



GLOBAL CLIMATE AND ENERGY PROJECT | STANFORD UNIVERSITY



Energy Tutorial: Solar Energy 101

GCEP RESEARCH SYMPOSIUM 2010 | STANFORD, CA

Professor Nate Lewis

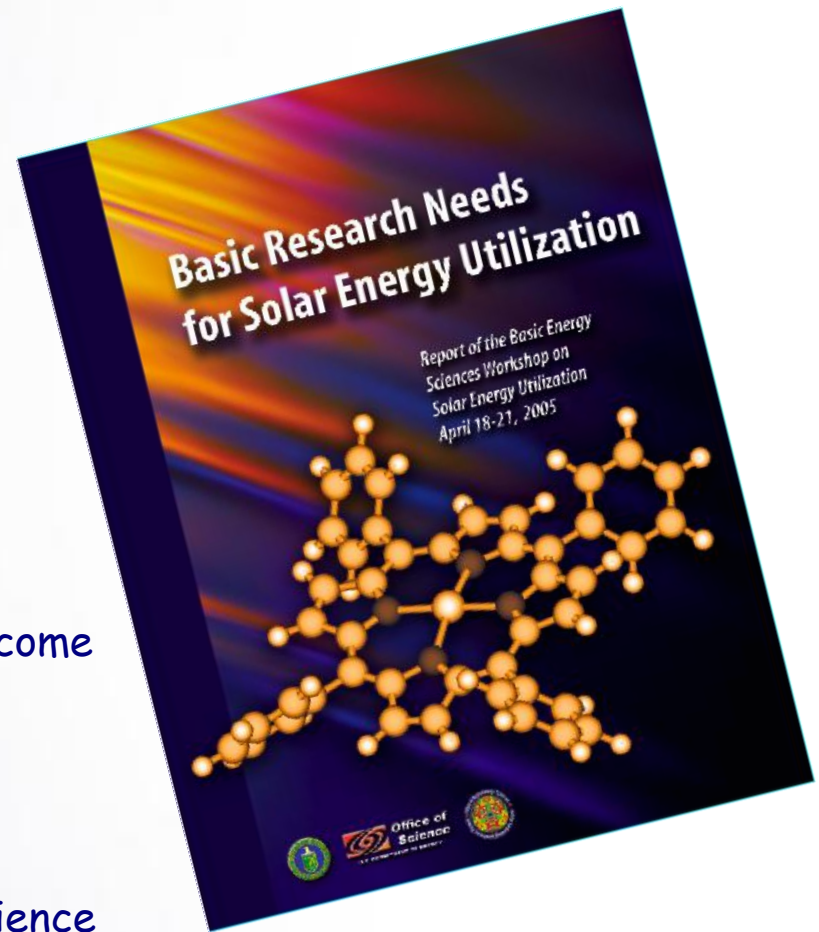
Chemistry Department, California Institute of Technology
GCEP Theme Leader – Solar Energy, Stanford University

SEPTEMBER 28, 2010

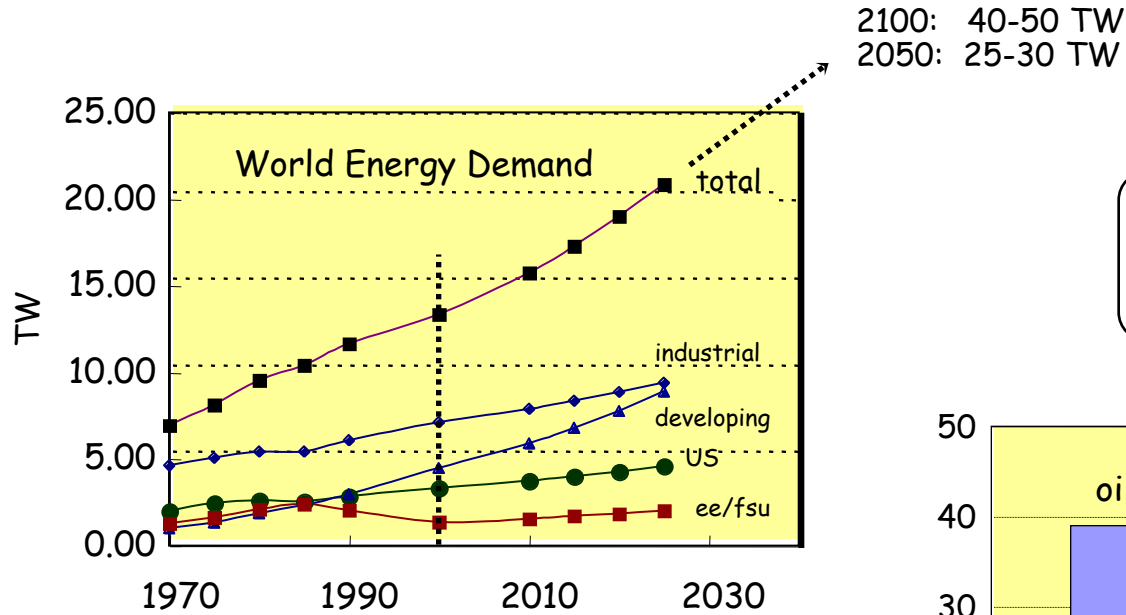
GLOBAL CHALLENGES – GLOBAL SOLUTIONS – GLOBAL OPPORTUNITIES

Basic Research Needs for Solar Energy

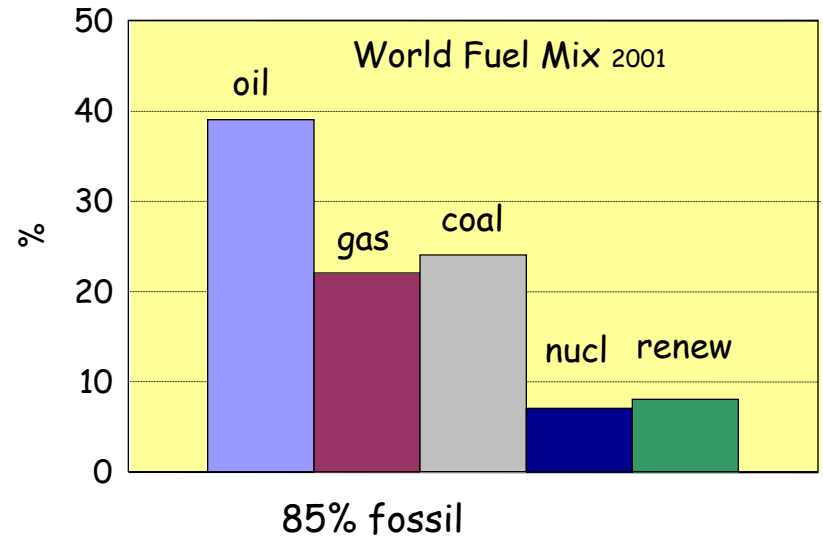
- ***The Sun is a singular solution to our future energy needs***
 - capacity dwarfs fossil, nuclear, wind . . .
 - sunlight delivers more energy in one hour than the earth uses in one year
 - free of greenhouse gases and pollutants
 - secure from geo-political constraints
- ***Enormous gap between our tiny use of solar energy and its immense potential***
 - Incremental advances in today's technology will not bridge the gap
 - Conceptual breakthroughs are needed that come only from high risk-high payoff basic research
- ***Interdisciplinary research is required***
physics, chemistry, biology, materials, nanoscience
- ***Basic and applied science should couple seamlessly***



World Energy Demand



energy gap
 ~ 14 TW by 2050
 ~ 33 TW by 2100



EIA Intl Energy Outlook 2004
<http://www.eia.doe.gov/oiaf/ieo/index.html>

Hoffert et al Nature 395, 883,1998

Renewable Energy

Solar

1.2×10^5 TW at Earth surface
600 TW practical

energy gap
~ 14 TW by 2050
~ 33 TW by 2100

Wind

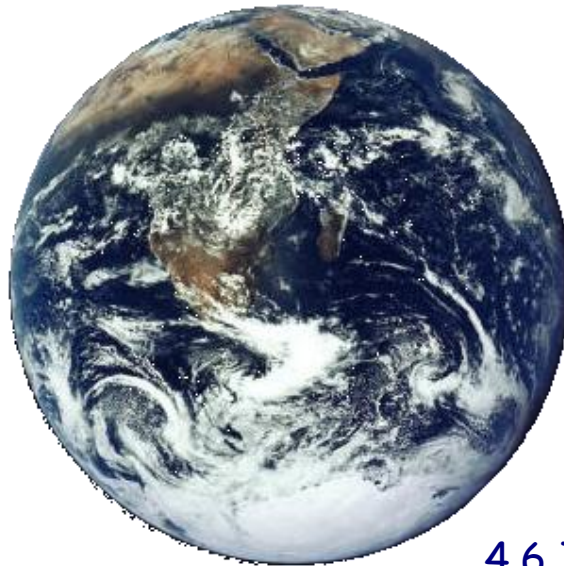
2-4 TW extractable

Tide/Ocean Currents

2 TW gross

Geothermal

12 TW gross over land
small fraction recoverable



Biomass

5-7 TW gross
all cultivatable
land not used
for food

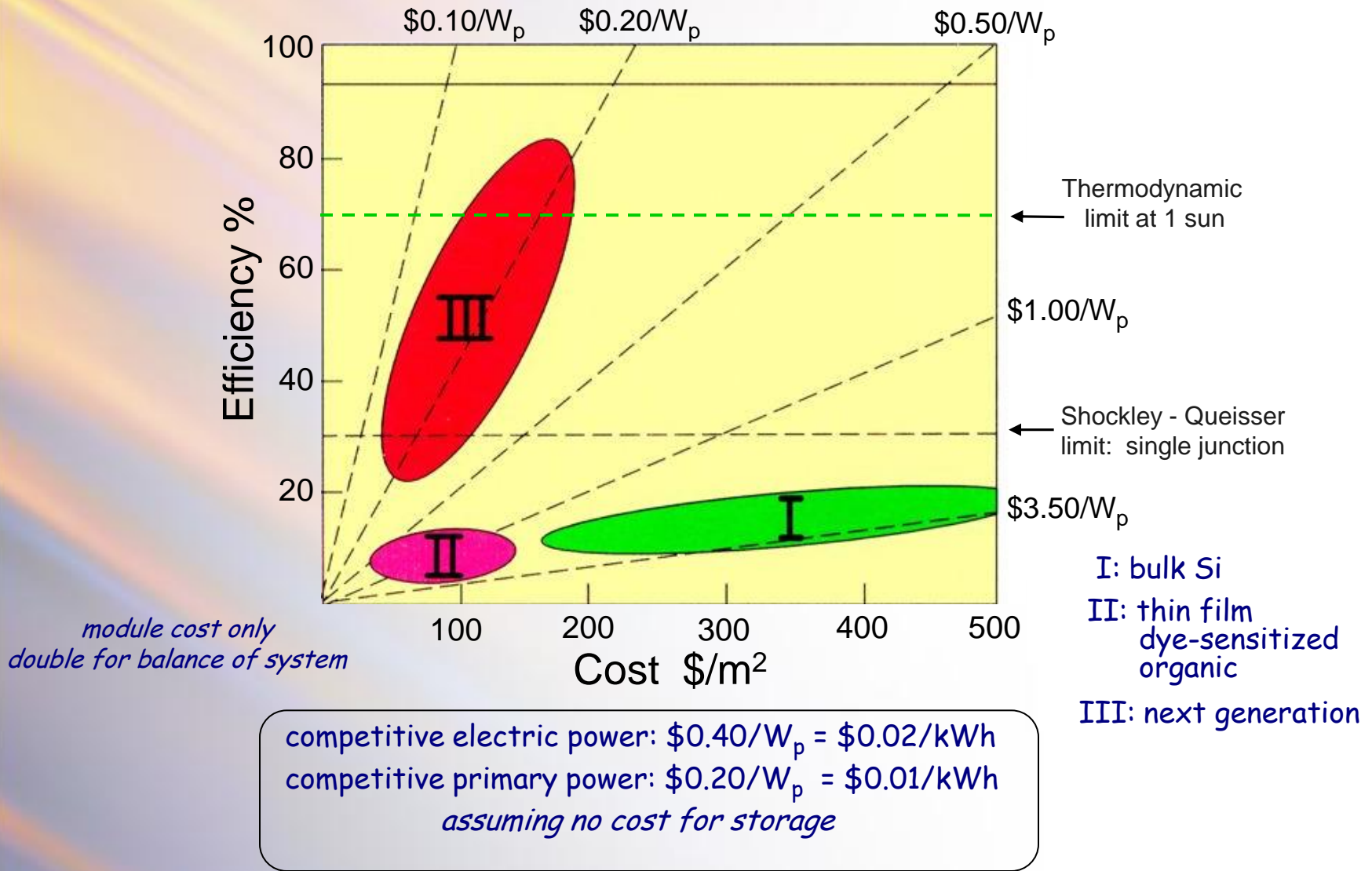
Hydroelectric

4.6 TW gross
1.6 TW technically feasible
0.9 TW economically feasible
0.6 TW installed capacity

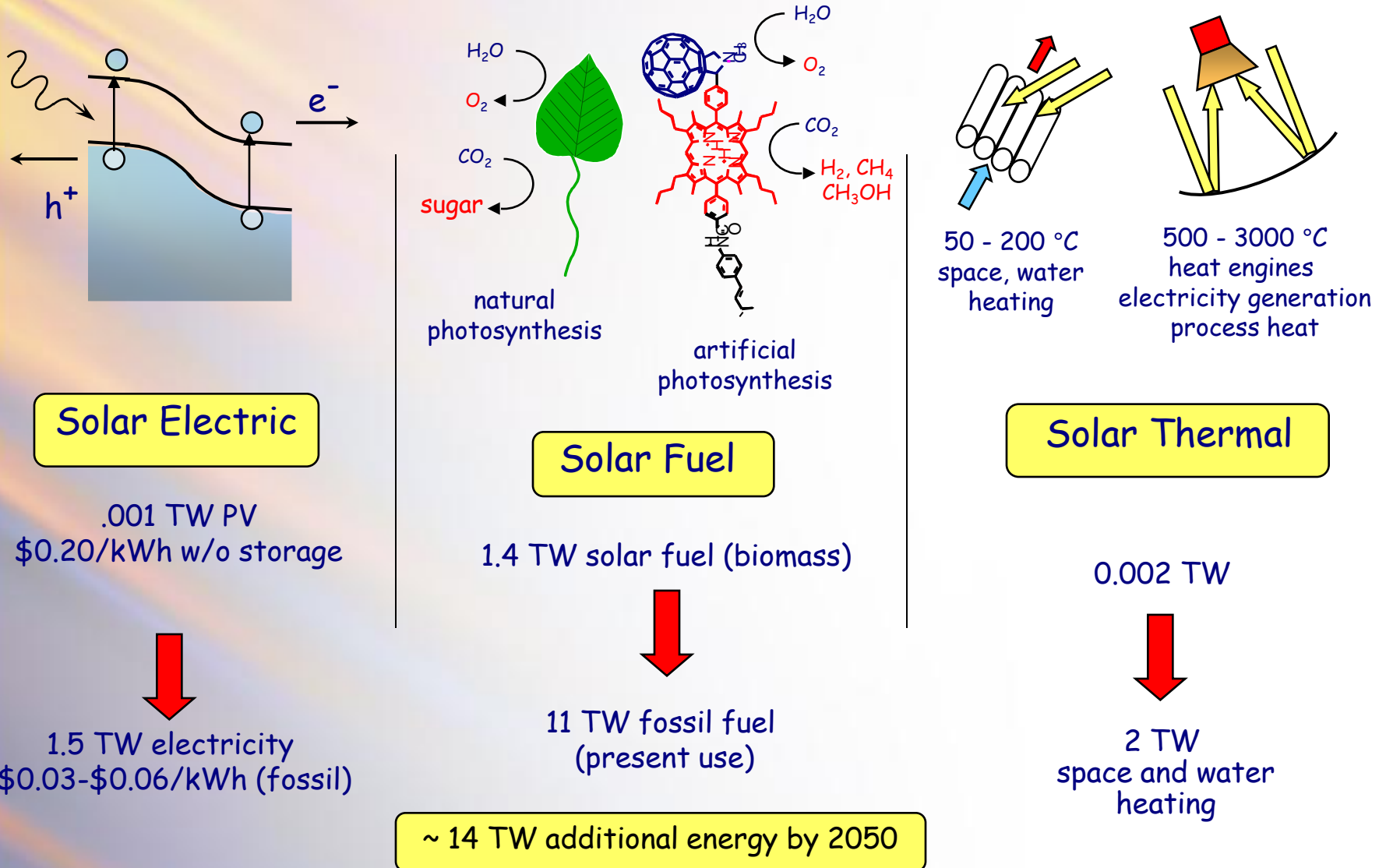
Solar Land Area Requirements



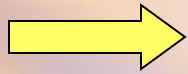
Cost of Solar Electric Power



Solar Energy Utilization



Solar Energy Challenges



Solar electric

Solar fuels

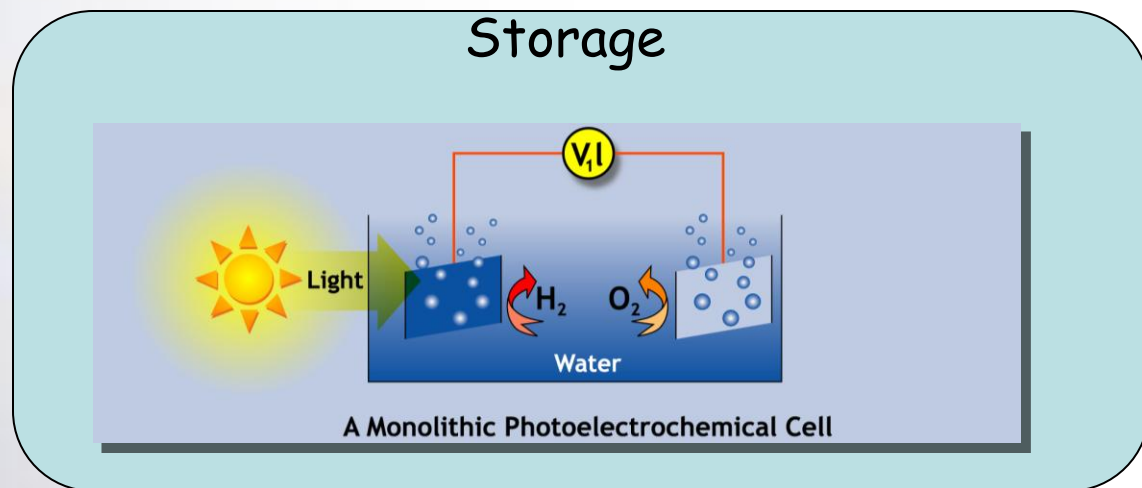
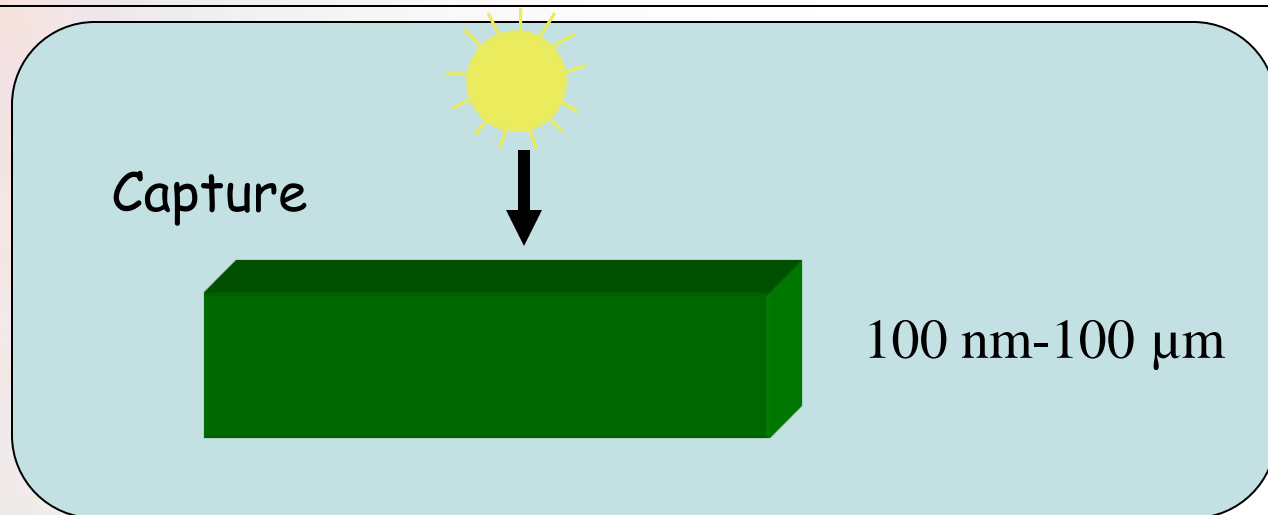
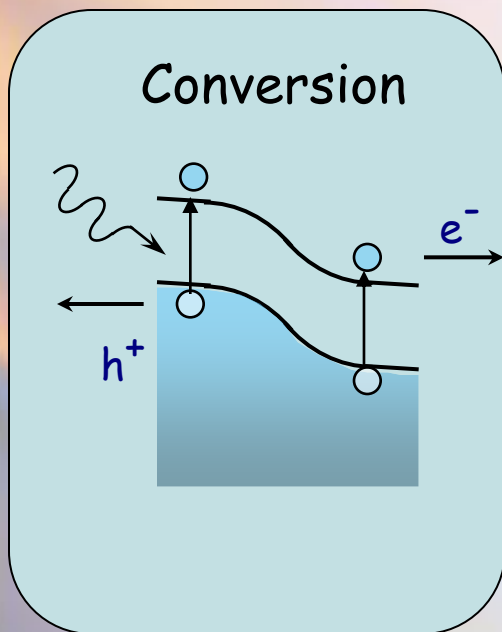
Solar thermal

Cross-cutting research

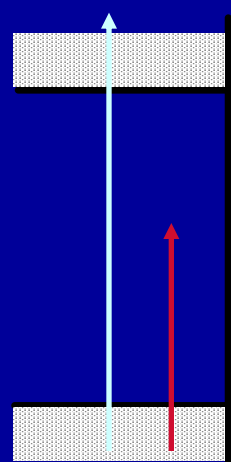
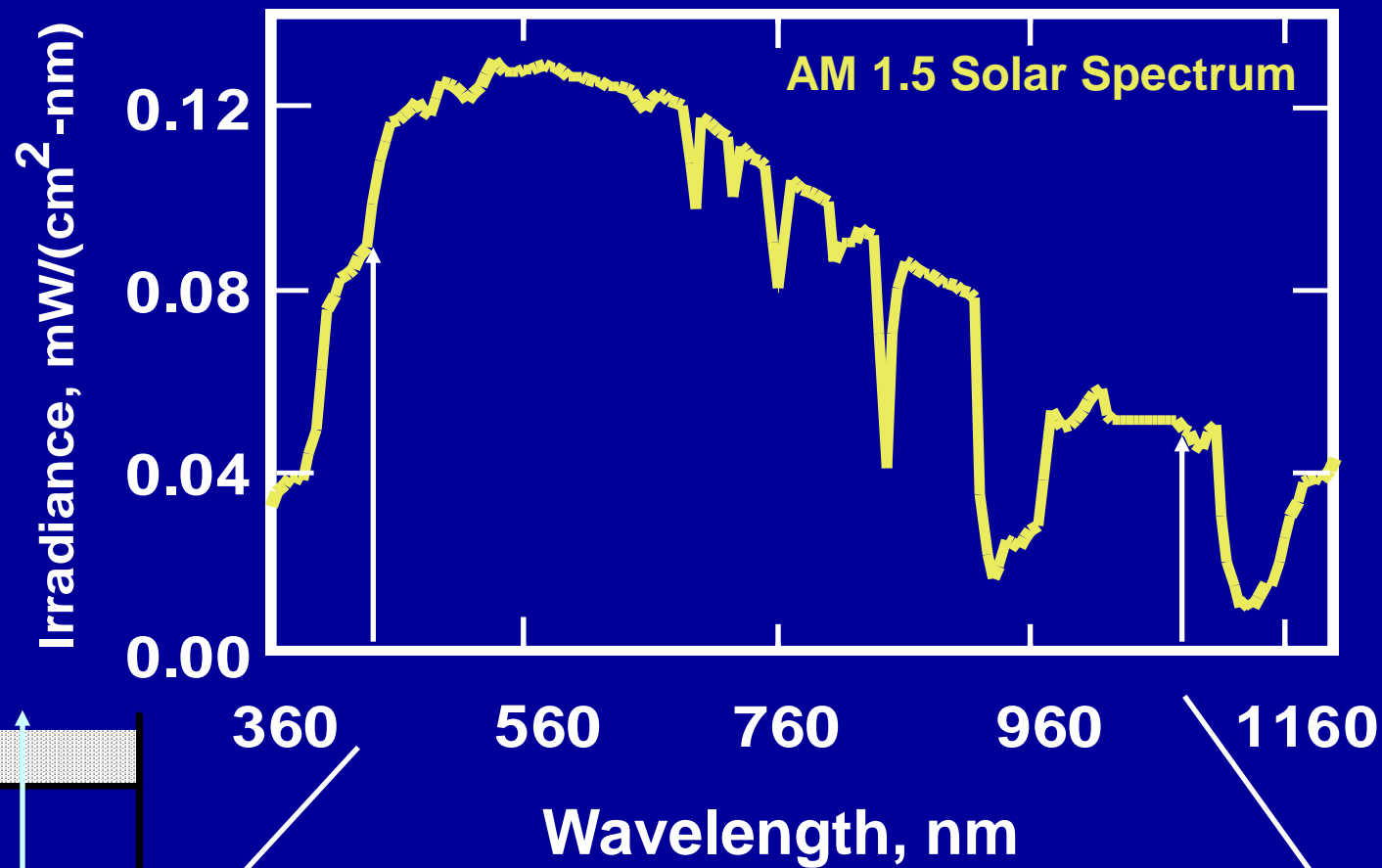
Solar Electric

- Despite 30-40% growth rate in installation, photovoltaics generate
 - less than 0.1% of our electricity*
 - less than 0.01% of total energy*
- Decrease *cost/watt* by a factor 10 - 25 to be competitive with fossil electricity (without storage)
- Find effective method for *storage* of photovoltaic-generated electricity

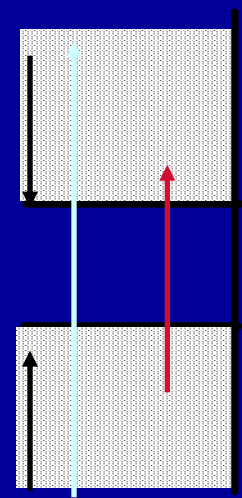
Solar Energy Conversion



Optimum Absorption Threshold

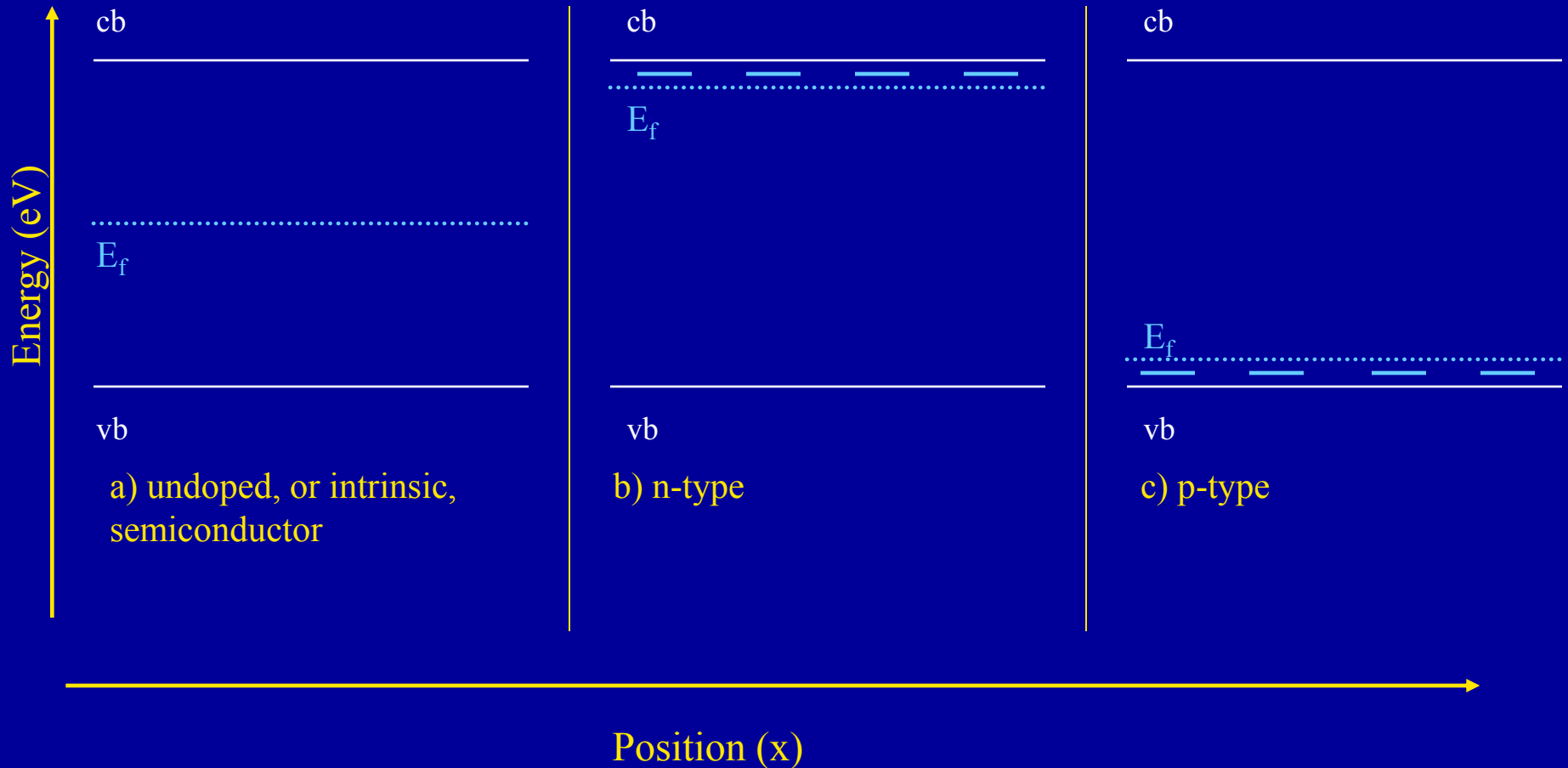


Too Large Band Gap

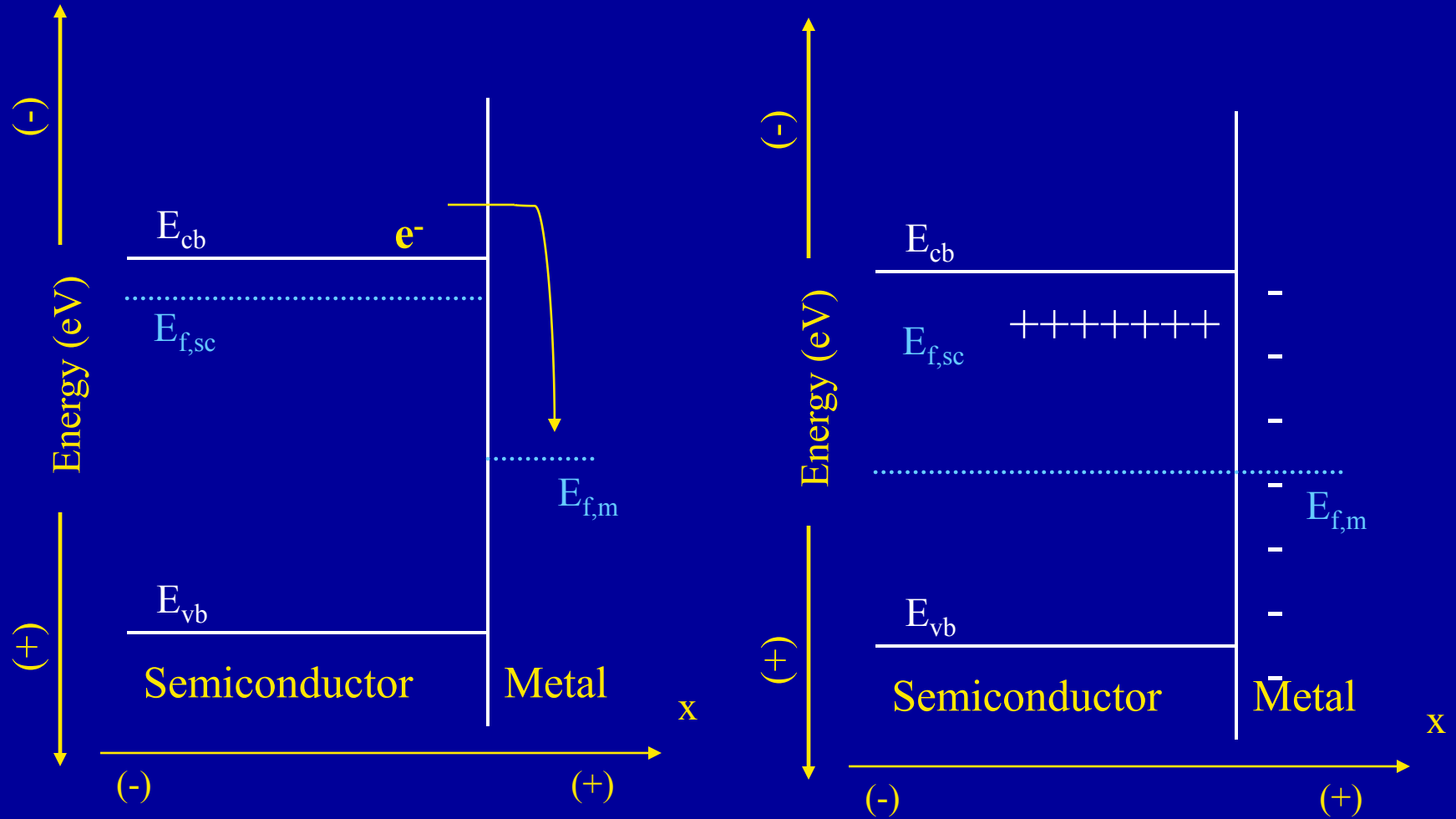


Too Small Band Gap

Semiconductor Doping

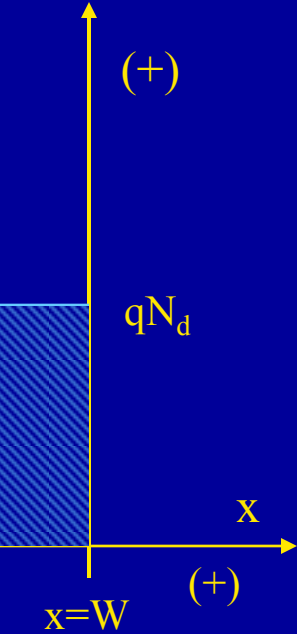


Band Bending at SC/Metal Junctions

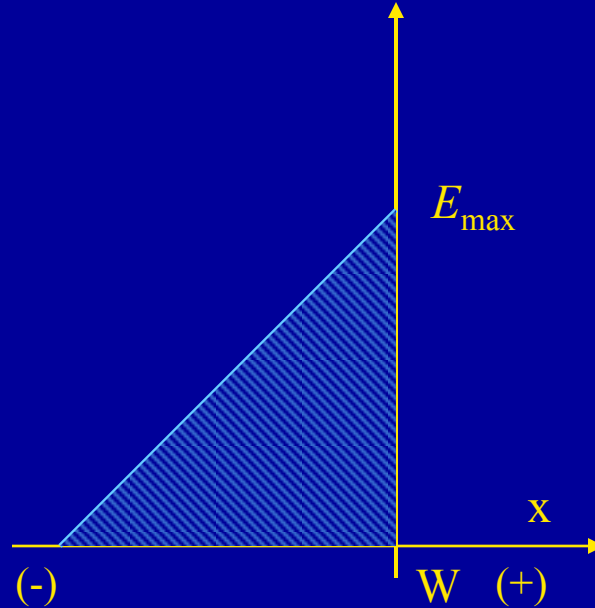


The Depletion Region

Charge
Density

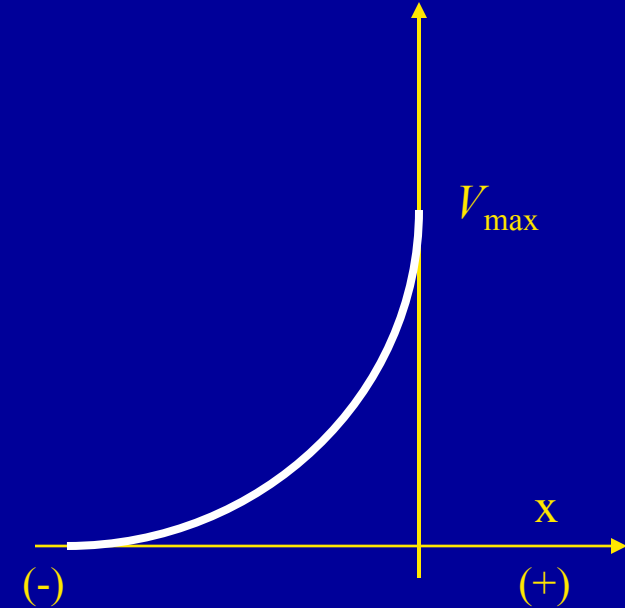


Electric Field
Strength



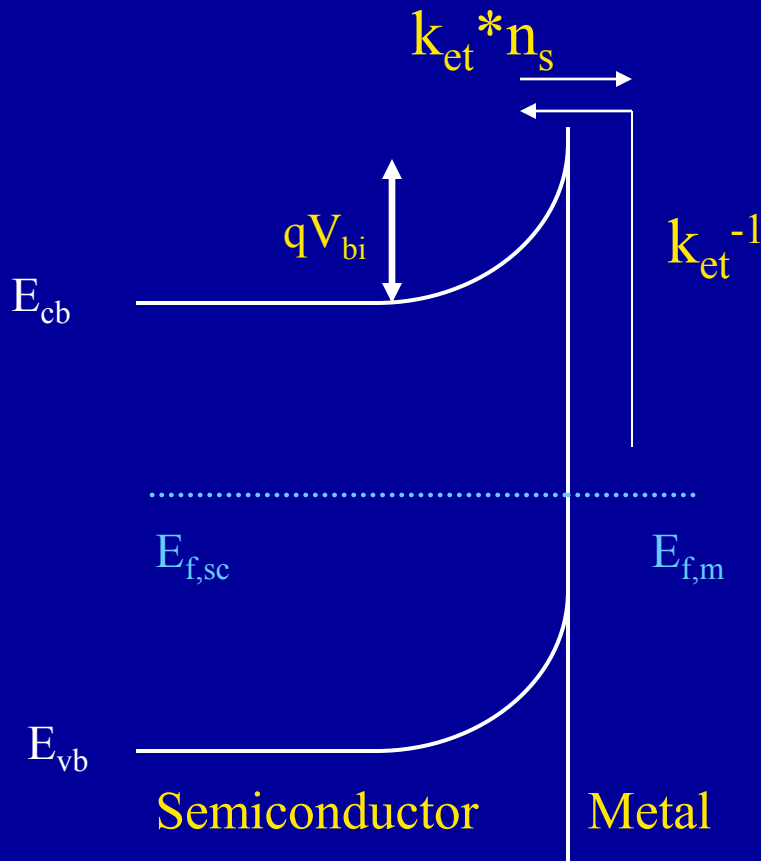
$$E_{\max} = \left(\frac{qN_d}{\epsilon_s} \right) W$$

Electric
Potential



$$|V_{\max}| = \left(\frac{qN_d}{2\epsilon_s} \right) W^2$$

Thermionic Emission



Thus, always

$$-dn/dt = k_{et} * n_s - k_{et}^{-1}$$

Rewrite it as:

$$-dn/dt = k_{et}(n_s - n_{so})$$

Now relate flux to current density:

$$J = -q(-dn/dt) = -q k_{et}(n_s - n_{so}) = -qk_e n_{so} (n_s/n_{so} - 1)$$

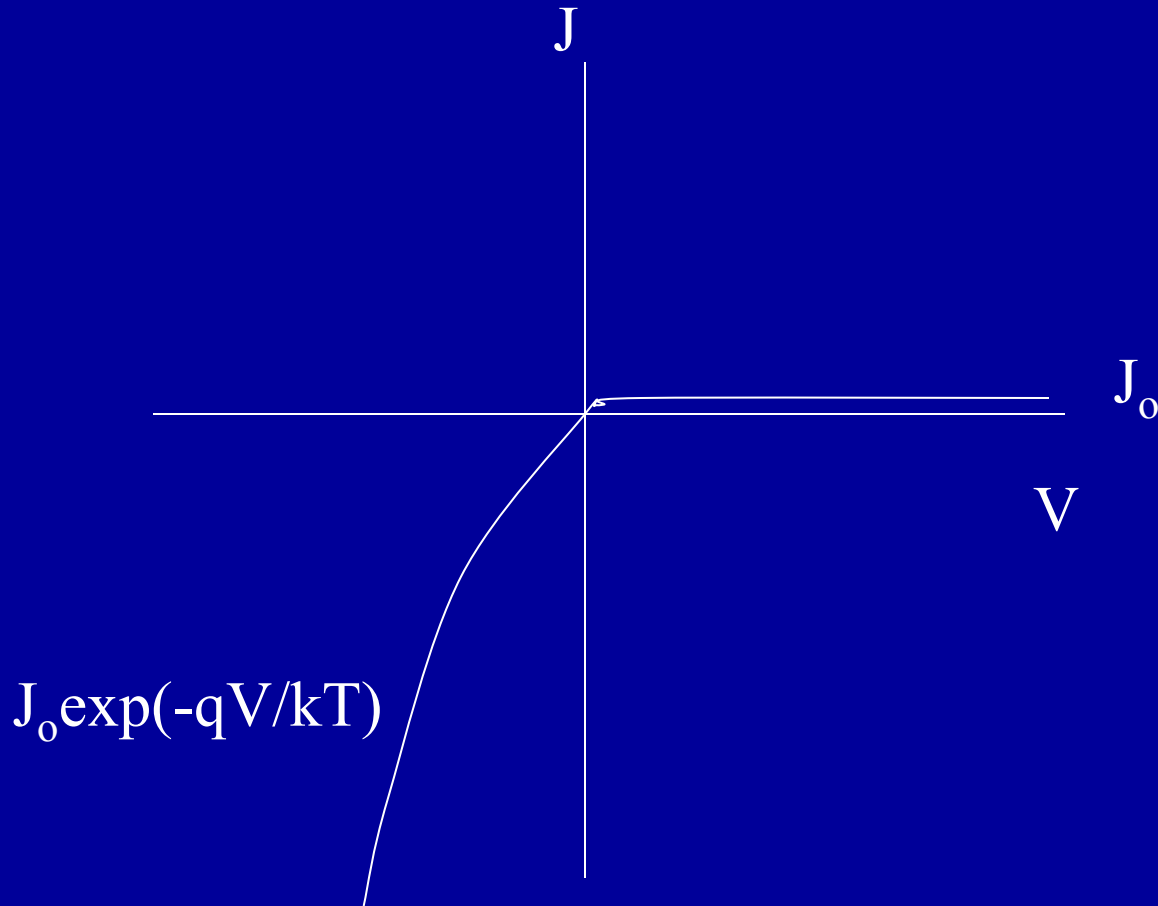
By substituting for n_s/n_{so} , we obtain:

$$J = -qk_{et}n_{so} \left[\exp\left(\frac{-qV}{kT}\right) - 1 \right] = -J_o \left[\exp\left(\frac{-qV}{kT}\right) - 1 \right]$$

The Dark Current

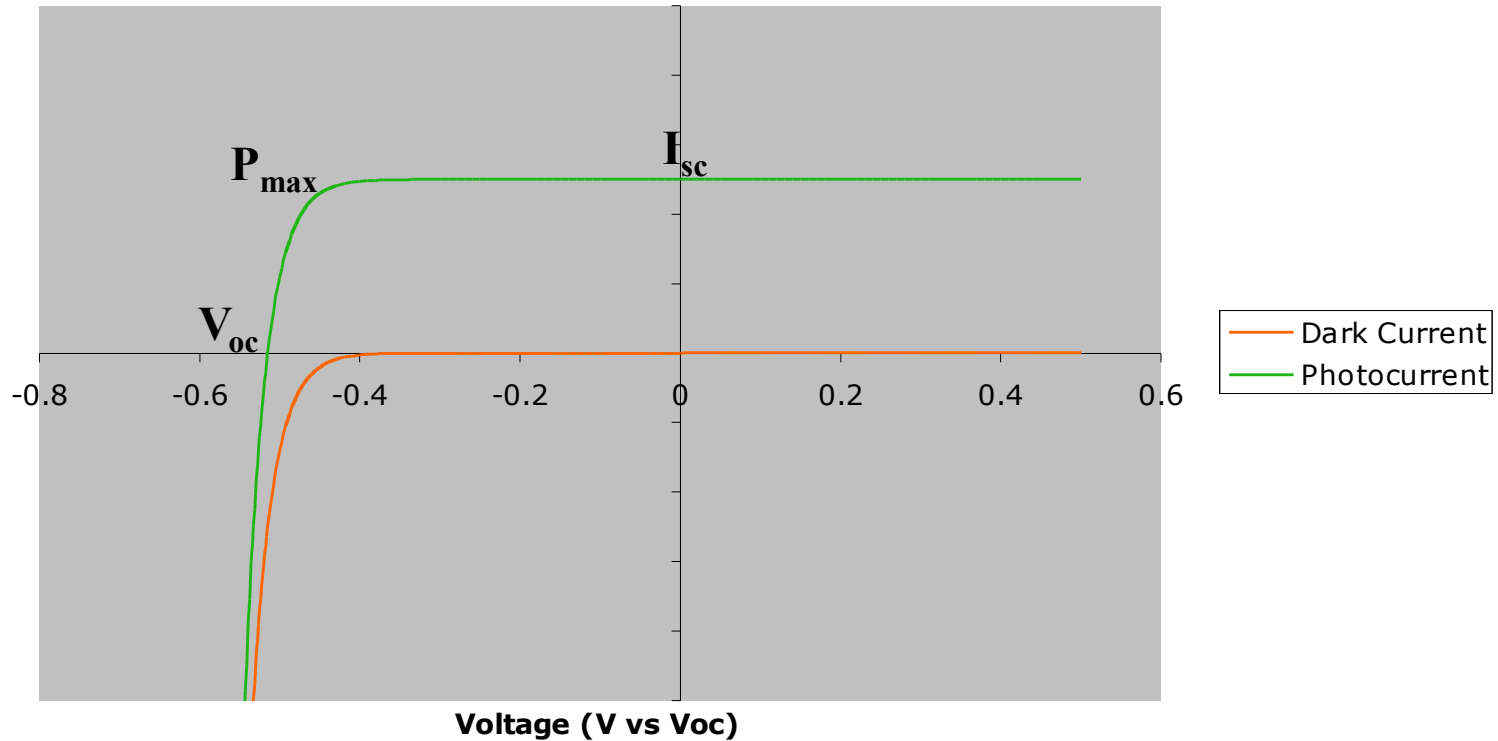
The current given by the equation:

$$J = -J_0 \left[\exp\left(\frac{-qV}{kT}\right) - 1 \right]$$



I-V Curves

Photovoltaic I-V Curve



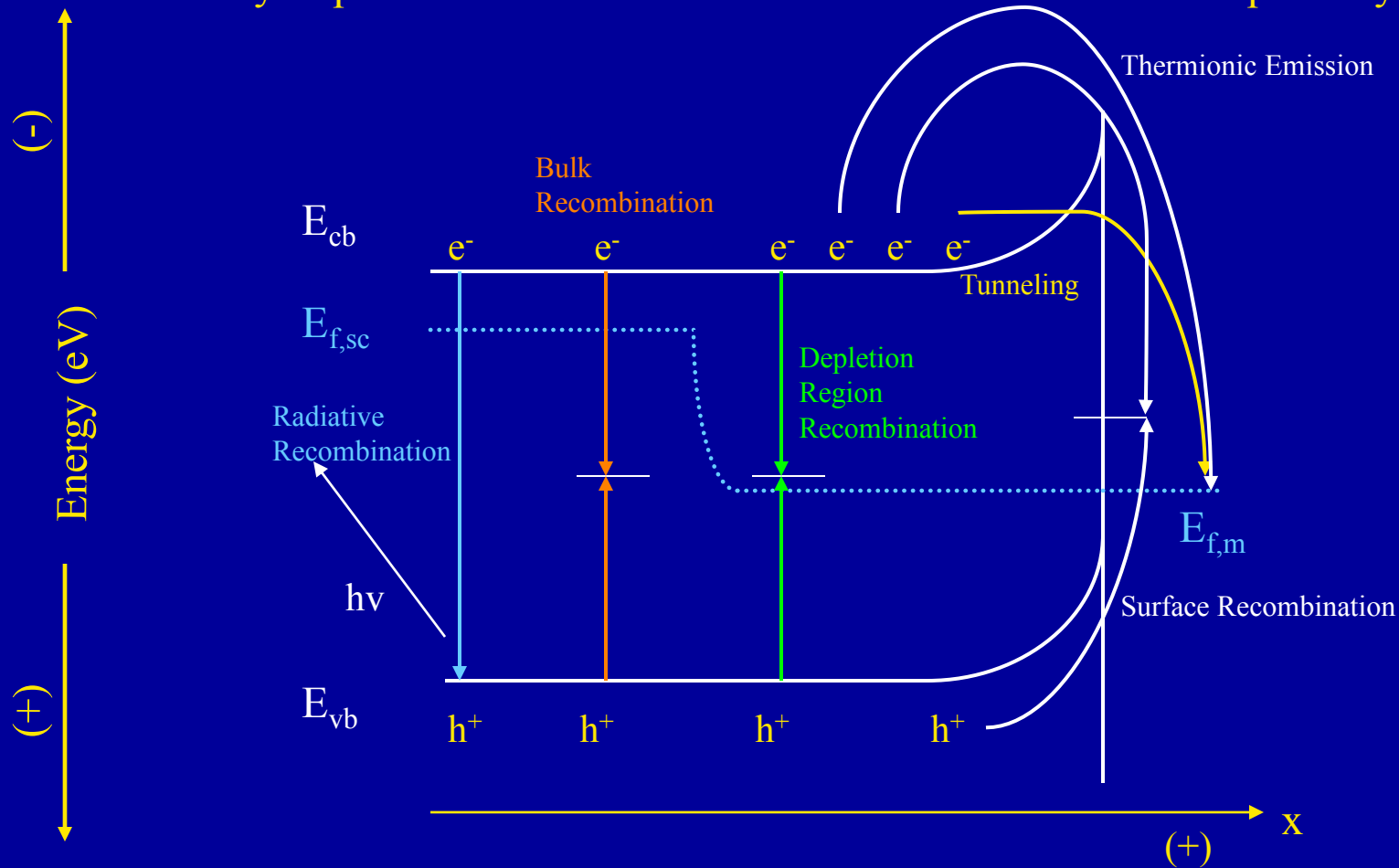
V_{oc} : Open circuit voltage, the voltage when no current flows. $J_{ph} = -J_0$

I_{sc} : Short circuit current, current where $V = 0$

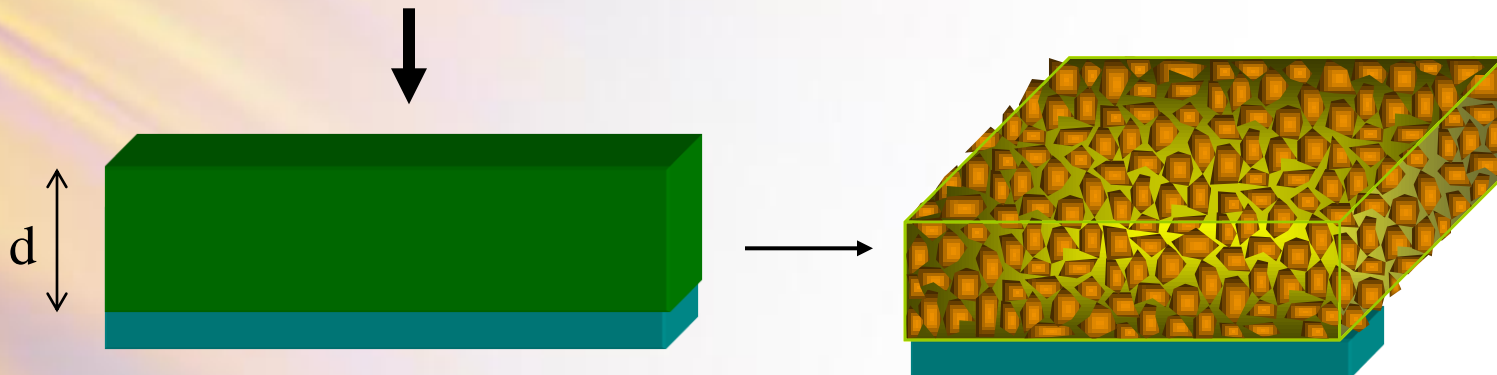
P_{max} : Maximum power point, greatest value of $I * V$

Carrier Recombination

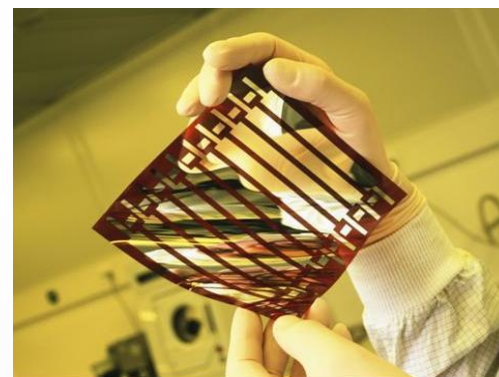
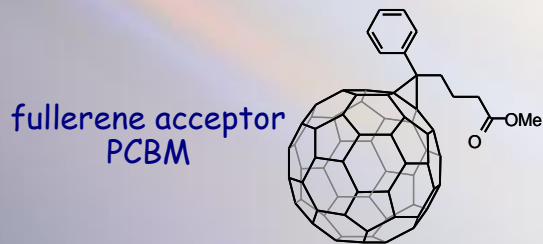
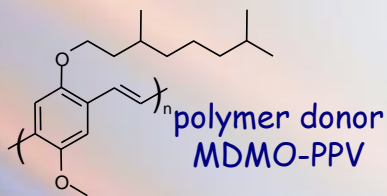
In an ideal system, electrons and holes will only recombine at the back face of the semiconductor after they have performed work. In a real system, alternative pathways for recombination will shorten the effective carrier lifetime of the sample and lower the efficiency of photovoltaic devices. The dominant recombination pathways are:



“Solar Paint”

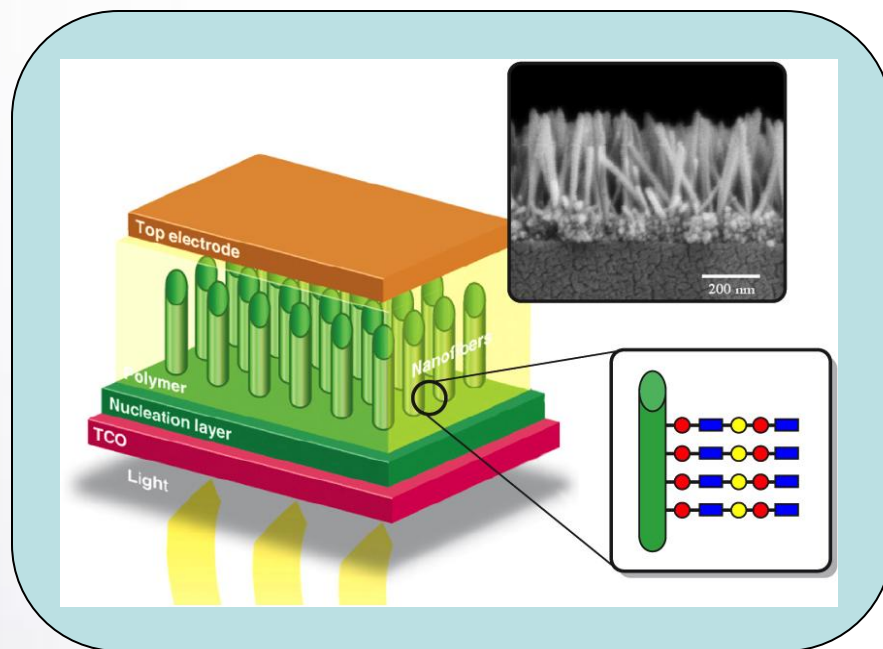
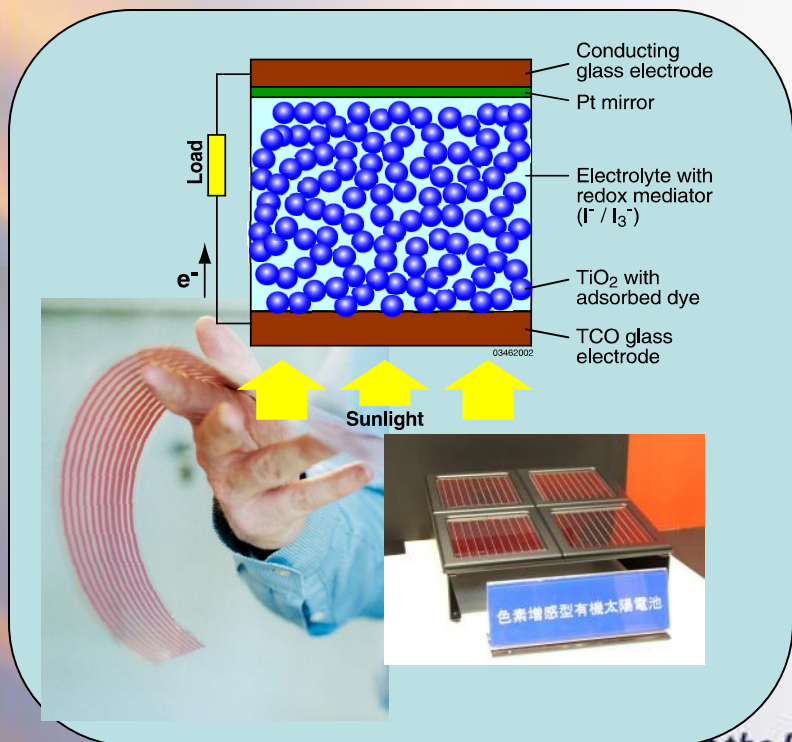
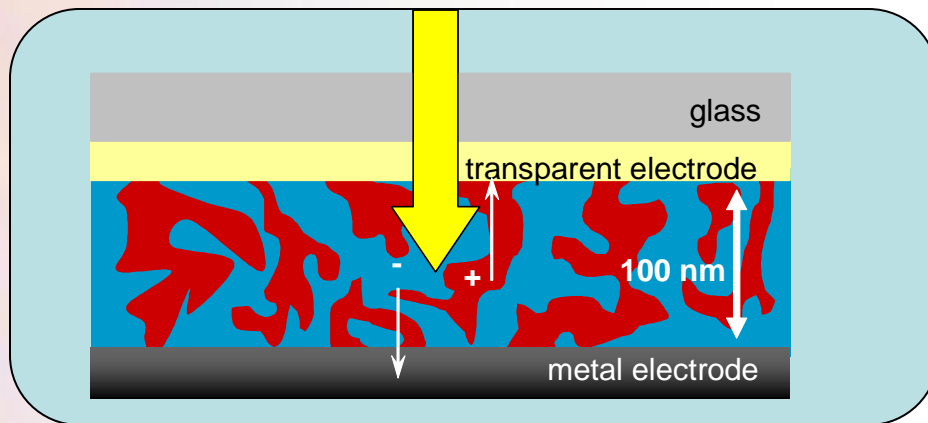


“Fooling” inexpensive particles into behaving as single crystals



inexpensive processing, conformal layers

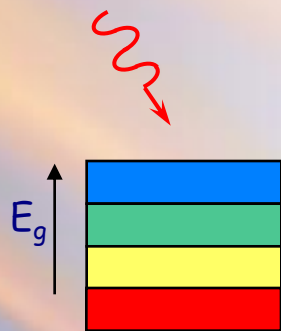
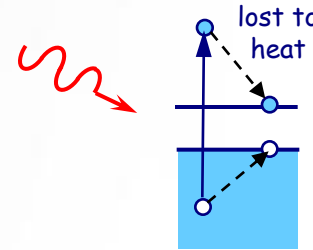
Interpenetrating Nanostructured Networks



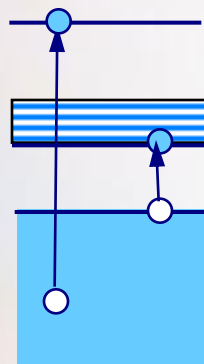
Revolutionary Photovoltaics: 50% Efficient Solar Cells

present technology: 32% limit for

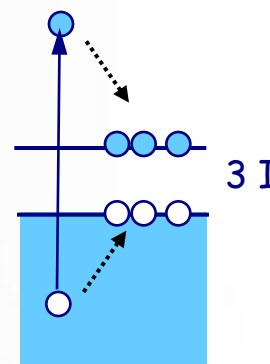
- single junction
- one exciton per photon
- relaxation to band edge



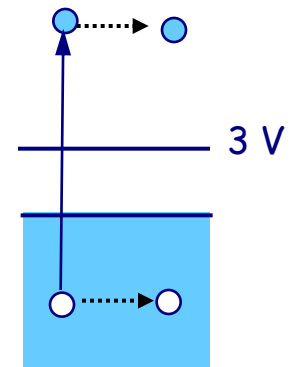
multiple junctions



multiple gaps



multiple excitons
per photon

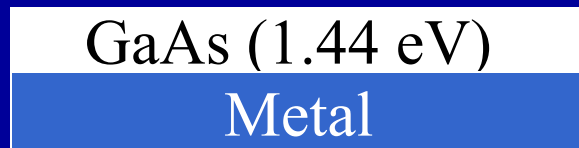


hot carriers

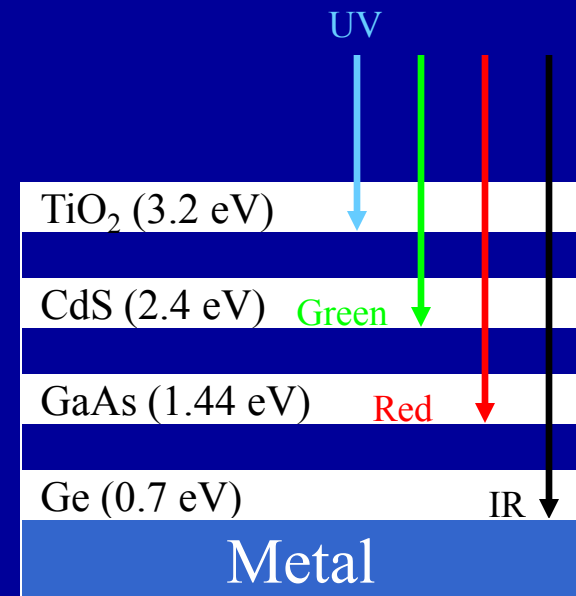
rich variety of new physical phenomena
understand and implement

Concentrator vs. Flat Plate Arrays

Why not stack several semiconductors to get better energy conversion? A large band gap semiconductor can get higher voltage out of the more energetic photons, then smaller band gap semiconductors underneath can extract additional energy from the remaining photons.

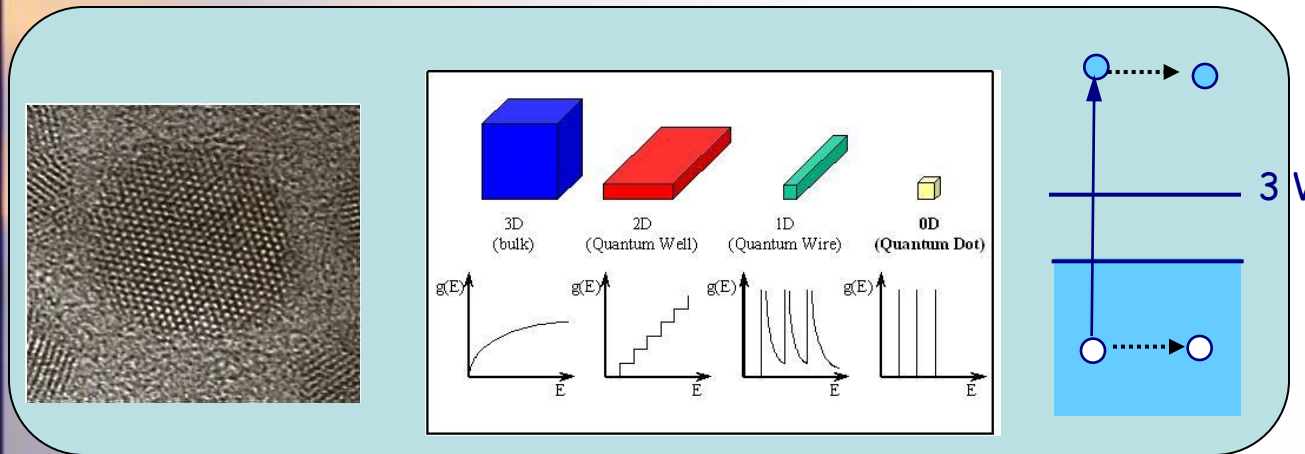
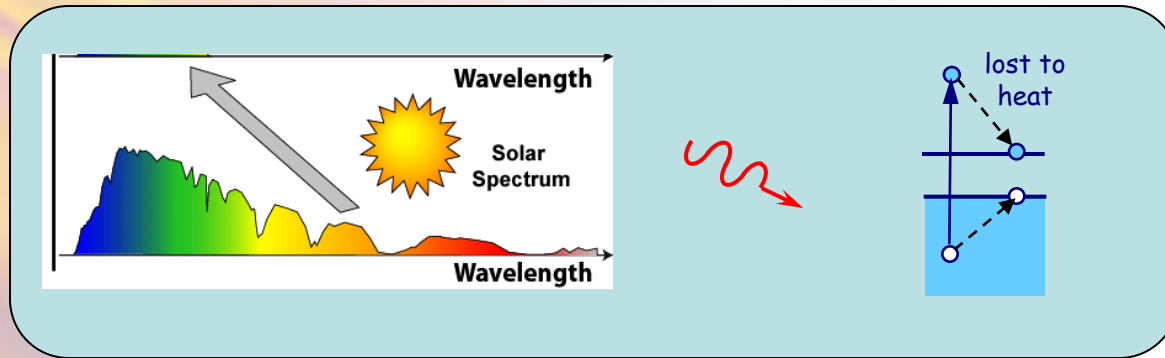


Flat Plate Array

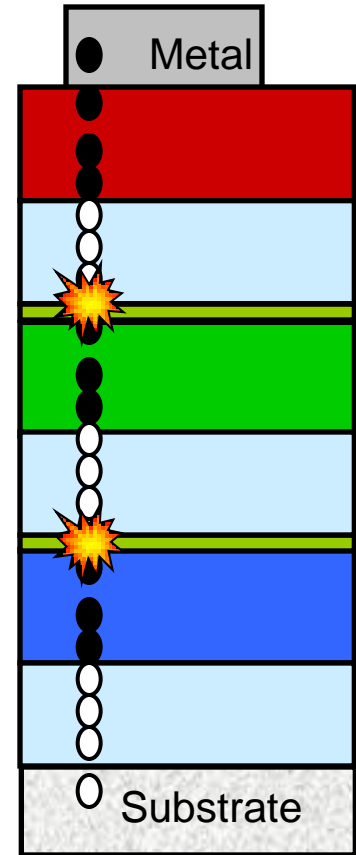


Concentrator Array

Ultra-high Efficiency Solar Cells

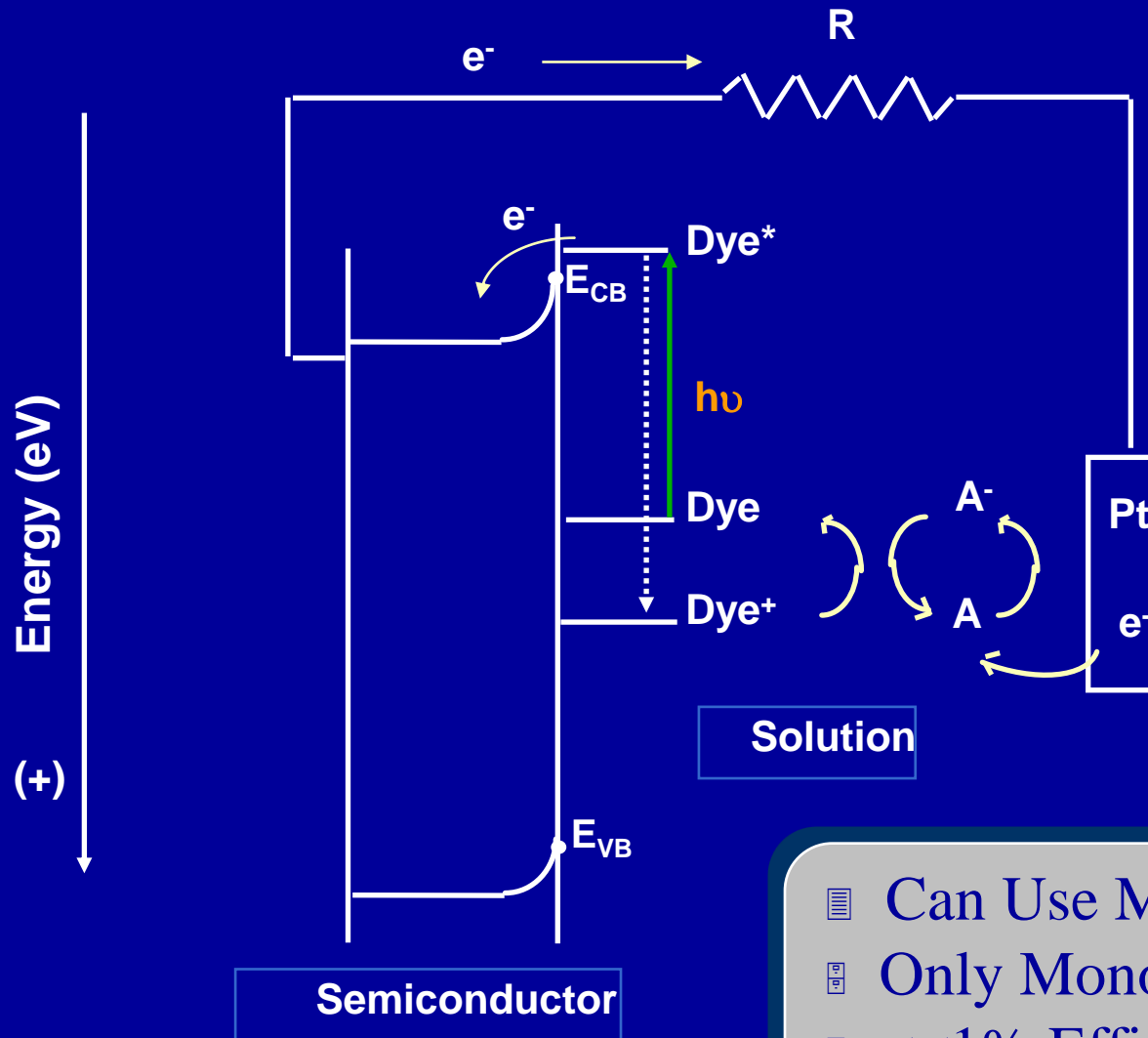


rich variety of new physical phenomena
understand and implement



multiple junctions

Dye Sensitization

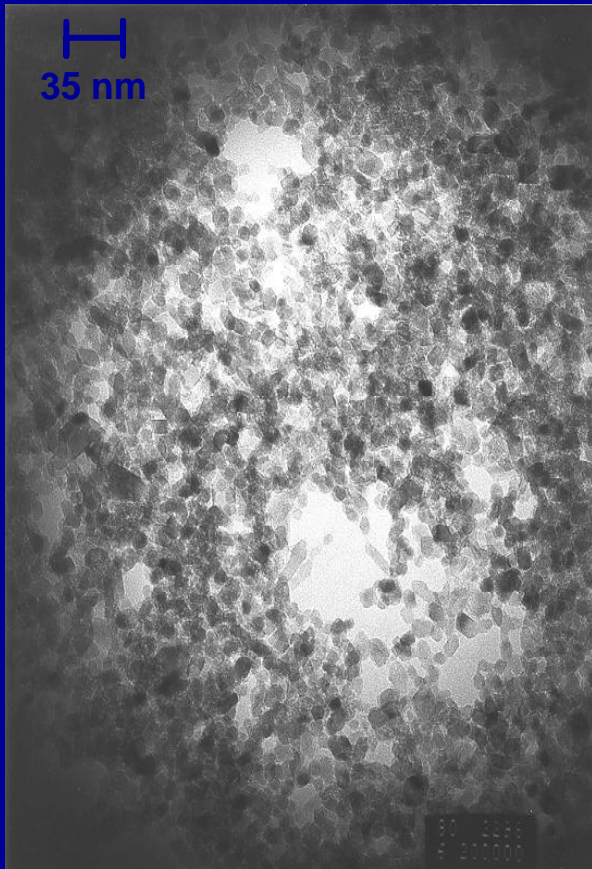


- ☰ Can Use Metal Oxides
- ☰ Only Monolayer of Dye
- ☰ <<1% Efficiency

Semiconductor Photoelectrochemistry



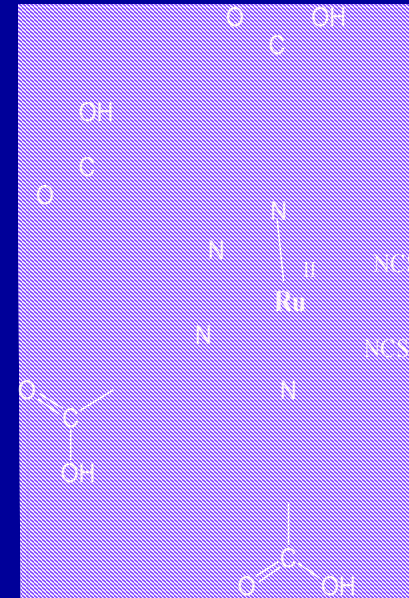
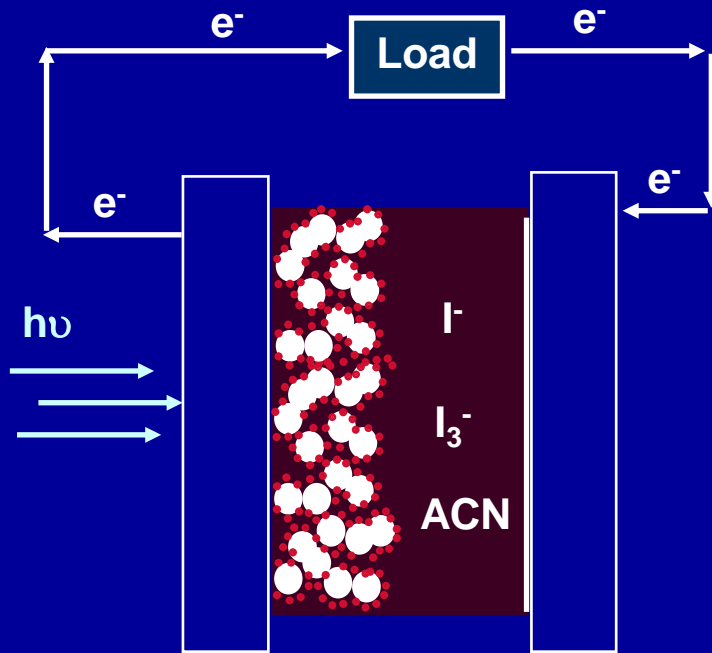
Nanocrystalline Titanium Dioxide



- Particle Size $\sim 15\text{nm}$
- Surface Area
*is larger than single crystal
 ~ 1000 times*
- No Quantum Size Effects
(large electron effective mass)
- Different Electrochemistry
from single crystal semiconductors

TEM of nanostructured TiO_2

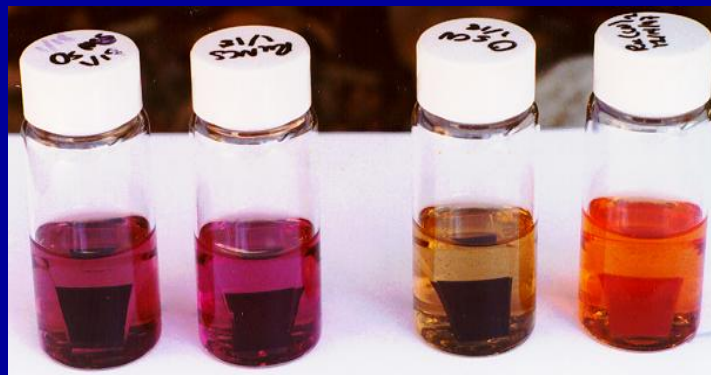
Dye Sensitized Solar Cells



$RuL'_2(NCS)_2$

- 8-10% Efficient
- >15% Efficiency Possible
- Stability

Dye-Coated TiO₂ Electrodes



$\text{OsL}'_2(\text{NCS})_2$ $\text{RuL}'_2(\text{NCS})_2$ $\text{OsL}'_2(\text{CN})_2$ $\text{RuL}'_2(\text{CN})_2$

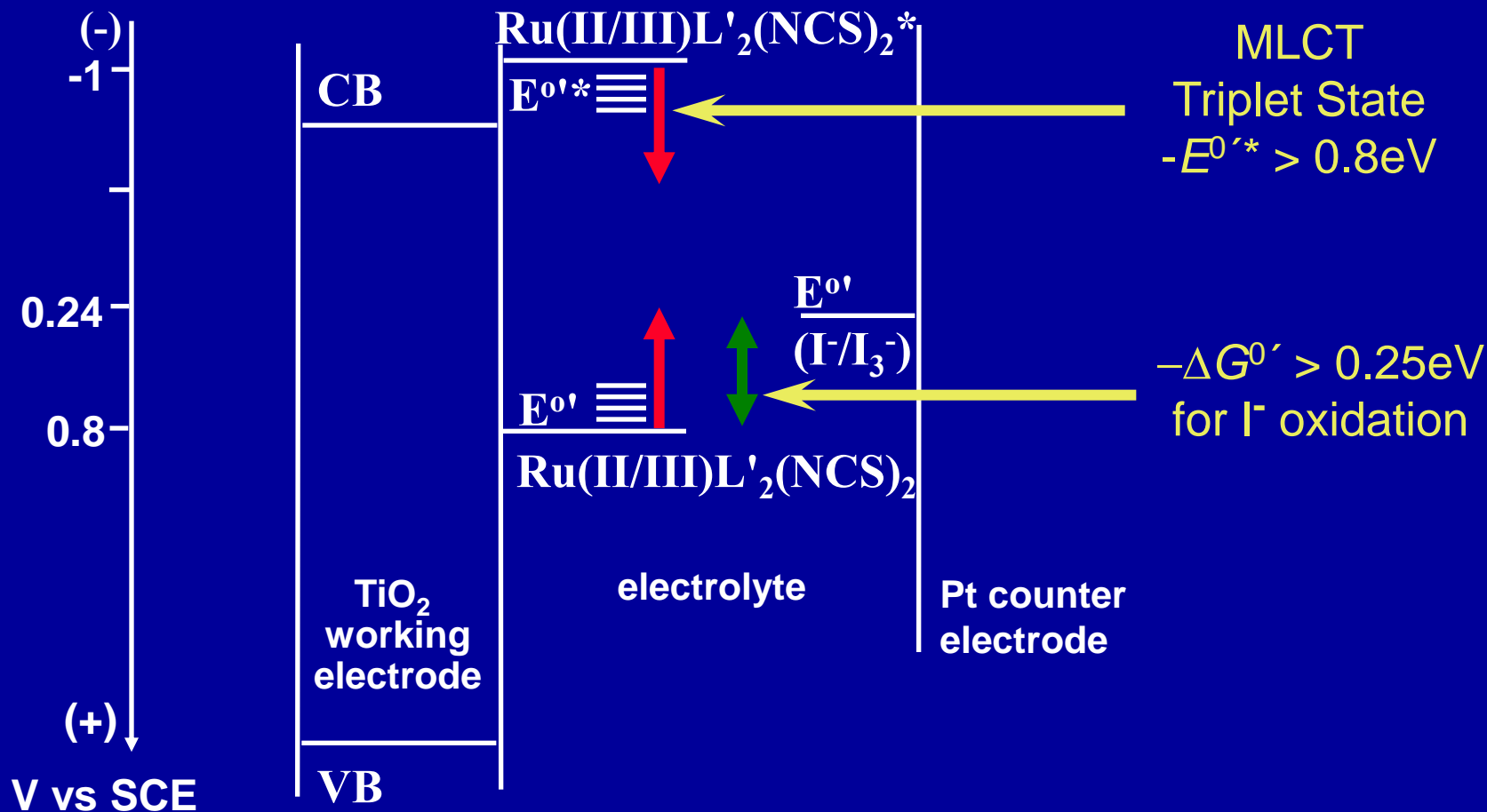


$\text{OsL}_2\text{L}'$ $\text{RuL}_2\text{L}'$ OsL'_3 RuL'_3

TiO₂ coated on conducting glass (INAP), deposited TiCl₄ overnight, heated 450 °C for 30 min, cooled to 120 °C, immersed in ethanolic dye solution for 15-24 h

Energetics of Sensitized TiO₂ Solar Cell

To red-shift the absorption spectra, require:
More positive excited state potential, or more negative ground state potential



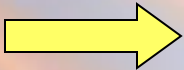
Solar Energy Challenges

Solar electric

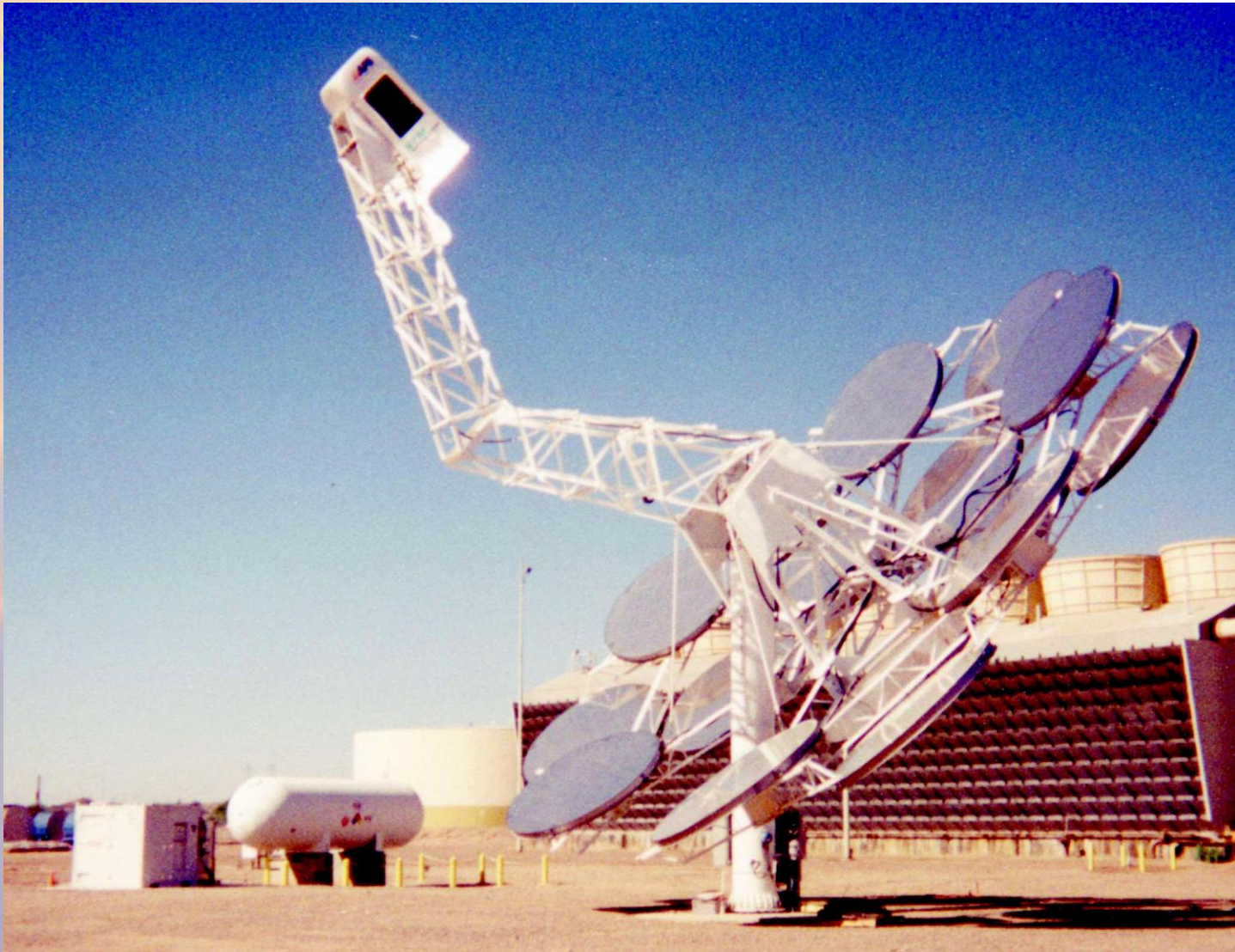
Solar fuels

Solar thermal

Cross-cutting research

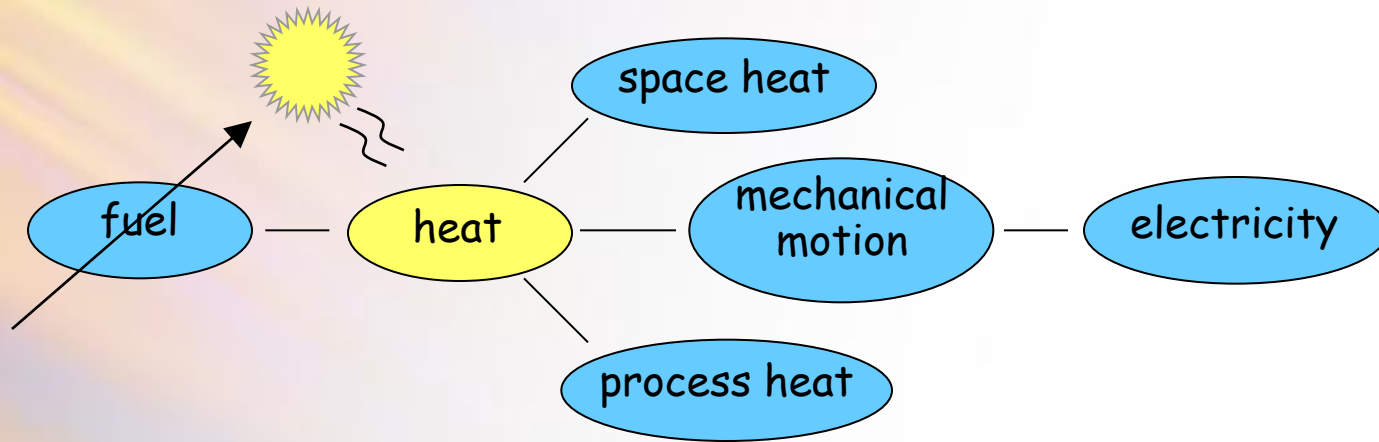


Solar Thermal + Electrolyzer System



Report of the Basic Energy Sciences Workshop on Solar Energy Utilization

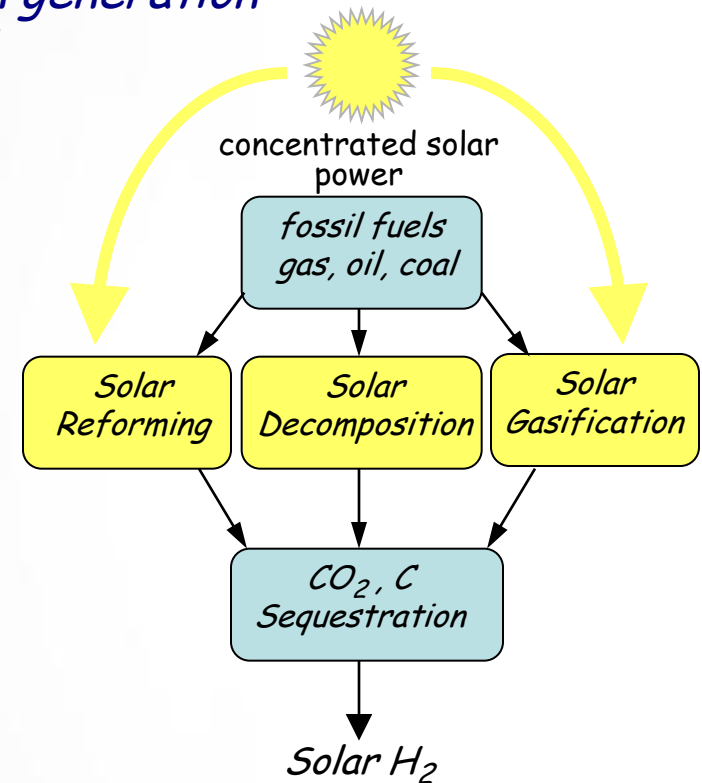
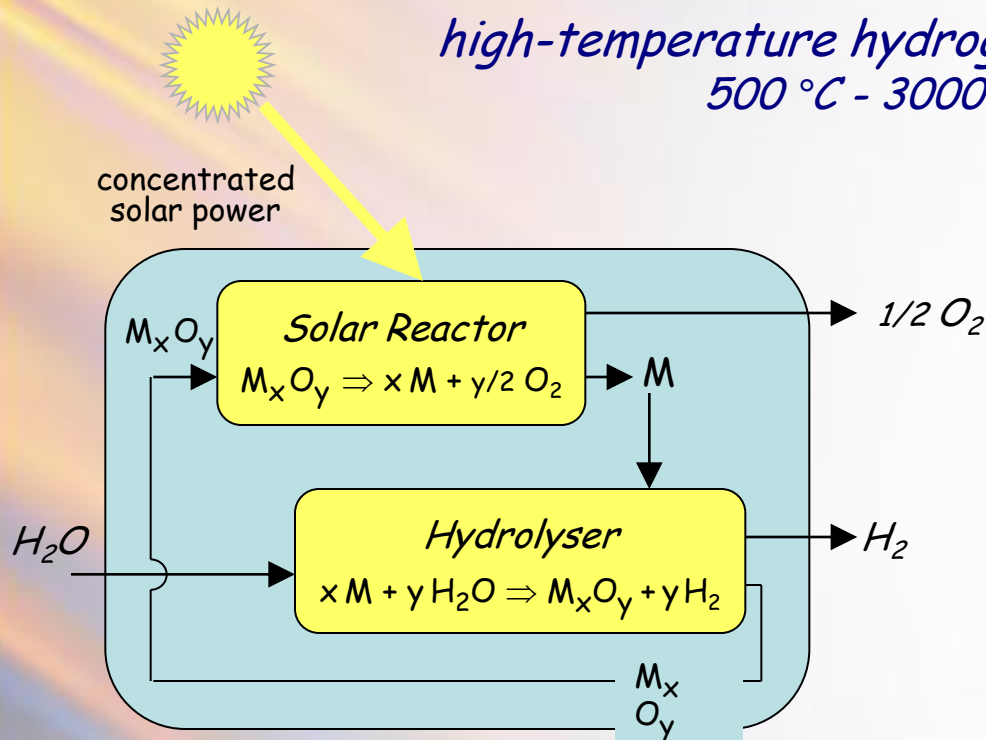
Solar Thermal



- heat is the first link in our existing energy networks
- solar heat replaces combustion heat from fossil fuels
- solar steam turbines currently produce the lowest cost solar electricity
- challenges:
 - new uses for solar heat
 - store solar heat for later distribution

Solar Thermochemical Fuel Production

high-temperature hydrogen generation
500 °C - 3000 °C

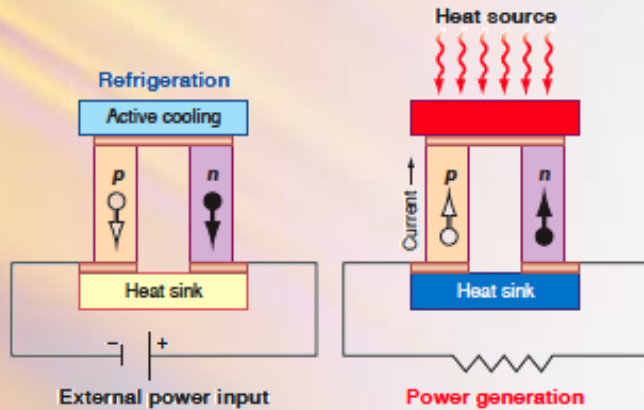


Scientific Challenges

- high temperature reaction kinetics of
 - metal oxide decomposition
 - fossil fuel chemistry

robust chemical reactor designs and materials

Thermoelectric Conversion



thermal gradient \leftrightarrow electricity

figure of merit: $ZT \sim (\sigma/\kappa) T$

$ZT \sim 3$: efficiency \sim heat engines
no moving parts

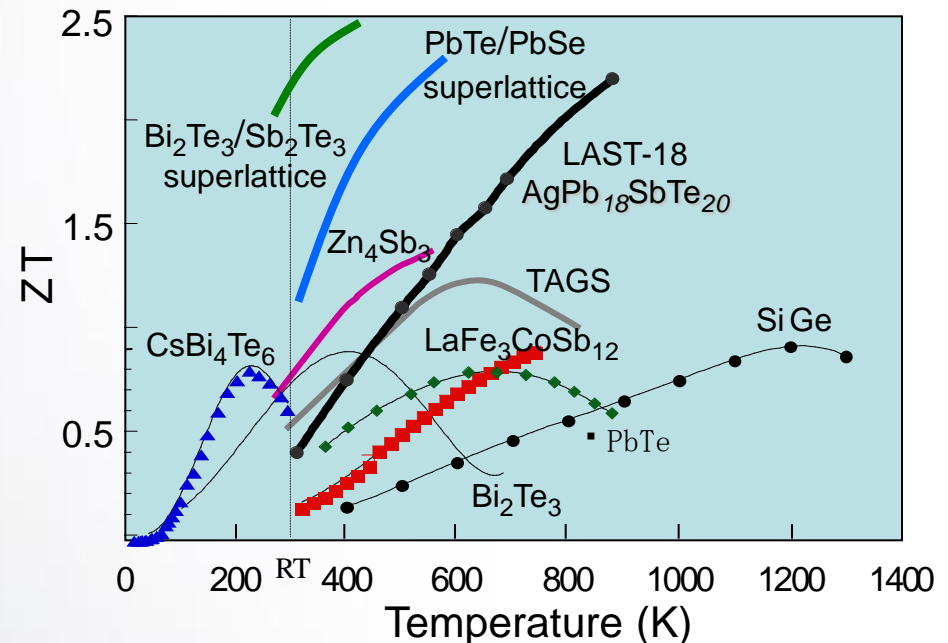
Scientific Challenges

increase electrical conductivity
decrease thermal conductivity



nanowire superlattice

nanoscale architectures
interfaces block heat transport
confinement tunes density of states
doping adjusts Fermi level



Solar Energy Challenges

Solar electric

 **Solar fuels**

Solar thermal

Cross-cutting research

Leveraging Photosynthesis for Efficient Energy Production

- photosynthesis converts ~ 100 TW of sunlight to sugars: nature's fuel
- low efficiency (< 1%) requires too much land area



switchgrass

Modify the biochemistry of plants and bacteria

- improve efficiency by a factor of 5-10
- produce a convenient fuel
methanol, ethanol, H₂, CH₄



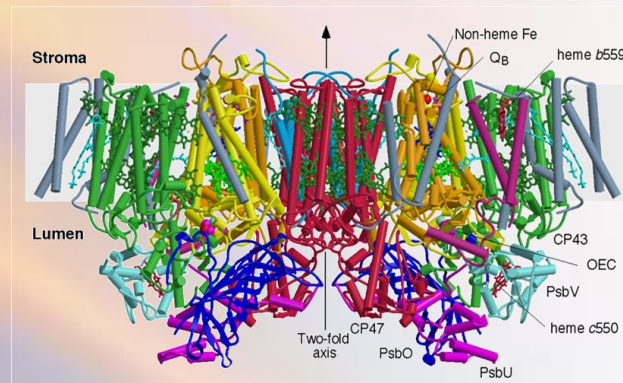
hydrogenase
 $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$

Scientific Challenges

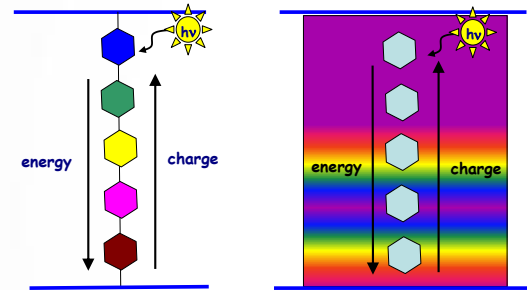
- understand and modify genetically controlled biochemistry that limits growth
- elucidate plant cell wall structure and its efficient conversion to ethanol or other fuels
- capture high efficiency early steps of photosynthesis to produce fuels like ethanol and H₂
- modify bacteria to more efficiently produce fuels
- improved catalysts for biofuels production

Smart Matrices for Solar Fuel Production

- Biology: protein structures dynamically control energy and charge flow
- Smart matrices: adapt biological paradigm to artificial systems



photosystem II

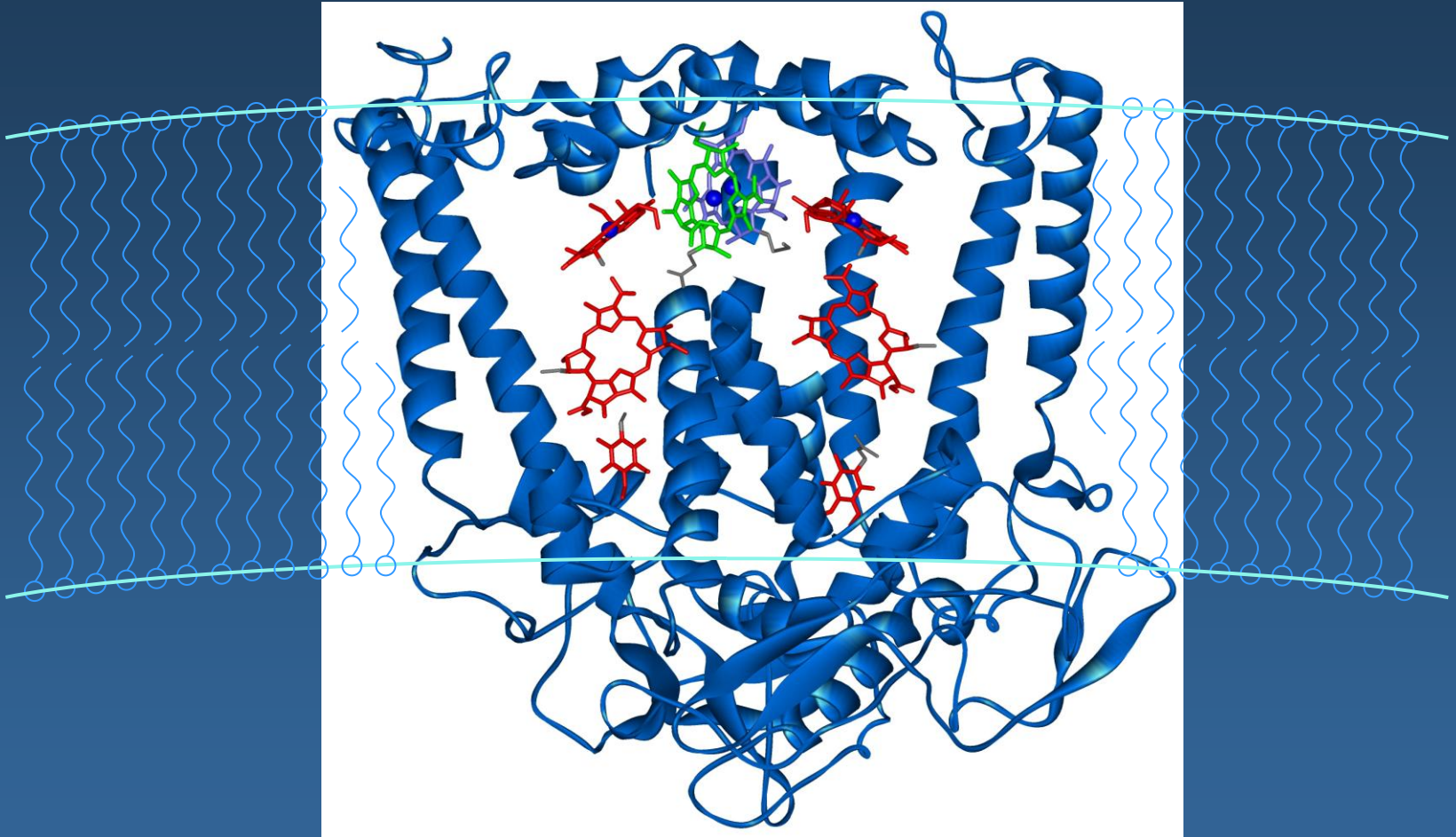


smart matrices carry energy and charge

Scientific Challenges

- engineer tailored active environments with bio-inspired components
- novel experiments to characterize the coupling among matrix, charge, and energy
- multi-scale theory of charge and energy transfer by molecular assemblies
- design electronic and structural pathways for efficient formation of solar fuels

Bacterial Photosynthetic Reaction Center



rhodobacter sphaeroides

Stowell, M.H.B.; Rees, D.C.; *et. al.* *Science* **1997**, 276, 882.

photons in
1 oxidant & reductant out

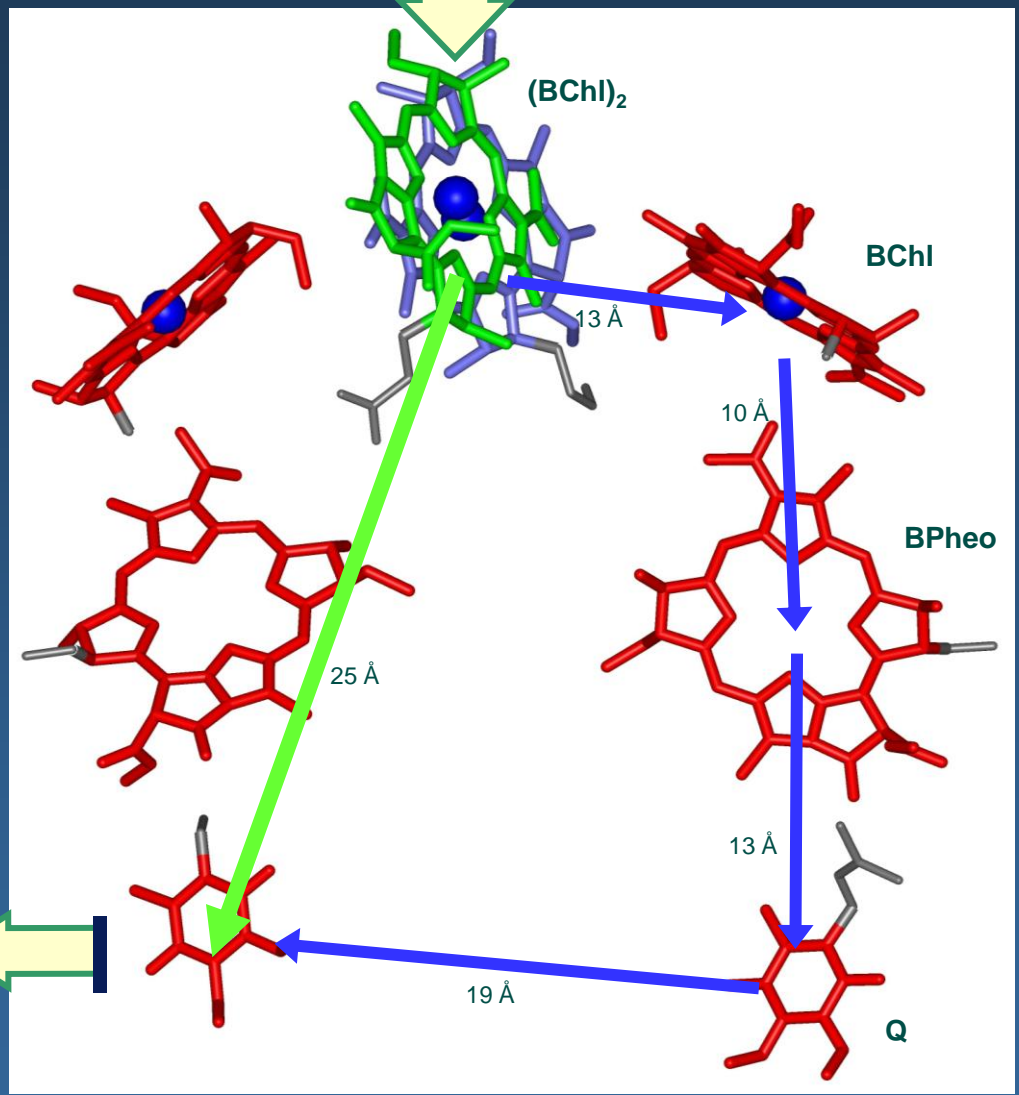
Energy In

BChl bacteriochlorophyll
BPheo bacteriopheophytin
Q quinone

1 step distance : 25 Å
calculated time : ~100 ps

4 steps
ET distance : 55 Å
total time : < 1 ns

reducing
equivalents

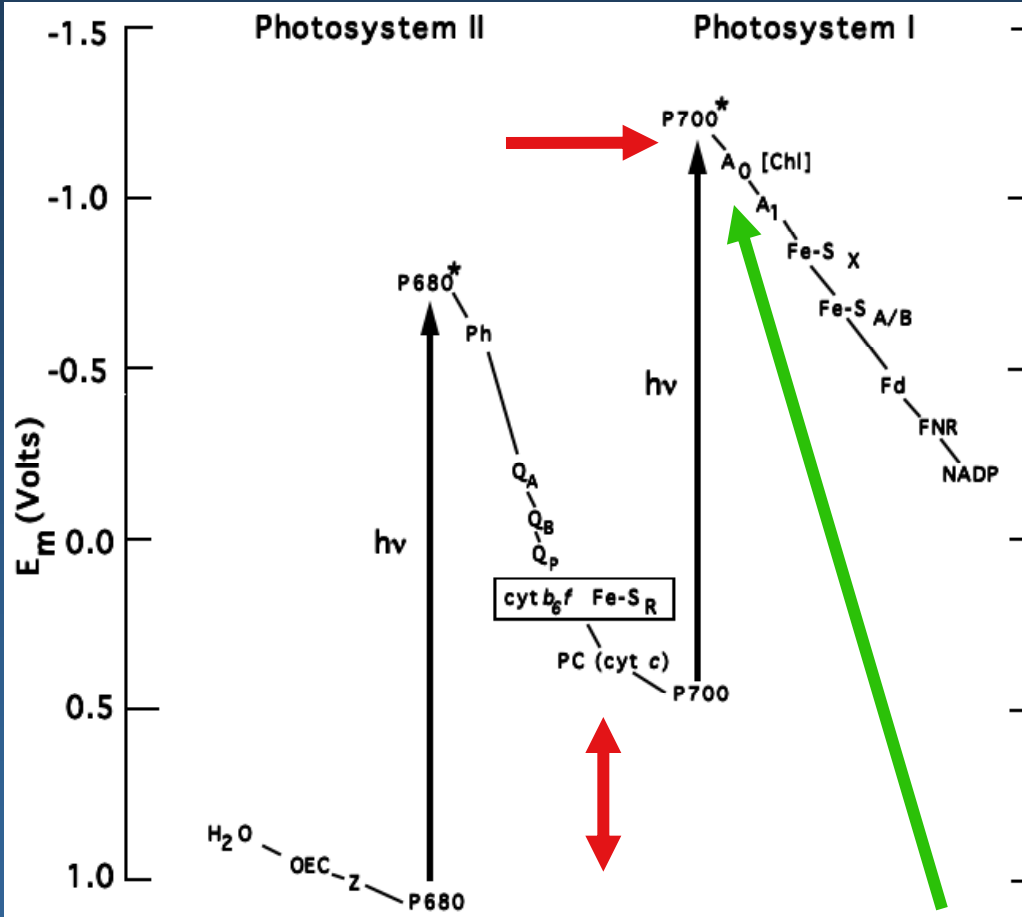


Boxer, S.G. *Annu. Rev. Biophys. Biophys. Chem.* 1990, 19, 267.

Nature uses two photosystems to span the redox space from O_2/H_2O to $NAD^+/NADH$

QuickTime™ and a TIFF (LZW) decompressor are needed to see this picture.

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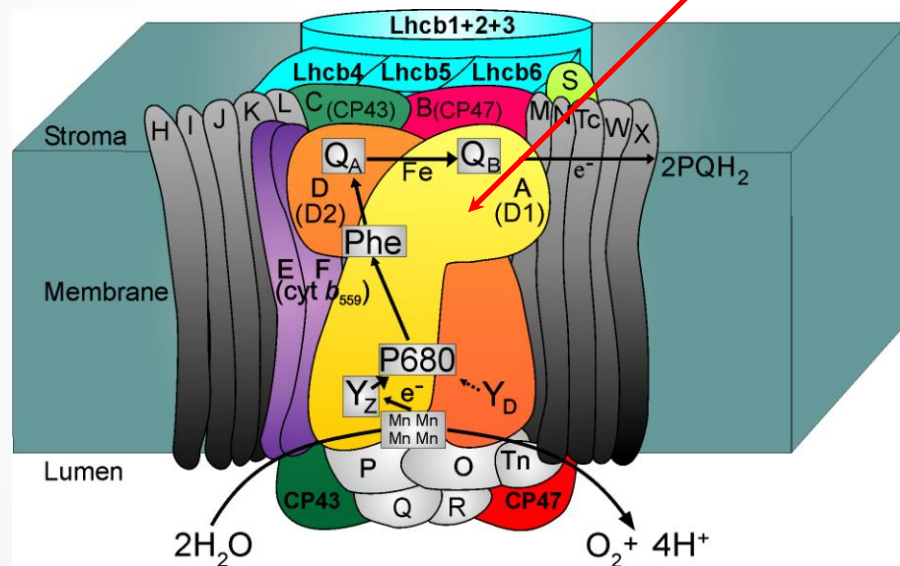
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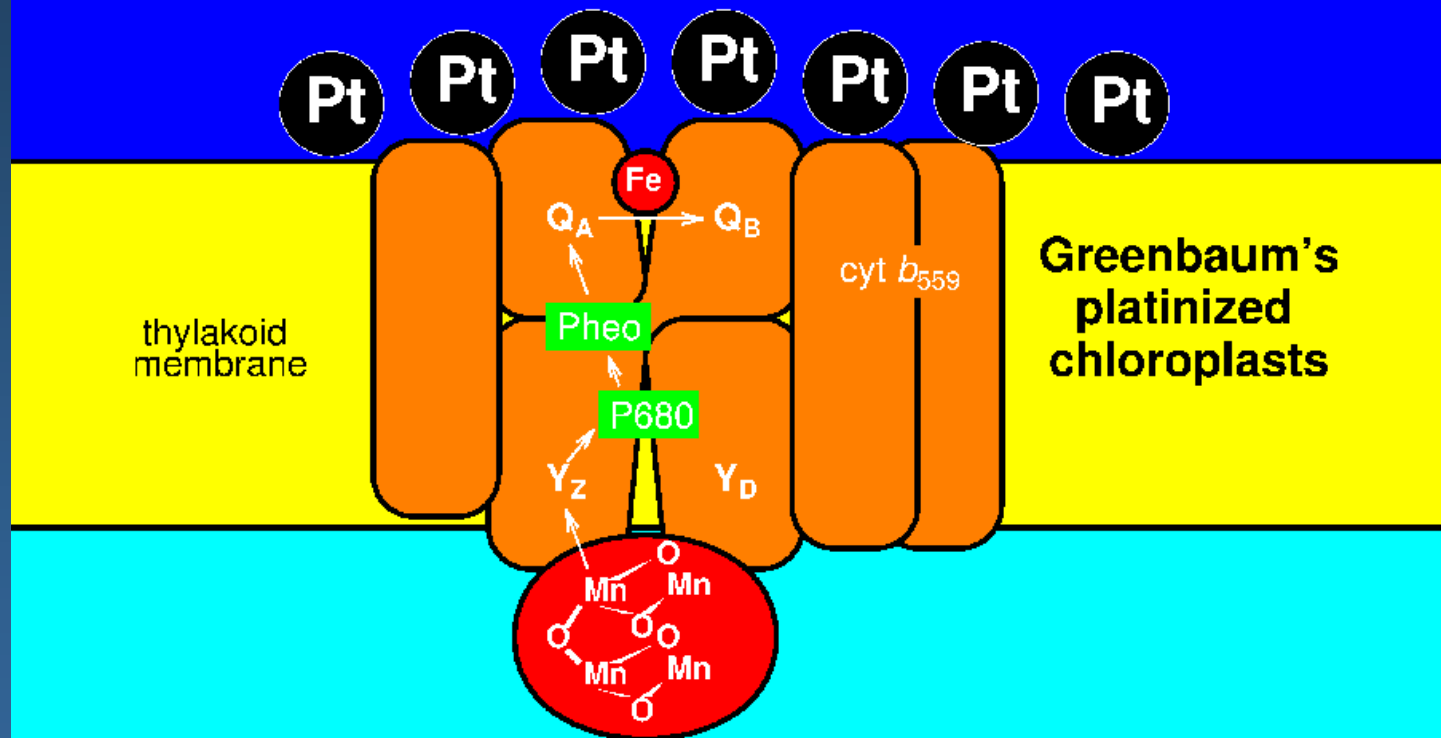
Giving more thermodynamic push to synthesis

Defect Tolerance and Self-repair

- Understand defect formation in photovoltaic materials and self-repair mechanisms in photosynthesis
- Achieve defect tolerance and active self-repair in solar energy conversion devices, enabling 20-30 year operation

the water splitting protein in Photosystem II is replaced every hour!



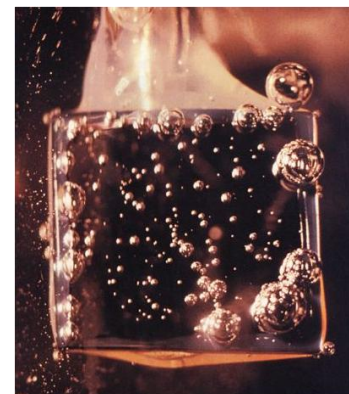
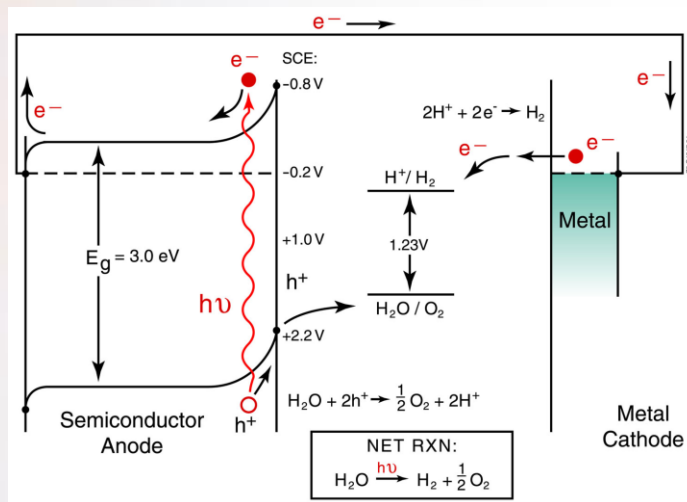
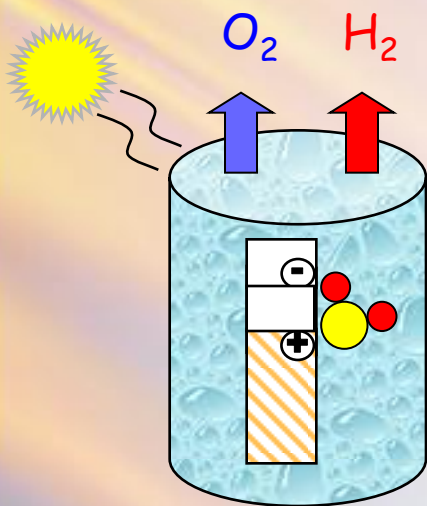


thylakoid
membrane

Greenbaum's
platinized
chloroplasts



Efficient Solar Water Splitting



demonstrated efficiencies 10-18% in laboratory

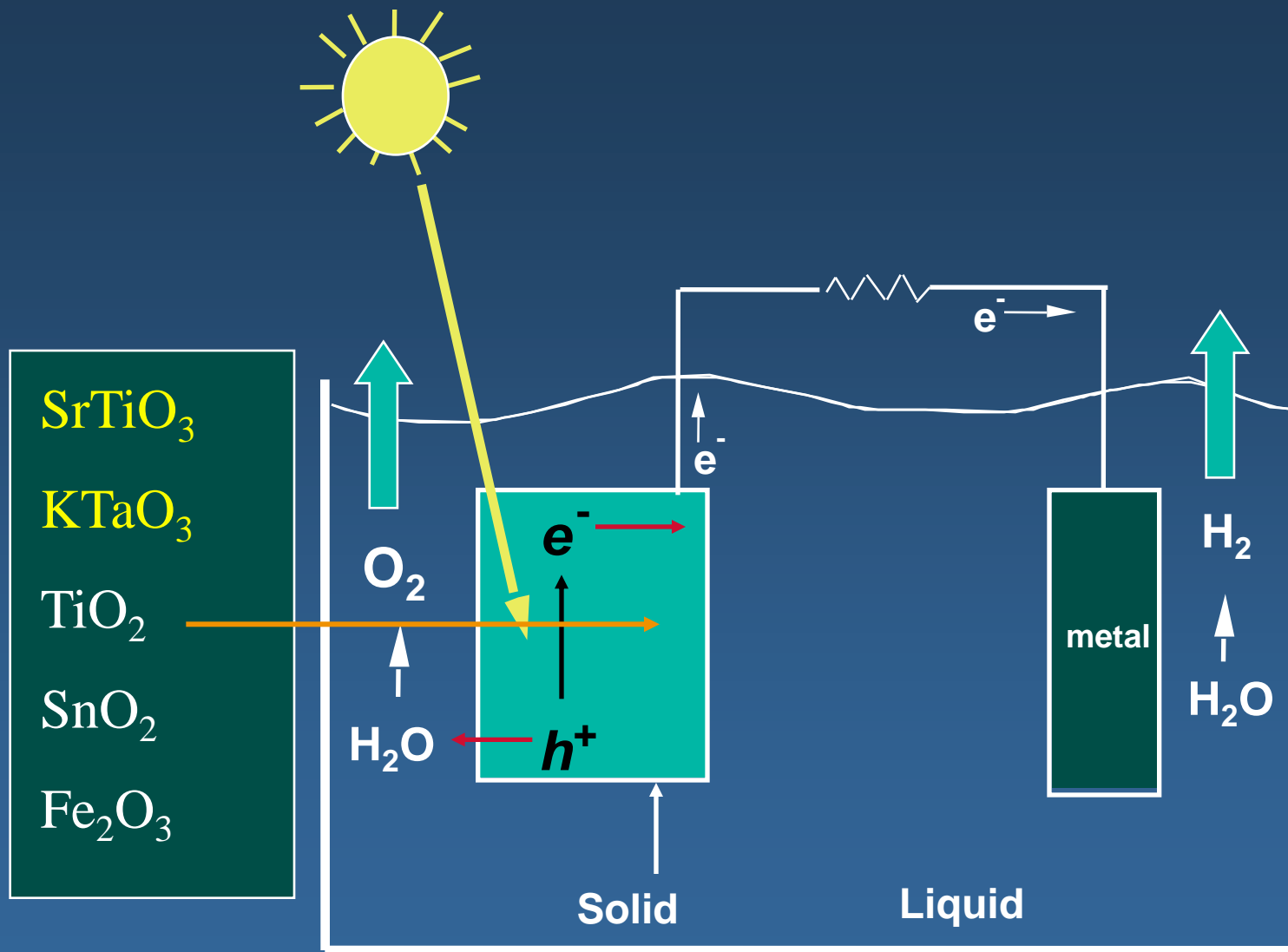
Scientific Challenges

- cheap materials that are robust in water
- catalysts for the redox reactions at each electrode
- nanoscale architecture for electron excitation \Rightarrow transfer \Rightarrow reaction

Fuel from Sunlight

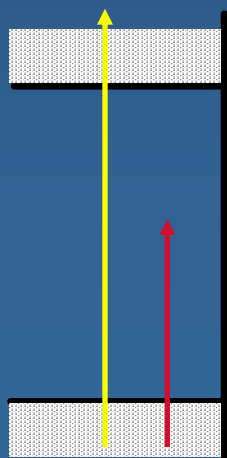
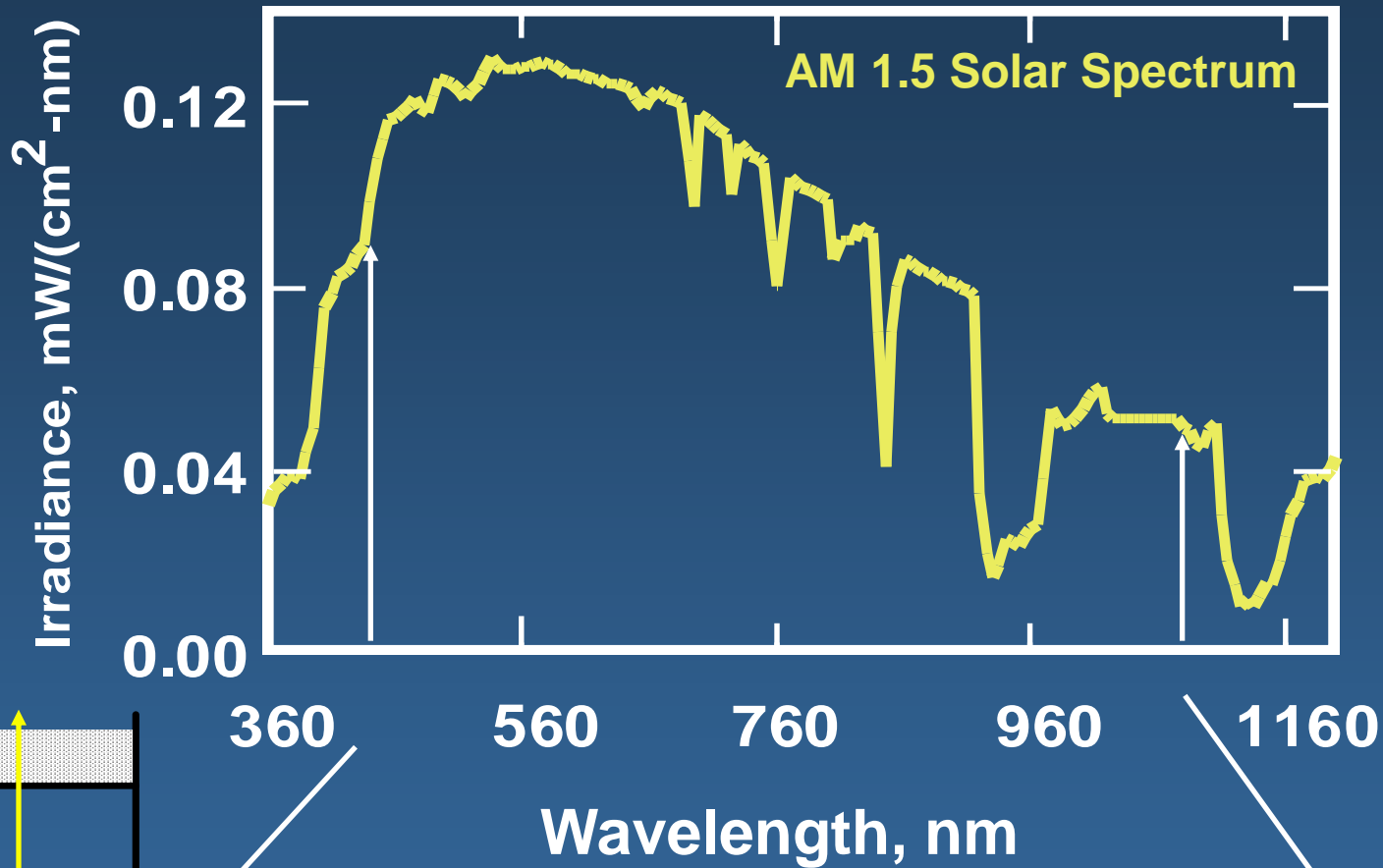
QuickTime™ and a
YUV420 codec decompressor
are needed to see this picture.

Photoelectrochemical Cell

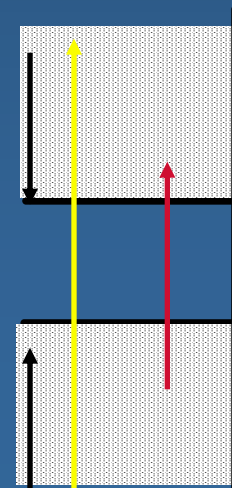


Light is Converted to Electrical+Chemical Energy

Optimum Absorption Threshold



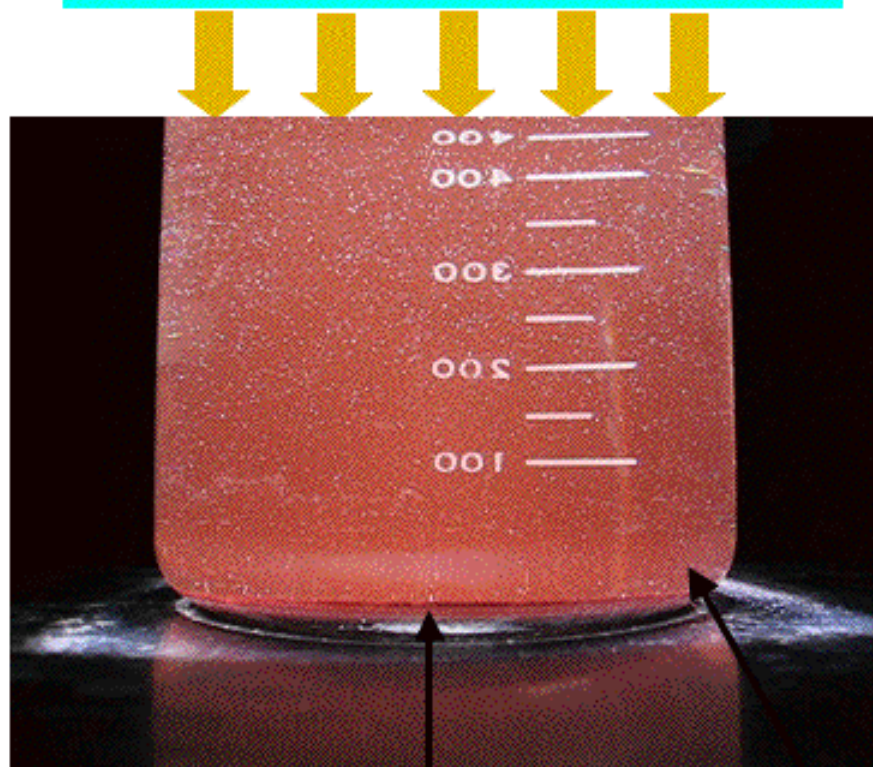
Too Large
Band Gap



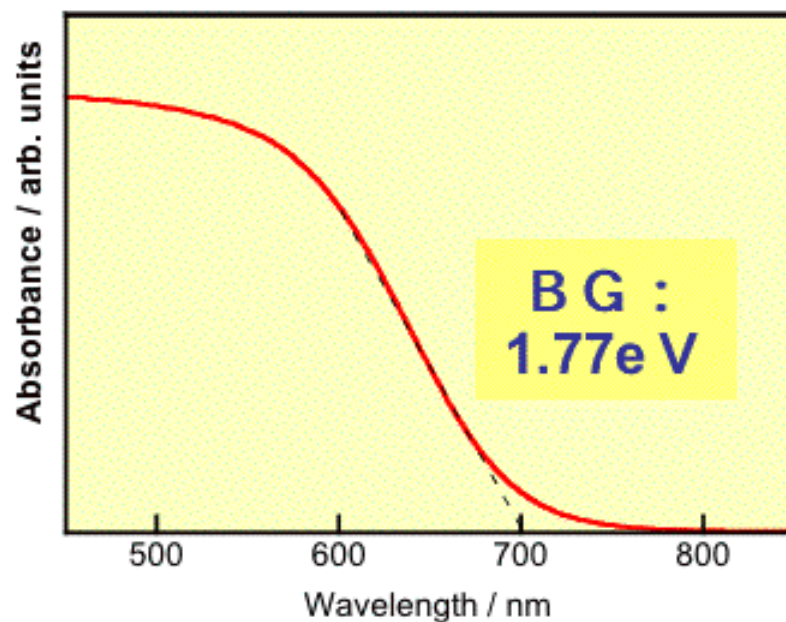
Too Small
Band Gap

Solar H₂ production on Ru/CuInS₂-AgInS₂-ZnS solid solution photocatalyst

Solar simulator(AM-1.5)



Rate of H₂ evolution
8L/h·m²

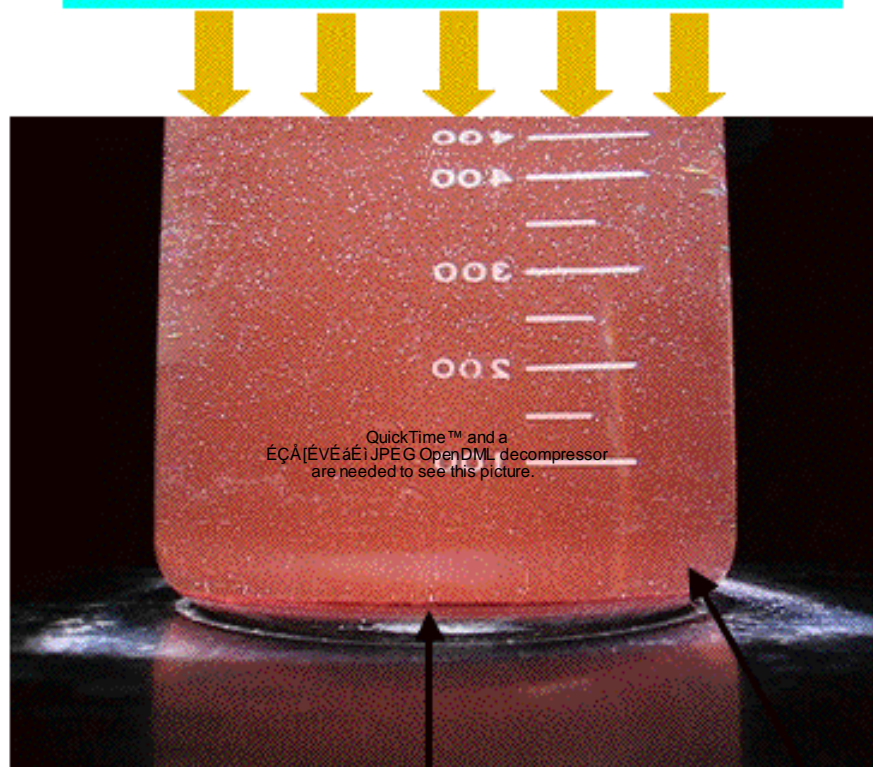


Photocatalyst Reactant: K₂SO₃ + Na₂S

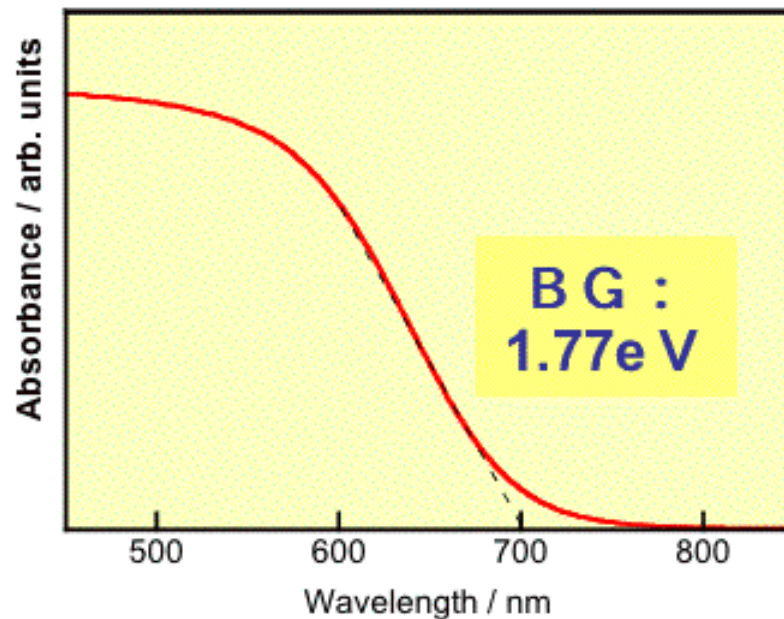
I. Tsuji, H. Kato, and A. Kudo,
Angew. Chem., Int. Ed., 44, 3565 (2005), *Chem. Mater.*, 18, 1969 (2006).

Solar H₂ production on Ru/CuInS₂-AgInS₂-ZnS solid solution photocatalyst

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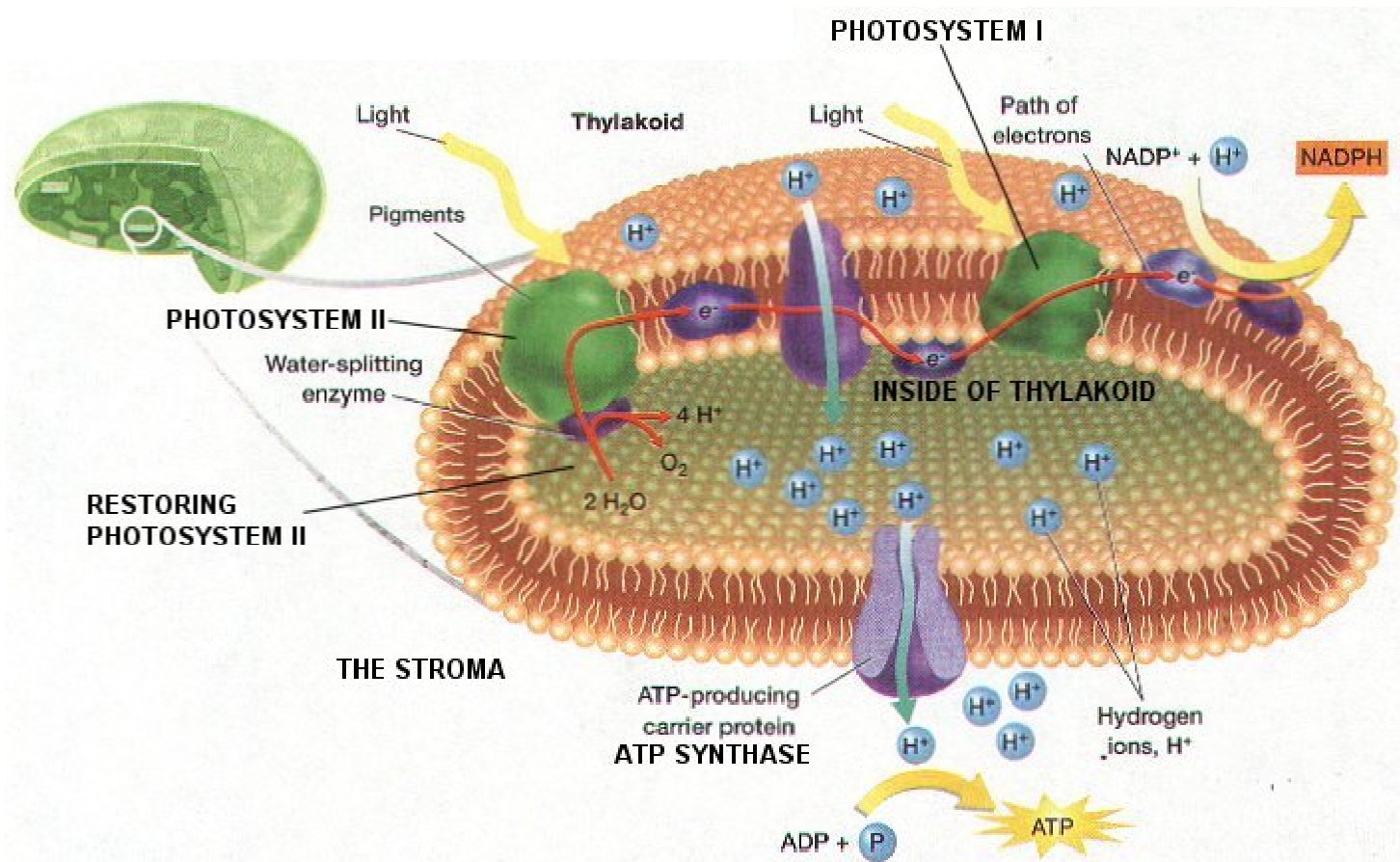


Photocatalyst

Reactant: K₂SO₃ + Na₂S

I. Tsuji, H. Kato, and A. Kudo,
Angew. Chem., Int. Ed., 44, 3565 (2005), *Chem. Mater.*, 18, 1969 (2006).

Lessons from Photosynthesis

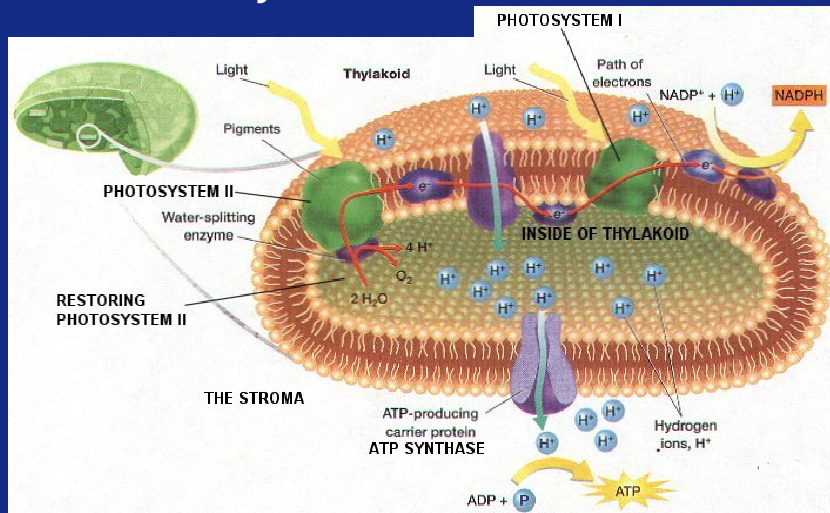


April 18-21, 2005

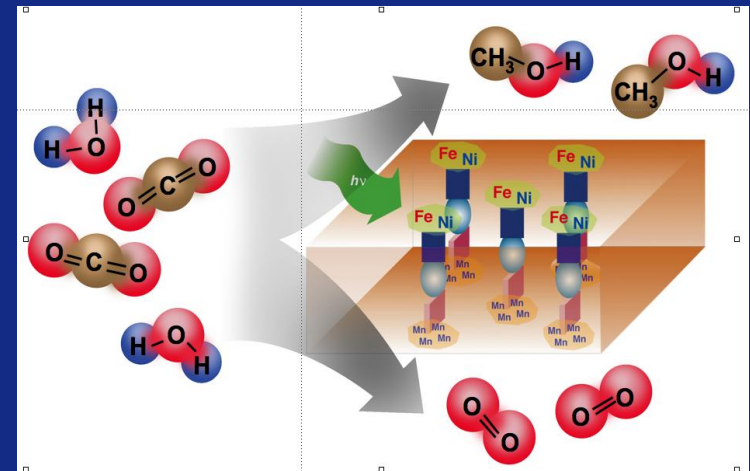
Mission of JCAP

- **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 efficiently than (current) crops

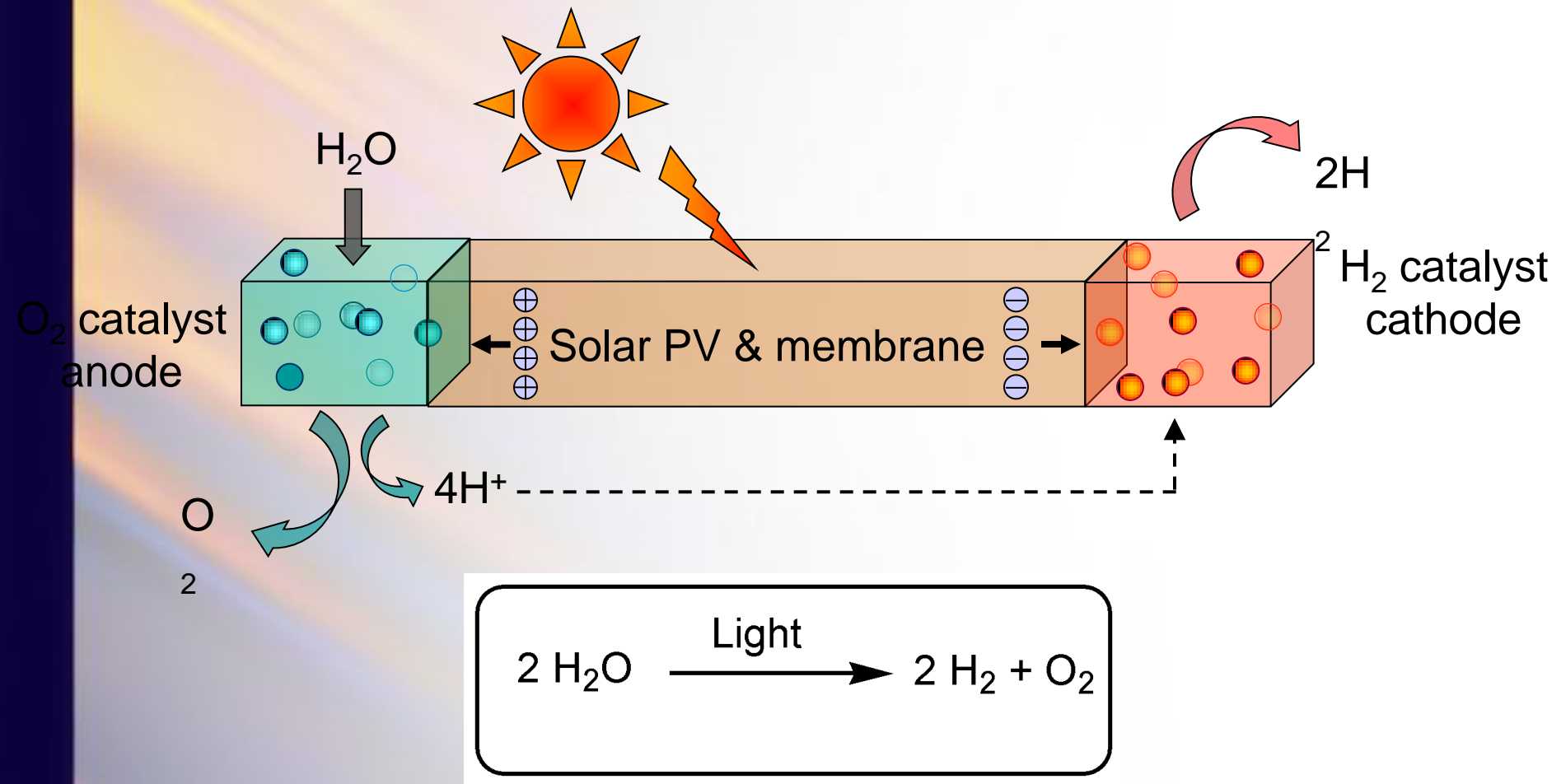
Photosynthesis



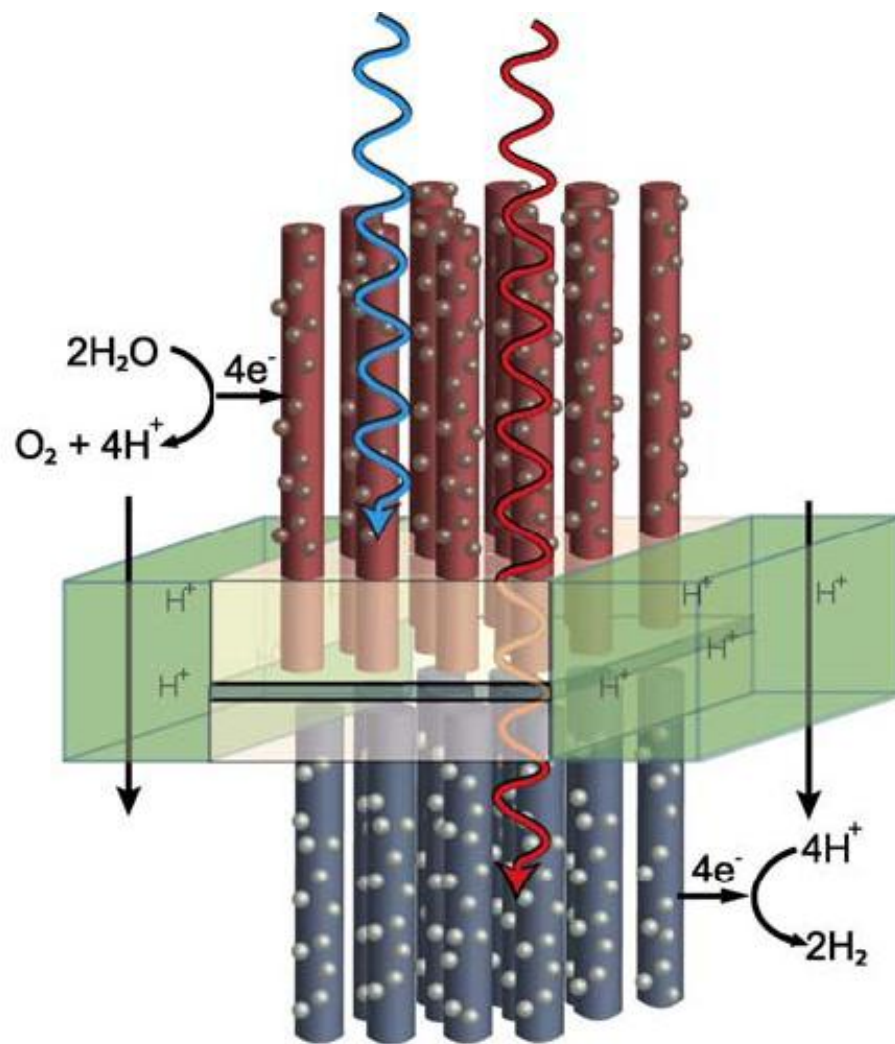
Artificial Photosynthesis



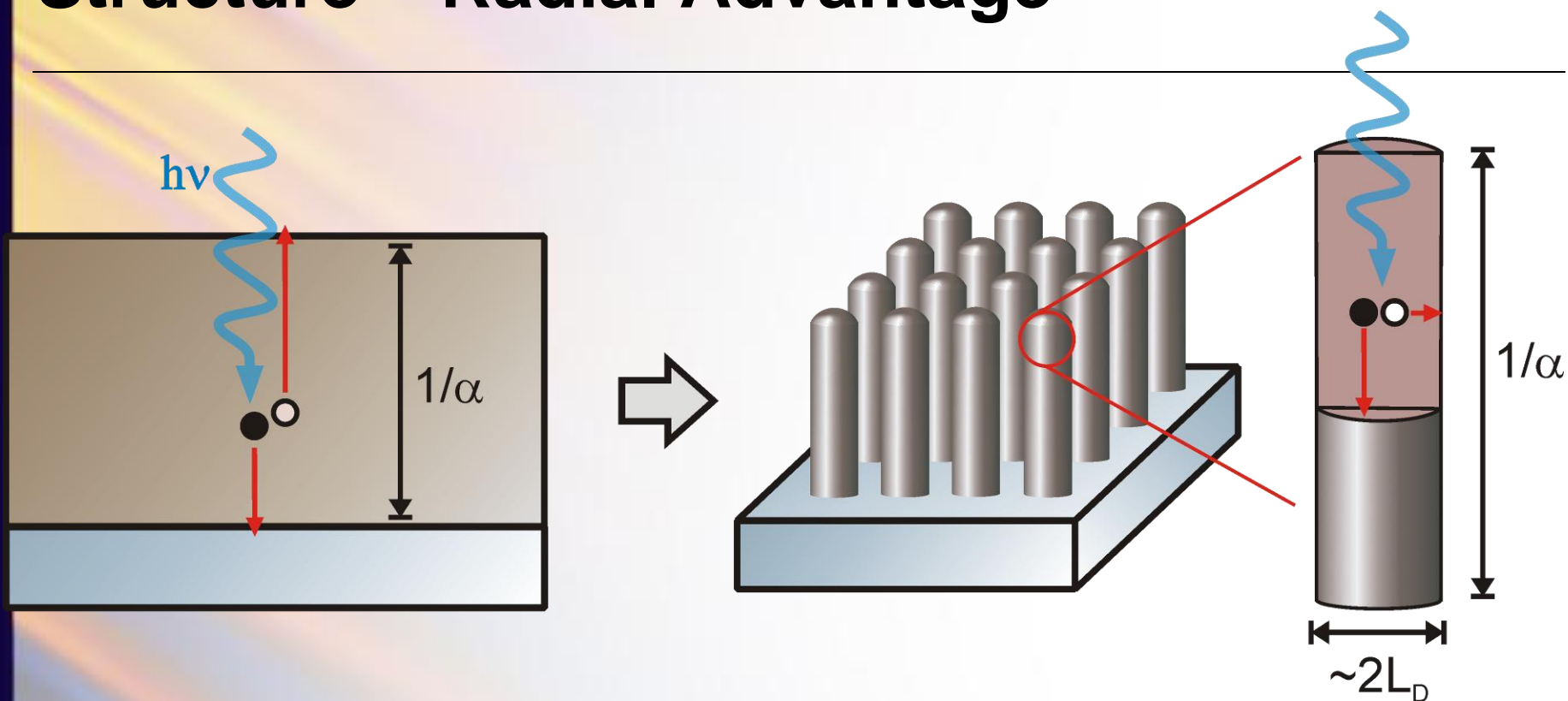
System Concept



Constructing the Pieces of a Solar (H₂) Fuel Generator



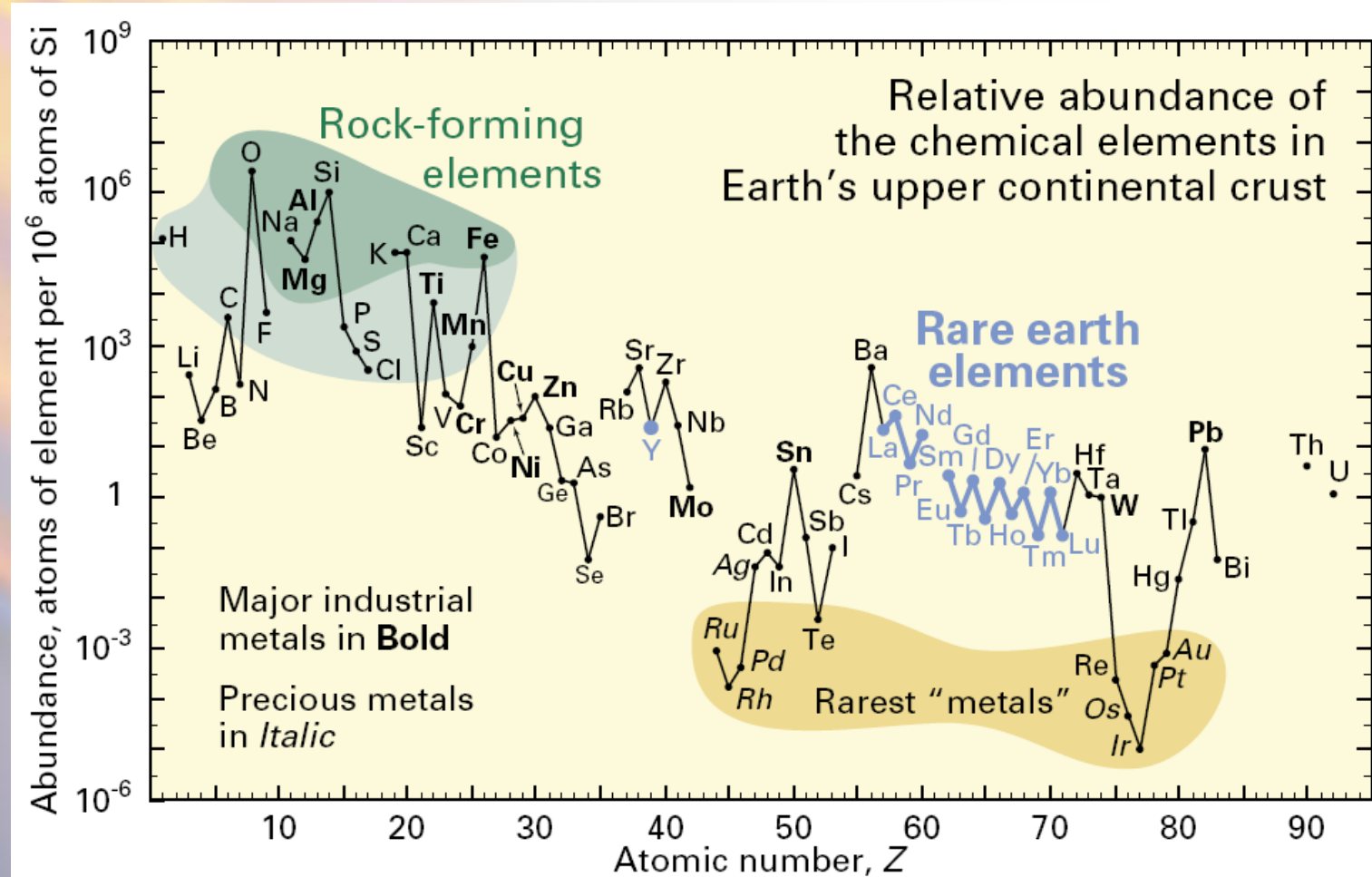
Structure – Radial Advantage



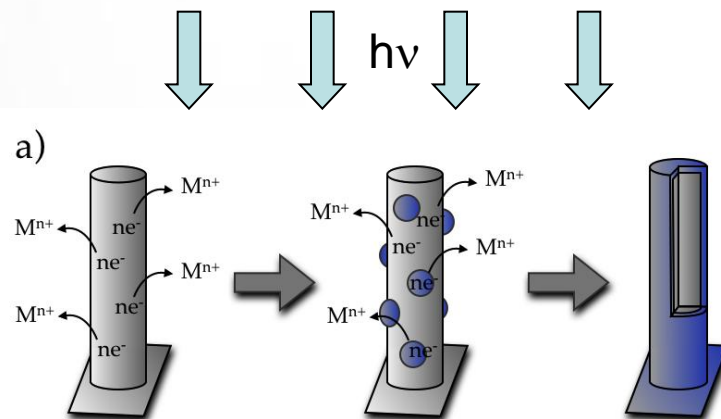
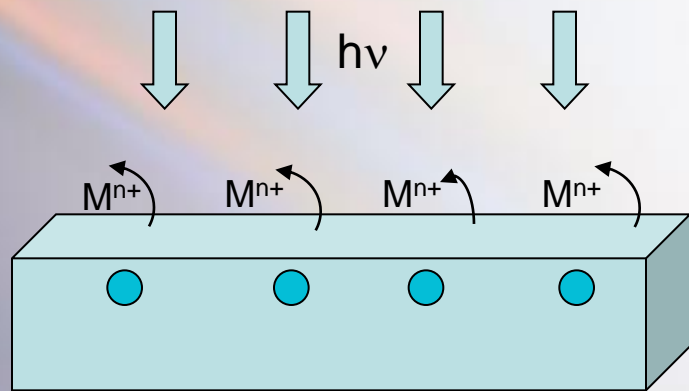
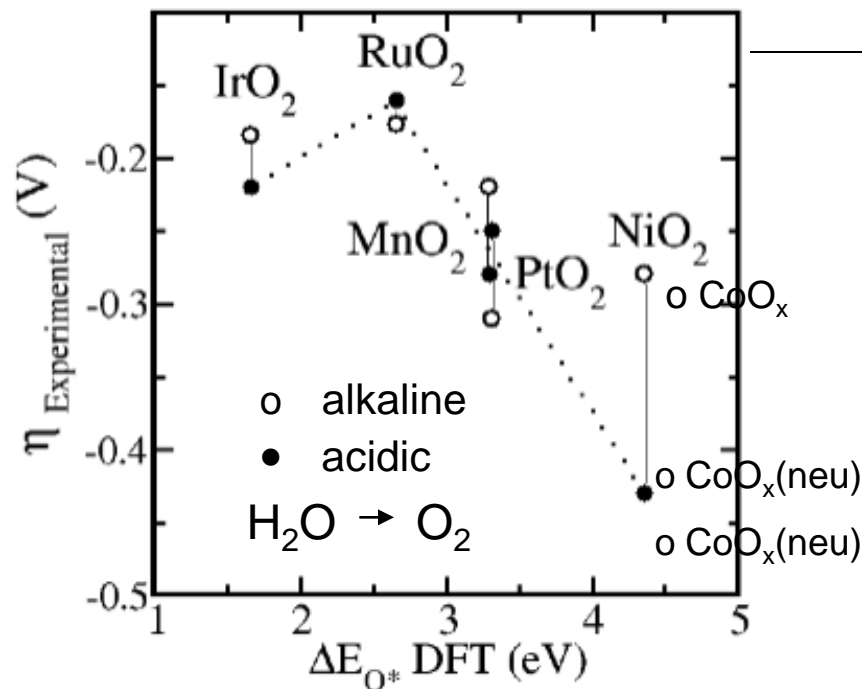
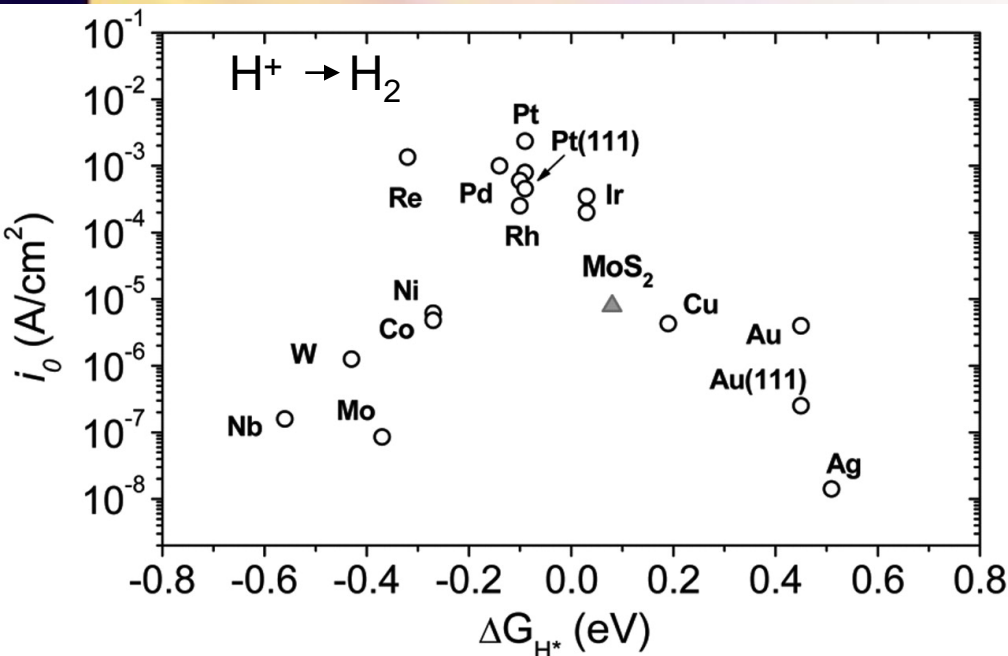
L_D ✪ purity ✪ materials cost

Impure material but high performance

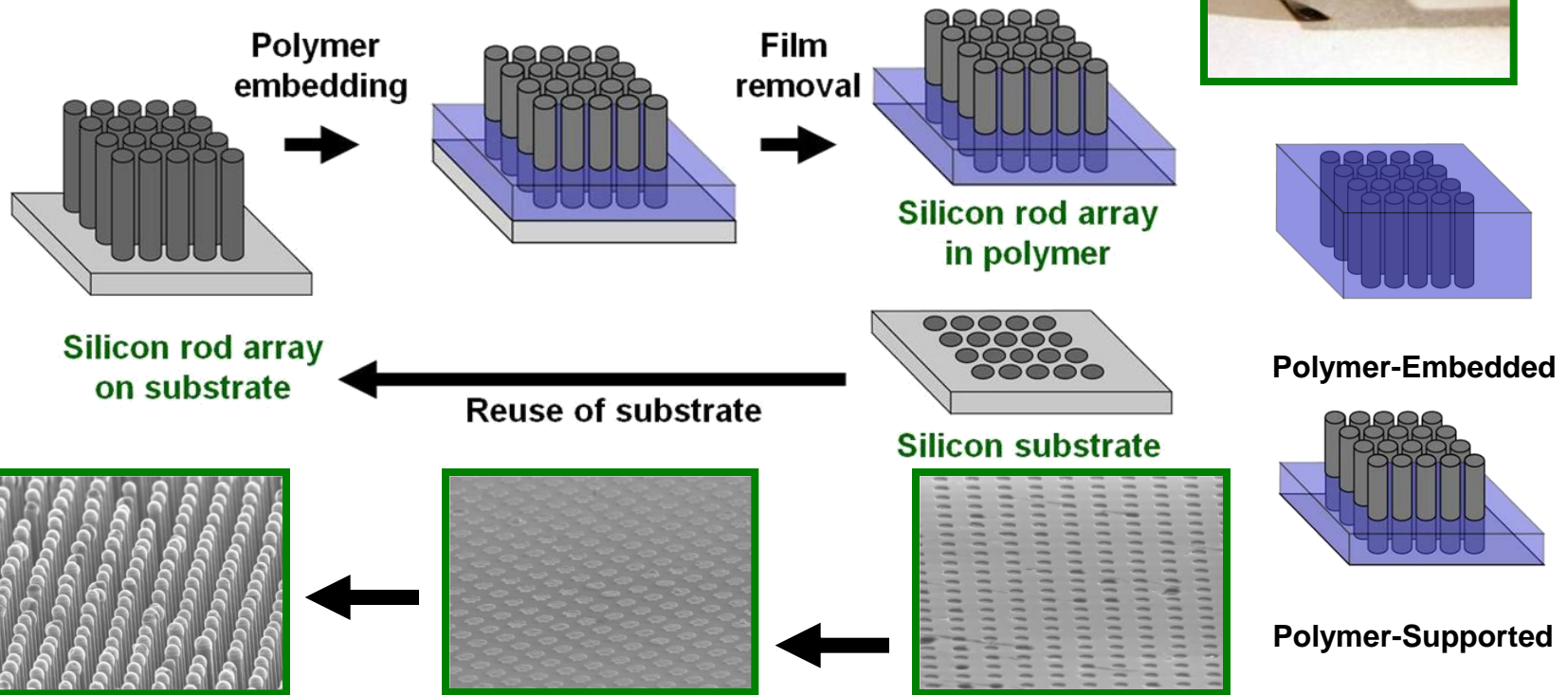
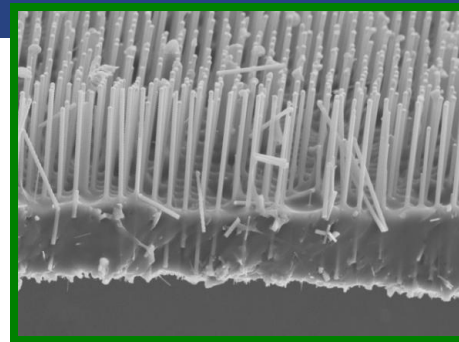
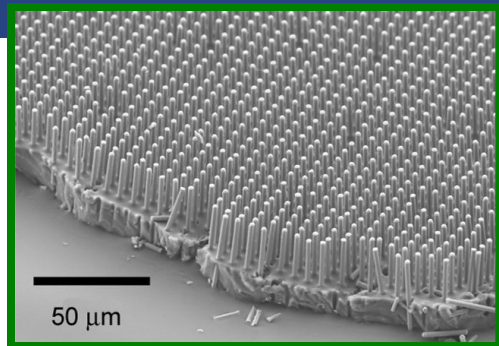
Enables Application of New Materials



Relaxes Catalyst Activity Requirements



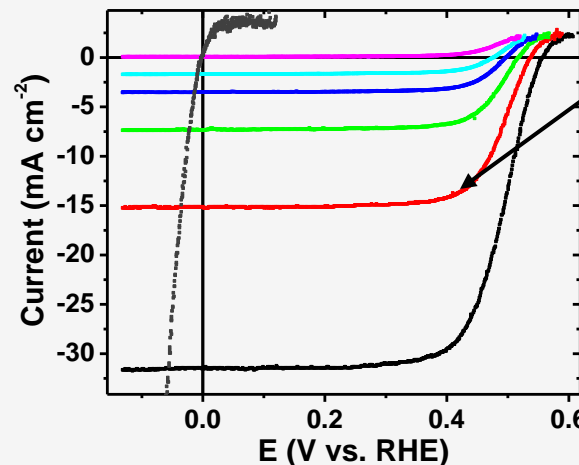
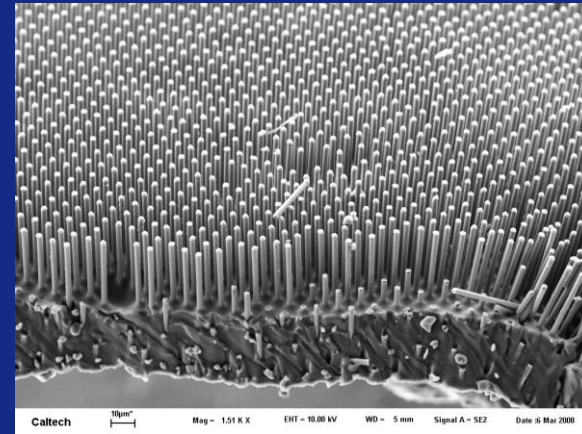
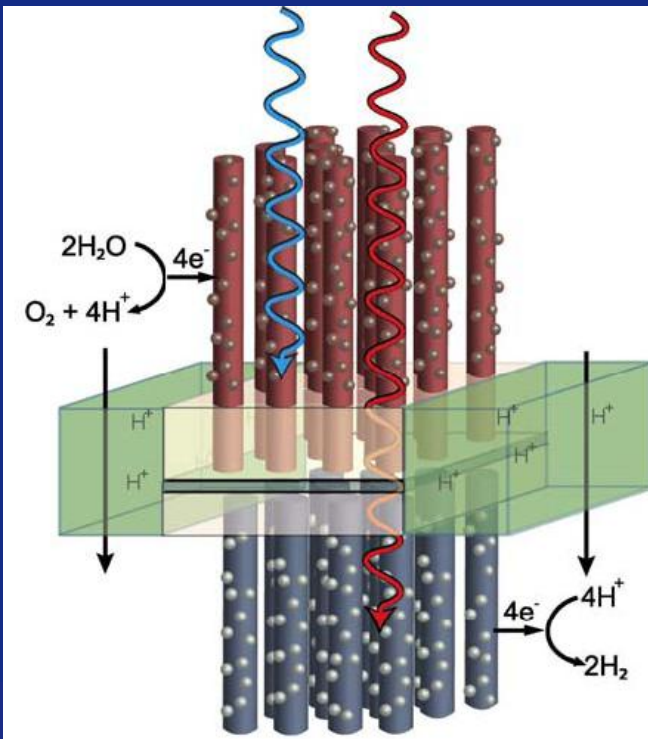
Flexible PDMS-Si Wire Composites



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

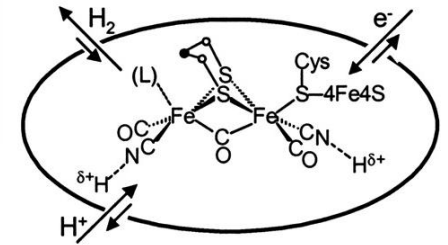
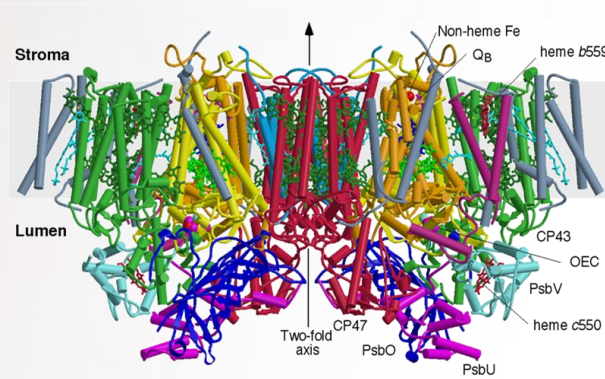
Fundamental Design Principles and Progress

- Require >1.23 V of photovoltage
- Require membrane to neutralize pH gradient and separate products
- Require catalytic sites to transform individual e^-h^+ pairs into multi-electron transfer reactions

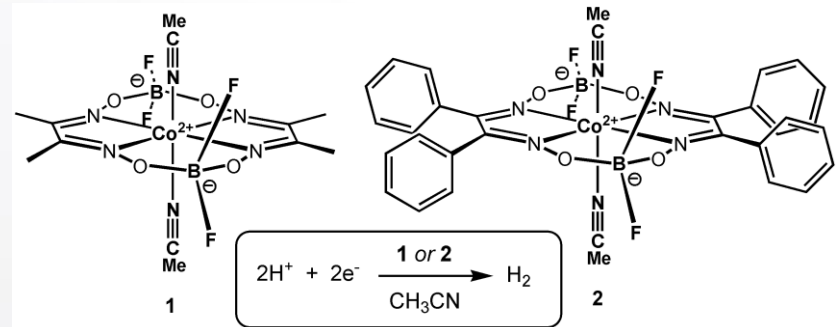
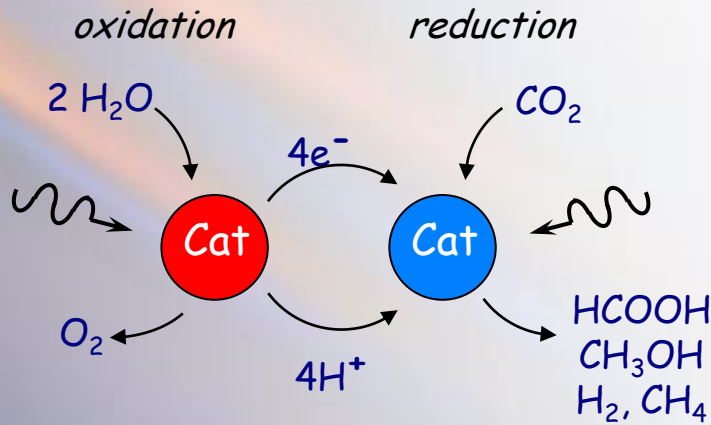
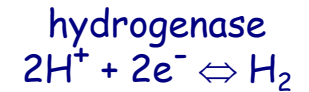


7% to H_2
(w only 60%
absorption)

Solar-Powered Catalysts for Fuel Formation



photosystem II

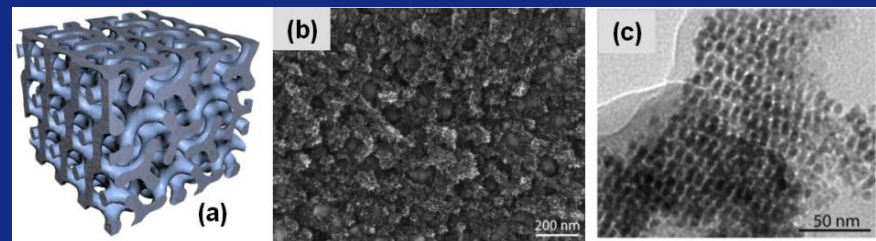
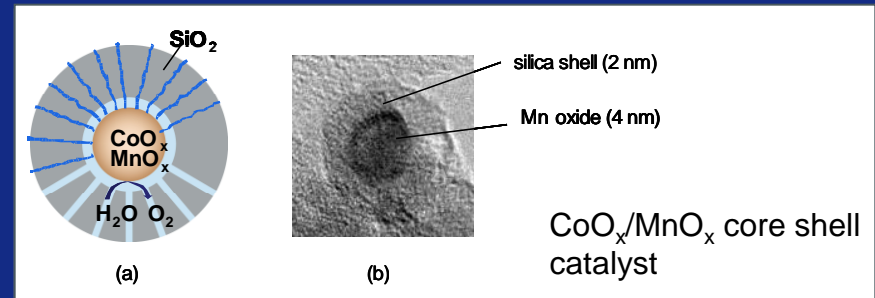
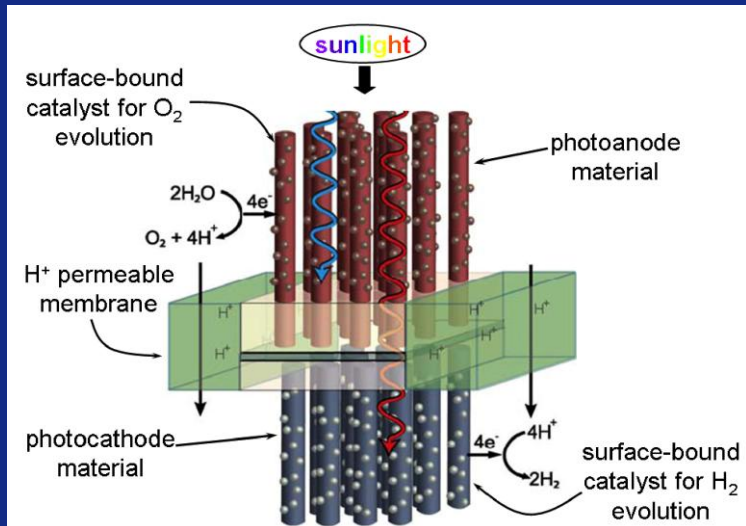


Molecular-Nanoscale Interface

Gaps: How to combine components into working system; functionality of components individually vs collectively

Approach: Control functionality of integrated components

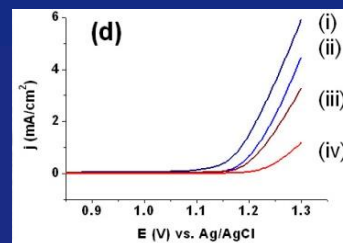
Exploit 3-D to achieve desired activity and/or functionality



Starting

Points:

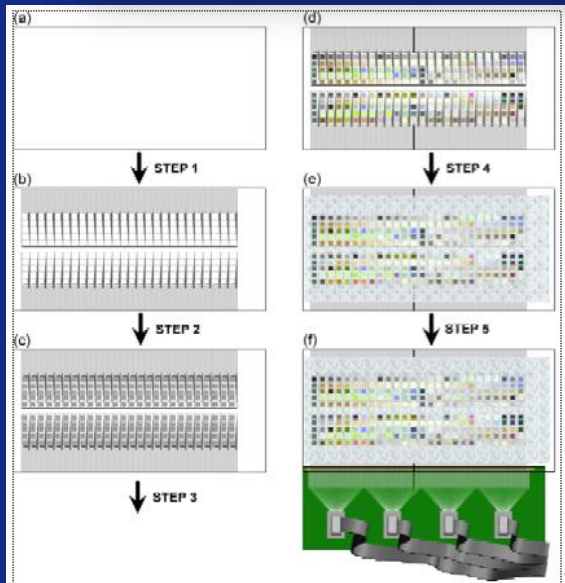
MnO_x; CoO_x
Ni-Mo



Synthesis and catalytic activity of Ru double gyroid vs planar Ru for O₂ evolution

Heterogeneous Catalyst Discovery

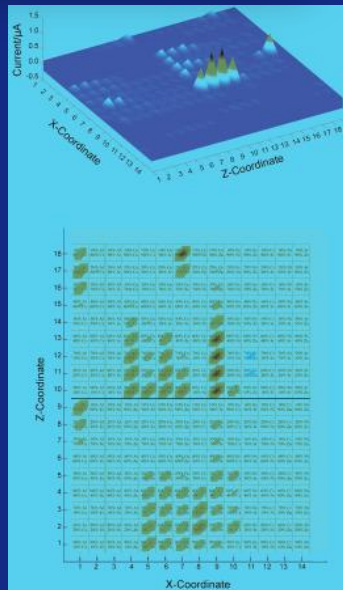
Gaps: Complement with Ultra-high Throughput Experimentation



Schematic of the process of preparing the substrate and making electrical contact to 130 individual materials on a single piece of FTO-coated glass.

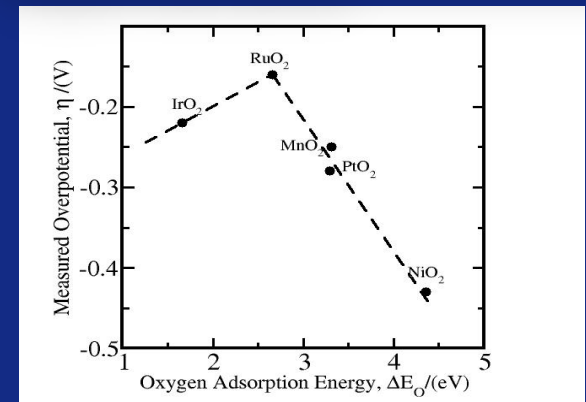
Starting Points:

H_2/CO_2 : MS_x ; O_2 : MO_x , MO_xN_y



False color images of the photocurrent of a slide that contained spots of binary mixed-metal oxides (top). Three-dimensional plot (bottom). Top-down view.

Outputs: Tie together theory, surface science, electrochemistry, X-ray spectroscopy, high-throughput experimentation

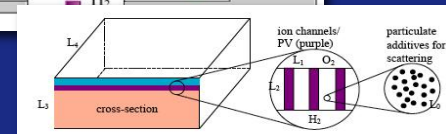
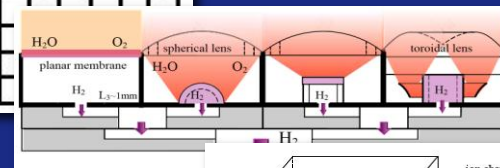
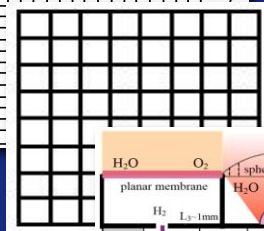
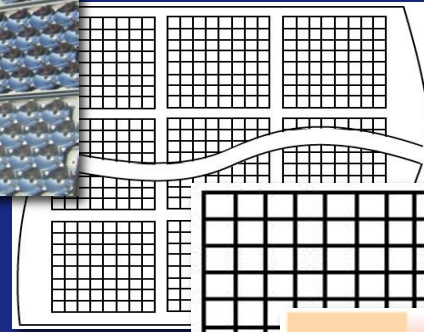
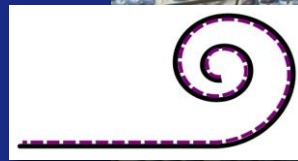
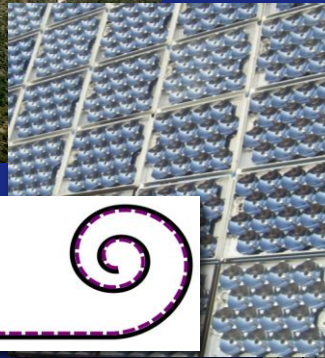


Measured OER overpotential vs calculated adsorption energy

Activity Metrics/Goals:

$\sim x 10^2$ for H_2 ; $\sim x 10^4$ for O_2
 $> x 10^5$ for CO_2

Envisioning JCAPs Products



System/design/process level

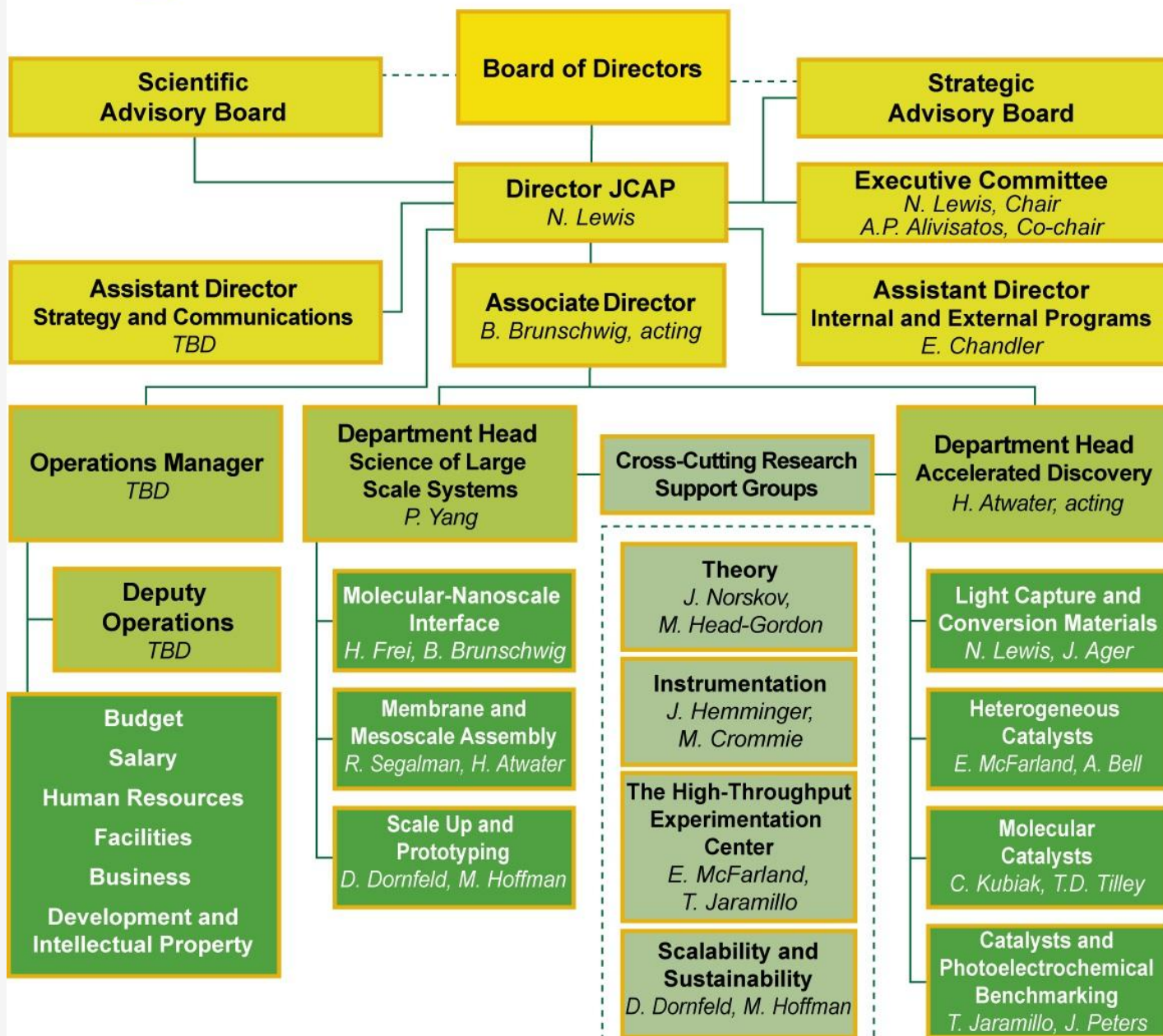
Flow channel building blocks

Diagram illustrating the system/design/process level, showing various flow channel building blocks and their arrangement. The blocks are represented by icons: a square with an 'X', a square with a blue and pink flow path, and a square with a grid and flow path. The text "Flow channel building blocks" is written in blue.

Device/physics level

Diagram illustrating the device/physics level, showing a cross-section of a flow channel with various layers and components. The text "Device/physics level" is written in white on a blue arrow pointing downwards.

JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS



Basic Research Needs for Solar Energy Utilization

*Report of the Basic Energy Sciences Workshop on Solar Energy
Utilization*

Nathan S. Lewis
Caltech

with

George Crabtree, ANL

Arthur Nozik, NREL

Mike Wasielewski, NU

Paul Alivisatos, UC-Berkeley

April 18-21, 2005



**Office of
Science**
U.S. DEPARTMENT OF ENERGY



CONCLUSIONS

- Without **massive** quantities (10-20 TW by 2050) of clean energy, CO₂ levels will continue to rise
- The only sufficient supply-side cards we have are “clean” coal, nuclear fission (with a closed fuel cycle), and/or cheap solar fuel
- We need to pursue globally scalable systems that can efficiently and cost-effectively capture, convert, and store sunlight in the form of chemical fuels
 - He that can not store, will not have power after four
- Semiconductor/liquid junctions offer the *only* proven method for achieving this goal, but we have a great deal of fundamental science to learn to enable the underpinnings of a cost-effective, deployable technology
 - Nanorods, randomly ordered junctions to generate the needed potential
 - Catalysts to convert the incipient electrons into fuels by rearranging the chemical bonds of water (and CO₂) into O₂ and a reduced fuel

BES Workshop on Basic Research Needs for Solar Energy Utilization

April 21-24, 2005

Workshop Chair: Nathan Lewis, Caltech

Co-chair: George Crabtree, Argonne

Panel Chairs

Arthur Nozik, NREL: Solar Electric

Mike Wasielewski, NU: Solar Fuel

Paul Alivisatos, UC-Berkeley: Solar Thermal



Topics

Photovoltaics

Photoelectrochemistry

Bio-inspired Photochemistry

Natural Photosynthetic Systems

Photocatalytic Reactions

Bio Fuels

Heat Conversion & Utilization

Elementary Processes

Materials Synthesis

New Tools

Plenary Speakers

Pat Dehmer, DOE/BES

Nathan Lewis, Caltech

Jeff Mazer, DOE/EERE

Marty Hoffert, NYU

Tom Feist, GE

200 participants

universities, national labs, industry

US, Europe, Asia

EERE, SC, BES

Charge

To identify basic research needs and opportunities in solar electric, fuels, thermal and related areas, with a focus on new, emerging and scientifically challenging areas that have the potential for significant impact in science and technologies.