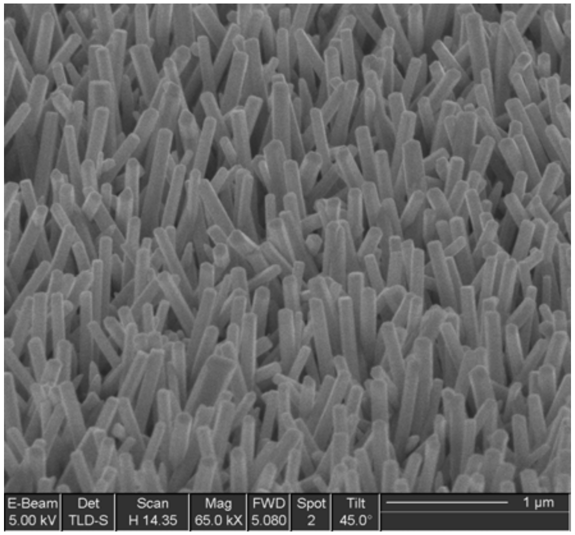
Challenges in semiconductor design: the anode materials

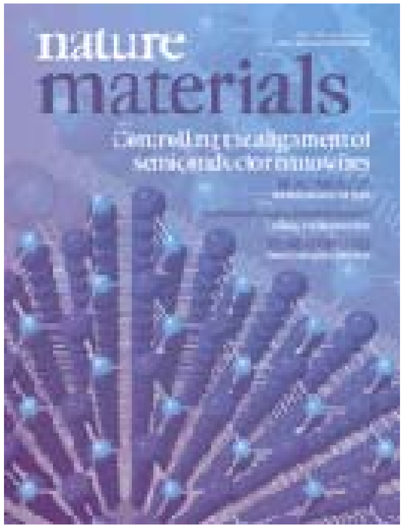


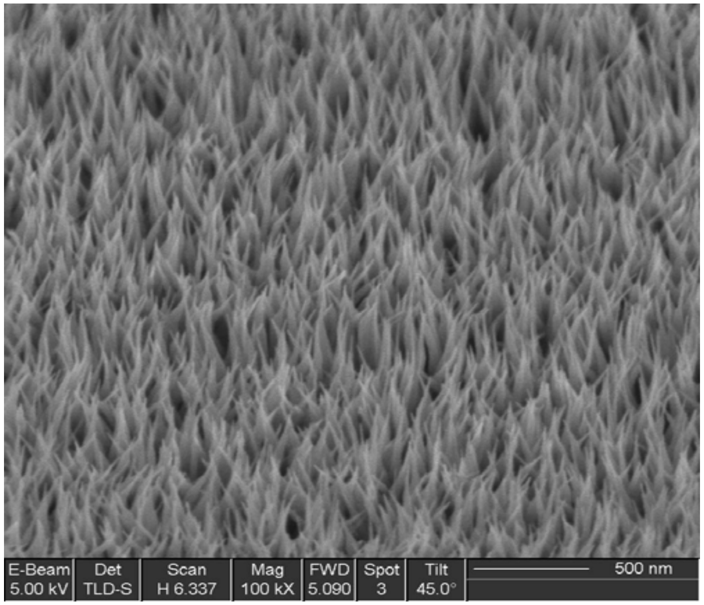
Sources
Walukiewicz, Physica B **302–303** 123 (2001)
Van de Walle, Nature **423** 626 (2003)
Bak, Int. J. Hydrogen Energy **27**, 991 (2002)

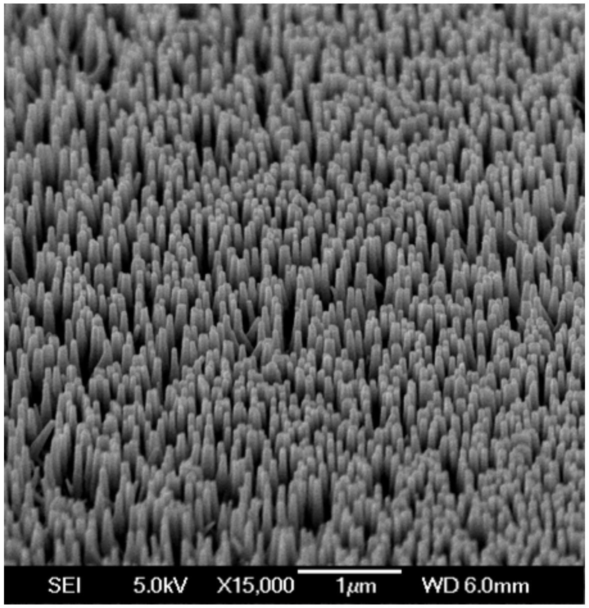
Single crystalline InGaN Nanowires for solar water splitting





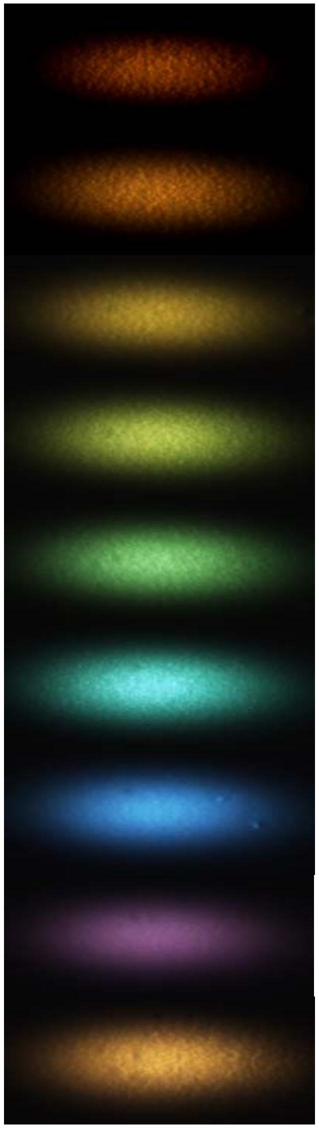


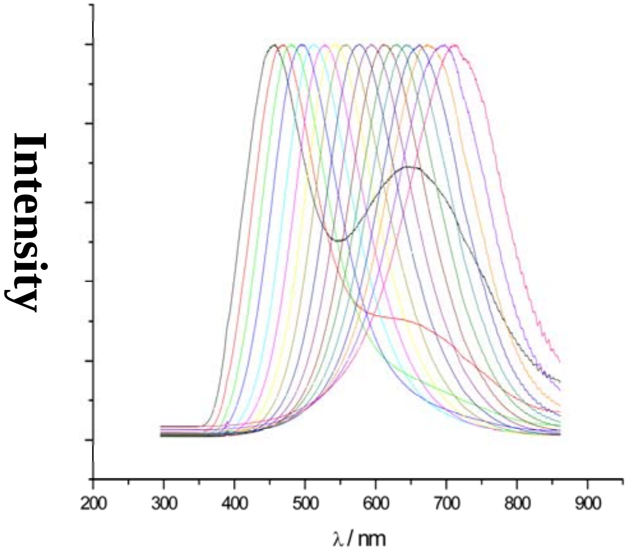


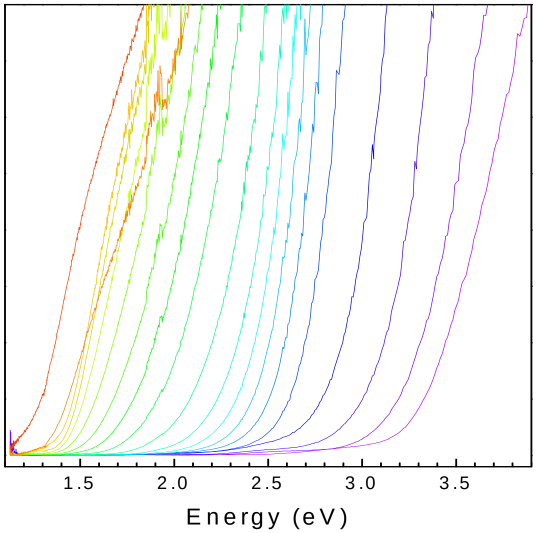


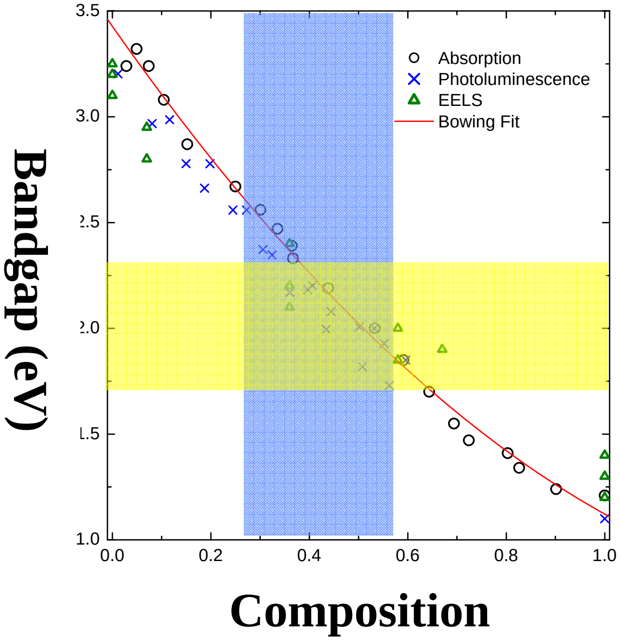
T. Kuykendall et al. ***Nature Mater, 3, 528,*** *2004;* ***Nature Materials****, 6, 951, 2007*

Alloyed Nanowires: Full Color Spectrum



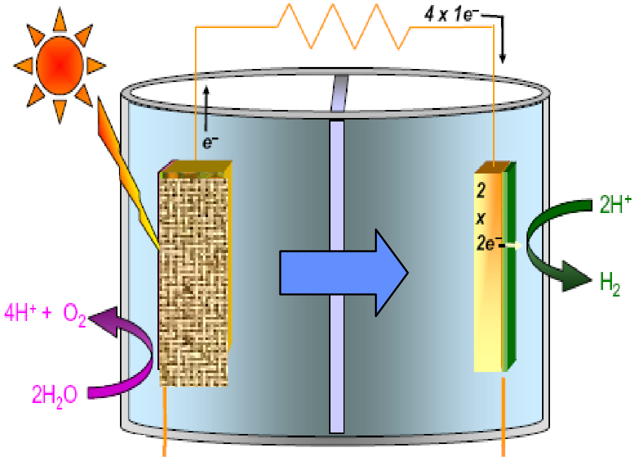


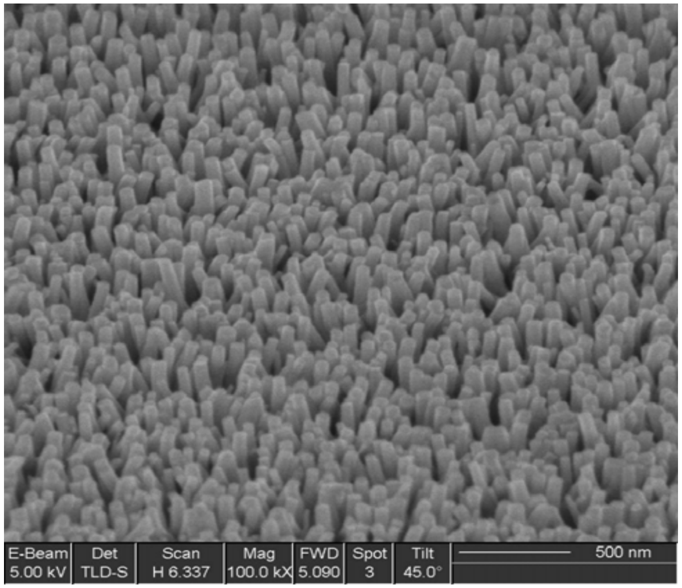


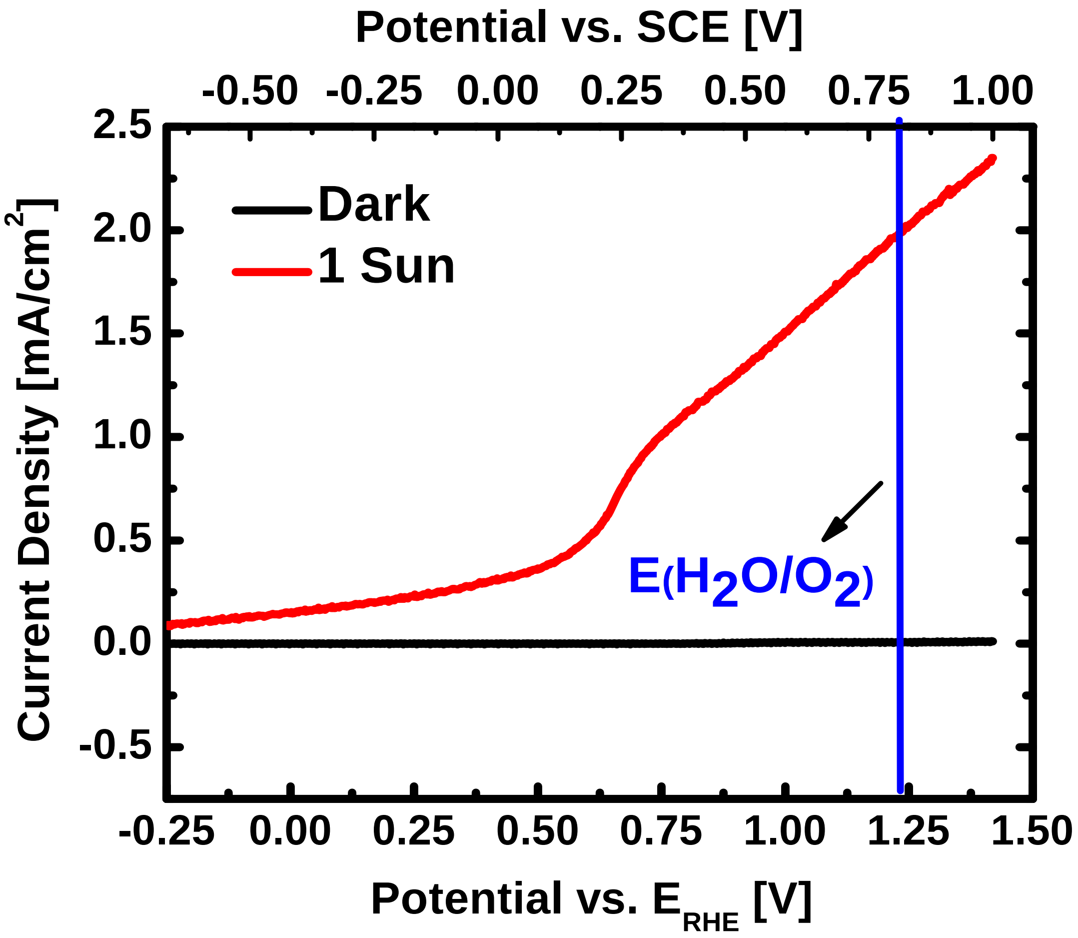


- Solid state lighting
- Solar cell
- Solar water splitting

$In_xGa_{1-x}N$ Photocurrent Measurements pH3



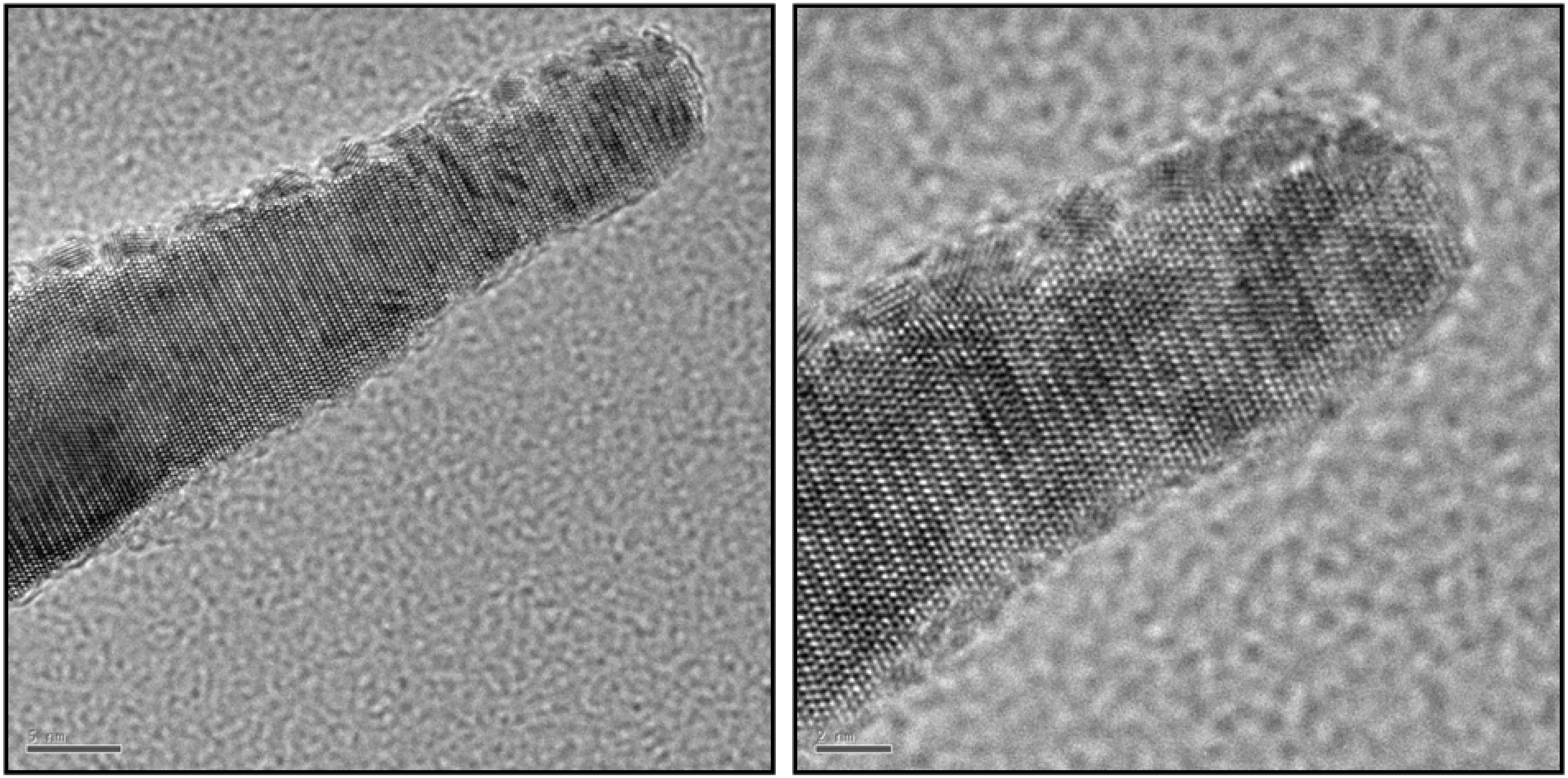




C. Hahn, unpublished results

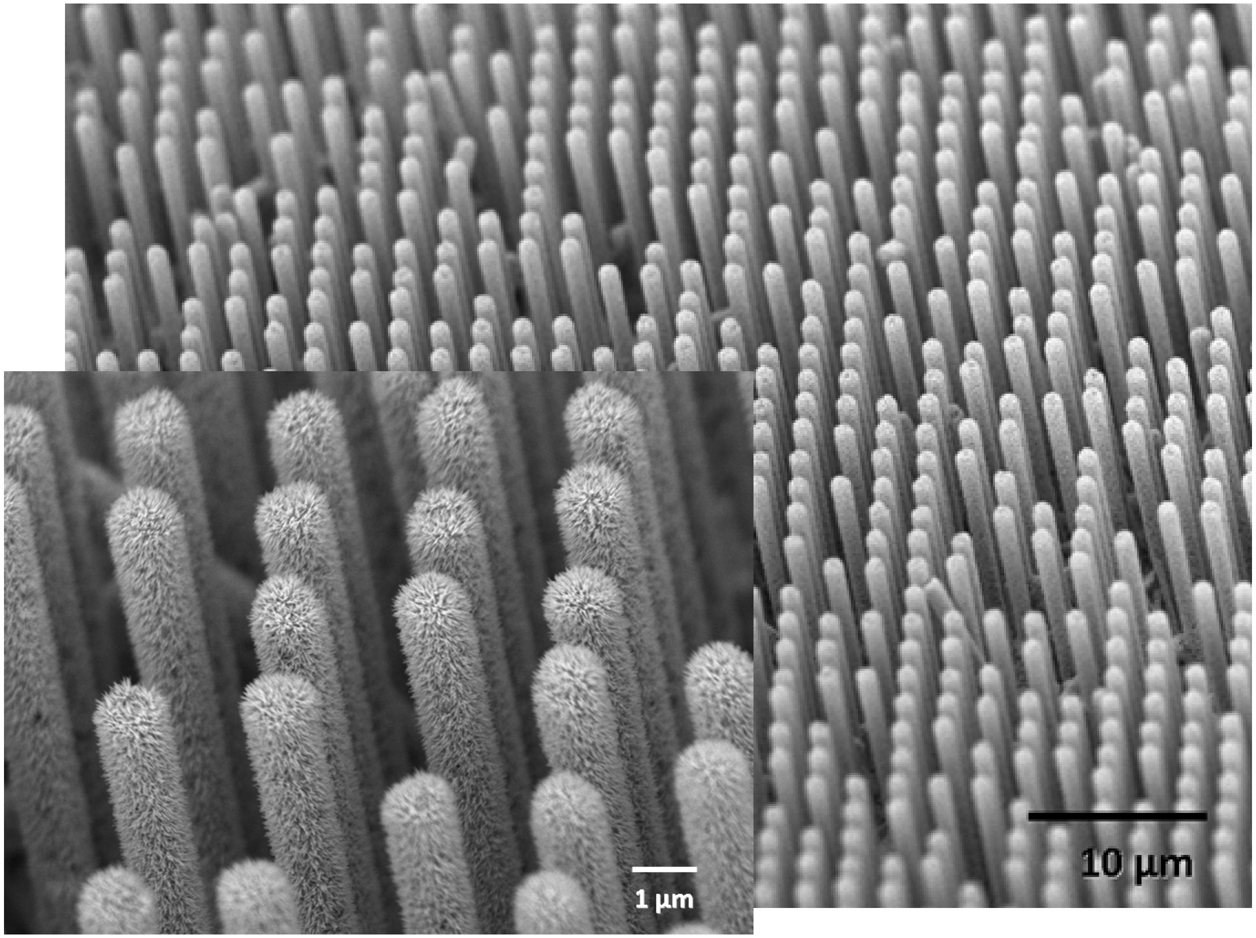
$In_xGa_{1-x}N$ Photocorrosion Test

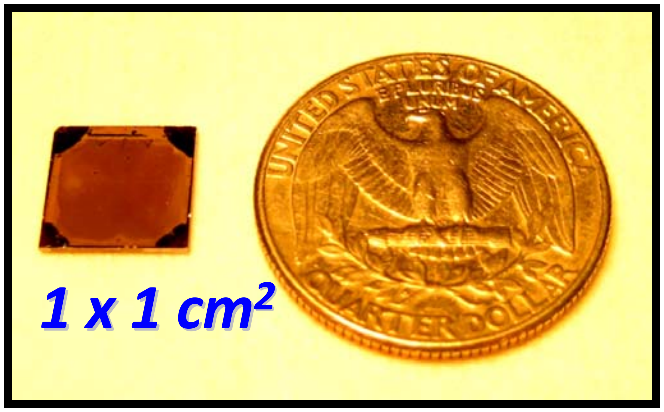
24 Hr, 4.5 Suns Illumination, pH 3 0.5 M Na_2SO_4 Solution, Pt Clusters



InGaN is a promising photoanode material.

Si/InGaN Core/Shell Wire

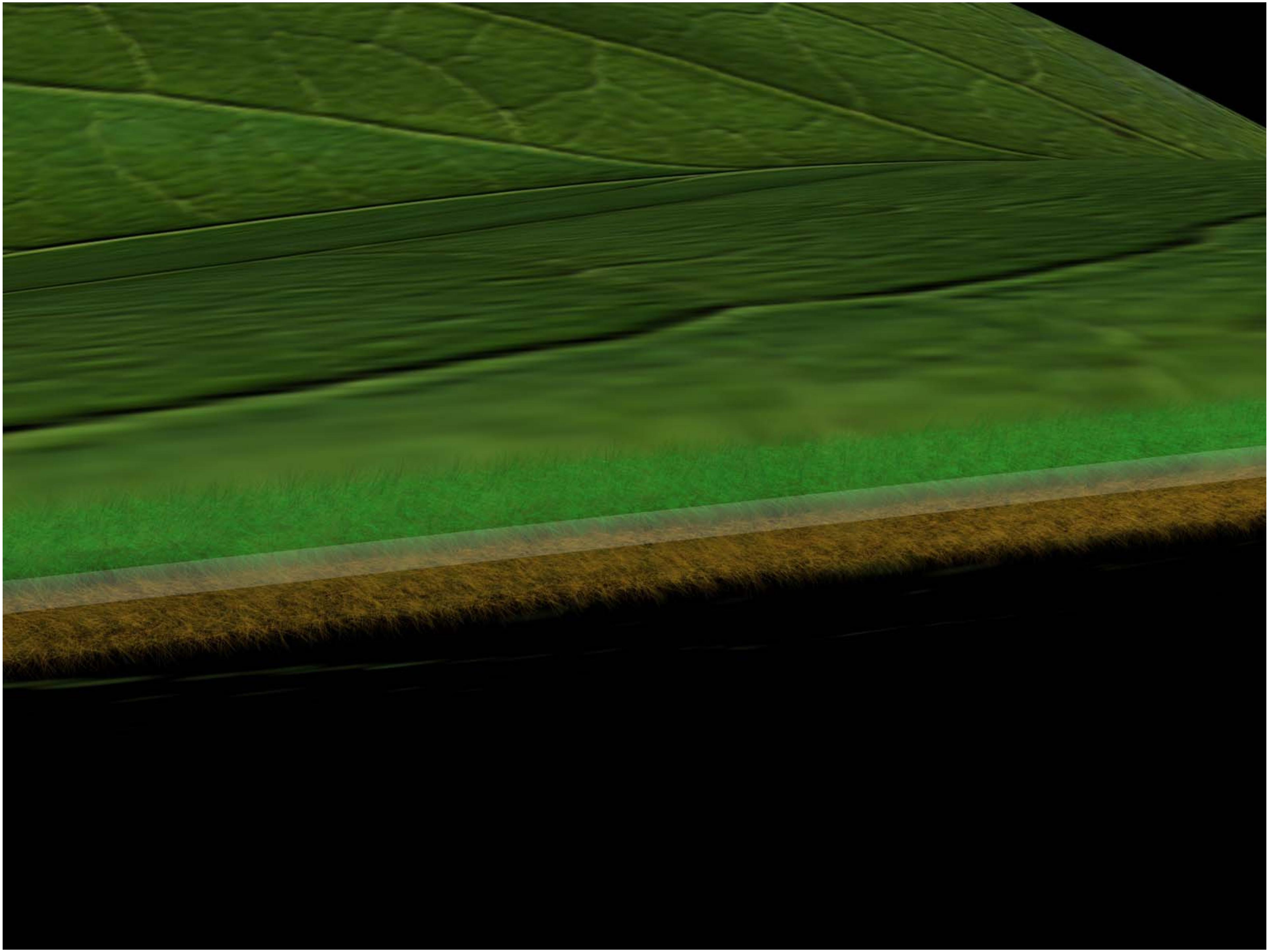


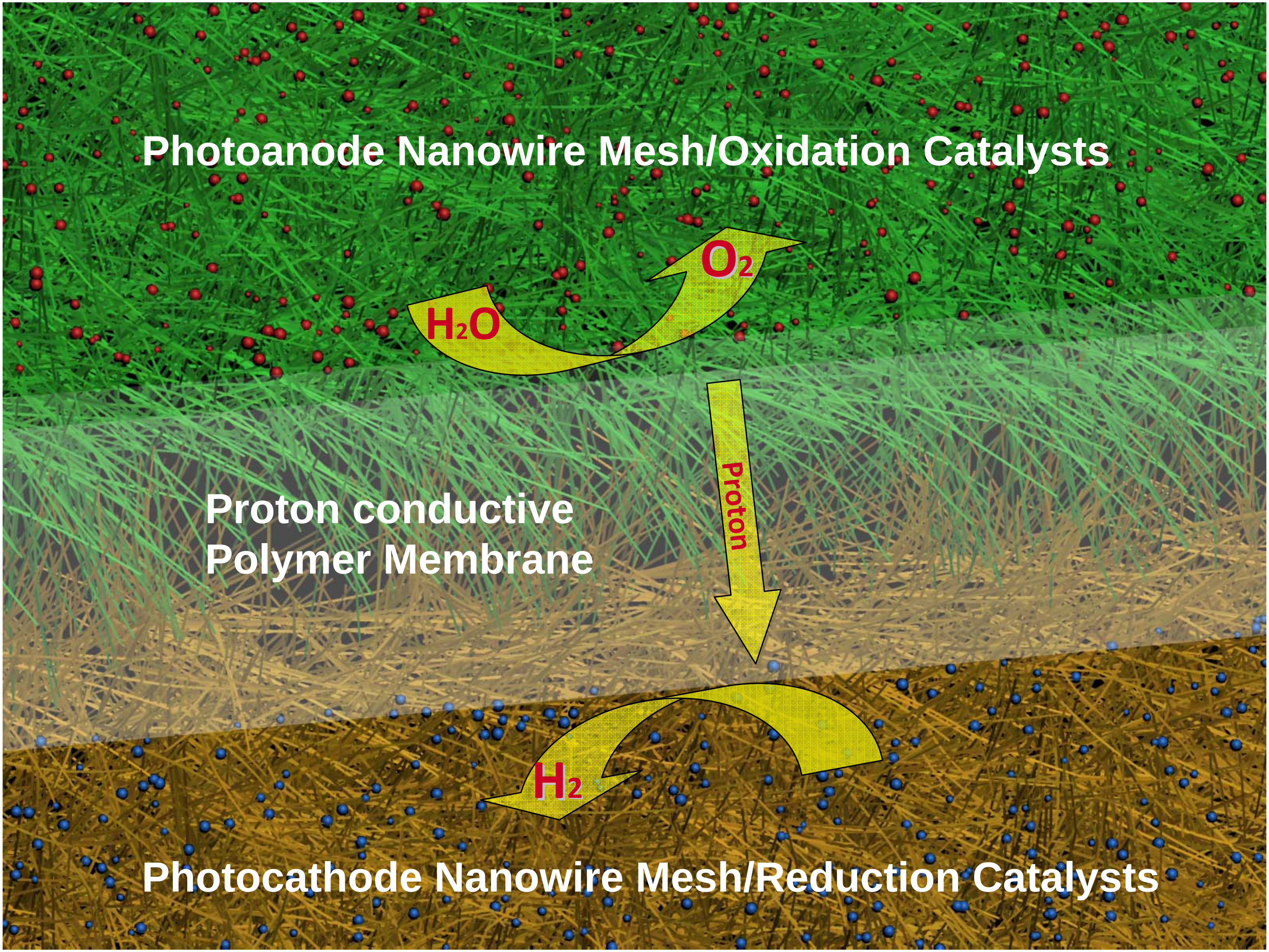


- In$_x$Ga$_{1-x}$N nanorod shell grows on the patterned Si wire arrays, which provide high surface area as well as light trapping.

-Spectrally splitting light absorption, tunable bandgap, and bandedge

Artificial Leaf: Nanowire Bilayer Paper Solar-Fuels Generators

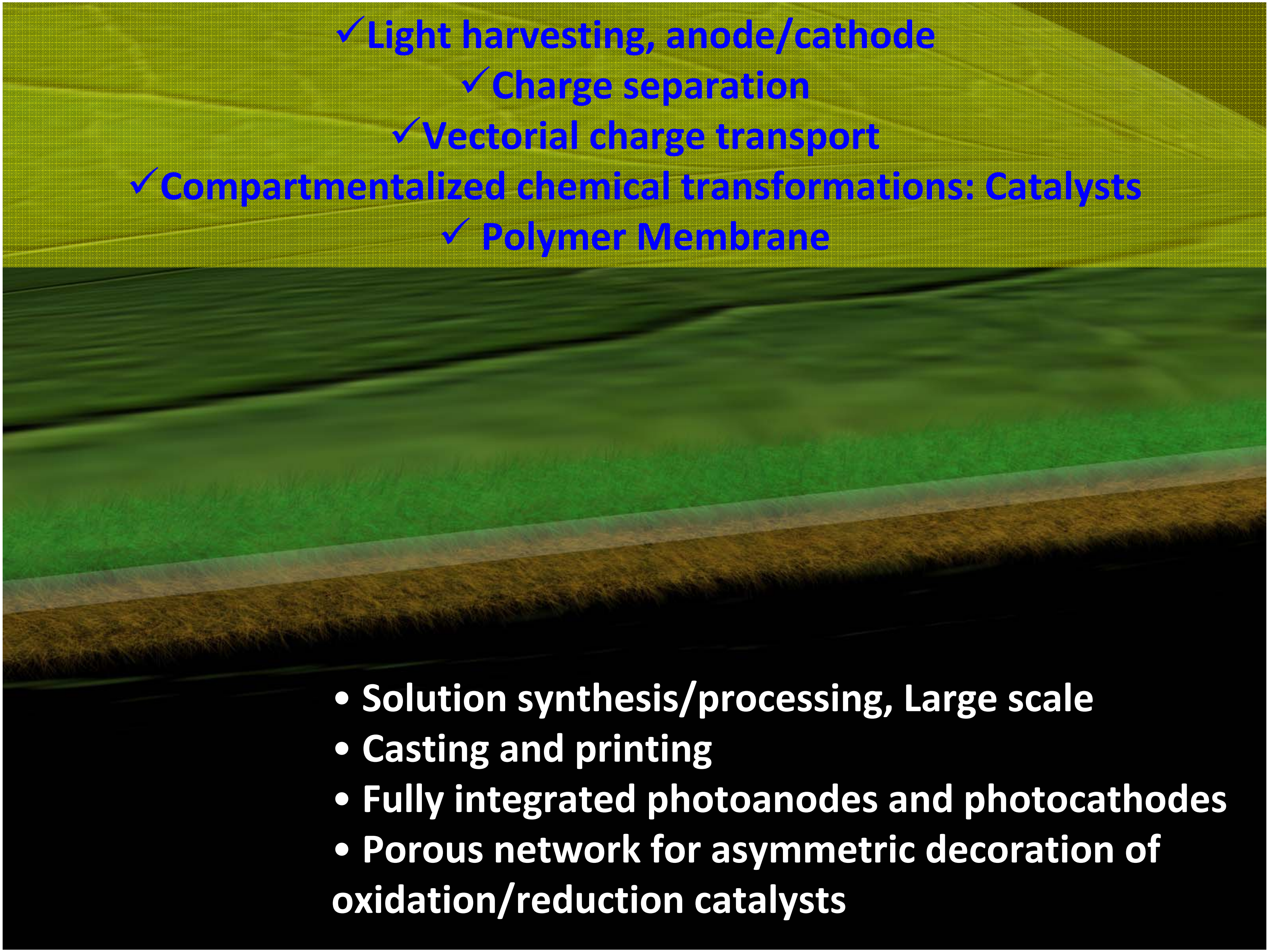




Photoanode Nanowire Mesh/Oxidation Catalysts

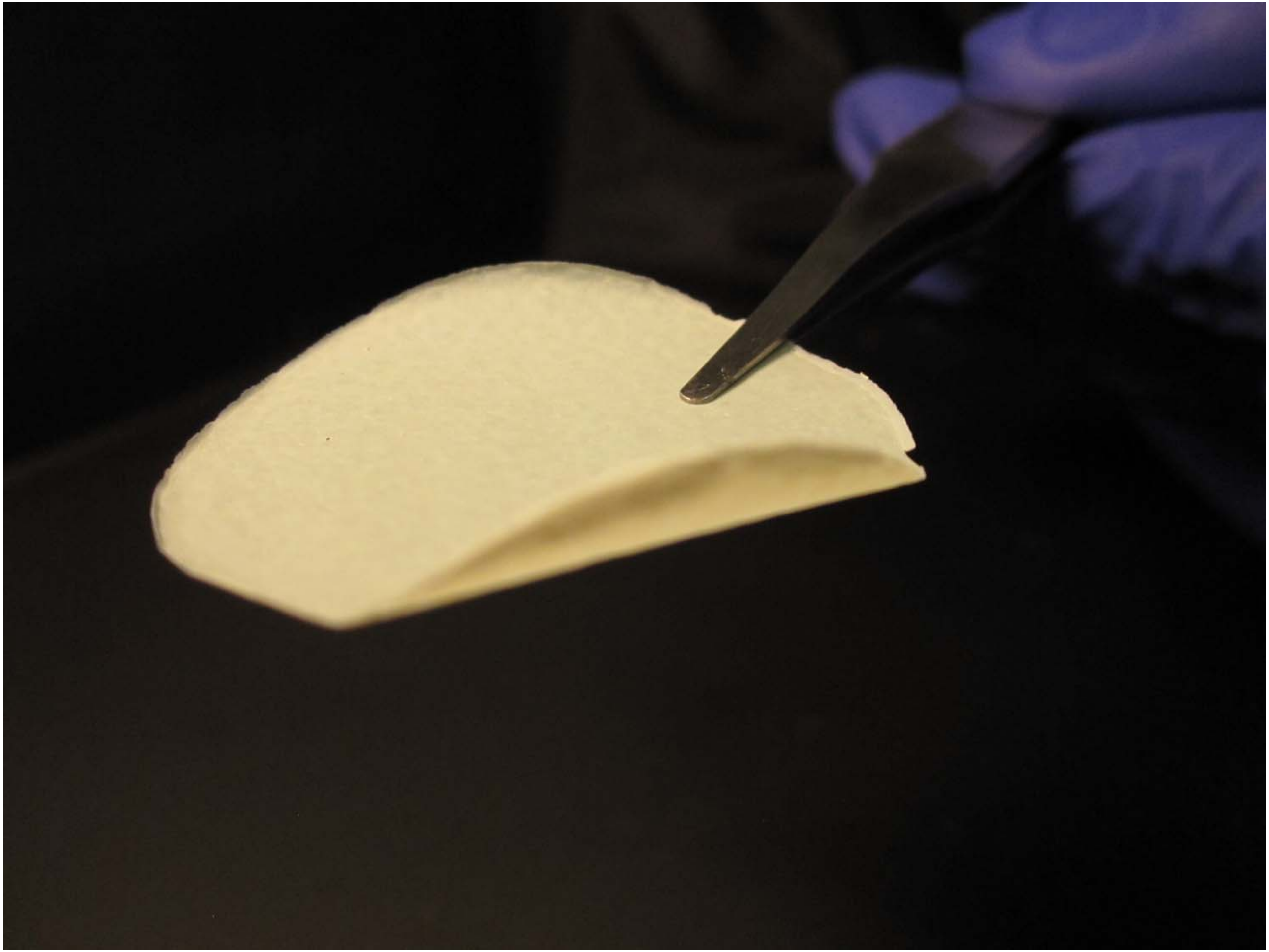
Proton conductive
Polymer Membrane

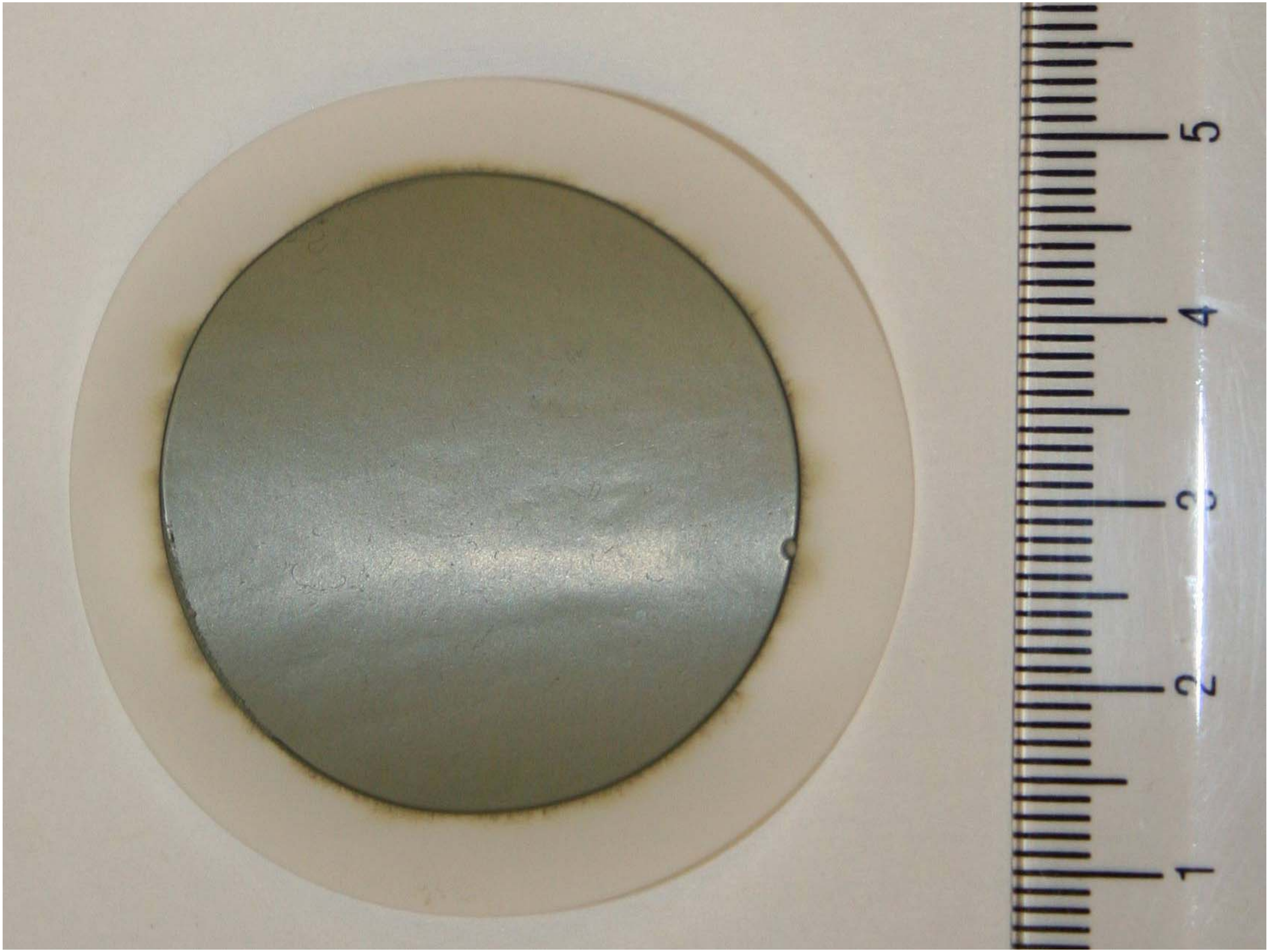
Photocathode Nanowire Mesh/Reduction Catalysts



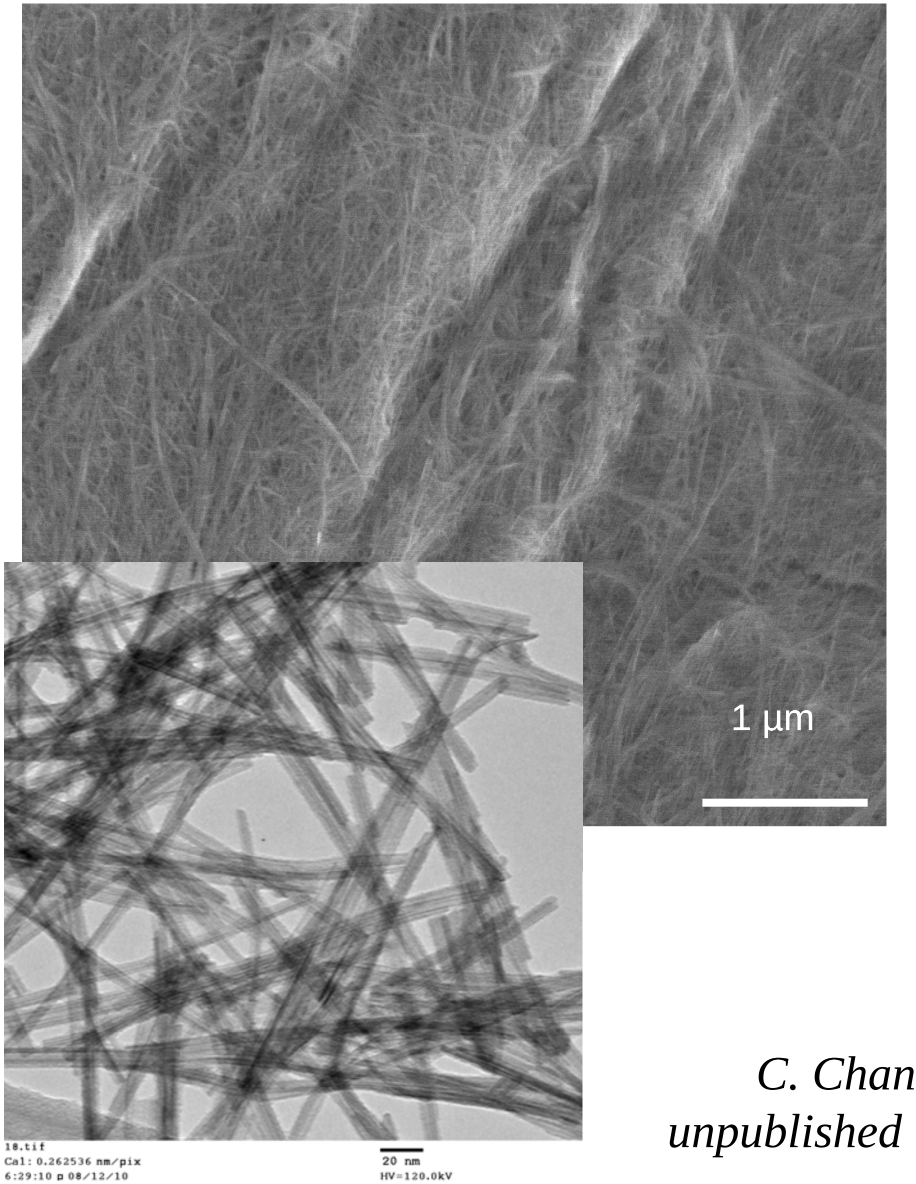
✓Light harvesting, anode/cathode
✓Charge separation
✓Vectorial charge transport
✓Compartmentalized chemical transformations: Catalysts
✓ Polymer Membrane

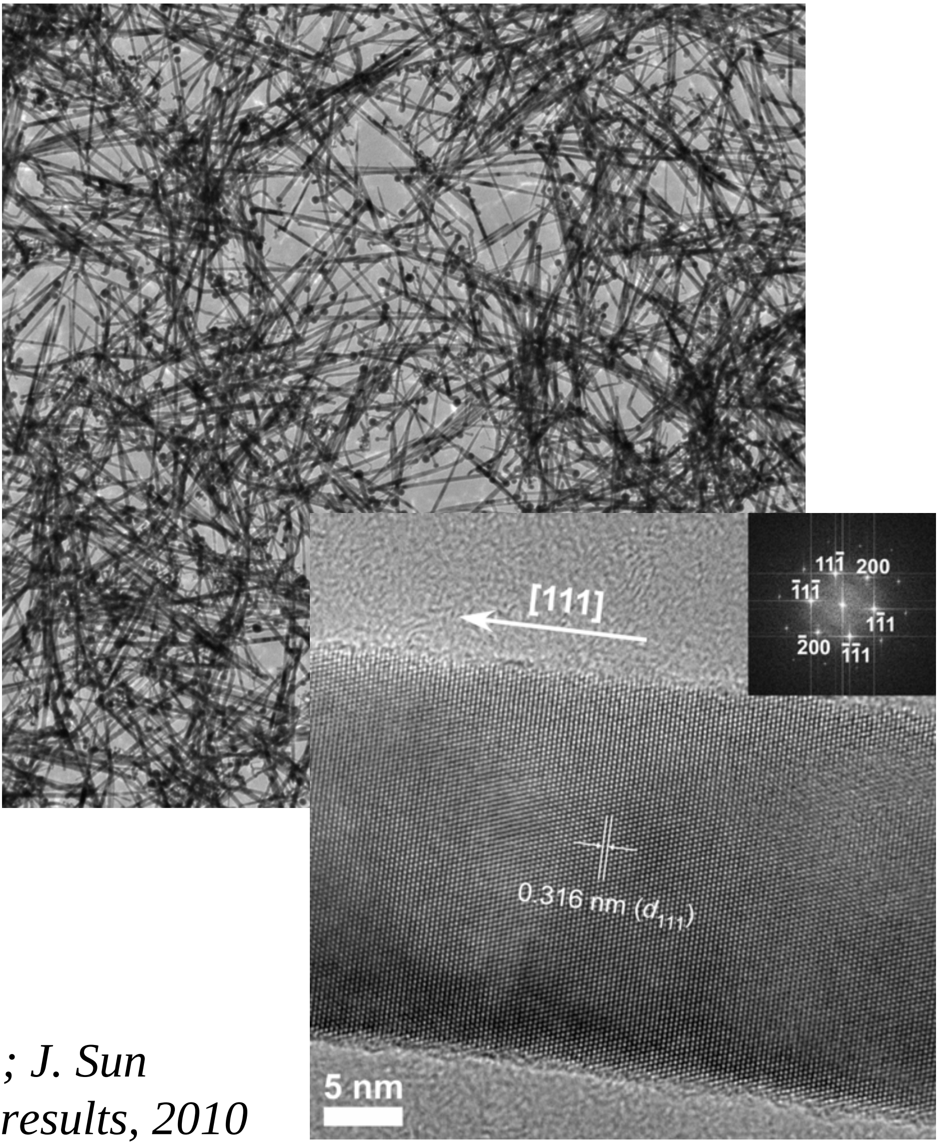
- Solution synthesis/processing, Large scale
- Casting and printing
- Fully integrated photoanodes and photocathodes
- Porous network for asymmetric decoration of oxidation/reduction catalysts




1
2
3
4
5

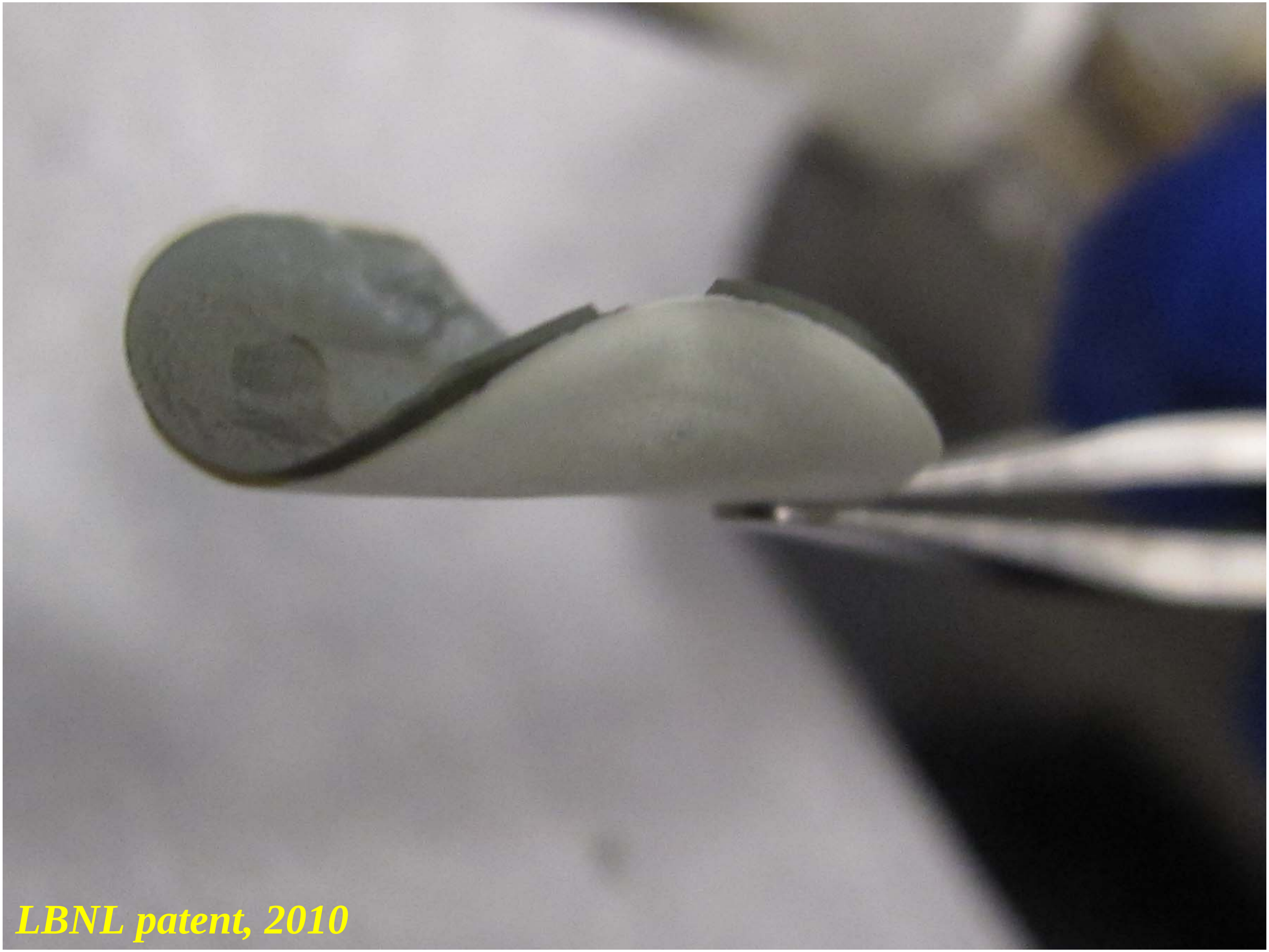
Bilayer Nanowire Mesh





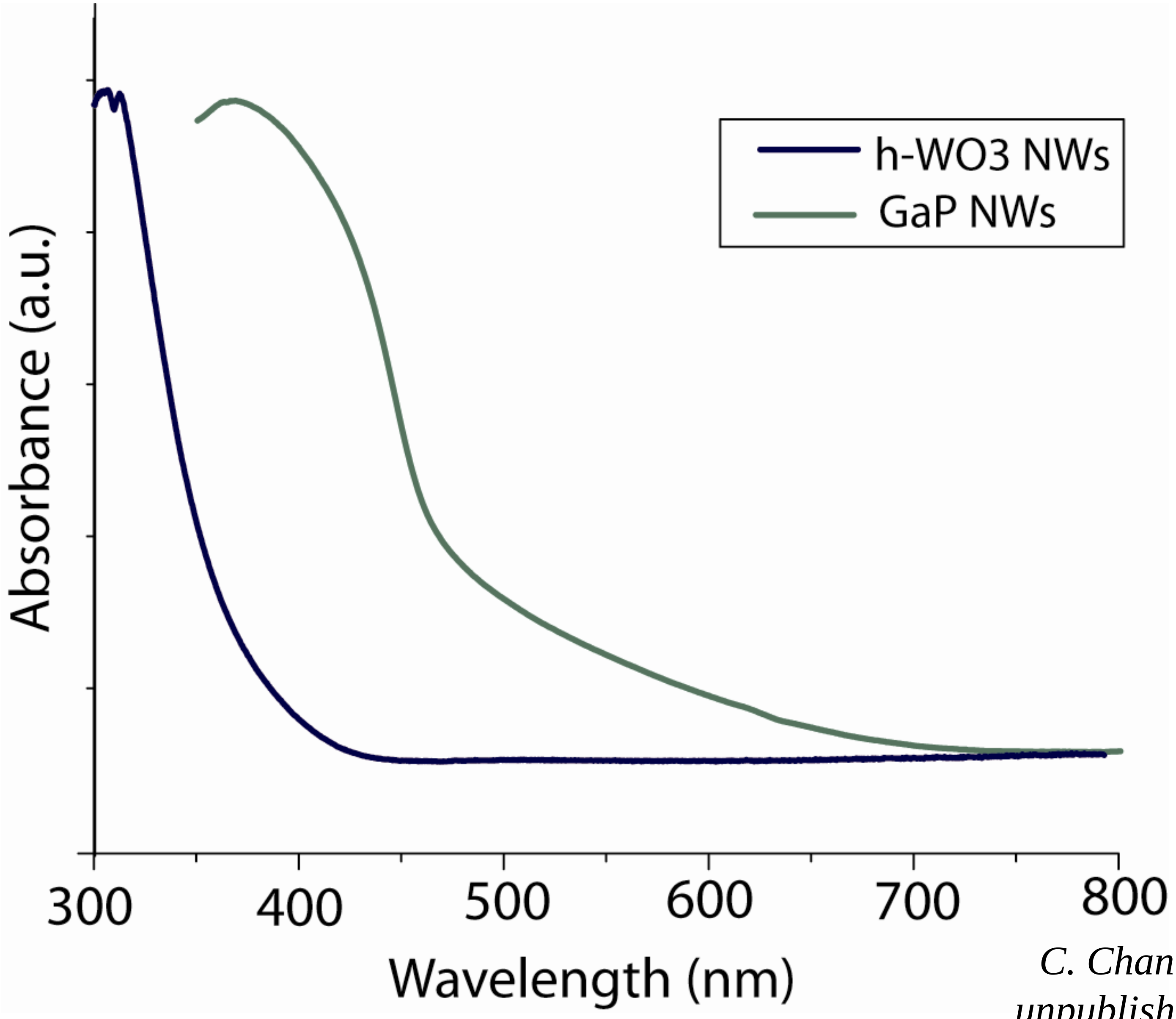
C. Chan; J. Sun

unpublished results, 2010



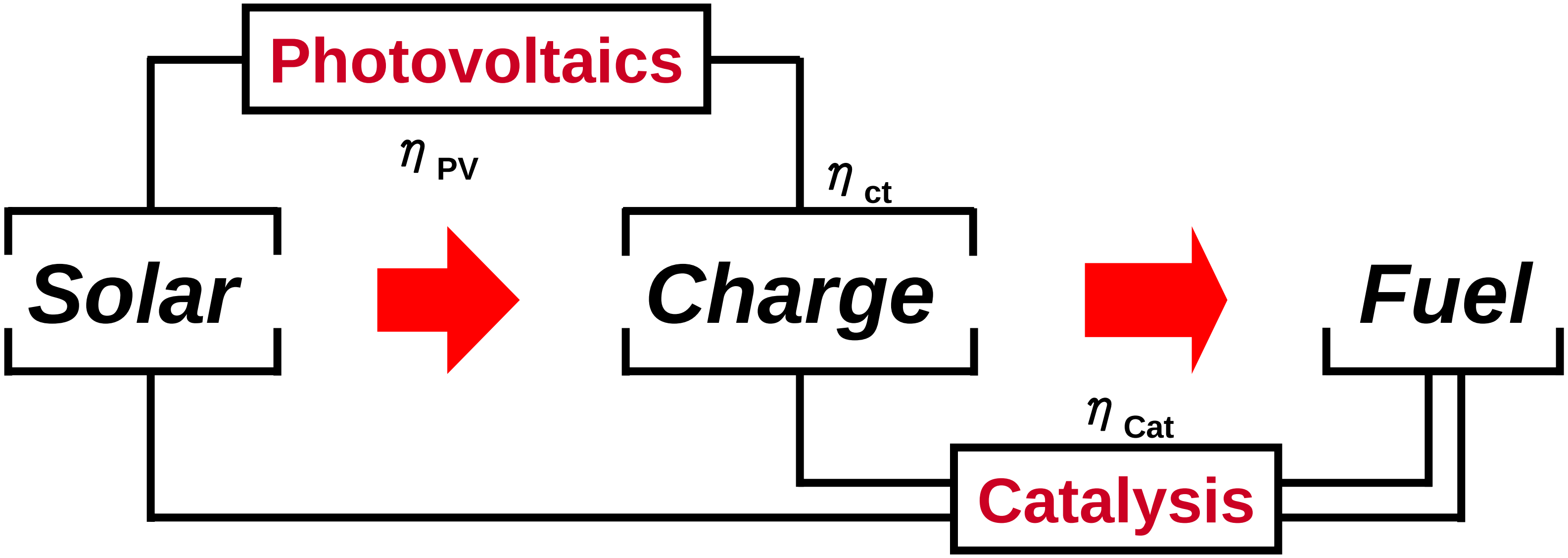
LBNL patent, 2010

Bilayer Nanowire Mesh: Light Absorption



C. Chan; J. Sun
unpublished results

Solar-to-Fuel Conversion



The overall efficiency for the conversion of available sunlight to fuel:

$\eta_{overall}$ = η_{PV} **(photovoltaic efficiency)**

• η_{CT} **(charge transfer efficiency)**

• η_{cat} **(catalysis efficiency)**

Candidate Energy-Storing Reactions

Dual oxidation/reduction components needed for overall catalytic cycles

- **Water Splitting**

$$2\,H_2O \xrightarrow{\text{light/catalyst}} 2\,H_2 + O_2$$

Oxidation $2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-$

Reduction $2\,H^+ + 2\,e^- \longrightarrow H_2$

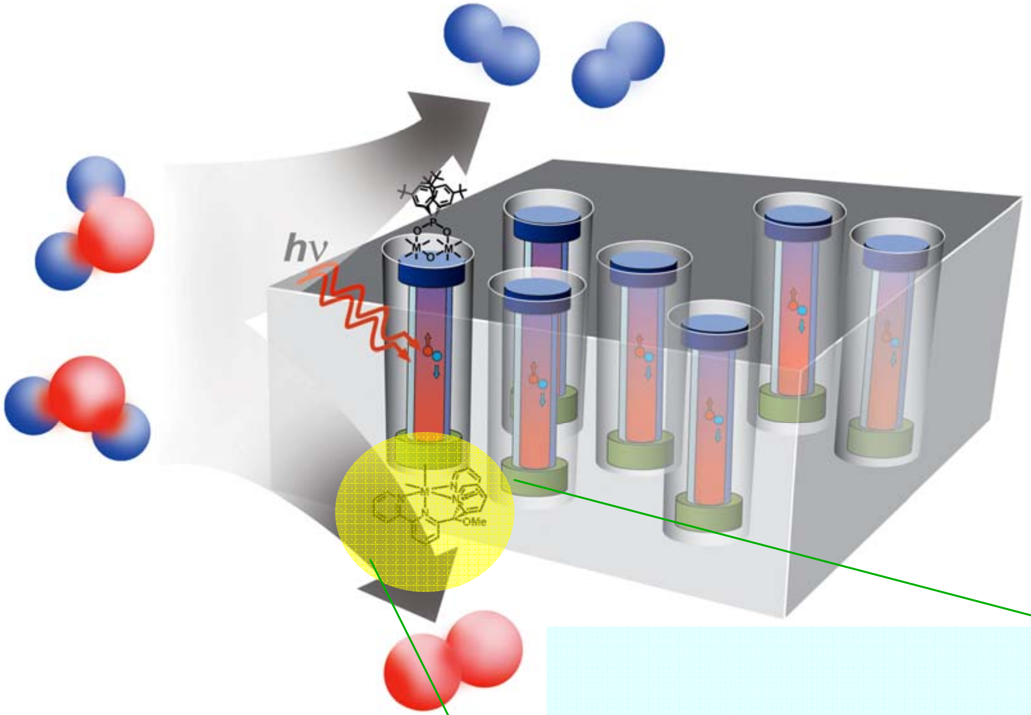
- **Carbon Dioxide Fixation**

$$CO_2 \xrightarrow{\text{light/catalyst}} CO + 1/2\,O_2$$

Oxidation $2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-$

Reduction $CO_2 + 2\,H^+ + 2\,e^- \longrightarrow CO + H_2O$

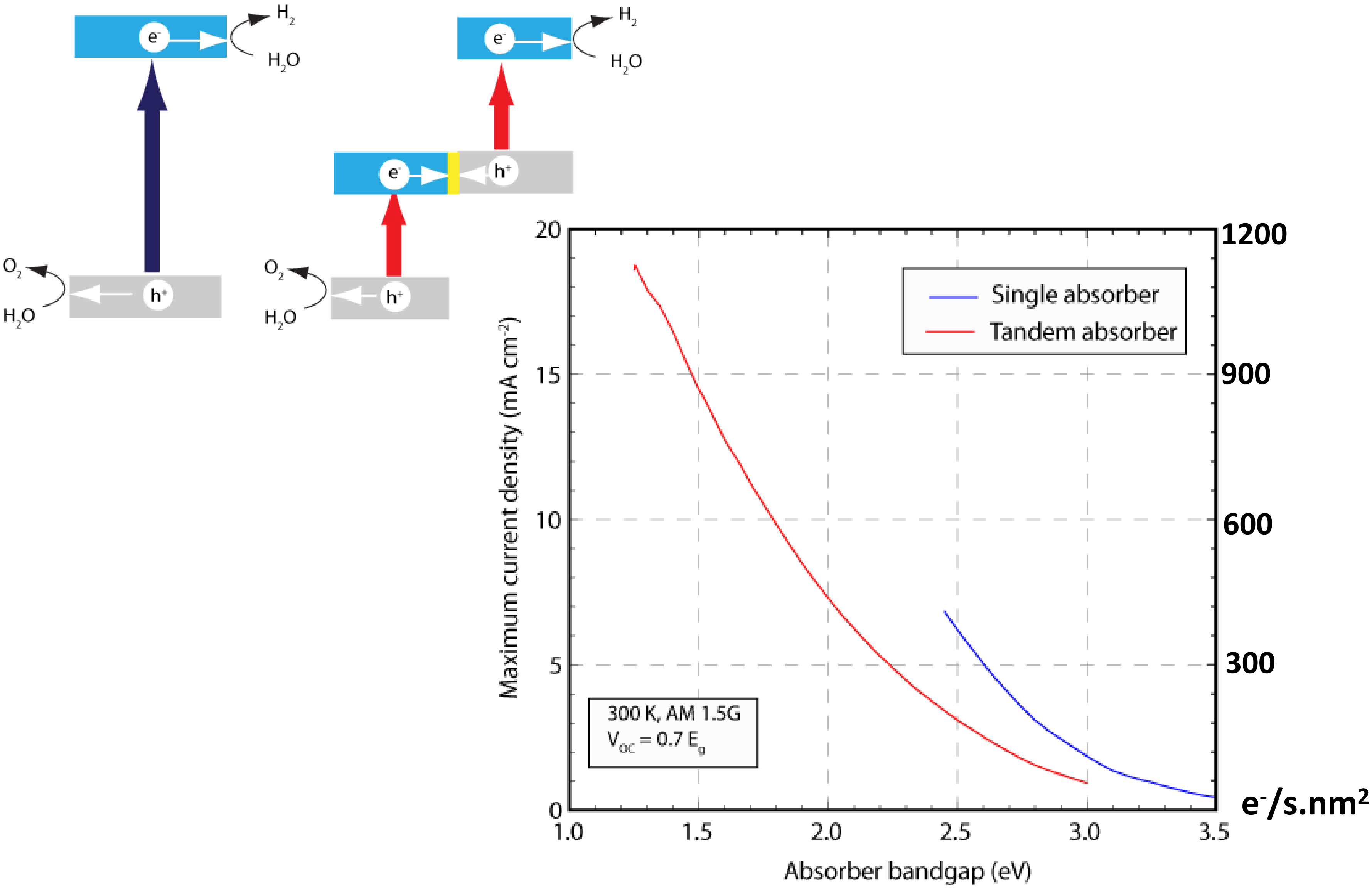
Catalysis



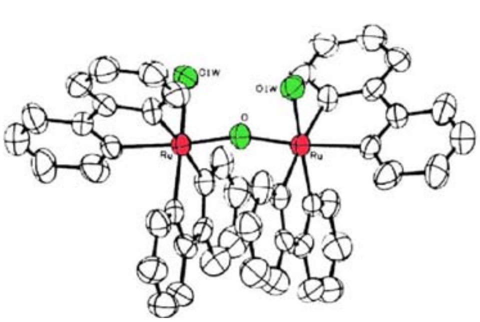
$\eta_{\text{cat}} \propto$

- Γ_{cat} (catalyst coverage)
- TOF (turnover frequency)
- E_0 (potential for water splitting)

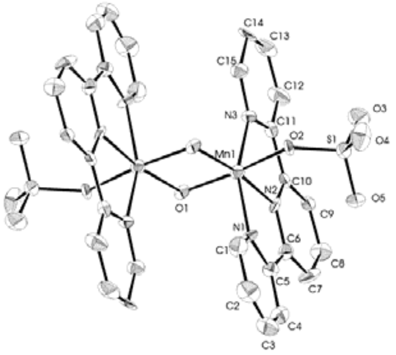
Matching solar flux with catalytic activity



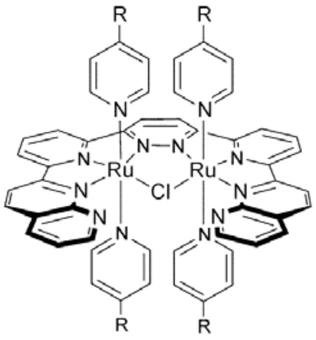
Molecular catalysts for water oxidation



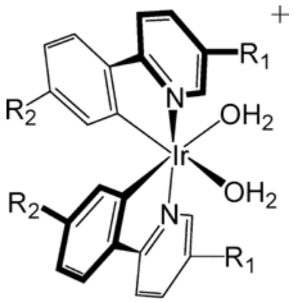
Meyer
1982



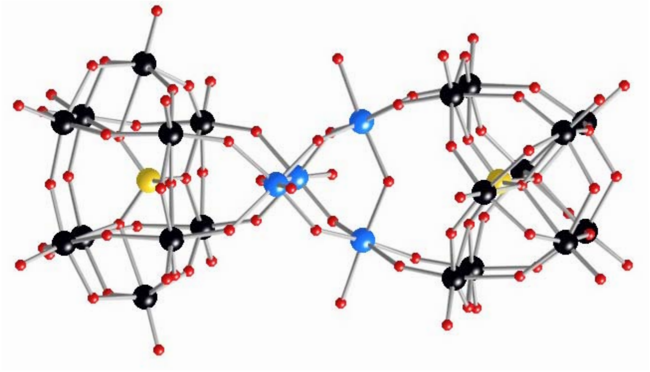
Brudwig, Crabtree
2001



Thummel
2005



Bernhard
2008



Hill, 2008

Molecular catalysts are structurally and mechanistically well understood.

Turnover rates (10^{-3} to 10^{0} s^{-1}) are generally too slow to compete with back ET in non-sacrificial systems.

Turnover frequencies (TOF) for oxygen evolution at Co and Mn oxide materials

Activity Metrics/Goals:

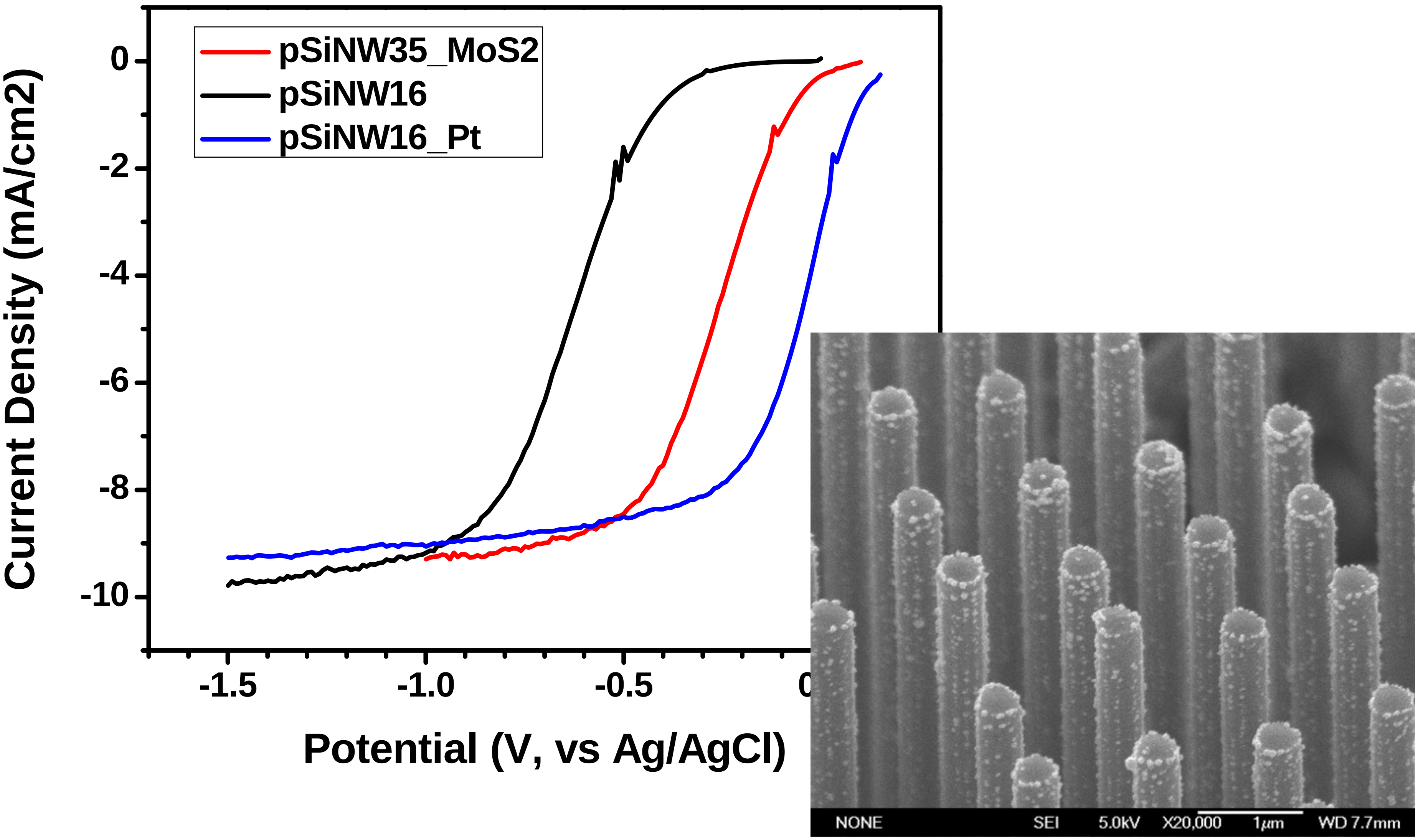
~x 10^2 for H_2; ~x 10^4 for O_2

>x 10^5 for CO_2

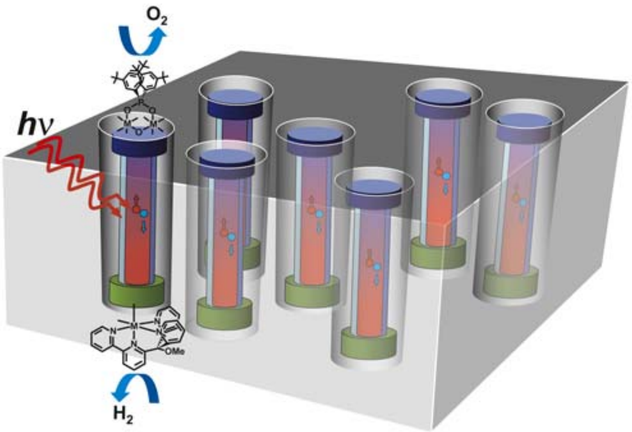
Oxide	TOF (sec^{-1})	Overvoltage, η (mV)	pH	T (^oC)	Quantum yield	Reference
Co_3O_4	0.035	325	5	RT	58%	Harriman (1988) [1]
Co_3O_4	$\geq$ 0.0025	350	14	30	--	Tamura (1981) [2]
Co_3O_4	$\geq$ 0.020	295	14	120	--	Wendt (1994) [3]
Co_3O_4	$\geq$ 0.0008	414	14.7	25	--	Tseung (1983) [4]
Co_3O_4	$\geq$ 0.006	235	14	25	--	Singh (2007) [5]
Co,P film	$\geq$ 0.0007	410	7	25	--	Nocera (2008) [6]
MnO_2	$\geq$ 0.013	440	7	30	--	Tamura (1977) [7]
Mn_2O_3	0.055	325	5	RT	35%	Harriman (1988) [1]

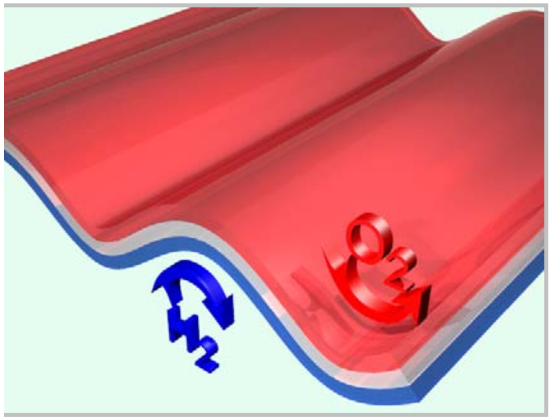
[1] Harriman, A.; Pickering, I.J.; Thomas, J.M.; Christensen, P.A. *J. Chem. Soc., Farad. Trans. 1* **1988**, *84*, 2795-2806.
[2] Iwakura, C.; Honji, A.; Tamura, H. *Electrochim. Acta* **1981**, *26*, 1319-1326.
[3] Schmidt, T.; Wendt, H. *Electrochim. Acta* **1994**, *39*, 1763-1767.
[4] Rasiyah, P.; Tseung, A.C.C. *J. Electrochem. Soc.* **1983**, *130*, 365-368.
[5] Singh, R.N.; Mishra, D.; Anindita; Sinha, A.S.K.; Singh, A. *Electrochem. Commun.* **2007**, *9*, 1369-1373.
[6] Kanan, M.W.; Nocera, D.G. *Science* **2008**, *321*, 1072-1075.
[7] Morita, M.; Iwakura, C.; Tamura, H. *Electrochim. Acta* **1977**, *22*, 325-328.

p-Si Nanowire Photocathode



AP: Challenges & Opportunities

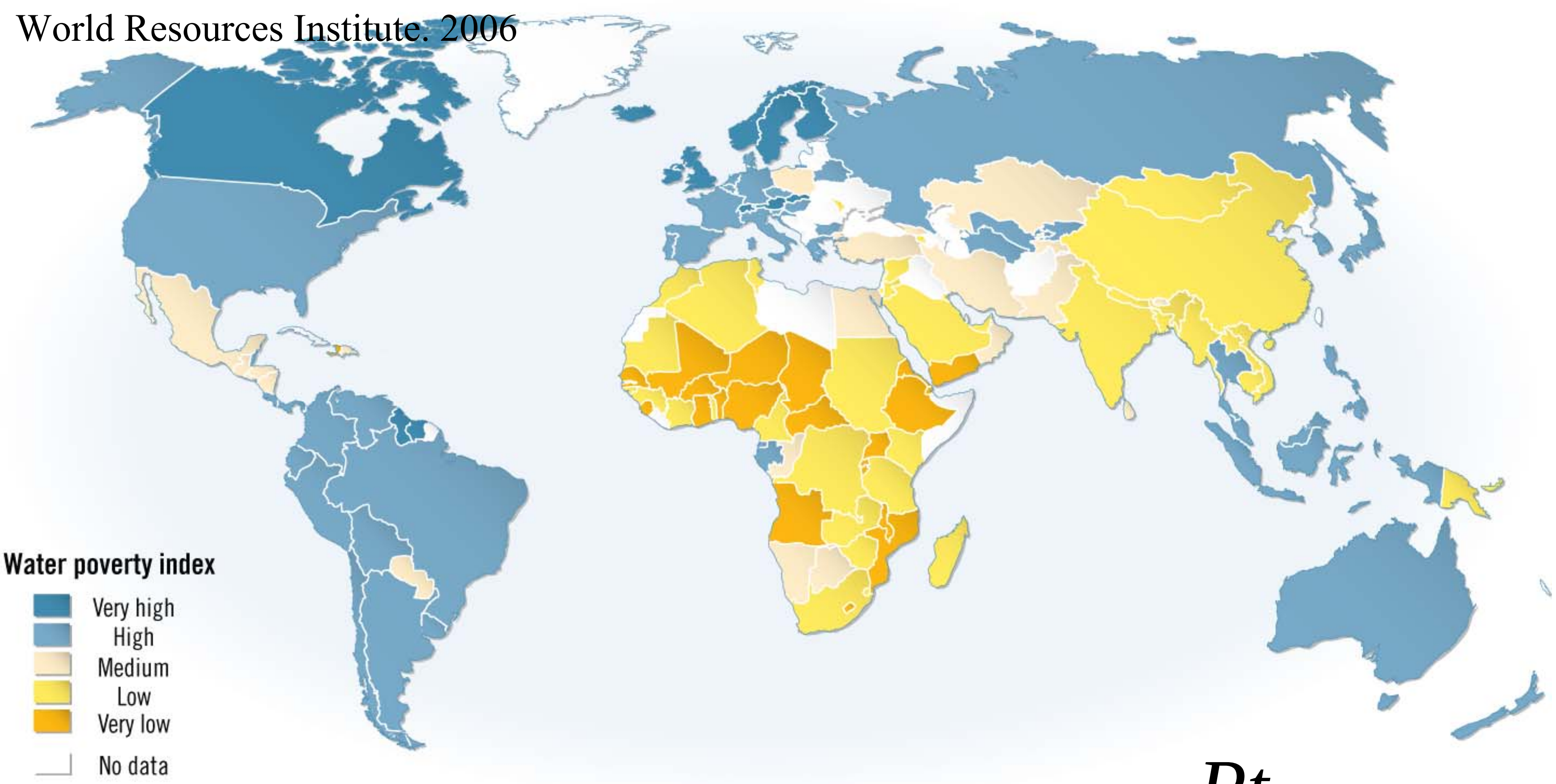




Photoanode materials critical part of the solar Fuels Technology.

Dual bandgap Configuration-Integrated Photocanode/cathode, mimicking photosynthesis in Nature

Catalysts with much higher TOF, and Lower overpotential.



World Resources Institute: 2006

To supply 15 TW from renewable hydrogen, $m = \dfrac{Pt}{E}$

Total mass of water used to power the world each second: 1.25 x10^{6} kg

Total mass of water on the whole planet: 1.36 x10^{21} kg

**** Disclaimer: Water is recycled through artificial photosynthesis & combustion! Same with CO2.***

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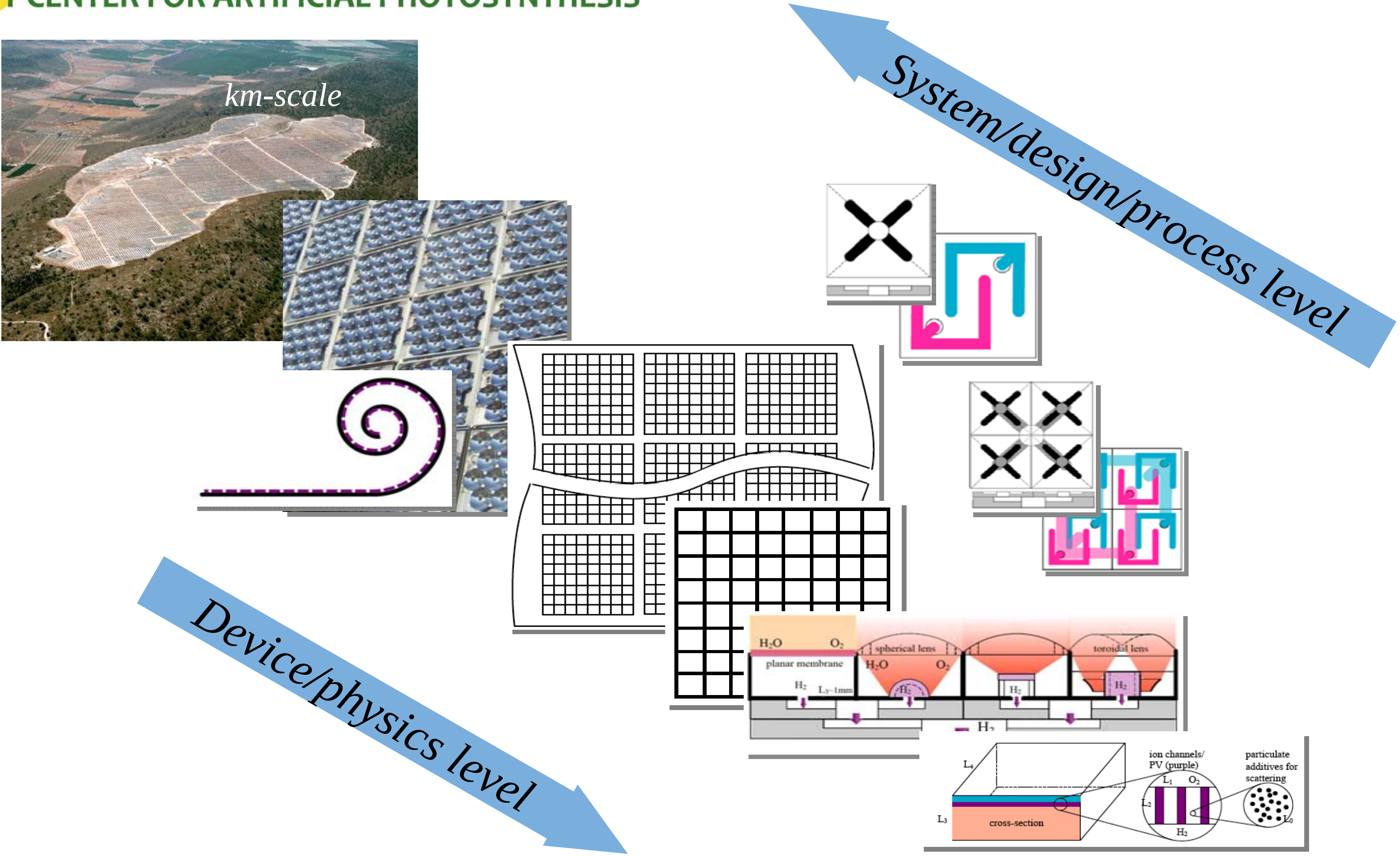
A Nanomanufacturing Challenge



System/design/process level

Device/physics level

Nanoscale to Macroscale

Gas Station of the Future

Thank You!