

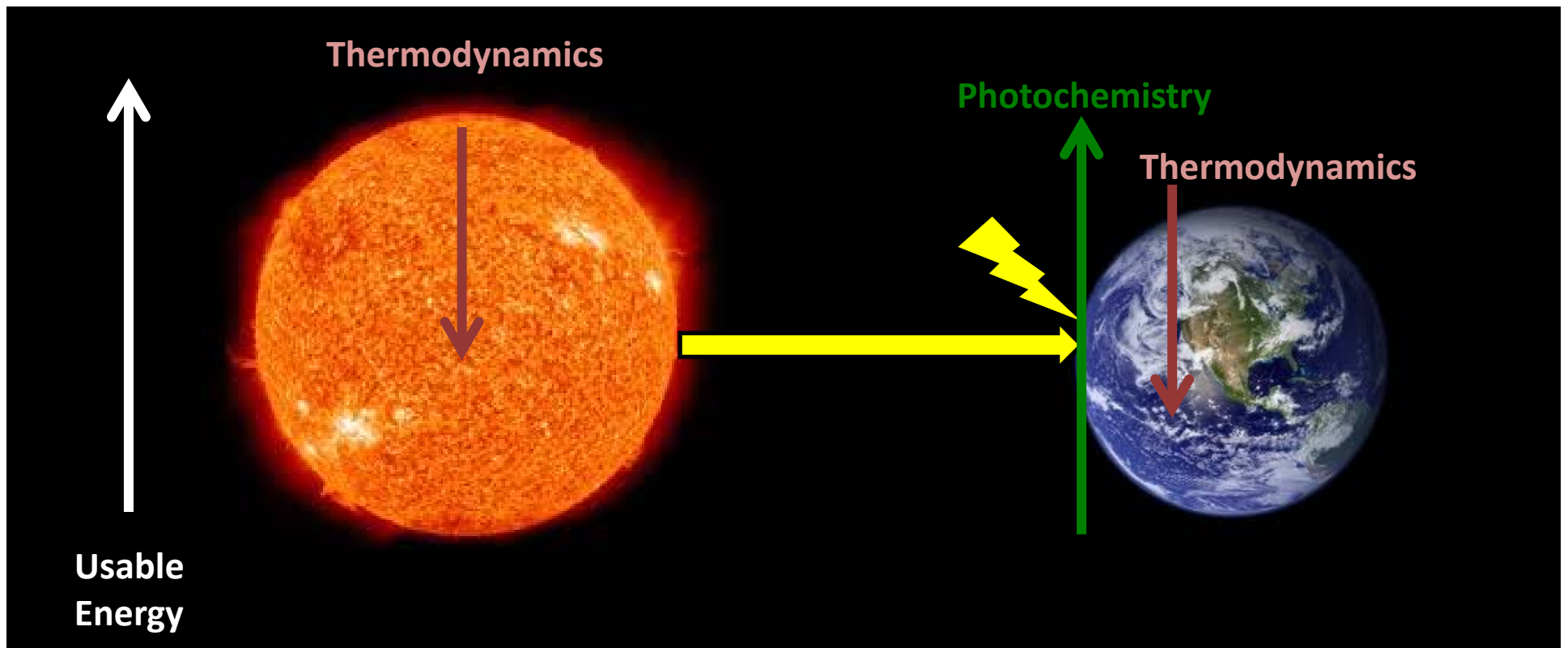
# Photochemistry- Fundamentals and Applications

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9-10-2014

# Energy

- *Thermodynamics*- Things will go to a lower energy state.
- *Photochemistry*- Takes photons and creates high energy states.

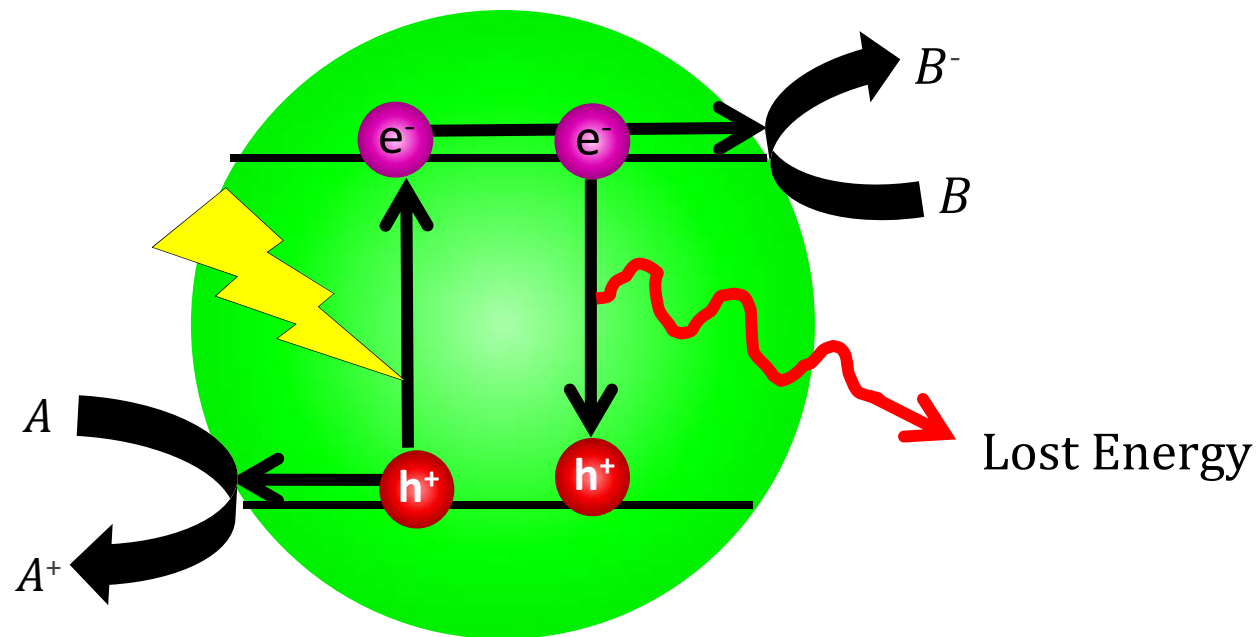


# Objectives

- *Photoabsorption*- You should be able to tell how much light any photocatalyst use to do useful amount of work
- *Doping*- You should be able to tell the difference between an n-type and p-type material.
- *Band Alignment*- You should know why band alignment to a redox reaction is important.
- *Applications*- You should be able to know multiple applications for photocatalyst and the basic approaches to making them successful.

# Breaking photocatalysis down to the fundamentals.

- A photon forces an electron to a higher energy level.
- The electron needs to get to the surface and react before it falls back down into it's initial/lower energy level.



# How much energy can we get from the sun?

- The x-axis is in wavelength, but we would like this axis to be energy.
- How do we do that?
- Speed of light equation:

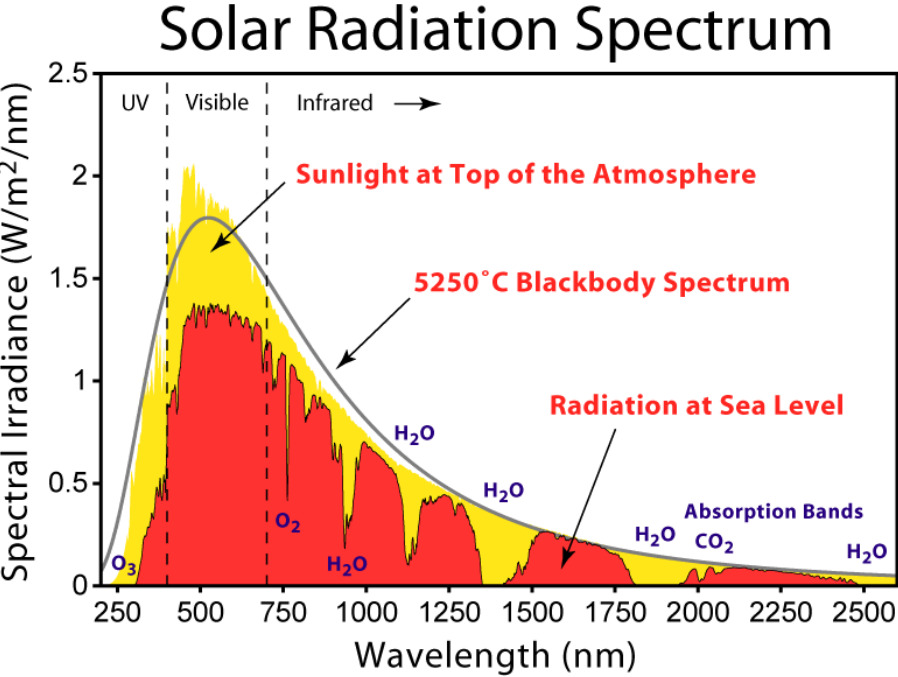
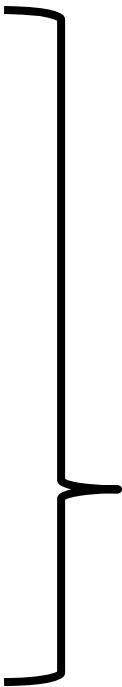
$$c = \lambda \nu$$

↑ Wavelength    ↑ Frequency

- Plank-Einstein relation:

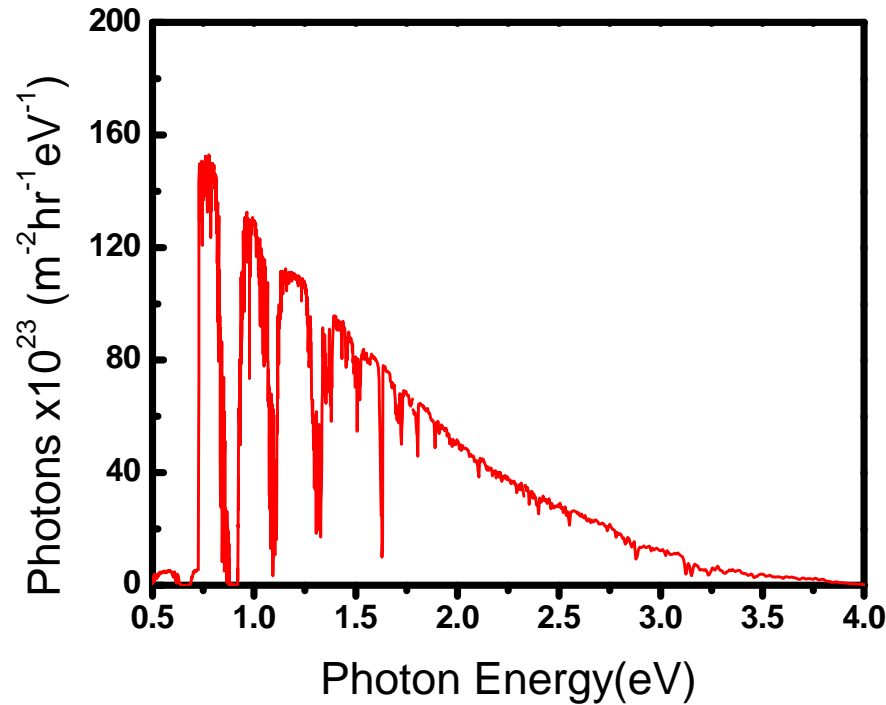
$$E = h \nu$$

↑ Energy    ↑ Frequency



<http://rredc.nrel.gov/solar/spectra/am1.5/>

$$E(eV) = \frac{1240}{\lambda(nm)}$$

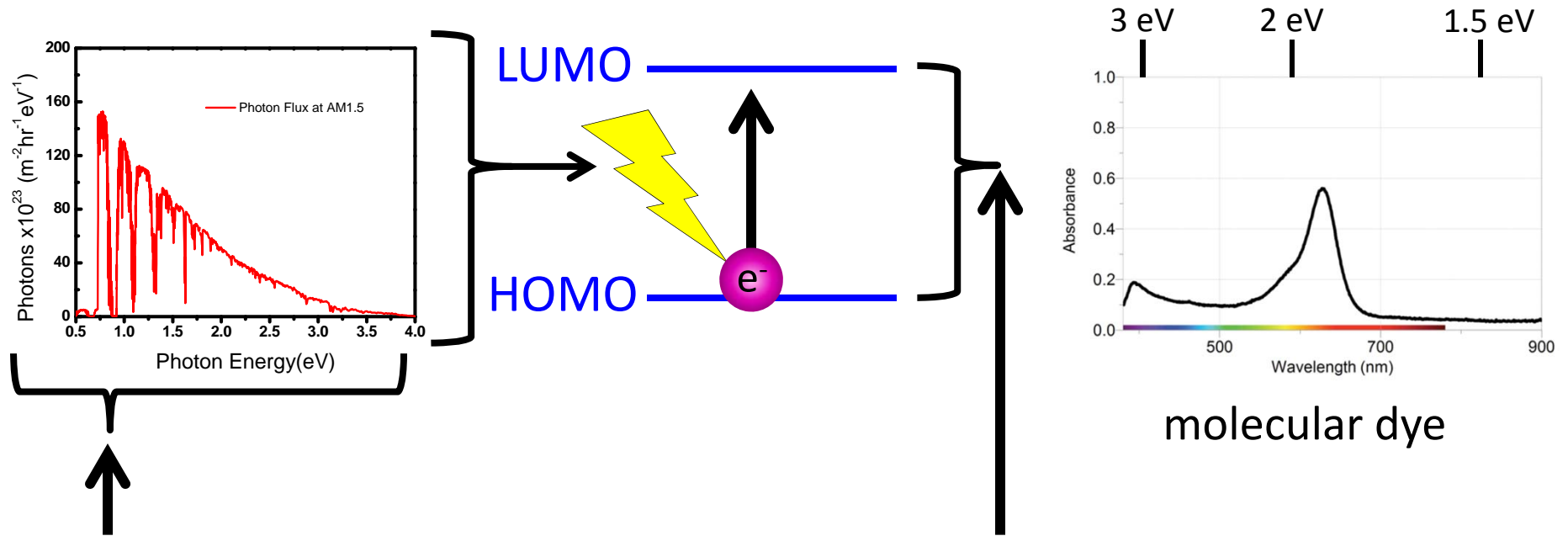


← This is the AM1.5 solar spectrum. ~average solar irradiation in the middle of the USA. See Wikipedia for exact details.

- This graph shows us the energy of all the photons coming from the sun.
- Important note:
  - The unit is ‘electron-Volt’, which is a unit of energy.
  - ‘Volt’ is a unit of potential.
  - 1 eV is the amount of energy it takes 1 electron to change its potential by 1 volt.

# Molecular Photocatalysts

- Molecular photocatalysts have distinct energy levels.

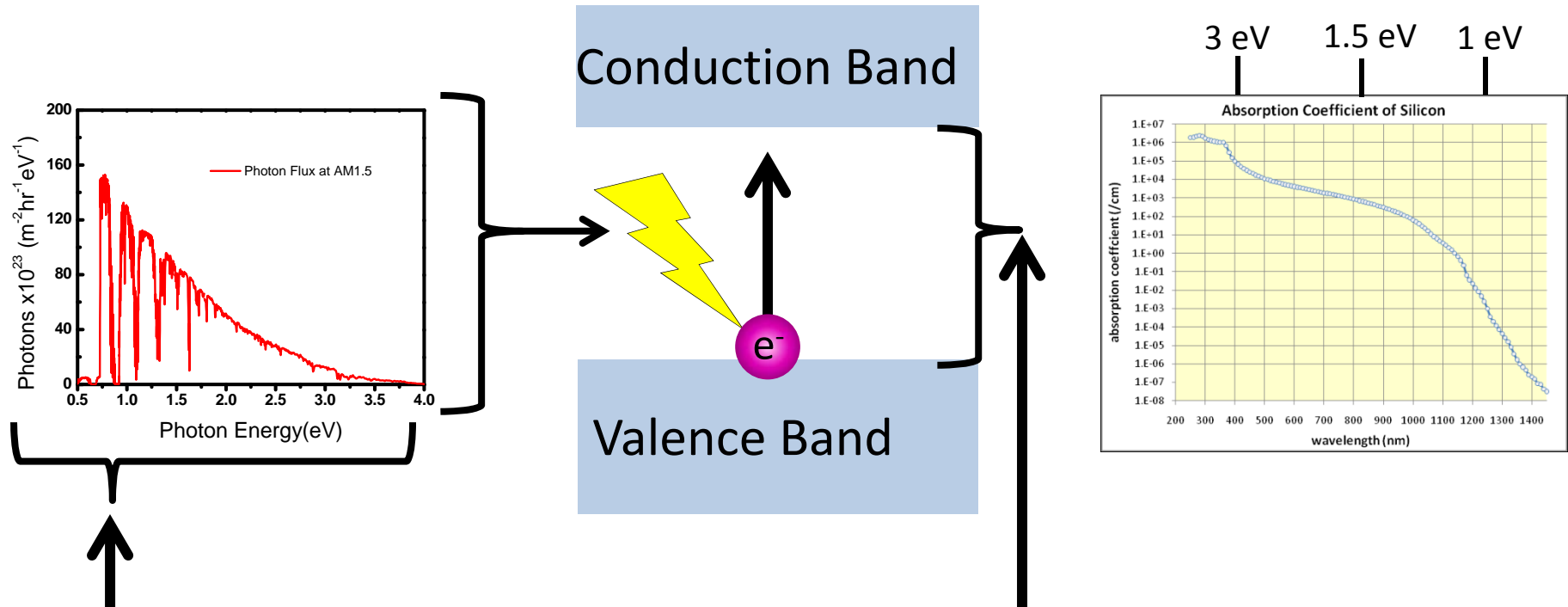


This photon energy needs to match this energy gap.

- Molecular photocatalyst only absorb efficiently at one wavelength.

# Semiconductor Photocatalysts

- Semiconductors have bands rather than distinct levels.



This photon energy needs to roughly this energy gap.

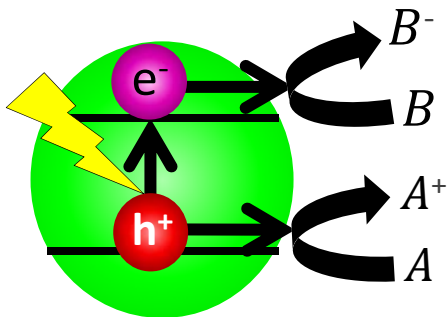
- Semiconductors can absorb a much broader range of light.



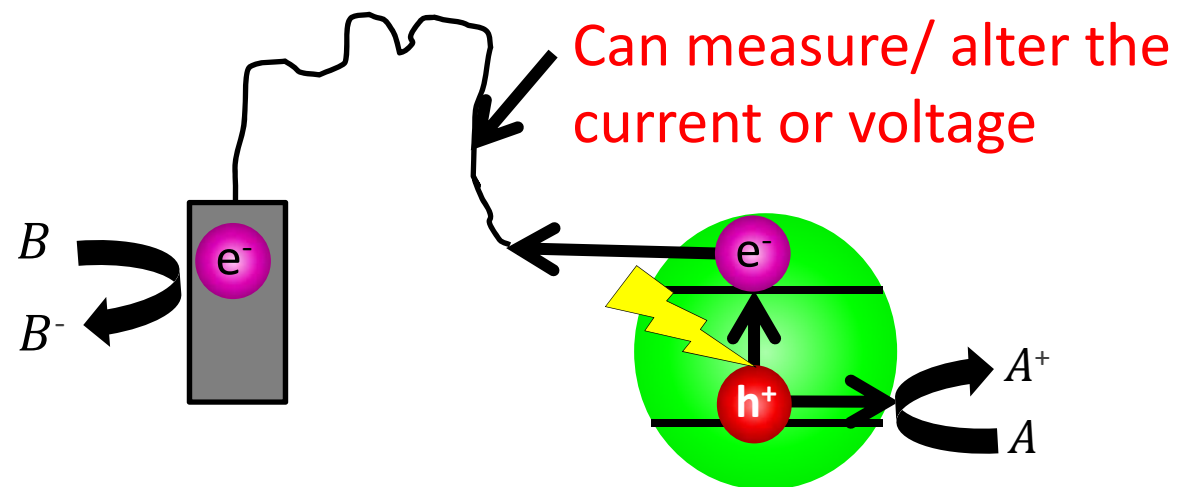
# Photochemistry vs. Photoelectrochemistry

- *Photochemistry*- having both the oxidation and reduction reaction take place on the same material
- *Photoelectrochemistry*- only having the photoabsorber doing oxidation (or reduction) and the electron (or hole) then goes through a wire to a counter electrode to do the other reaction

## Photochemistry



## Photoelectrochemistry

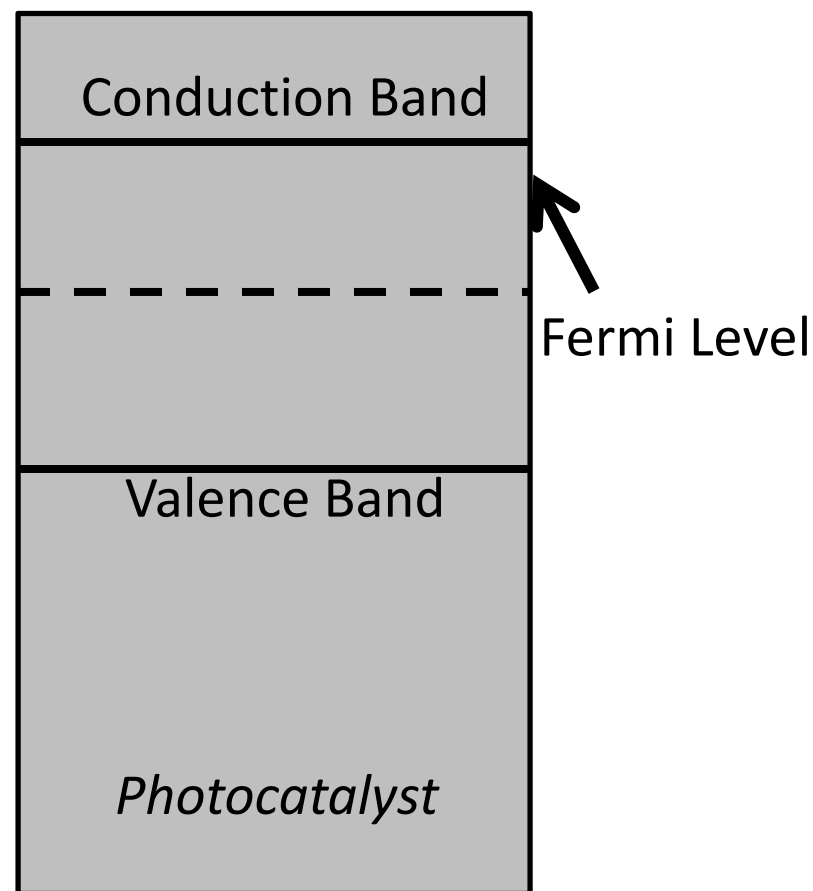


# Analysis

- It's hard to analyze what is going on in photochemistry.
- Analysis techniques include:
  - Measuring the products
  - Spectroscopy (normally expensive equipment)
- Photoelectrochemistry is much easier to analyze
- Common photo-electrochemical techniques include.
  - Standard electrochemical techniques- CV, CA...
  - Incident Photon to Current Efficiency (IPCE)
  - Faradaic Efficiency (electron to chemical product efficiency)
  - Impedance Techniques

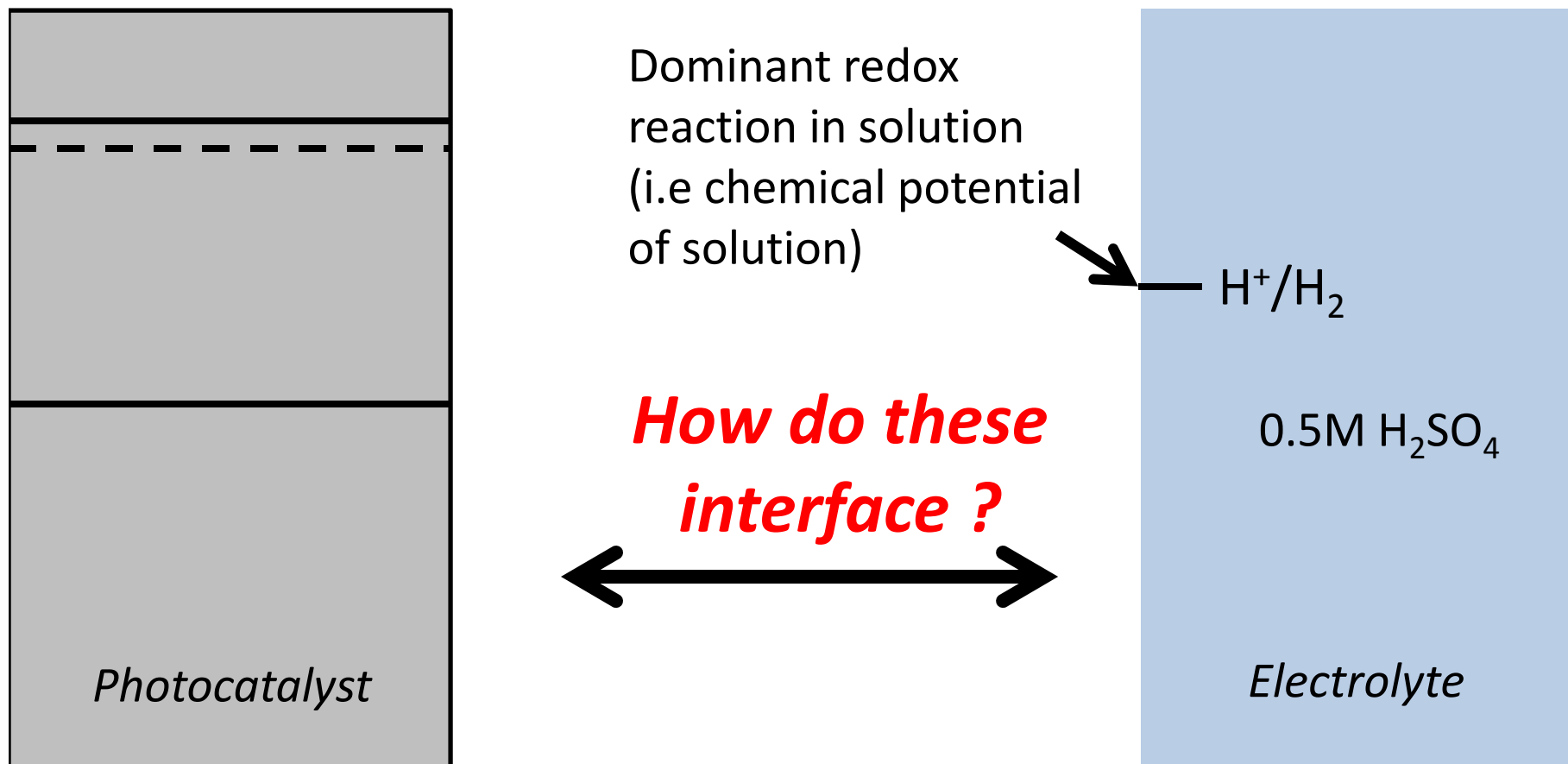
# Semiconductor Fundamentals

- Valence band are filled energy states.
- Conduction bands are empty states.
- The Fermi Level is electronic version of chemical potential.
- Undoped materials have a Fermi level  $\frac{1}{2}$  between VB and CB.
- p-type semiconductors have a Fermi level near the VB.
- n-type semiconductors have a Fermi level near the CB.



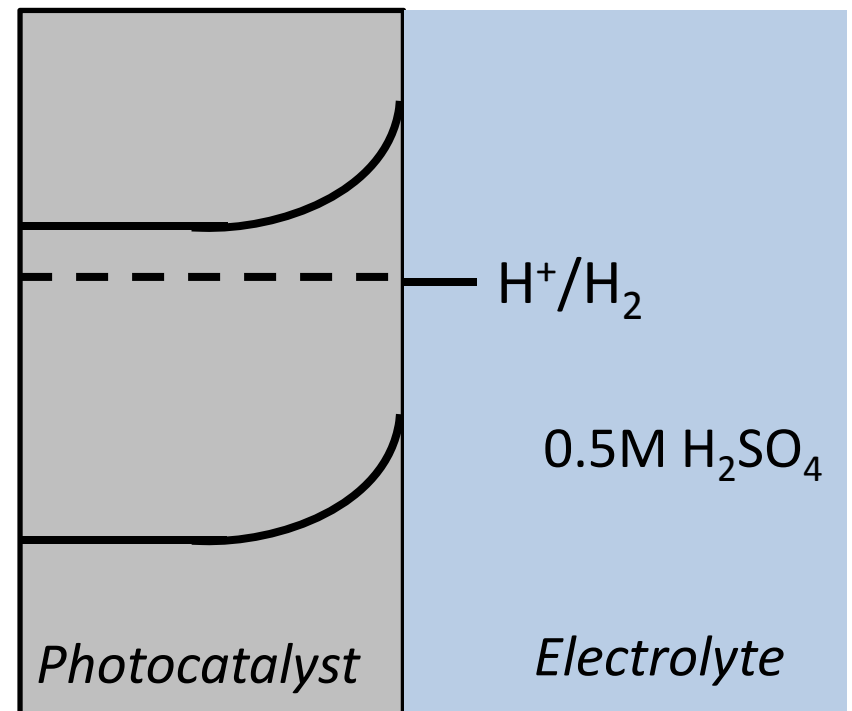
# PEC Fundamentals

- PEC is all about the semiconductor-electrolyte interface.
- Much of this work is purely semiconductor electrochemistry.
- Initially I will describe dark conditions.



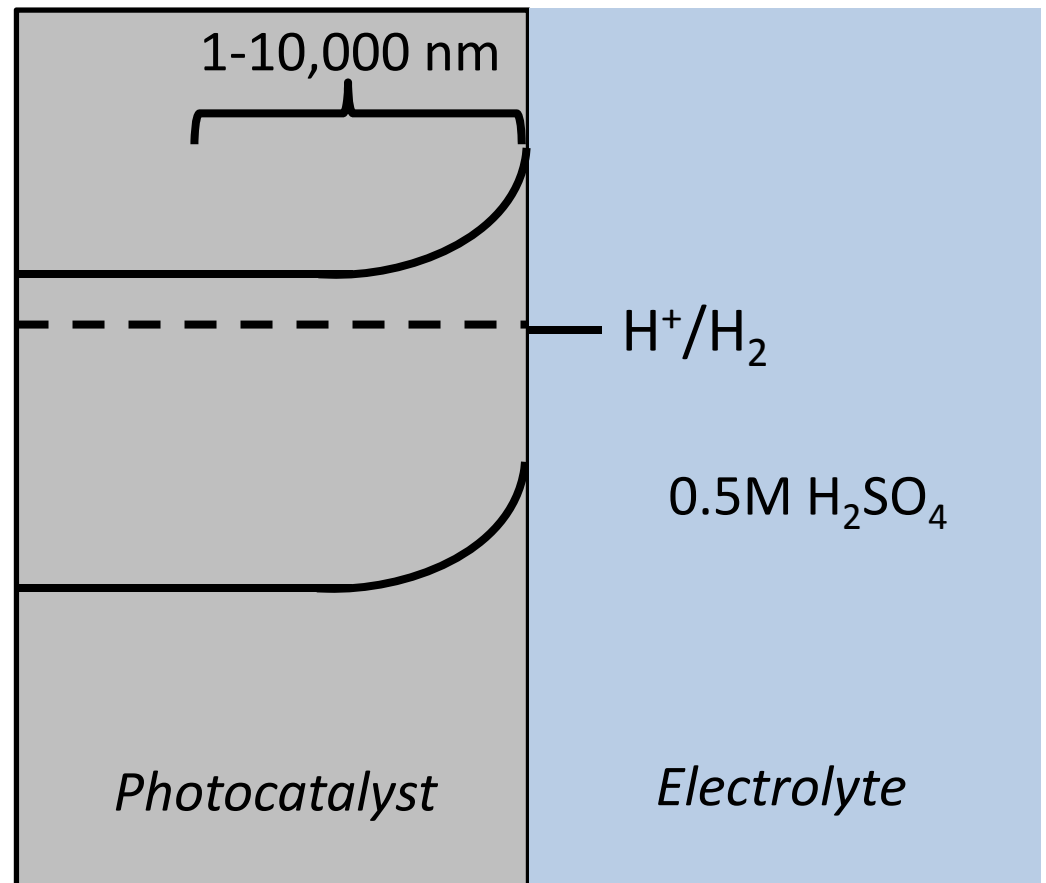
# PEC Fundamentals

- The electrolytes charge dominates the chemical potential of the system.
- The Fermi level matches the chemical potential of the solution.
- The VB and CB should move linearly with the Fermi level.
- The 1<sup>st</sup> few layers of water bind strongly to the semiconductor.
- There are so few carriers, the semiconductor can't balance this charging.
- This results in charging at the surface.



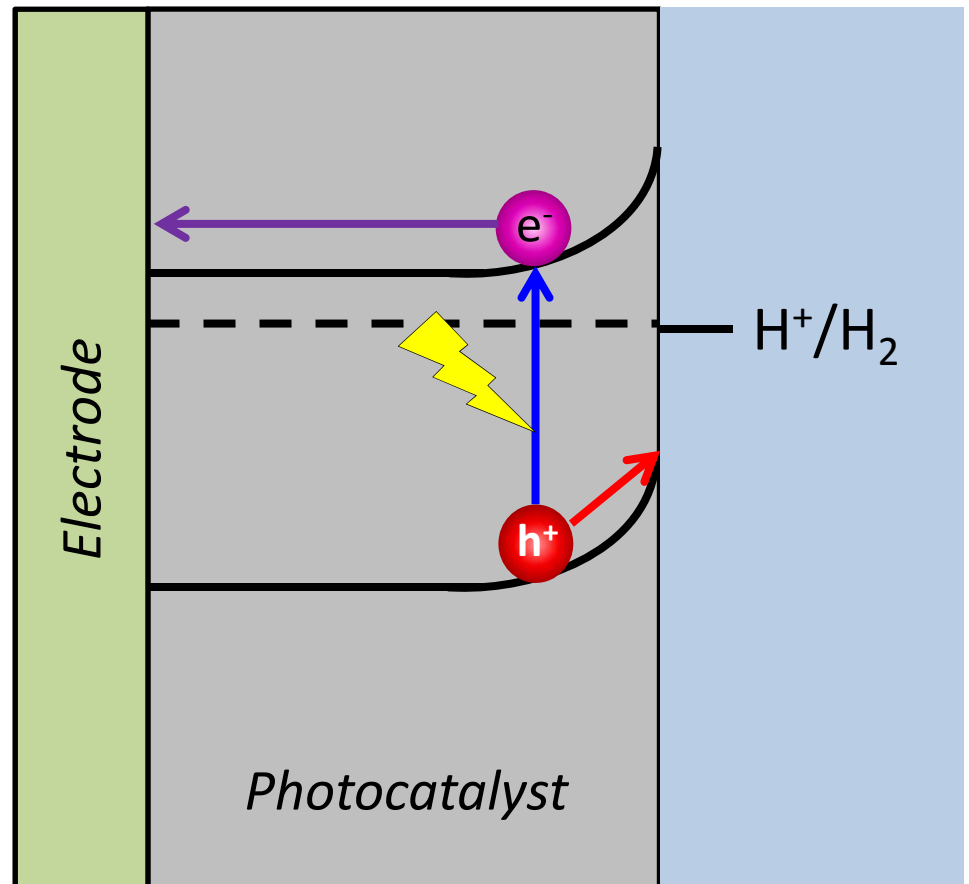
# PEC Fundamentals

- The semiconductor doesn't have many electronic states to conduct.
- Thus the charging must be dissipated over some distance.
- This dissipation results in band bending.
- The higher the dopant density, the smaller depletion width.
- Metals basically have no band bending.



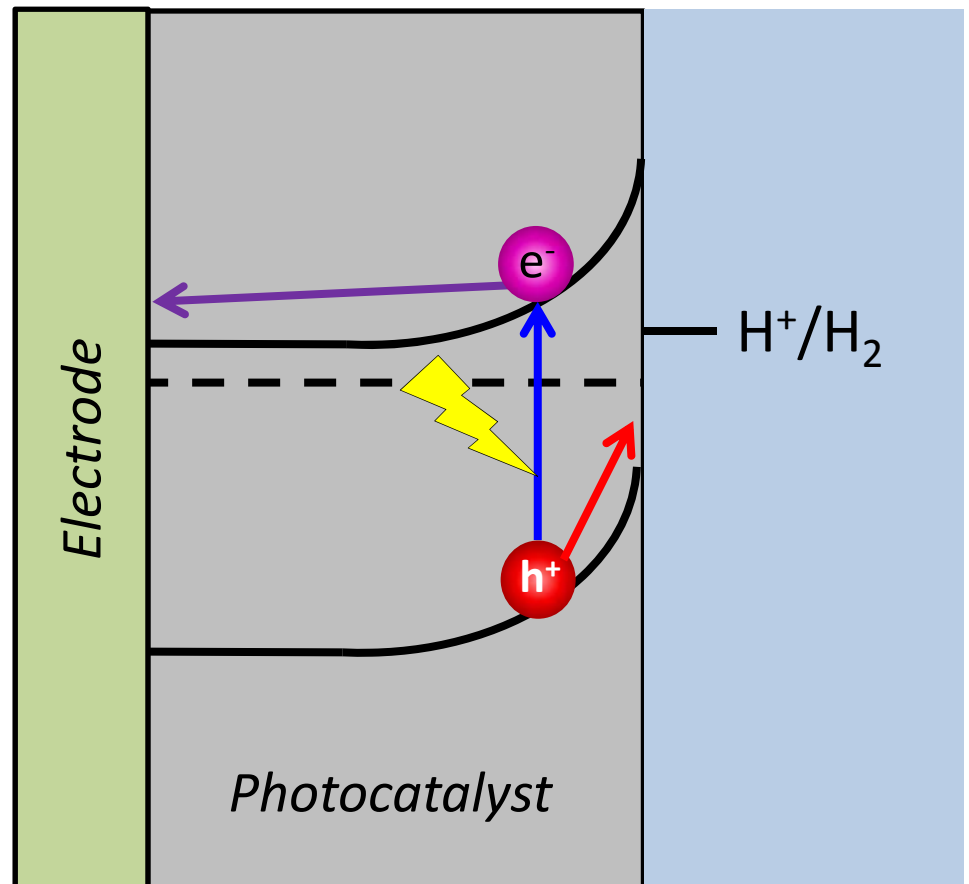
# Advantages of Band Bending

- **Band bending is great for photochemistry!!**
- Electrons love to go down hill, and holes (i.e. anti-electrons) like to go uphill.
- Thus band bending separates electrons and hole.
- Therefore they can not recombine.
- The holes go to the surface to react.
- The electrons go to the bulk/electrode.



# The Electrode

- Rather than have the electrolyte produce band bending, we can have an electrode do this.
- The electrode sets the Fermi level, but does not effect the solution chemical potential.
- This produces a non-equilibrium state.
- This also increases our band bending.
- Increased band bending means better electron-hole separation.

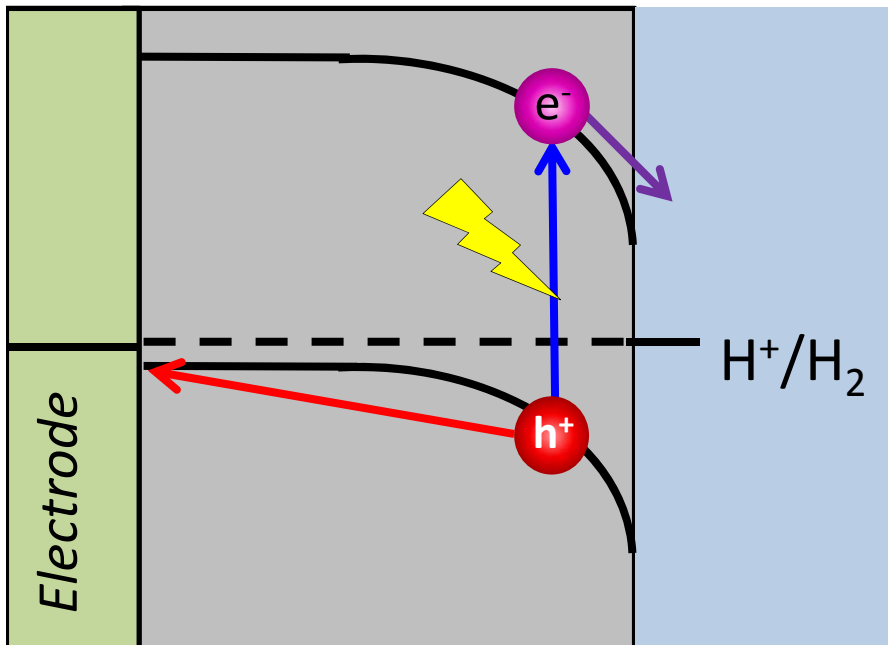




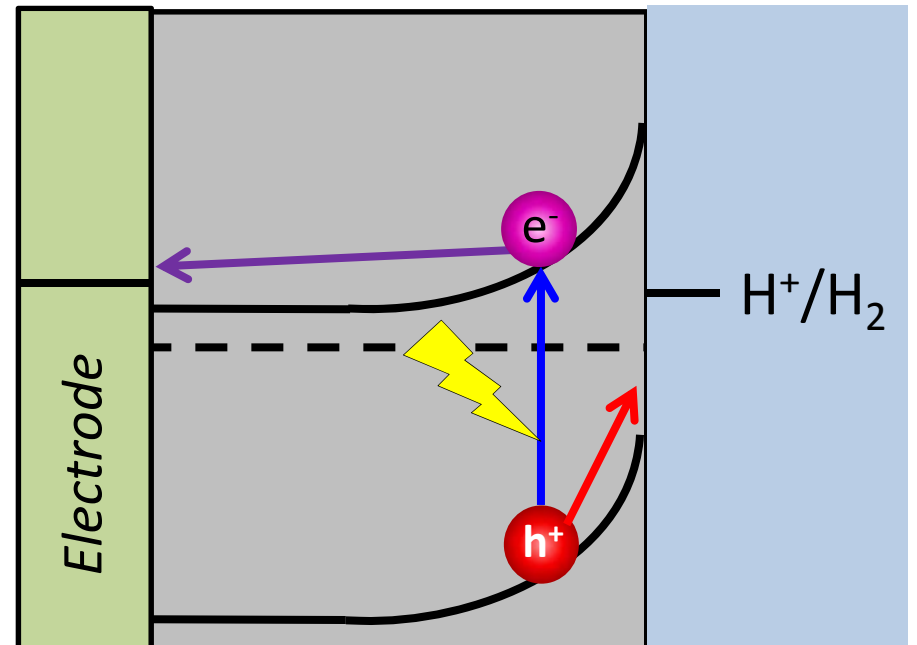
# n-type versus p-type

- n-type will almost always force holes to the surface.
- Holes oxidize, thus **n-type electrode do oxidation reactions.**
- p-type will almost always force electrons to the surface.
- Electrons reduce, thus **p-type electrode do reduction reactions.**

## p-type Semiconductor

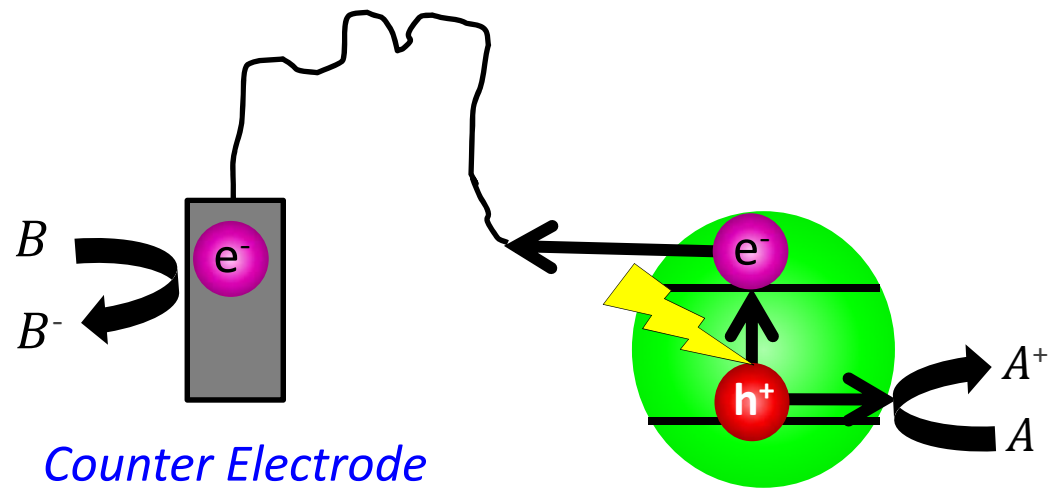


## n-type Semiconductor



# Counter Electrode

- If the semiconductor does either an oxidative (or reductive) reaction, where is the corresponding reductive (or oxidation) reaction?
- This takes place on the metallic counter electrode (in the dark).
- The transfer of  $e^-$  or  $h^+$  through the wire can be measured as current.



# What reactions to do?

- p-type reduction reactions:

- $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_2 + \text{OH}^-$
- $\text{CO}_2 + \text{e}^- \rightarrow \text{C}_x\text{H}_y\text{O}_z$  (hydrocarbons) +  $\text{OH}^-$
- $\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^*$  ← Superoxide/ $\text{O}_2$  radical – oxidizing agent
- $\text{Ag}^+\text{Cl}^- + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$  ← This is how photographic films are made.

- n-type oxidation reactions:

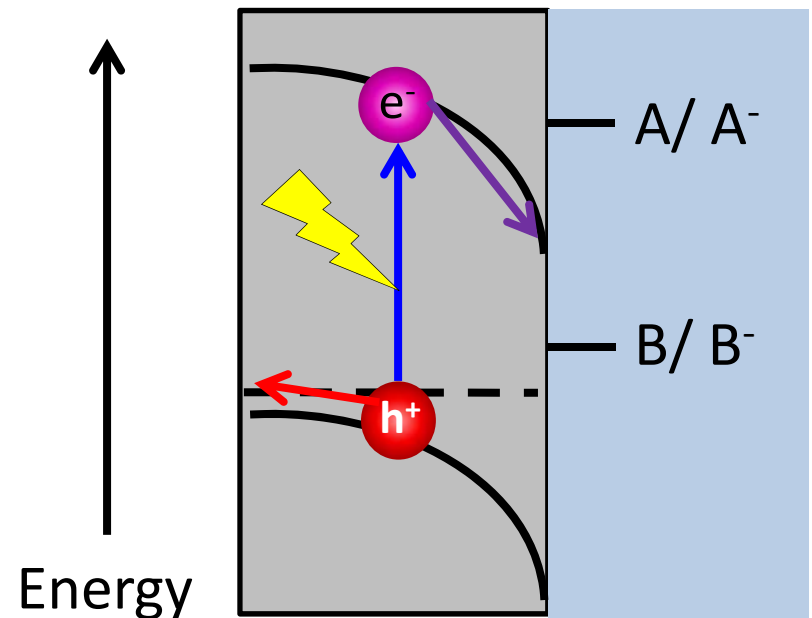
- $\text{OH}^- + \text{h}^+ \rightarrow \text{H}_2\text{O} + \text{O}_2$
- Carbon based pollutants +  $\text{h}^+$  →  $\text{CO}_2 + \text{H}^+$
- $\text{Cl}^- + \text{h}^+ \rightarrow \text{Cl}_2$

- Overall reactions (using counter electrode or 2 photoabsorbers):

- $\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2$
- Carbon based pollutants →  $\text{CO}_2 + \text{H}_2\text{O} + \text{others}$  (This is not well defined)
- $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{C}_x\text{H}_y\text{O}_z$  (hydrocarbons) +  $\text{O}_2$


# Issues with Band Levels

- For a p-type material, the electron will go to the electrolyte at an potential no higher than the conduction band.
- The conduction band is pinned at the semiconductor/water interface.
- Thus photo-electrons can only reduce species, which can get reduced at or below the conduction band.
- In the case to the right, A can not be reduced, whereas B can be reduced.
- Even if we bias the electrode to increase band-bending, we still can't get the electron to reduce A.



# Trick with Band Positions

- The band levels of oxides in water can be modified.
- Changes in pH, modify the oxide surface.
- For all oxides the valence band (and conduction band) vary via the following equation.

$$VB = VB(@ pH = 0) + \frac{RT}{nF} \times pH$$


- The VB or CB position are always relative to some reference such as Ag/AgCl, SCE, or normal hydrogen electrode.
- The general rule is every increase in pH gives you 59 mV of reducing power.
- *However the redox potential of any reaction that has an H<sup>+</sup> as a reactant needs 59 mV/pH more of reducing power.*

# Band Positions and Redox Reactions

- Below are a list of band positions and redox reactions.
- For the semiconductors, more negative means more reducing power.

## Semiconductor

Material	VB	CB
Si	0.6	-0.5
TiO <sub>2</sub>	3.0	-0.1
WO <sub>3</sub>	2.8	0.2
CdS	1.75	-0.5
GaP	1.25	-1.0
Cu <sub>2</sub> O	1.0	-1.0
Fe <sub>2</sub> O <sub>3</sub>	2.4	0.3

All potentials are vs. NHE

## Reduction Reactions

Reaction	Potential
$\text{H}^+ + \text{e}^- \rightarrow \text{H}_2$	-0.0
$\text{CO}_2 + \text{e}^- + \text{H}_2\text{O} \rightarrow \text{CH}_4 + \text{OH}^-$	0.1
$\text{CO}_2 + \text{e}^- + \text{H}_2\text{O} \rightarrow \text{CO} + \text{OH}^-$	-0.14
$\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^*$	-0.5

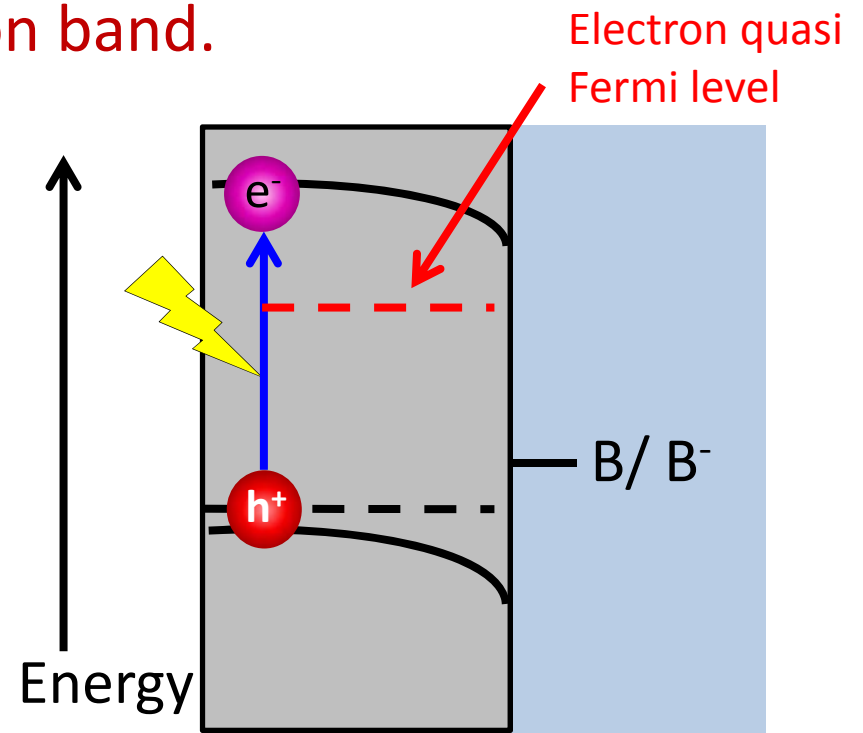
## Oxidation Reactions

Reaction	Potential
$\text{H}_2\text{O} + \text{h}^+ \rightarrow \text{O}_2 + \text{H}^+$	1.23
$\text{Cl}^- + \text{h}^+ \rightarrow \text{Cl}_2$	1.4
$\text{HCOOH} + \text{h}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O}$	0.25

All potentials are vs. NHE

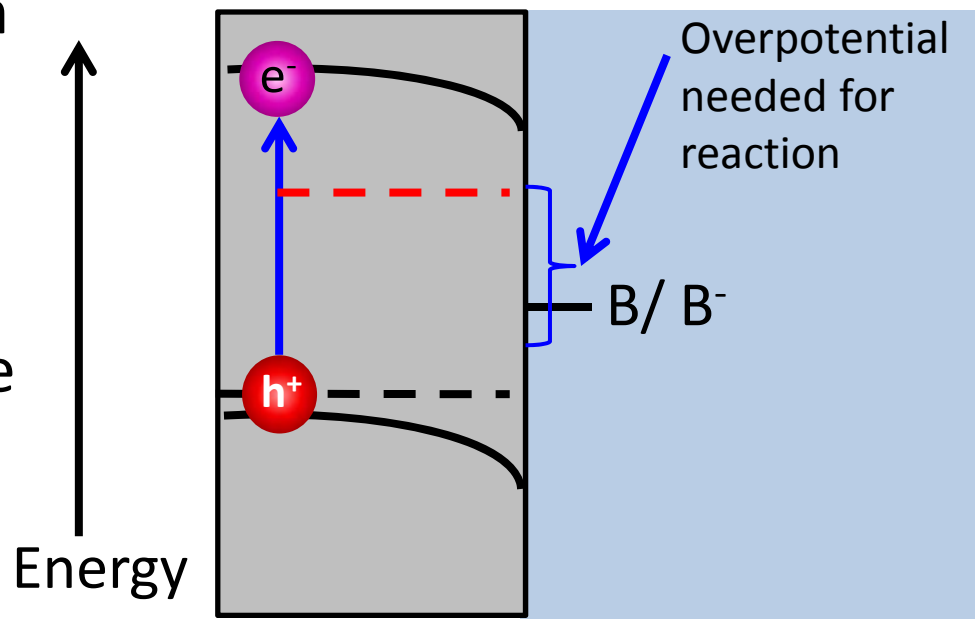
# More Issues with Semiconductors

- Just because an electron is in the conduction band, doesn't mean that is the chemical potential of the electron.
- Just because an electron is in the conduction band, doesn't mean that is the chemical potential of the electron.
- The photo-electron has a quasi Fermi-level, which is somewhere below the conduction band.
- The quasi-Fermi level is based on light intensity and the ability to efficiently separate electrons and holes.
- Ole Hansen will discuss this in detail when he presents.



# Even More Issues with Semiconductors

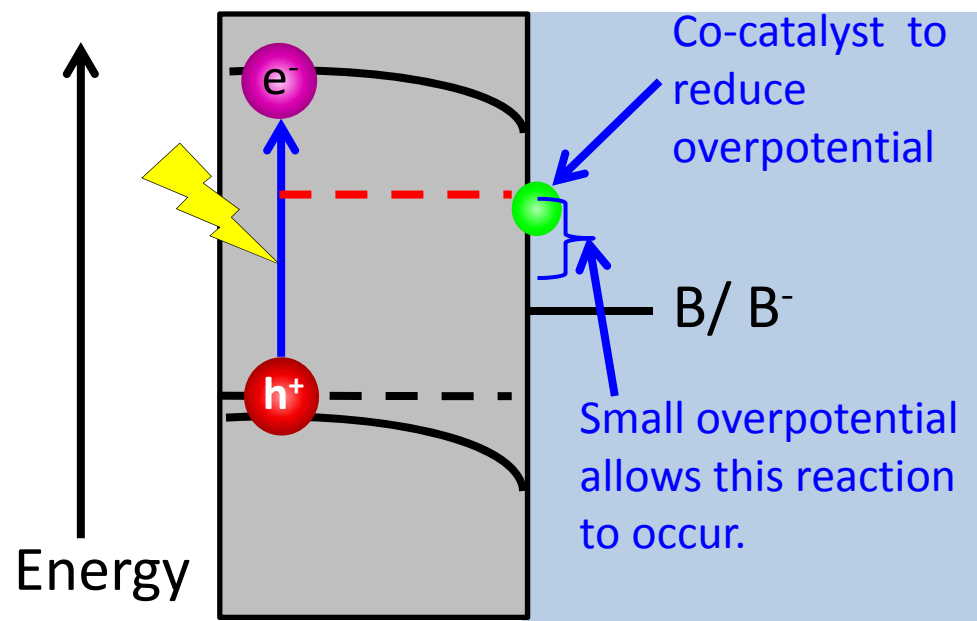
- **Issue #1-** the electron quasi-Fermi level needs to have a higher energy than the redox couple to reduce it.
- I know of no pure way to determine where your quasi-Fermi level is located at.
- If you apply bias, you can increase band bending, which may help increase the Quasi-Fermi level.
- **Issue #2-** If the redox reaction isn't easy, you will also have catalytic overpotentials.
- If overpotential is too large, you still won't be able to have reduction.





# Photoabsorber + Catalyst

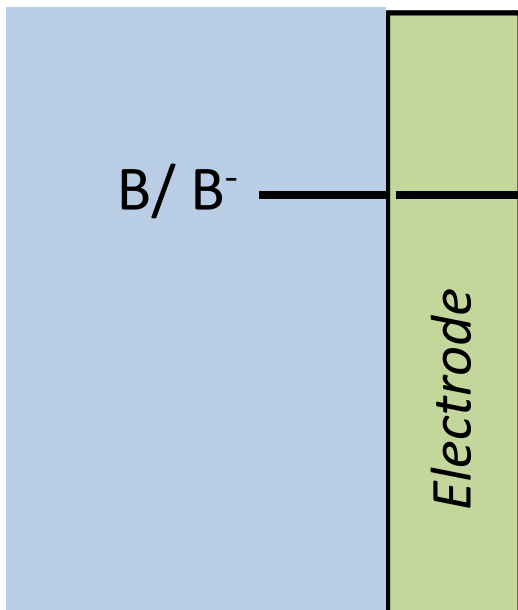
- Unless you are extremely lucky, the photoabsorber will not be the best electro-catalyst for your reaction.
- Thus you need a co-catalyst.
- At this point you are doing coupled photo-absorption and electrochemistry.
- Ifan Stephens explained the electrochemistry in a previous lecture.
- *If all this becomes electrochemistry, why do we do photoelectrochemistry?*



# Photovoltage

- PEC lets us do electrochemistry with less/no applied bias.
- The electrode potential matches the Fermi level of the hole quasi-Fermi level.
- Thus the difference between the hole quasi-Fermi level and electron quasi-Fermi level is the extra voltage the PEC gives us.

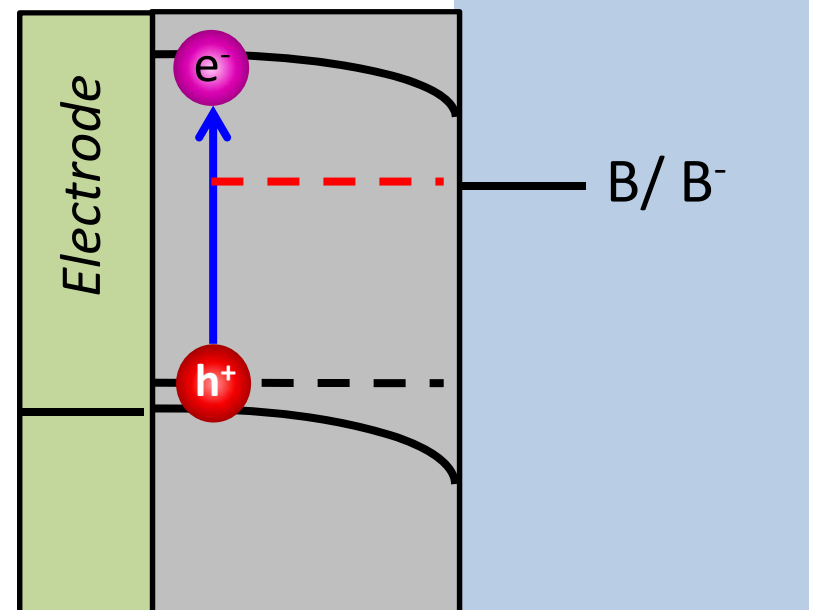
## Electrochemistry



← This reaction takes more energy than this reaction.

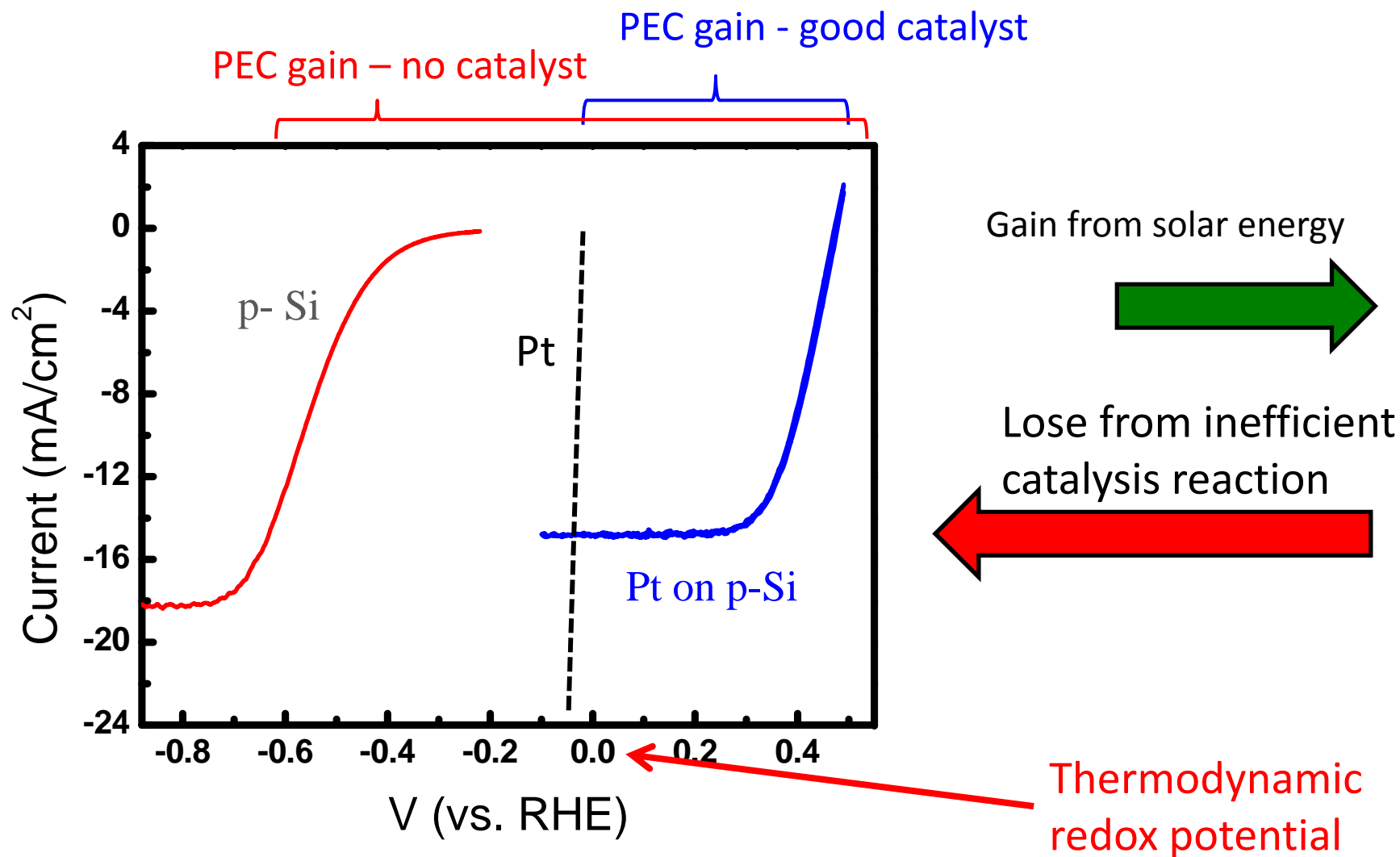


## Photo-electrochemistry



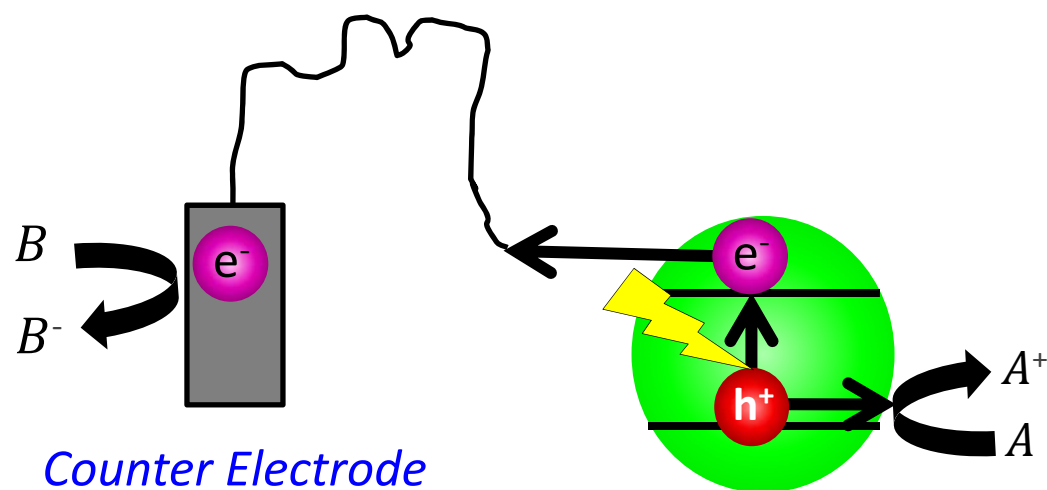
# Results

- Below is a cyclic voltammogram of various electrodes for the  $H^+/H_2$  reaction.



# Losses at the Counter Electrode

- Since the photocatalyst has catalytic losses the counter electrode will also have catalytic losses.
- To eliminate counter electrode losses, we use a 3-electrode cell.
- In a 3 electrode cell the voltage is measured between the photocatalyst and reference electrode.
- The current still runs between the photocatalyst and counter.
- In a 3 electrode cell, the system provides extra voltage to the counter electrode to mitigate the catalytic losses.

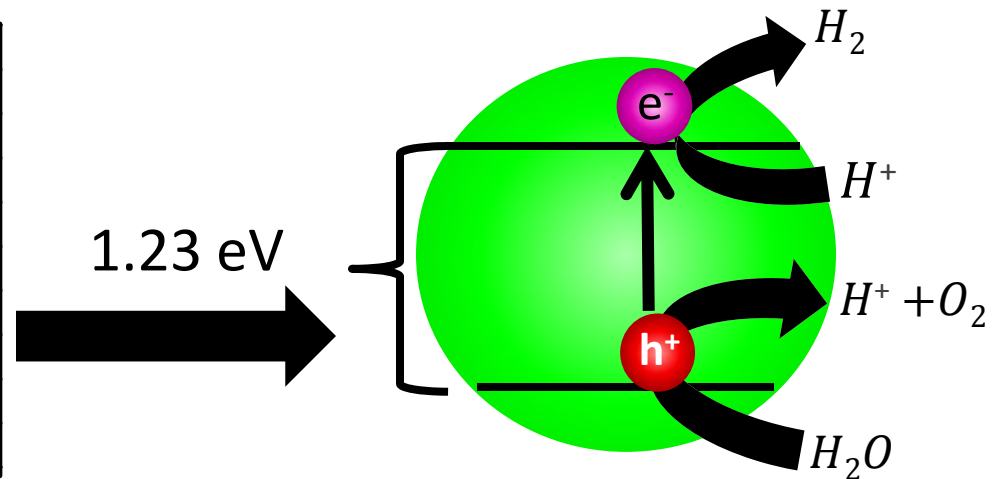
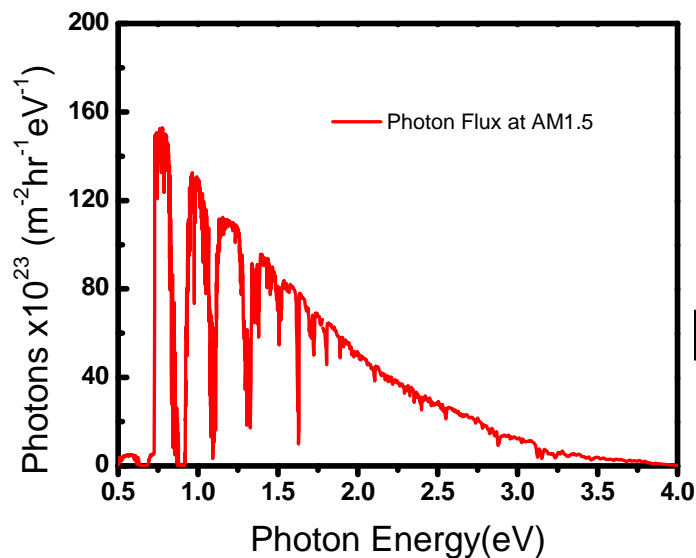


# Applications of Photochemistry and Photoelectrochemistry

- [Water Splitting](#)
- [CO<sub>2</sub> Reduction](#)
- [Pollutant Degradation](#)
- [Dye-Sensitized Solar Cells](#)
- [Perovskite Solar Cells](#)
- [Sensors](#)

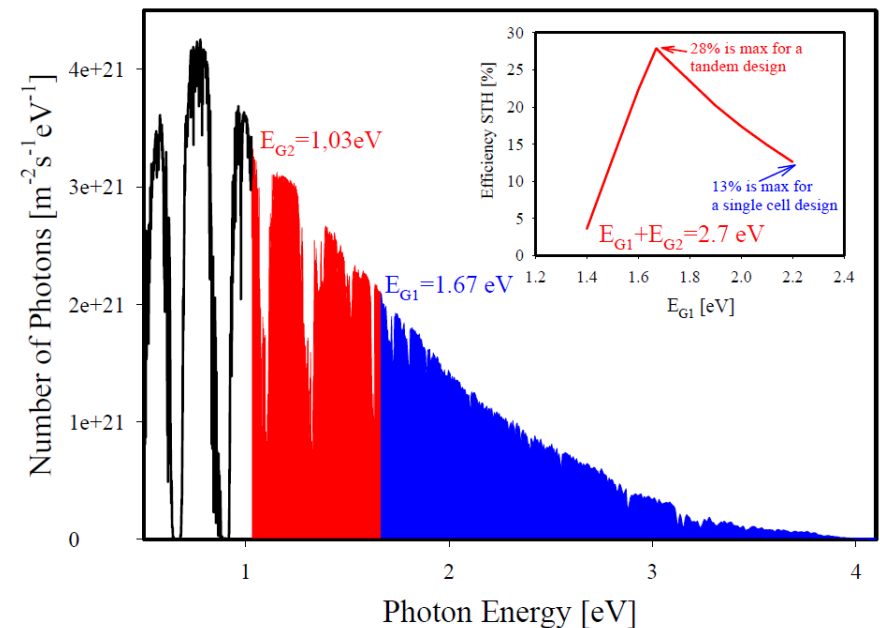
# Water Splitting

- $H_2O \rightarrow H_2 + O_2$
- The main idea behind this reaction is to produce hydrogen, which can replace fossil fuels as an energy source.
- Water is our reactant, and oxygen is a byproduct.
- Thermodynamically this reaction needs 1.2 eV.
- Realistically you need about 2.3 eV.

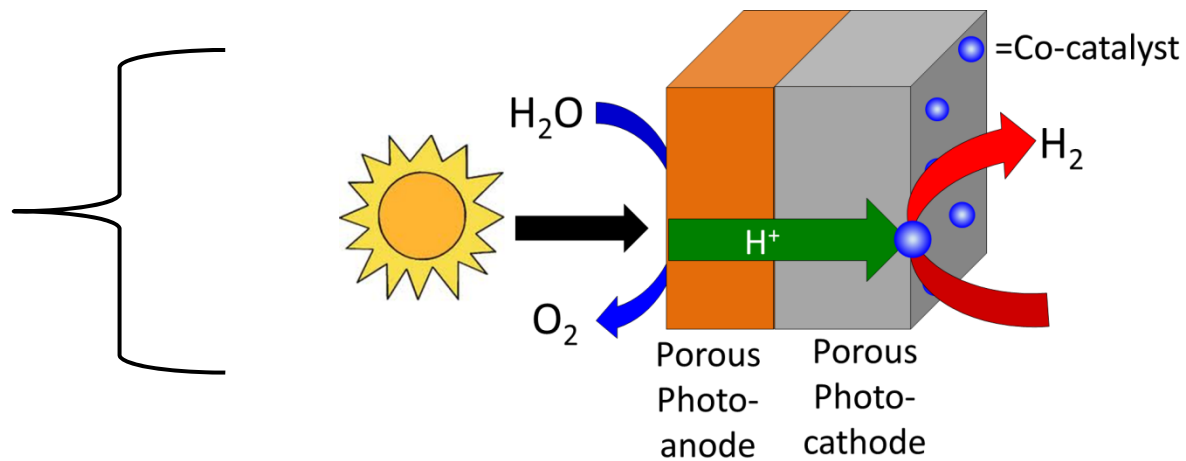


# Water Splitting

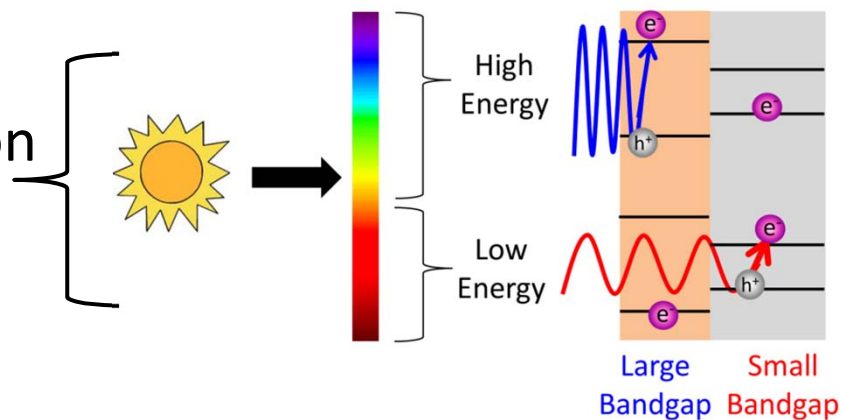
- $\text{H}_2$  has to compete with fossil fuels, which are extremely cheap.
- There are 2 approaches:
  - Do it really cheap, and then try to bring up efficiencies.
  - Do it really efficient and then bring down costs.
- I will discuss the high efficiency first approach because that is more of a physics way of doing it.
- To optimize water splitting you need 2 photocatalysts
  - 1 absorbs the blue light
  - 1 absorbs the red light
- A 2 photocatalyst design gives you just enough voltage to split water.



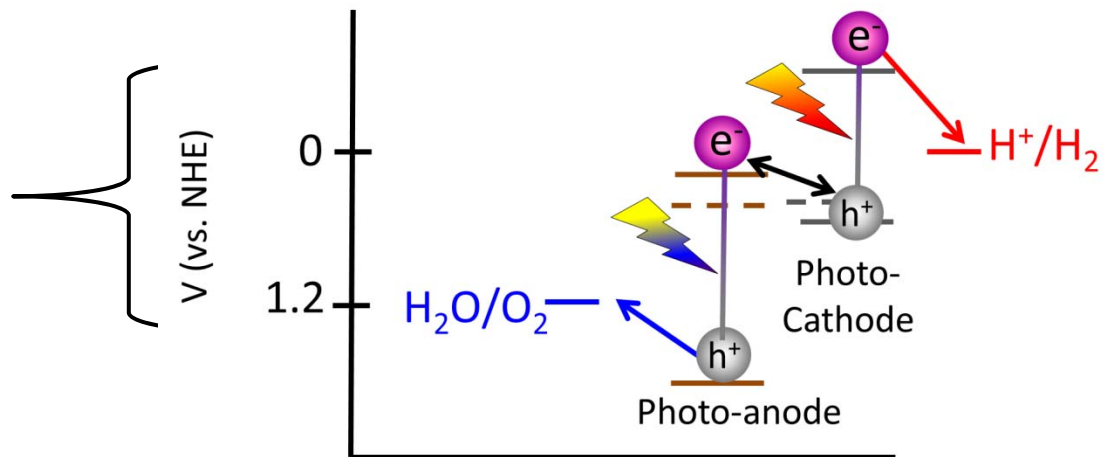
Physical Design



Optical Absorption Properties



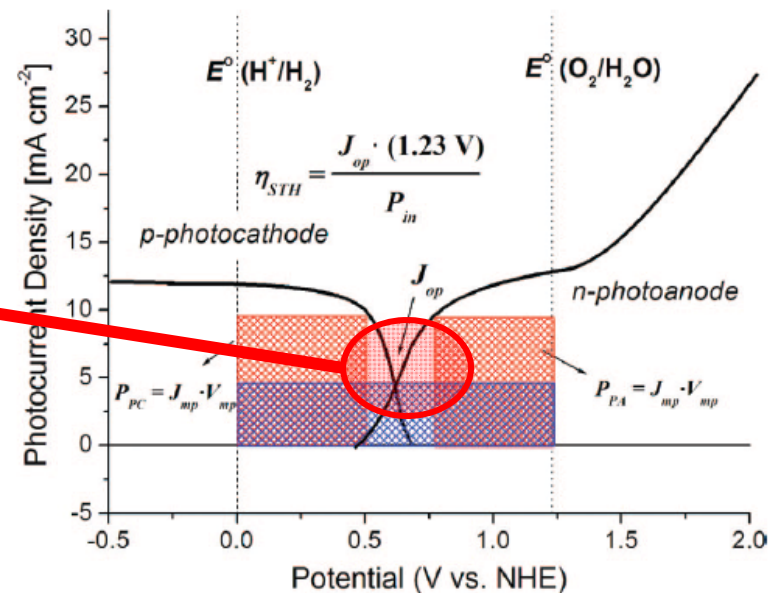
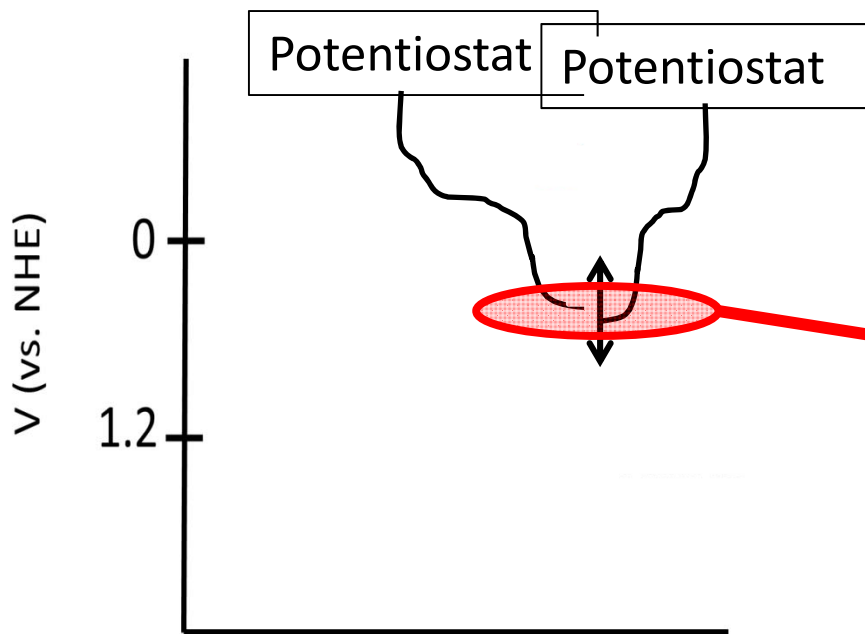
Energetic Properties





# Energy Levels of Our Processes

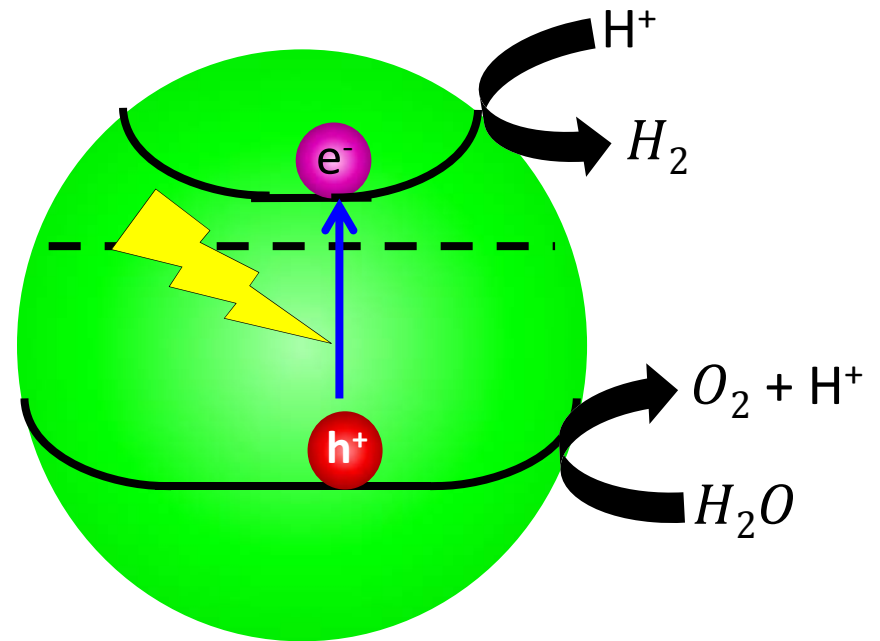
- The photoanode will oxidize water to oxygen while the silicon will reduce the protons to hydrogen.
- The Fermi levels of both photoabsorbers must equilibrate.
- Catalysts will be needed to improve reaction kinetics.



Walter et al. , Chem Review, 2010

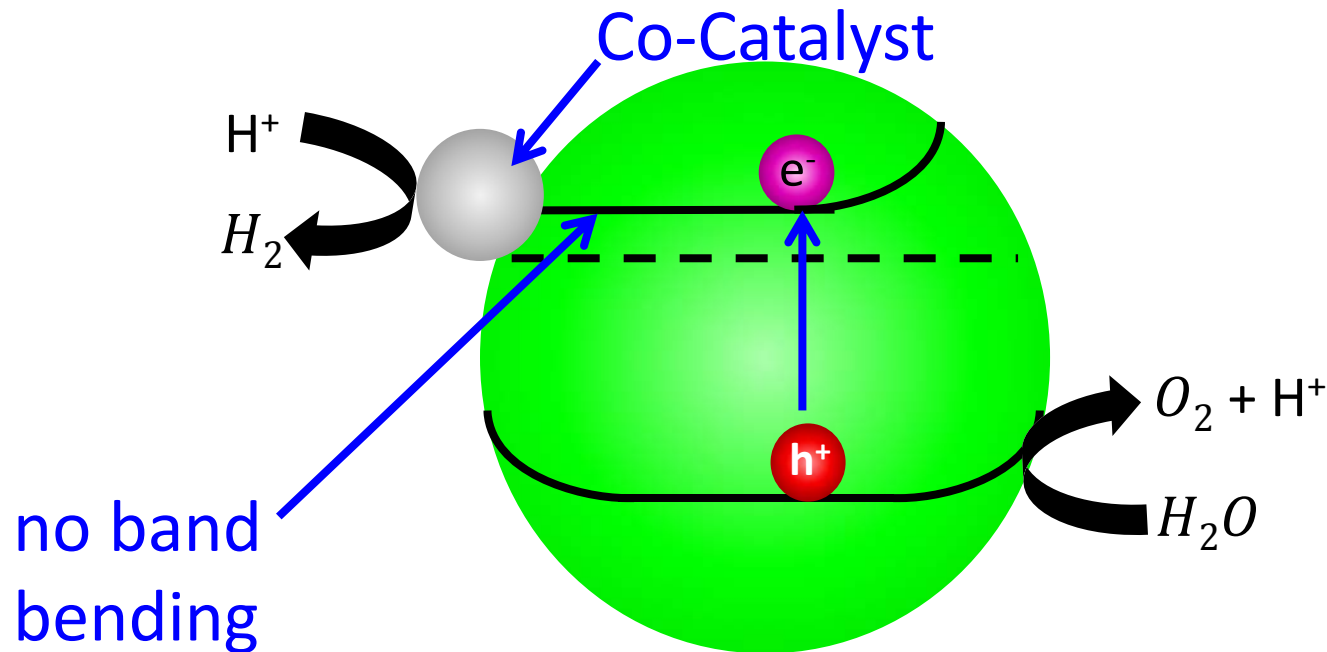
# 1-Photon Overall Water Splitting

- This is inherently a cheap method because you can use nanoparticles dispersed in water rather than aligned films.
- The problem is: *Should the photocatalyst be p-type or n-type?*
- There is no good answer to this.
- If it is n-type, holes will easily go to the surface, but electrons can't.
- If it is p-type, holes will easily go to the surface, but electrons can't.



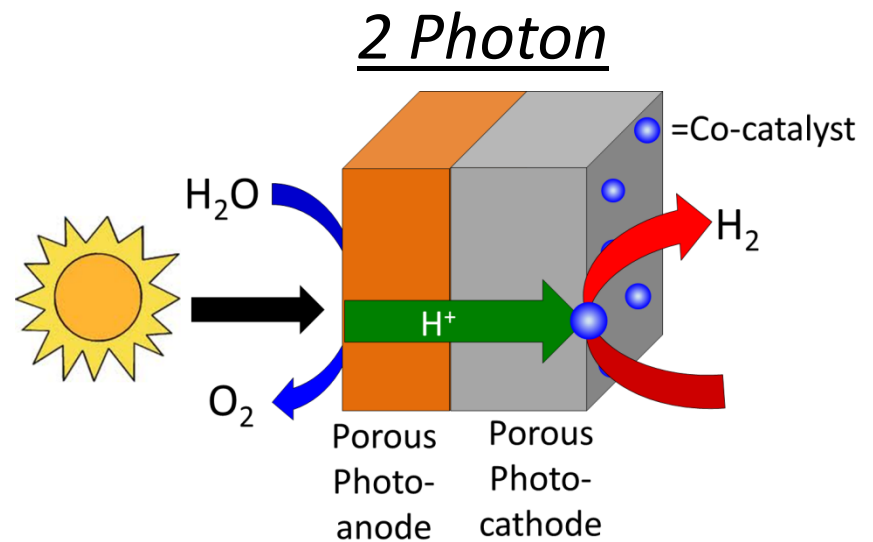
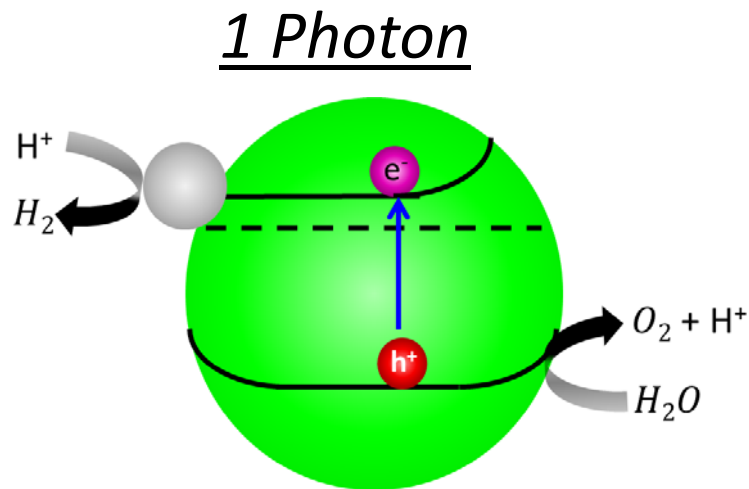
# 1-Photon Overall Water Splitting

- Approaches to resolving the band bending issue.
  - Don't dope the material, thus mitigating bandbending.
    - Creating a non-doped semiconductor is hard.
  - Have small particles.
    - Very small particles prevent band bending from building up (< 50 nm)
  - Have a co-catalyst create an ohmic contact.
    - Forming an ohmic contact prevents band bending at localized spots.



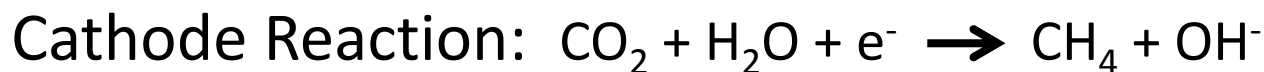
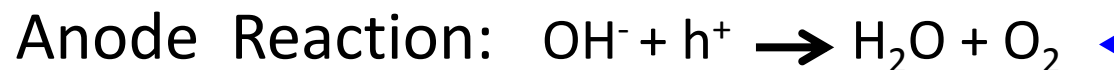
# Water Splitting- Recombination

- Electrons and holes can recombine to waste energy.
- In a 1 photon device it is very easy for the  $H_2$  and  $O_2$  to recombine to form water.
- Also the hole could oxidize  $H_2$  instead of  $H_2O$ . And the electron could reduce  $O_2$  rather than  $H^+$ .
- In a 2-photon/film these back reactions are less prevalent.



# CO<sub>2</sub> Reduction

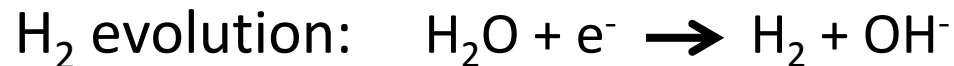
- CO<sub>2</sub> reduction to hydrocarbons is not easy electrochemically, thus it is even harder for PEC.
- If we simply look at CO<sub>2</sub> to methane.



Same as  
water splitting

8 electron transfer, thus hard reaction

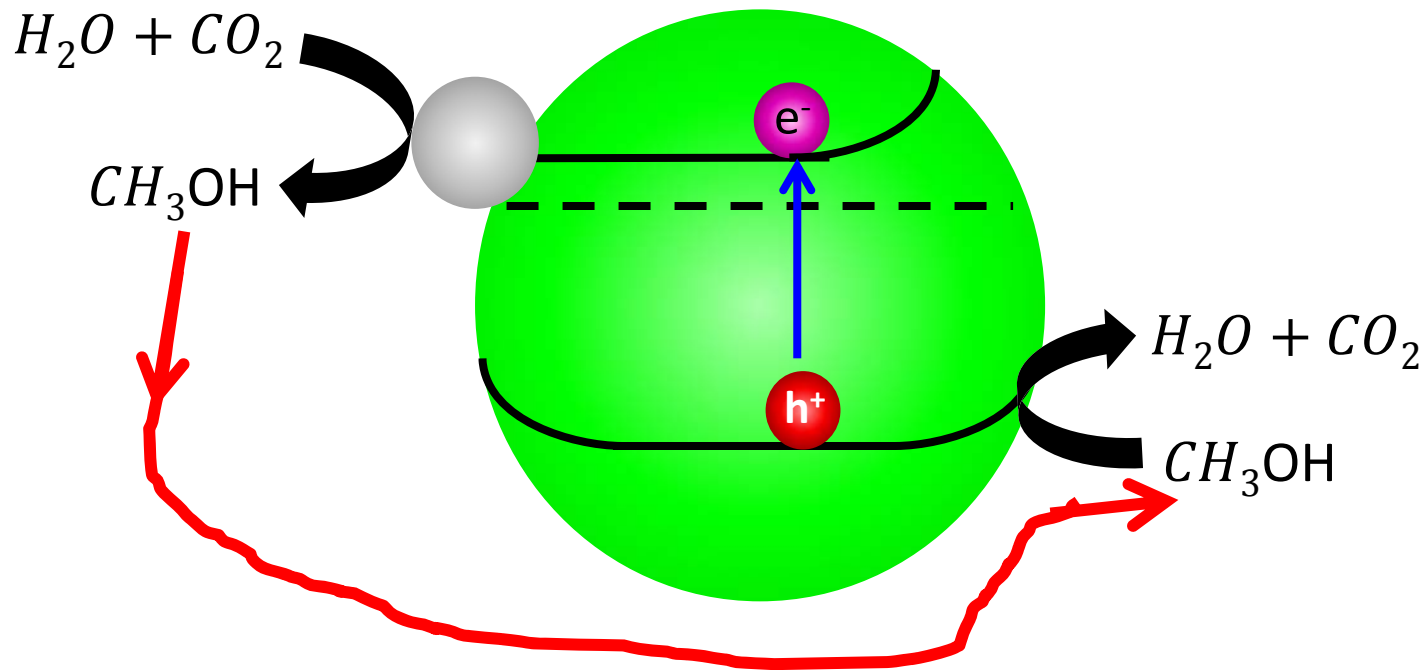
- The biggest impediment to CO<sub>2</sub> reduction is this cathode side reaction.



Most catalysts would rather do this reaction than CO<sub>2</sub> reduction.

# CO<sub>2</sub> Reduction-Recombination

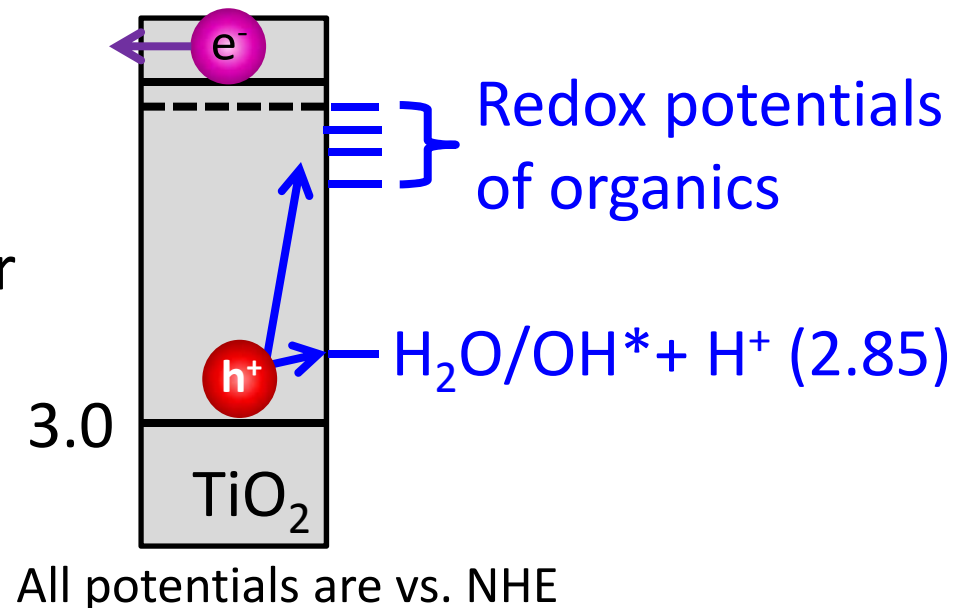
- Just like water splitting the hydrocarbons from CO<sub>2</sub> reduction, can be oxidized back to CO<sub>2</sub>.
- This recombination will happen more for liquid CO<sub>2</sub> reduction products rather than gaseous CO<sub>2</sub> reduction products.



- We can take advantage of this troublesome issue though.

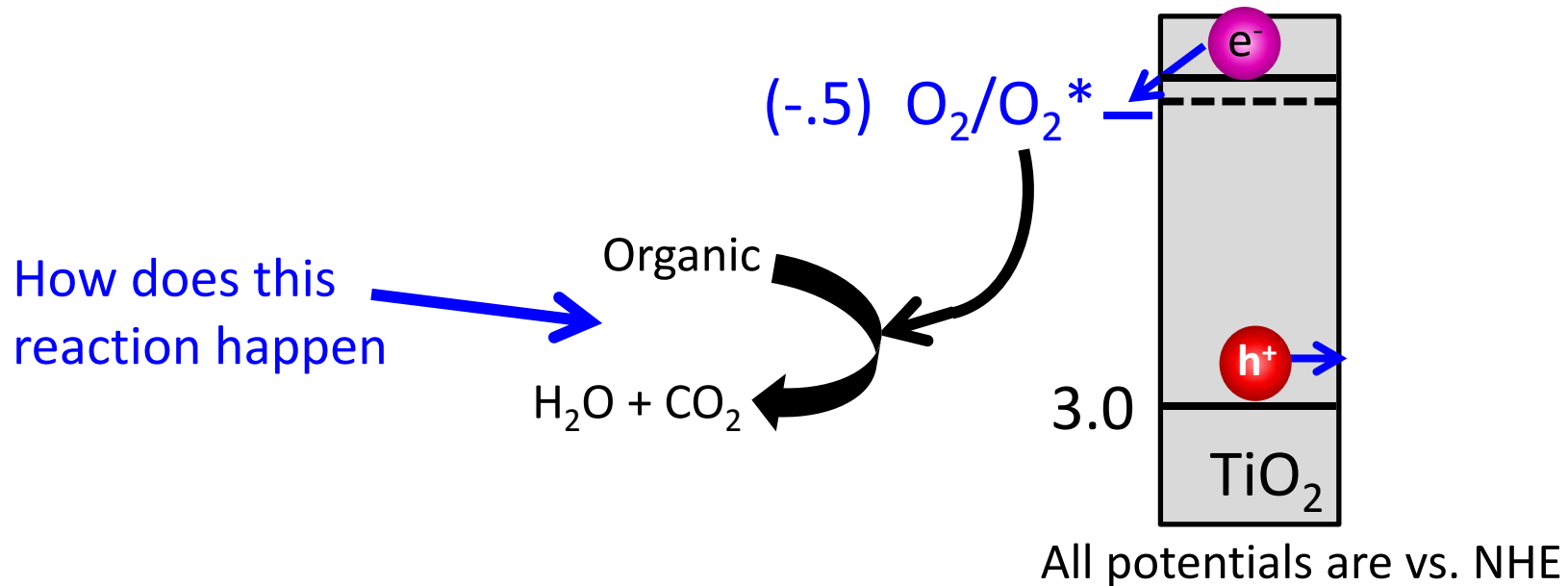
# Pollutant Removal

- Often there is organic pollutants that need to be removed for drinking or sanitation purposes.
- Most of these are very easy to oxidize with n-type semiconductors.
- Oxides are especially nice because they can produce OH radicals from water.
- OH radicals are highly oxidative and can migrate into solution.
- Thus either the photo-hole or the radical can oxidize the pollutant.



# Pollutant Removal

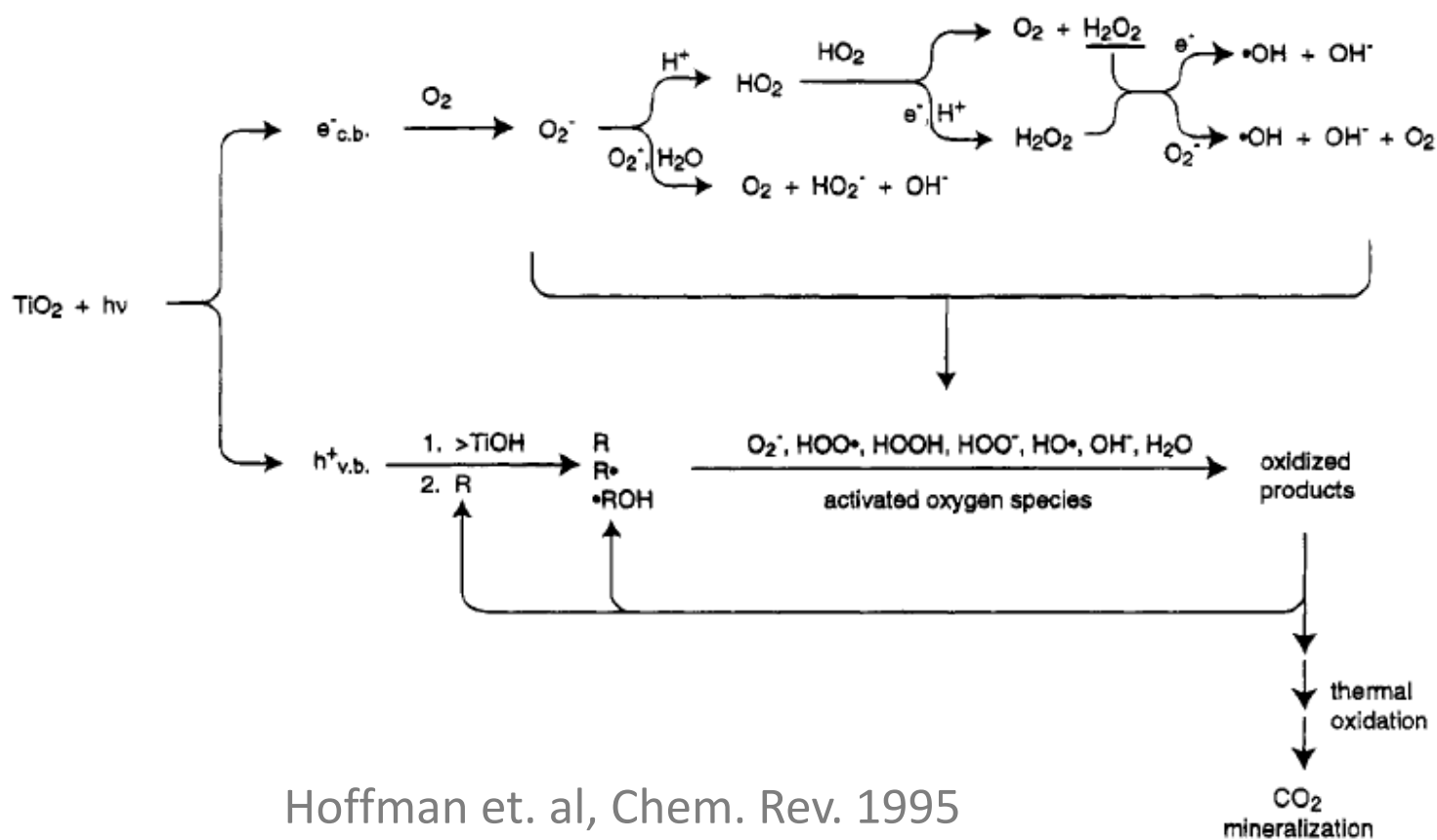
- While the hole oxidizes, *what does the electron do?*
- If there is oxygen in the system, which there always is, the electron can reduce the oxygen to form a superoxide (or oxygen radical.)
- Oxides are especially nice because they can produce OH radicals from water.





# Pollutant Removal

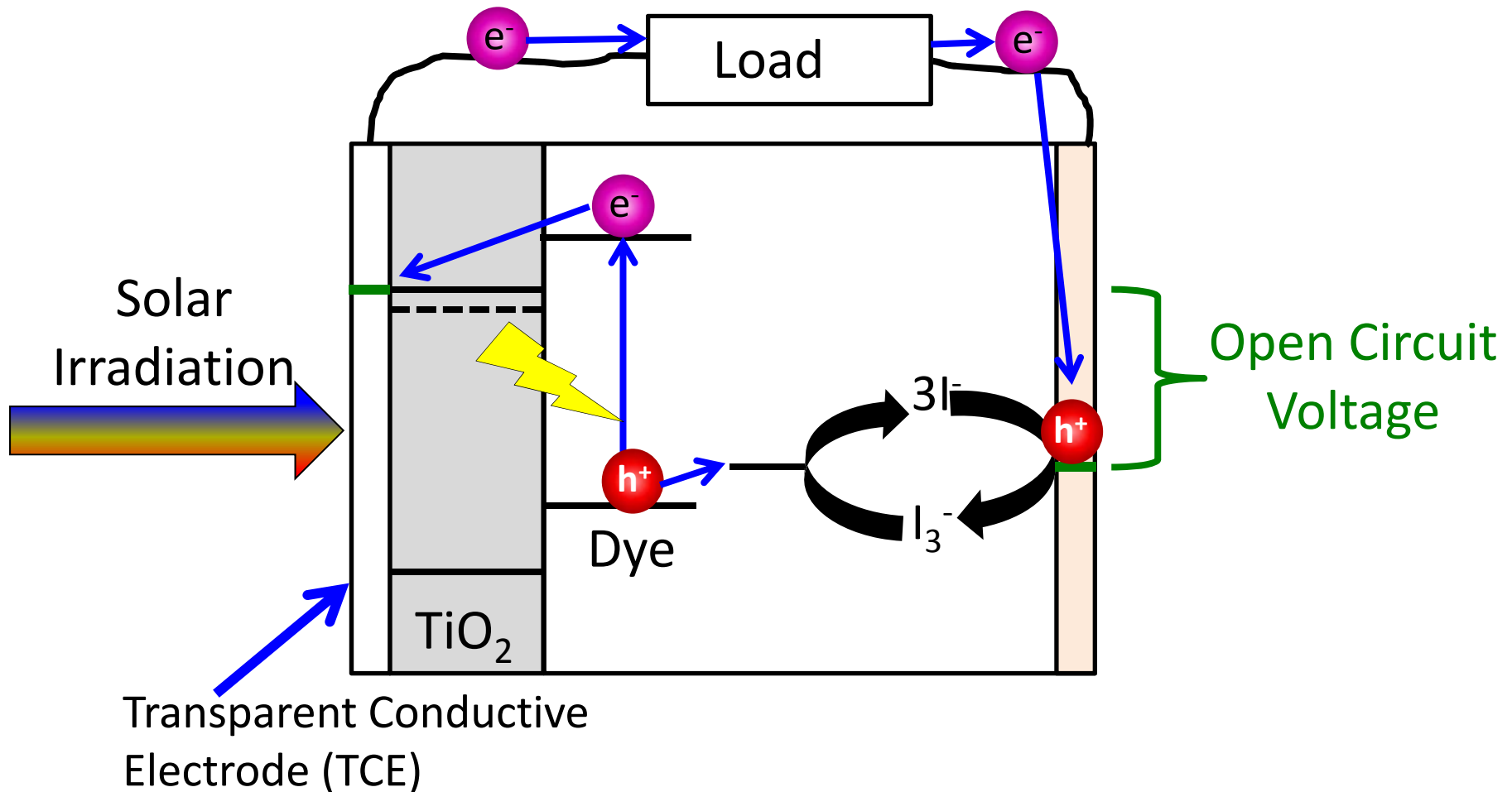
- Here is a more detailed mechanism for electron and hole degradation reactions for  $\text{TiO}_2$
- Radicals react very fast, thus it is hard to analyze mechanisms.



Hoffman et. al, Chem. Rev. 1995

# Dye Sensitized Solar Cell (DSSC)

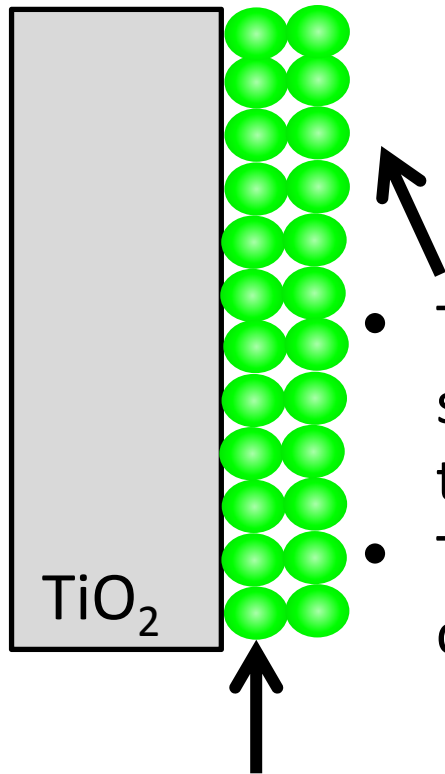
- Michael Gratzel popularized this approach to solar cells in 1991.



# Dye Sensitized Solar Cell (DSSC)

- The key to success in a nanoporous  $\text{TiO}_2$ .

## Ineffective Planar Approach

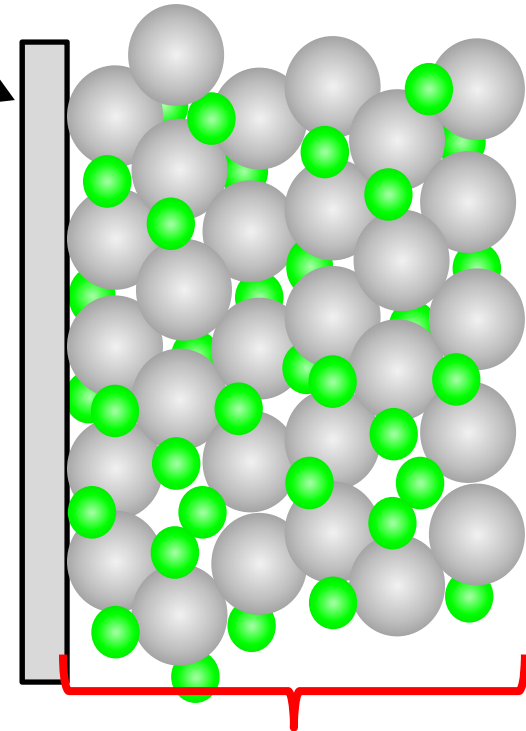


- There is no  $\text{TiO}_2$  surface area for these dyes.
- This gives low currents

Only first layer is active

## Effective Porous Approach

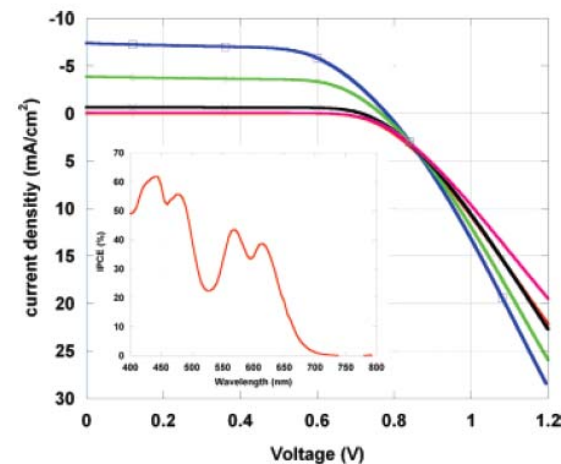
Blocking  $\text{TiO}_2$  layer to prevent back reactions



Porous  $\text{TiO}_2$  allows for much more dye adsorption.

# Dye Sensitized Solar Cell- Results

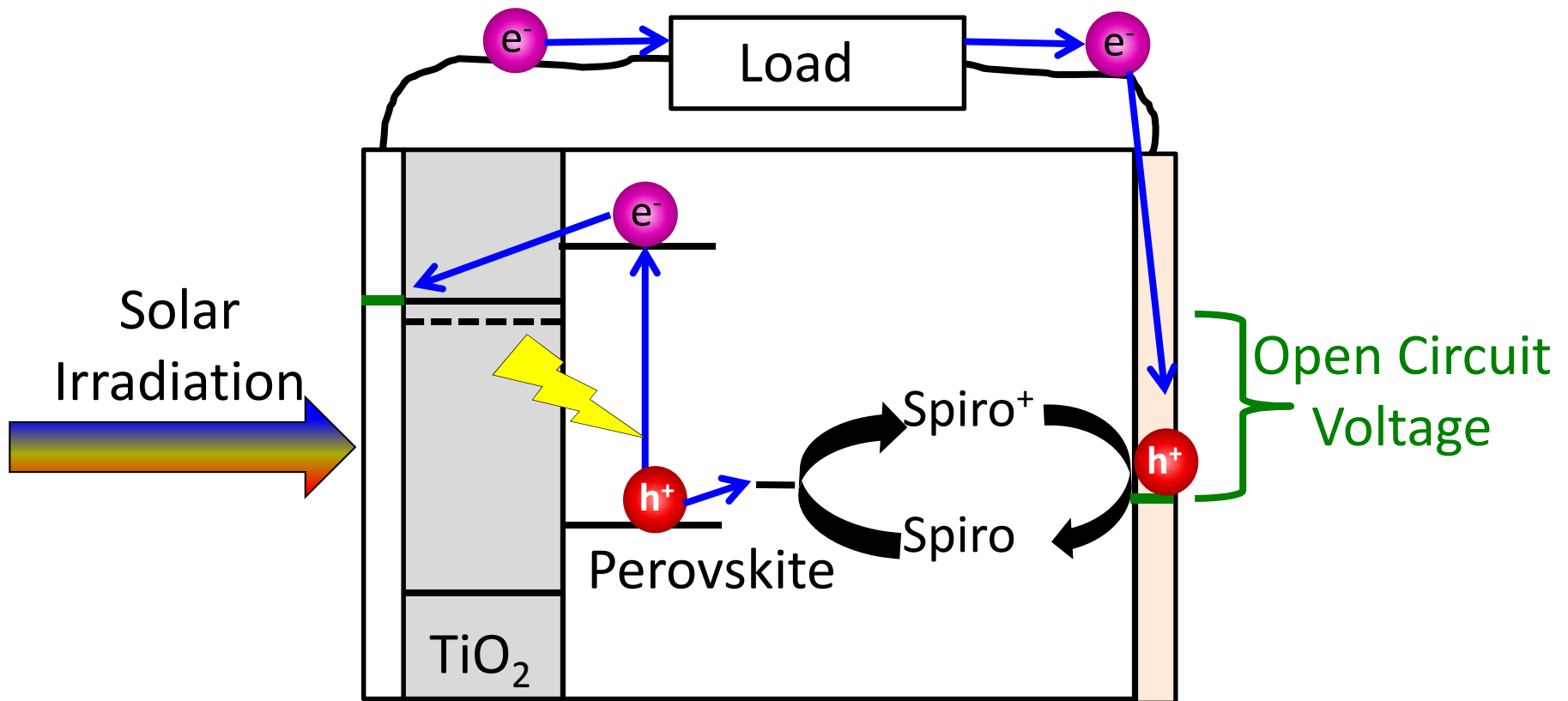
- In 1997 the record was 10% and in 2014 it is 11.9%.
- *The biggest issue is the liquid electrolyte leaking/evaporating over time.*
- The major focus is on finding good hole conductors to replace iodide.
- The annoying thing is a change in dye many times means a new hole conductor is needed.
- To the right is state of the art performing DSSC



**Figure 3.** Current–voltage characteristics measured in the dark (red line) and under simulated AM 1.5 solar illumination at 100 (blue line), 50 (green line), and 10 (black line) mW/cm<sup>2</sup> for a solid-state DSSC using **2** as the molecular sensitizer and *spiro*-MeOTAD as the hole transporting material. The inset shows the photocurrent action spectrum of the same cell.

# Perovskite Solar Cell

- These were initially an off-shoot of dye sensitized solar cells.
- The only difference was  $\text{PbCH}_2\text{NH}_3\text{I}_3$  replaced the dye.
- A hole conductor named 'SPIRO' is now used for DSSC and Perovskites instead of Iodide because it is more efficient.



# Perovskite Solar Cell

- Unlike DSSC, these do not need porous  $\text{TiO}_2$ .
- Electrons can hop from one perovskite until cell to another very efficiently.
- Perovskites naturally are undoped (i.e neither n-type nor p-type).

## Efficiencies

2006 - 2.2 %

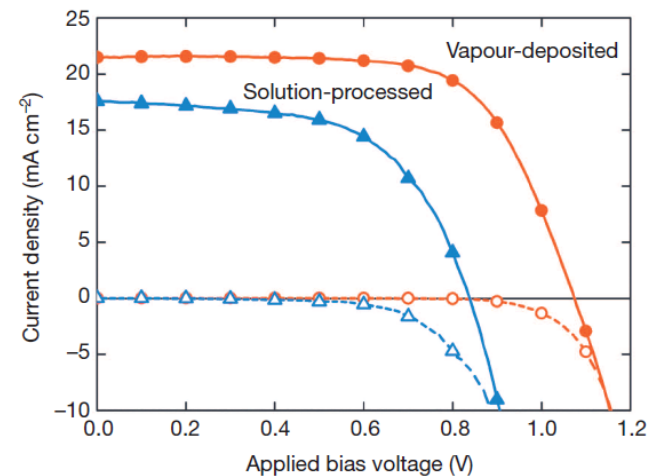
2009 - 3.8 %

Nov. 2012 - 10.9 %

July 2013 - 12.9 %

July 2014 - 17.9 % \*

\* Unpublished data

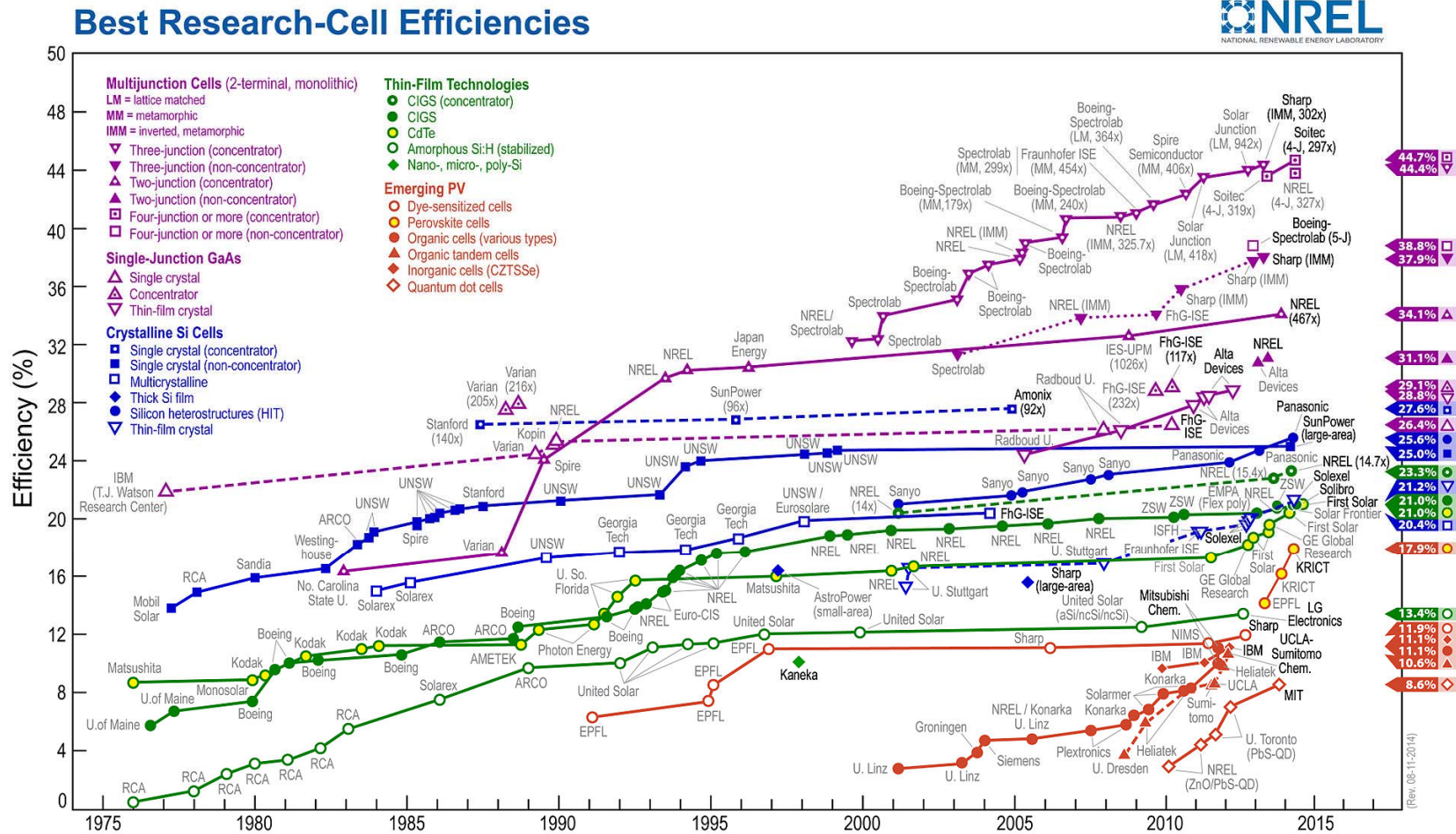


**Figure 3 | Solar cell performance.** Current-density/voltage curves of the best-performing solution-processed (blue lines, triangles) and vapour-deposited (red lines, circles) planar heterojunction perovskite solar cells measured under simulated AM1.5 sunlight of  $101 \text{ mW cm}^{-2}$  irradiance (solid lines) and in the dark (dashed lines). The curves are for the best-performing cells measured and their reproducibility is shown in Table 1.

Liu et. al, Nature, 2013

# Solar Cell Efficiencies

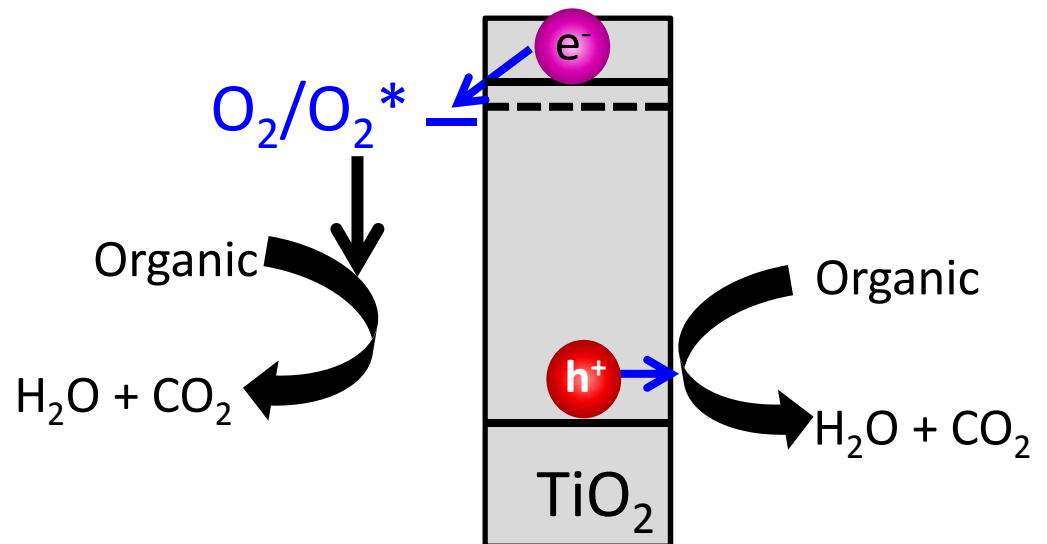
- NREL in the US tests and verifies all record solar cells. They frequently update the graph showing the best efficiencies



Greg Wilson and Keith Emery - National Renewable Energy Laboratory (NREL),

# Sensors

- One approach is just to monitor pollutants in water.
- In this case you use photocatalysts to oxidize a small fraction of the pollutants.
- To oxidize the pollutants the photocatalyst must use oxygen.
- You then use a detector to monitor changes in oxygen in the water.
- A decrease in  $O_2$  means an increase in pollutants.
- Once calibrated you can measure pollutants in solution via oxygen in solution.



All potentials are vs. NHE



# Sensors

- A non-photochemical way to use semiconductors is to use them as an electrical sensor.
- Hydrogen is known to intercalate/ react with  $\text{TiO}_2$ .
- Hydrogen can change the resistivity of  $\text{TiO}_2$  by orders of magnitude.
- Thus this is a phenomenal  $\text{H}_2$  sensor.

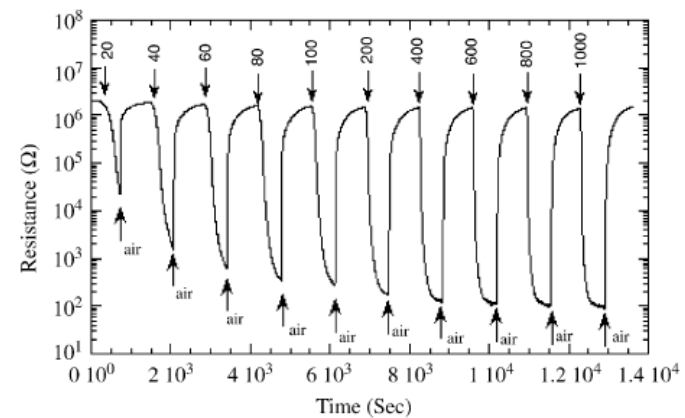
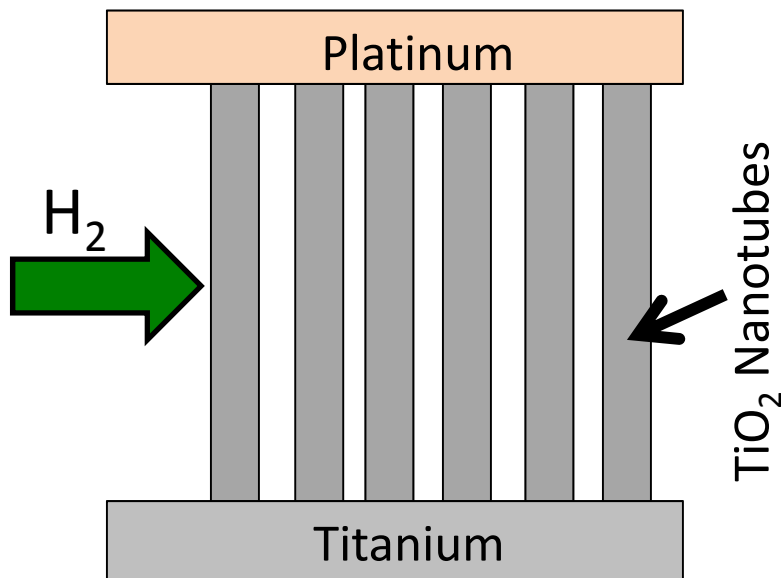


Fig. 43. Electrical resistance of 22nm diameter 360 nm long  $\text{TiO}_2$  nanotube array when exposed to different hydrogen concentrations at room temperature. The nanotube response is completely reversible without hysteresis or drift.

# Summary

## Fundamentally

- We kind of understand the general concepts such as band-bending, quasi-Fermi levels and redox reactions.
- We do not understand defect sites at the interface, and co-catalyst-semiconductor interactions.

## Applications

- The 2 main applications are energy production and contaminant removal.
- For energy production we need to increase efficiency and durability, while decreasing costs.
- For contamination removal, we need to understand degradation mechanisms and by-products.