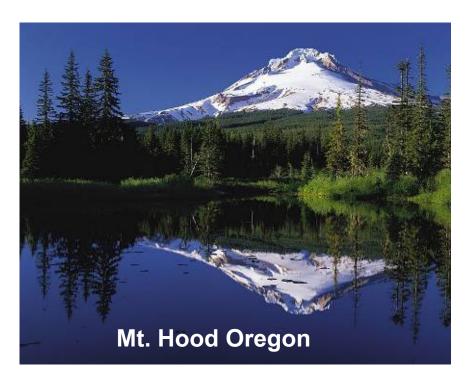


Tutorial Lecture: Semiconductor Photoelectrochemistry and Solar Water Splitting



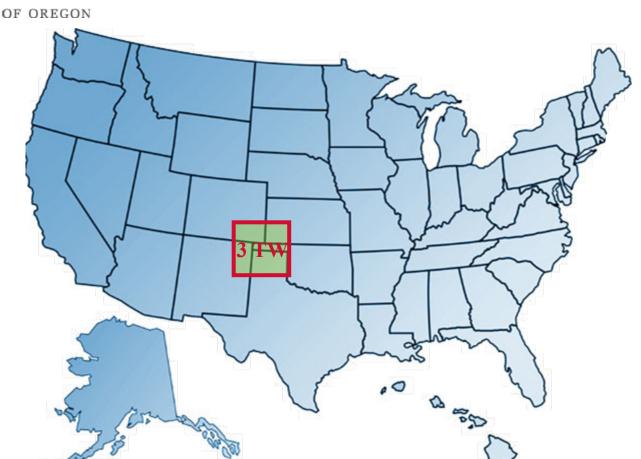
Shannon W. Boettcher Asst. Prof. of Chemistry University of Oregon Eugene, USA







Motivation: Powering the Planet



Global power consumption:

~18 TW

Worldwide potential*:

Wind < 4 TW
Biomass < 5 TW
Hydro < 1.5 TW
Geothermal < 1 TW
Solar ~ 120,000 TW

*Lewis, MRS Bulletin, (32) 808 2007.

Solar is the only renewable source capable of providing 20-50 TW of power worldwide.

Solar Energy Challenges

Solar Electricity > 15 ¢ per kWh (sunny climate, large installation)
Industrial Electricity ~ 5-10 ¢ per kWh

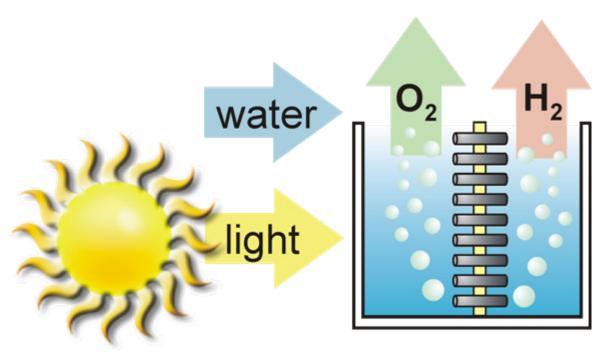


Cost of solar energy must be reduced to contribute significantly.

We must store that energy.



Vision for Storage: fuel from sunlight and water



Advantages:

- no wires / external electronics
- low-cost semiconducting absorbers
- direct energy storage in chemical bonds
- H₂ for fuel cells, turbines, liquid-fuel synthesis from CO₂
- closed-loop cycle

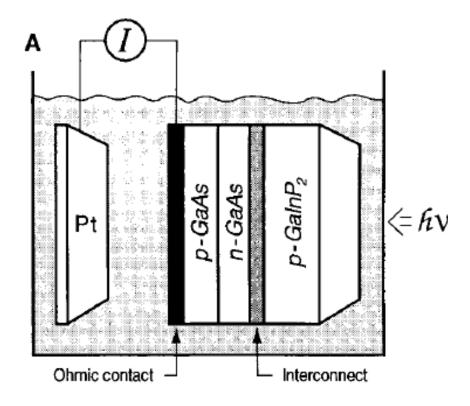
Disadvantages: Difficult to find right materials and to scale.



PEC H₂ production can work

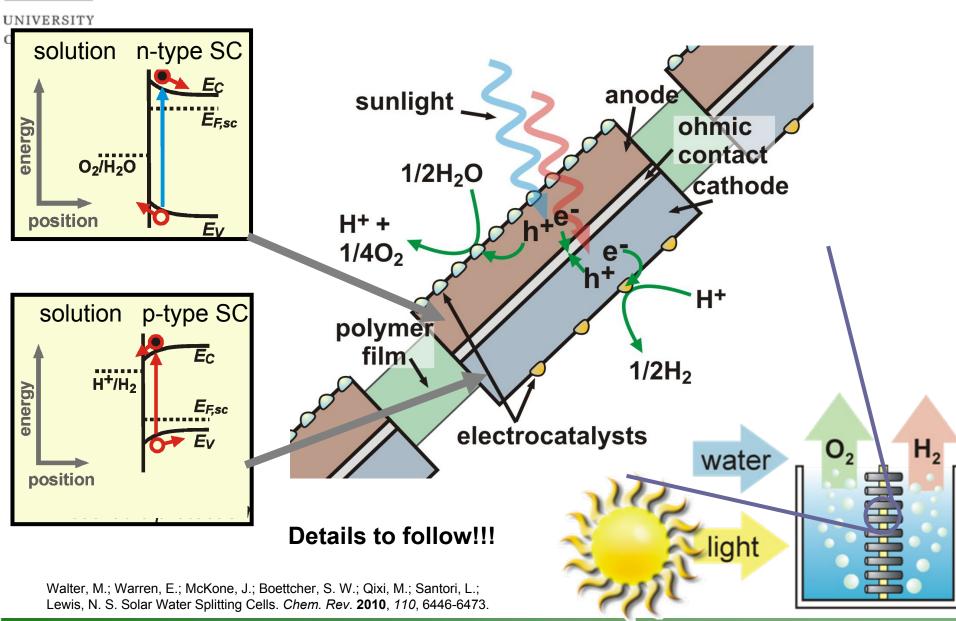
NREL Photoelectrolysis.mp4







Integrated architecture





Overview

PART 1:

- Thermodynamics and Electrochemical Reactions
- Semiconductors Physics
- Liquid junctions and Photoelectrochemistry (PEC)

PART 2:

- Electrocatalysis and Electrochemical Kinetics
- Integrated devices and Literature examples



Thermodynamics

OER:
$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$$
 E° = 1.23 V vs. NHE

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

overall:
$$H_2O \rightarrow \frac{1}{2}O_2 + H_2$$
 $E = E_{cath} - E_{ano} = -1.23 \text{ V}$

 $\Delta G = -nFE = 237 \text{ kJ mol}^{-1}$

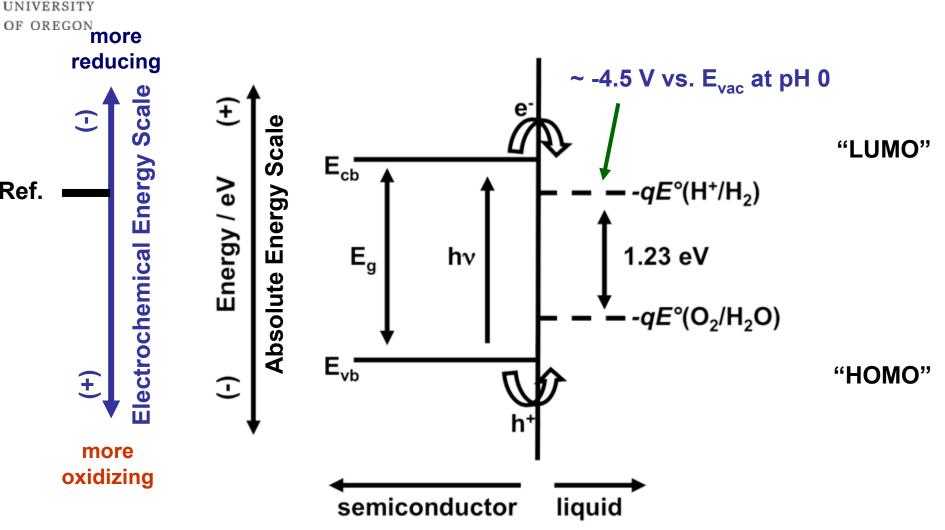
 $E^{\circ} = 0 \text{ V vs. NHE}$

Oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) for overall water splitting

Walter, M.; Warren, E.; McKone, J.; Boettcher, S. W.; Qixi, M.; Santori, L.; Lewis, N. S. Solar Water Splitting Cells. Chem. Rev. 2010, 110, 6446-6473.



(Over-)Simplified Picture



Basic Idea: **(a)** Semiconductor separates photoexcited electron-hole pairs. **(b)** ereduce H⁺ to make H₂ **(c)** h⁺ oxidizes water to make O₂



Review of Oxidation/Reduction

$$\Delta G^{\circ} = -RT \ln K$$

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$
 $\Delta G = -nFE$

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{a_{\text{Red}}}{a_{\text{Ox}}}$$
 Nernst Equation

$$E_{HER} = E^{\circ}_{HER} - \frac{RT}{2F} \ln \frac{P_{H_2}}{[H^+]^2}$$
 Both HER and OER are pH dependent. The total potential needed, E_{OER}-E_{HER} = 1.23 V, is not.

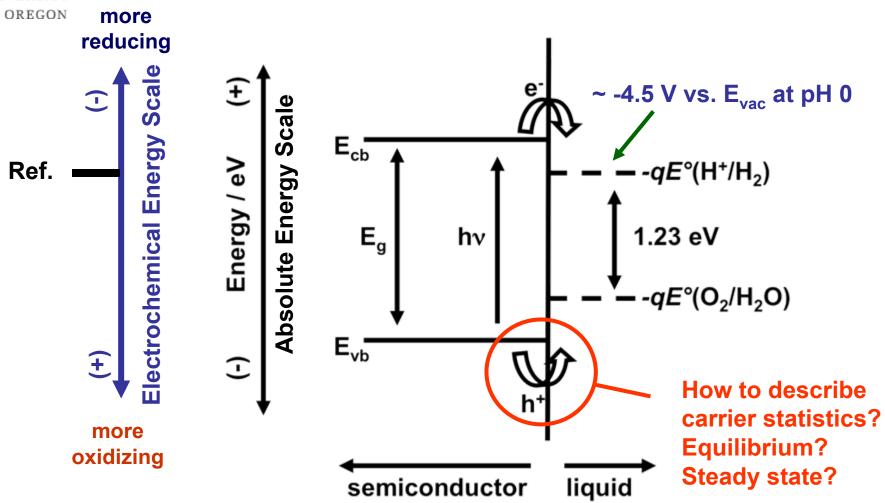
Both HER and OER are pH

$$E_{OER} = E^{\circ}_{OER} - \frac{RT}{2F} \ln \frac{1}{[H^{+}]^{2} (P_{O_{2}})^{\frac{1}{2}}}$$

Bard, A. J.; Faulkner, L. R. Electrochemical Methods: Fundamentals and Applications; Wiley, 2000.

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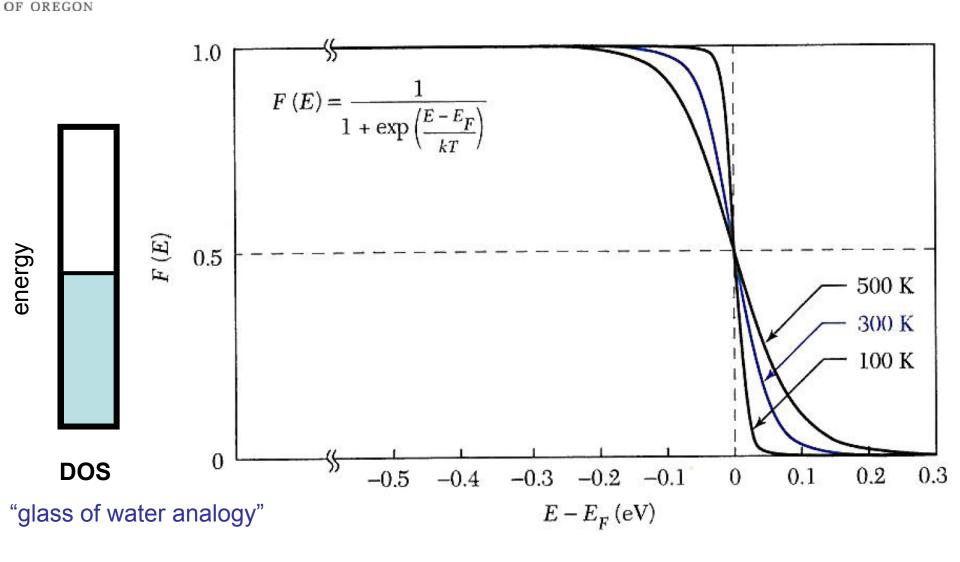
(Over-)Simplified Picture



Basic Idea: **(a)** Semiconductor separates photoexcited electron-hole pairs. **(b)** ereduce H⁺ to make H₂ **(c)** h⁺ oxidizes water to make O₂



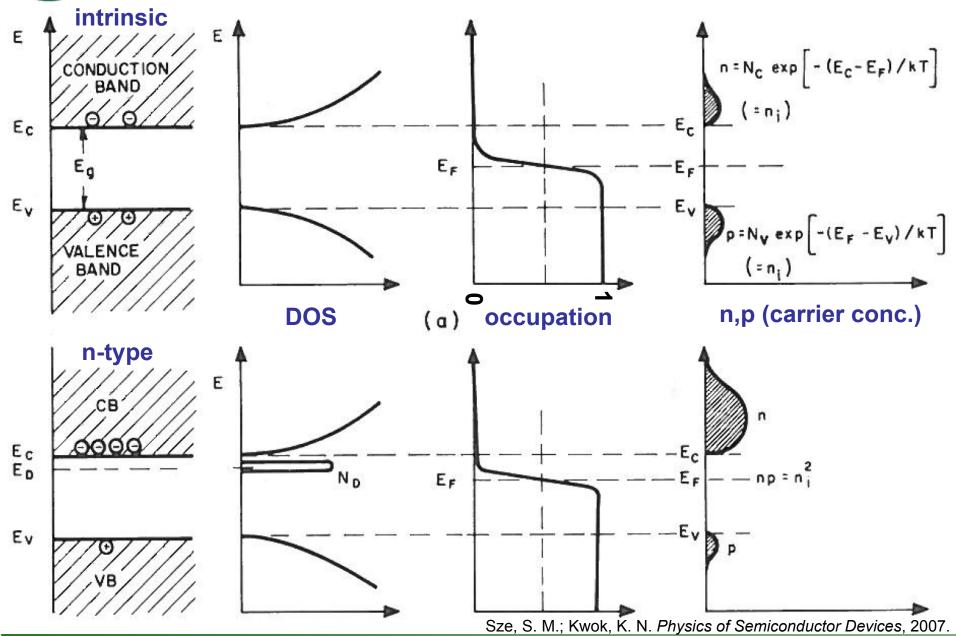
Fermi Levels Describe Energy of Carriers



Sze, S. M.; Kwok, K. N. Physics of Semiconductor Devices, 2007.

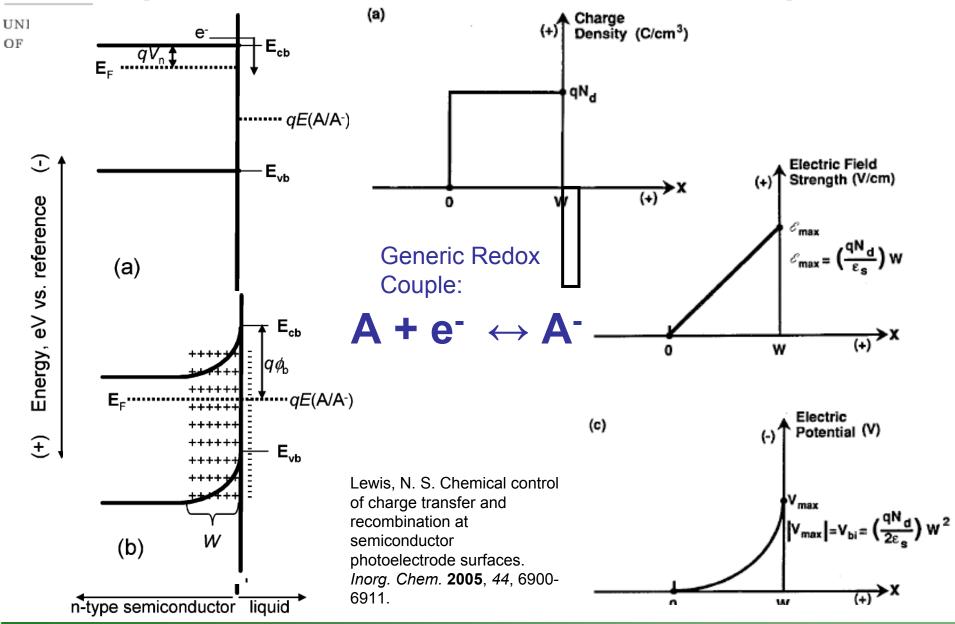
O

Semiconductor Properties and Doping



O

Equilibration with Solution Redox Couples





Dark Current-Voltage Behavior

Electron transfer at semiconductor-liquid interfaces is "simple" kinetics:

in forward bias

$$J_{et,f}(E) = -qk_{et,f}[A]n_s \qquad n_s = N_d e^{q(E_{fb}-E)/k_BT}$$

$$J_{et,r}(E) = -qk_{et,r}[A^-]$$

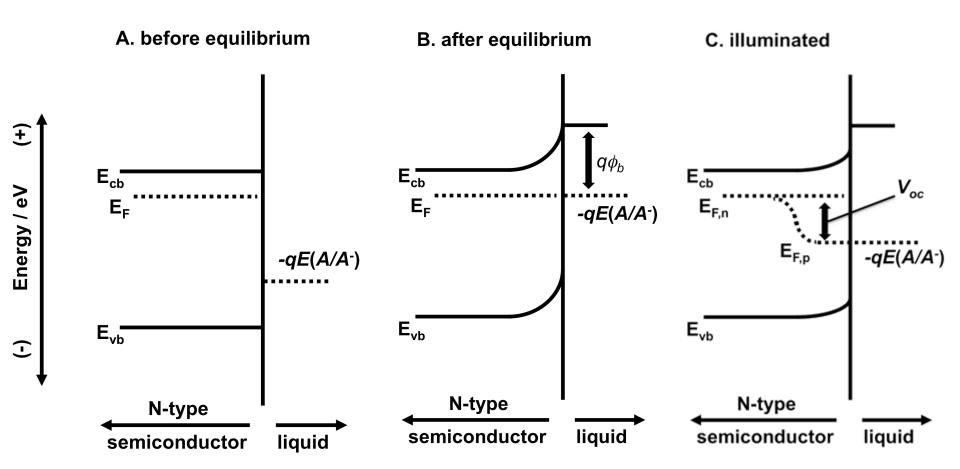
$$J_{et} = J_0 \left[e^{qV/k_BT} - 1 \right]$$

$$J_0 = qn_{so}k_{et}[A]$$
 Different
$$J_0 = qn_{so}k_{et}[A]$$

current



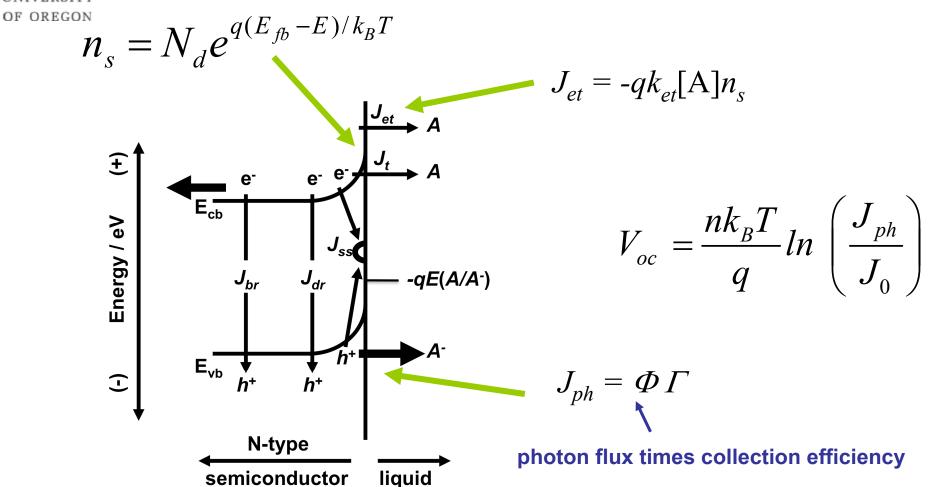
Semiconductor-solution contacts under illumination

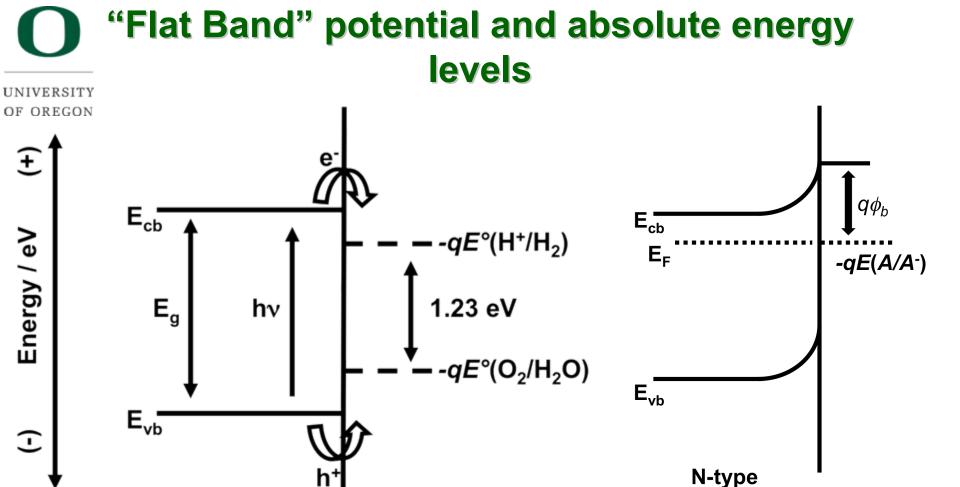


bands unbend; new quasi-equilibrium with different e- and h+ conc.



The measured current and voltage depends on the rates of fundamental processes





liquid

What determines the equilibrium barrier height ϕ_b ? What semiconductors can split water based on thermodynamics?

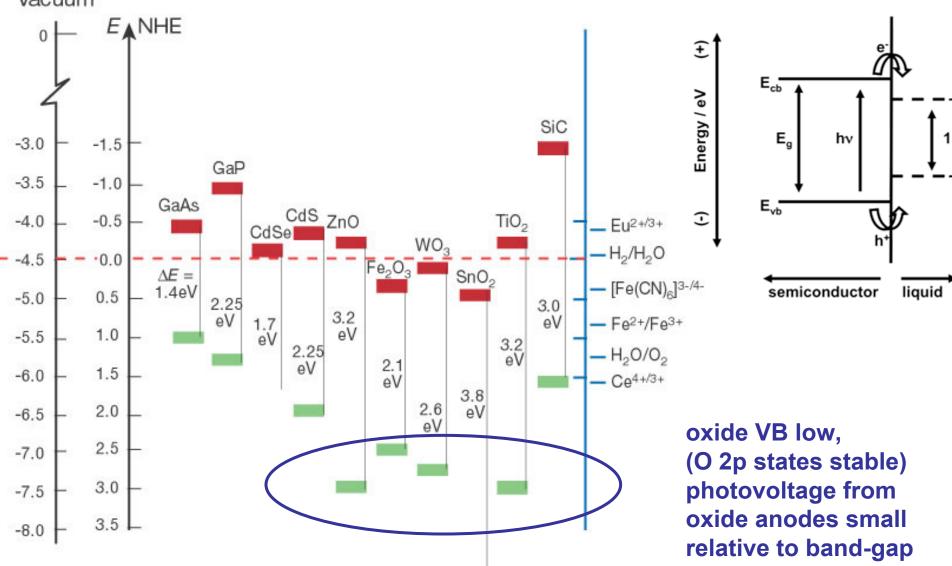
semiconductor

semiconductor

liquid



Absolute band-edge positions



Gratzel, M. Photoelectrochemical cells. *Nature* 2001, 414, 338-344.

Bak, T.; Nowotny, J.; Rekas, M.; Sorrell, C. C. Photo-electrochemical hydrogen generation from water using solar energy. Materials-related aspects. *Int. J. Hydrogen Energy* **2002**, *27*, 991-1022.



E_{vb}

N-type

semiconductor

Band-edges move via surface dipoles

OF OREGON A. Bare Interface B. "Negative" Dipole C. "Positive" Dipole interface interface interface $\mathsf{E}_{\mathsf{vac}}$ $\mathsf{E}_{\mathsf{vac}}$ E_{vac} E_{cb} E_{cb} E_{cb} Energy / eV E_{F} E_{F} \mathbf{E}_{\max} $-qE(A/A^{-})$

E_{vb}

Surface dipoles are the result of: absorbed ions, protonated/deprotonated surface hydroxyls, surface termination, charged surface states, etc.

N-type

semiconductor

 $-qE(A/A^{-})$

liquid

E_{vb}

N-type

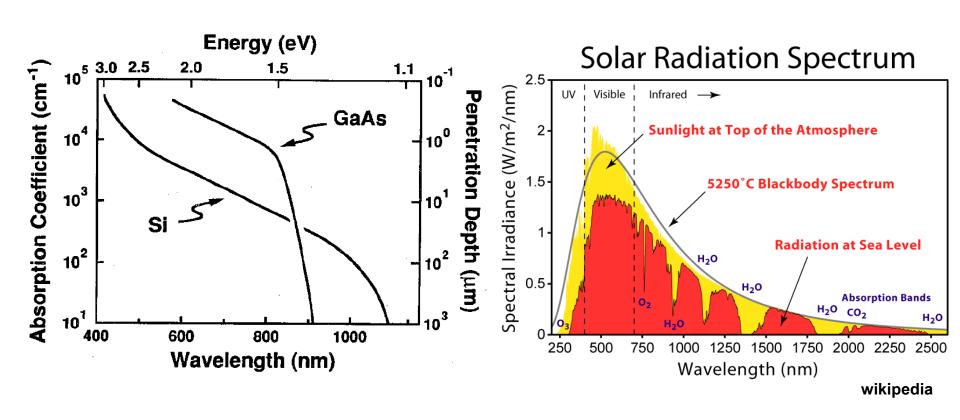
semiconductor

liquid

liquid



Semiconductors: Light Absorption

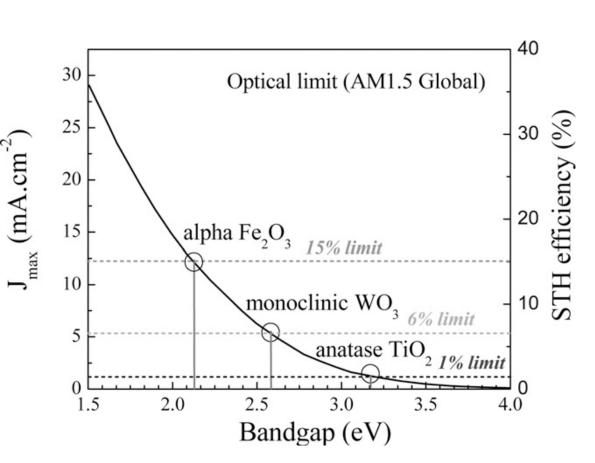


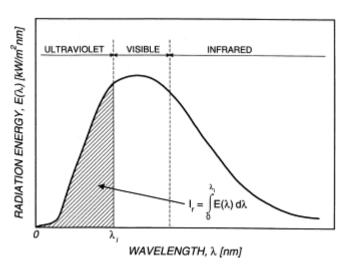
Tan, M. X.; Laibinis, P. E.; Nguyen, S. T.; Kesselman, J. M.; Stanton, C. E.; Lewis, N. S. Principles and application of semiconductor photoelectrochemistry. *Progress in Inorganic Chemistry, Vol 41* **1994**, *41*, 21-144.



Semiconductors: Light Absorption







Research challenge:

Design low-cost stable materials (oxides?) with smaller band-gaps? How do we make stabilize conventional semiconductors?

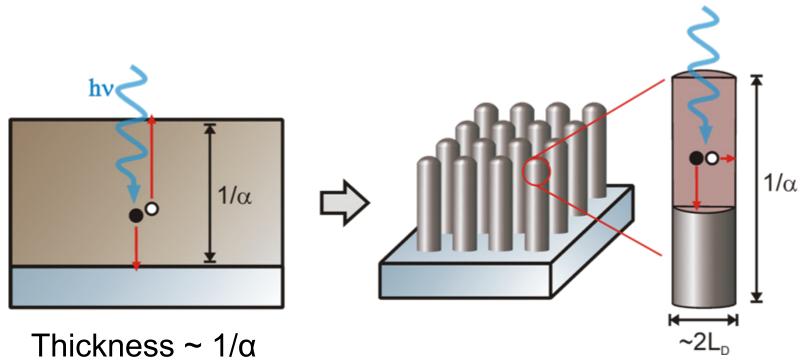
Chen, Z. B.; et. al. Accelerating materials development for photoelectrochemical hydrogen production: Standards for methods, definitions, and reporting protocols. *J. Mater. Res.* **2010**, *25*, 3-16.

Bak, T.; Nowotny, J.; Rekas, M.; Sorrell, C. C. Photo-electrochemical hydrogen generation from water using solar energy. Materials-related aspects. *Int. J. Hydrogen Energy* **2002**, *27*, 991-1022.



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Semiconductors: Carrier Collection



$$L_D = \sqrt{D \cdot \tau} \qquad D = \frac{\mu \cdot k_B \cdot T}{q}$$

Three dimensional geometry can enhance carrier collection... but at a price.

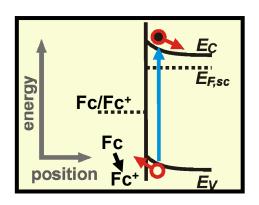
Comparison of the device physics principles of planar and radial p-n junction nanorod solar cells B. M. Kayes, H. A. Atwater and N. S. Lewis *Journal of Applied Physics*, 2005, *97*,

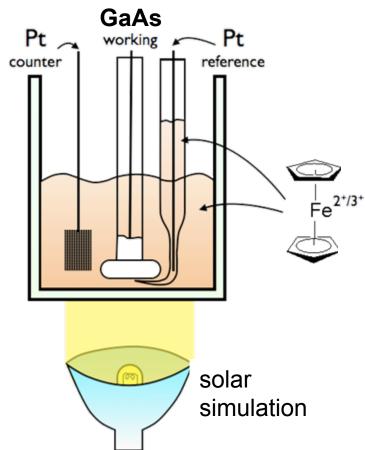


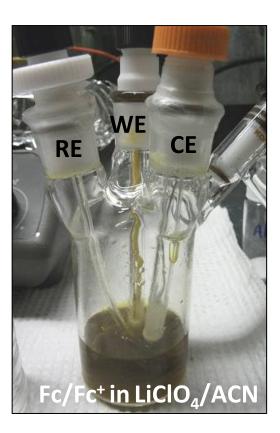
Non-aqueous photoelectrochemistry is a tool to characterize semiconductors for PEC



GaAs electrodes

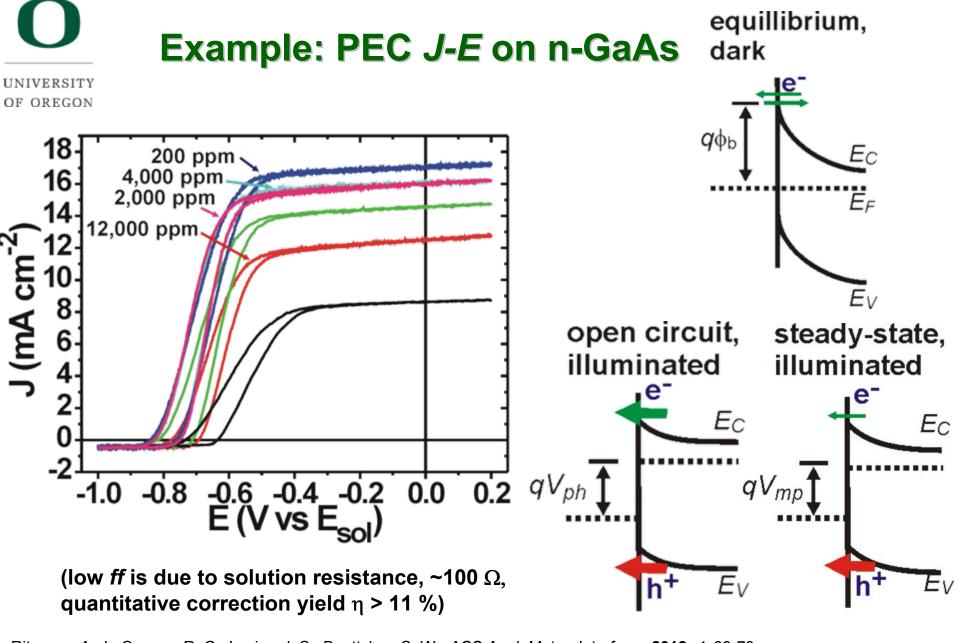






reversible redox couple with fast kinetics

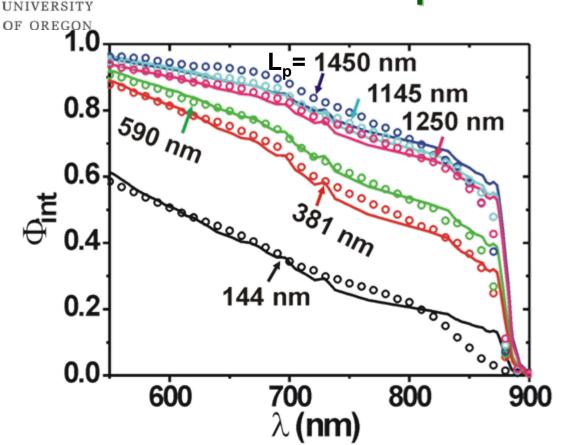
Gronet, C. M.; Appl. Phys. Lett. 43, 1, 115-117



Ritenour, A. J.; Cramer, R. C.; Levinrad, S.; Boettcher, S. W. *ACS Appl. Mater. Interfaces* **2012**, *4*, 69-73. Ritenour, A. J., Boettcher S. W. *IEEE PVSC 38* **2012**.



Diffusion length determination from quantum efficiency

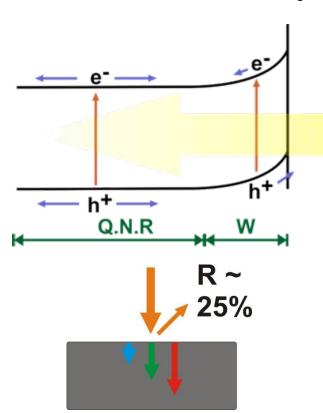


~1.5 um diffusion length sufficient to design high efficiency PV or PEC device. What defects are present? How can we eliminate them to improve response?

Ritenour, A. J., Boettcher S. W. IEEE PVSC 38 2012.

Gärtner Model:

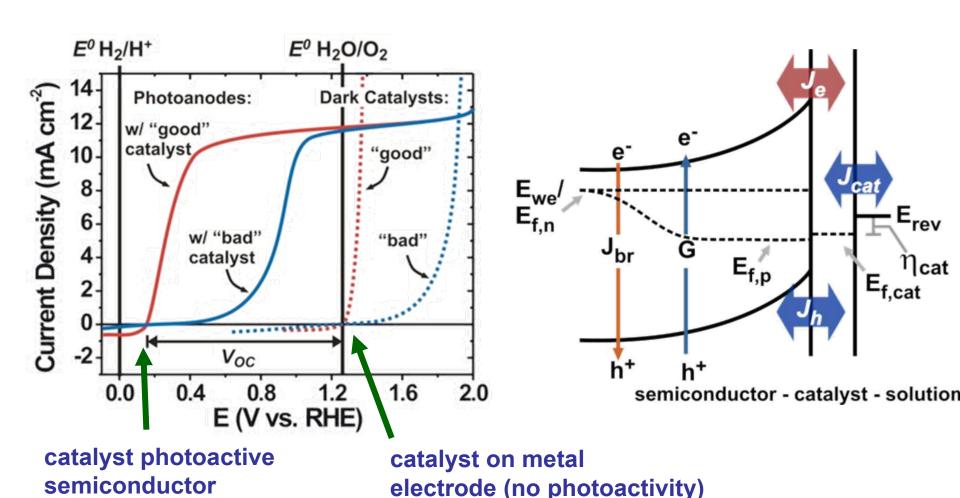
$$\phi_{int} = 1 - \frac{e^{-\alpha(\lambda)W}}{1 + \alpha(\lambda)L_p}$$



Gärtner, W. W. Phys. Rev. 1959 116, 84



PART 2: Surface Electrocatalysis and Integrated Architectures



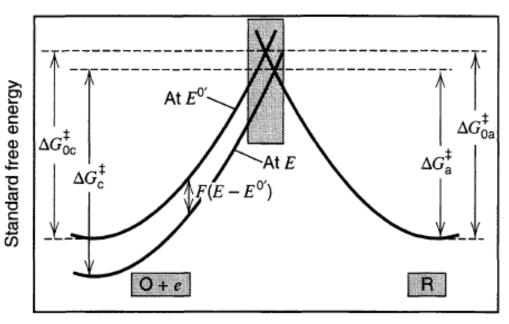


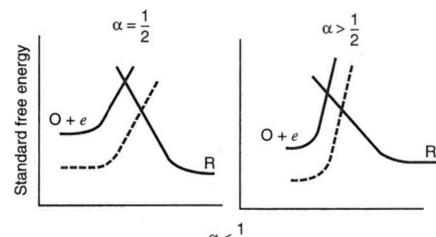
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Electrochemical Reaction Kinetics

$$O + e \stackrel{k_f}{\underset{k_b}{\rightleftharpoons}} R$$

O +
$$e \rightleftharpoons^{k_{\rm f}} R$$
 $k_{\rm f} = A_{\rm f} \exp{\left(-\Delta G_{\rm c}^{\ddagger}/RT\right)}$ $k_{\rm b} = A_{\rm b} \exp{\left(-\Delta G_{\rm a}^{\ddagger}/RT\right)}$

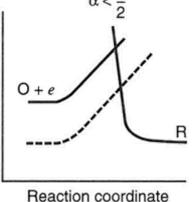




Reaction coordinate

$$k_{\rm f} = A_{\rm f} \exp{(-\Delta G_{0\rm c}^{\ddagger}/RT)} \exp{[-\alpha f(E-E^{0'})]}$$

$$k_{\rm b} = A_{\rm b} \exp{(-\Delta G_{0\rm a}^{\ddagger}/RT)} \exp{[(1-\alpha)f(E-E^{0'})]}$$

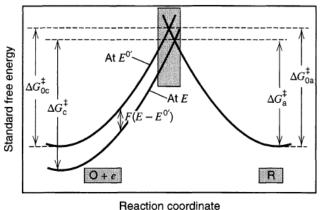


Bard, A. J.; Faulkner, L. R. Electrochemical Methods: Fundamentals and Applications; Wiley, 2000.



Electrochemical Reaction Kinetics

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Butler-Volmer Expression for a single electron-transfer step:

$$i = i_0 \left[\frac{C_{\rm O}(0, t)}{C_{\rm O}^*} e^{-\alpha f \eta} - \frac{C_{\rm R}(0, t)}{C_{\rm R}^*} e^{(1-\alpha)f \eta} \right]$$

$$i_0 = FAk^0 C_{\mathcal{O}}^{*^{(1-\alpha)}} C_{\mathcal{R}}^{*^{\alpha}}$$

Exchange Current Density

 α describes the shape of the potential barrier and is normally taken as 0.5. (f = F/RT)

$$i = i_0 \left[e^{-\alpha f \eta} - e^{(1-\alpha)f \eta} \right]$$
 assume fast mass transport

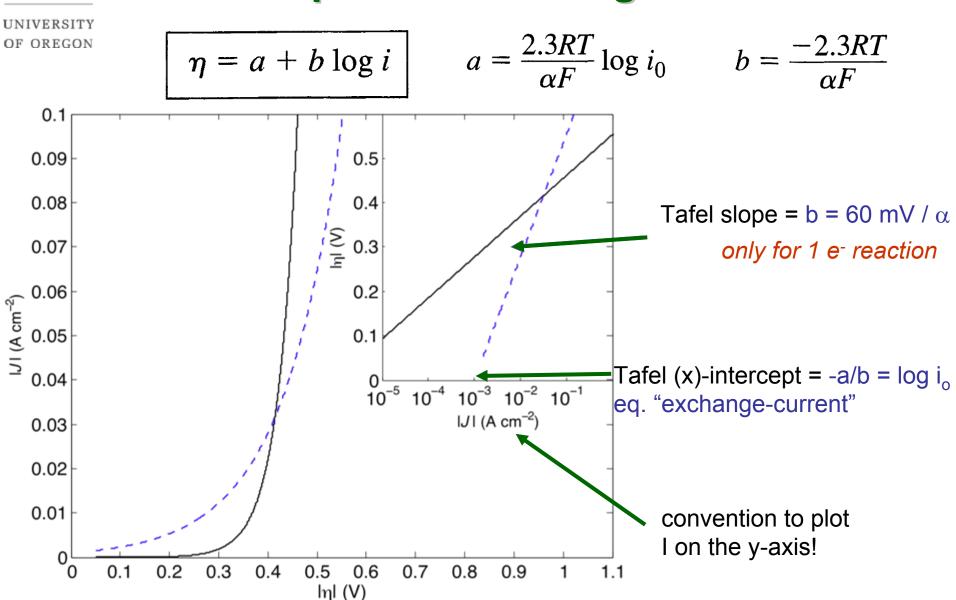
$$\eta = a + b \log i$$
 $a = \frac{2.3RT}{\alpha F} \log i_0$ $b = \frac{-2.3RT}{\alpha F}$

Ignore Reverse Reaction = Tafel Eqn. for Electrode Kinetics

Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; Wiley, 2000.



Tafel Slope and Exchange Current





Multistep reactions

Example:

$$H_2O \rightarrow *OH \rightarrow O* + H_2O \rightarrow *OOH \rightarrow O_2$$

* Indicates bonded to the surface

For multi-step ne- reaction:

$$i = i_0 [e^{-(n'+\alpha)f\eta} - e^{(n''+1-\alpha)f\eta}]$$

$$n = n' + n'' + 1$$

Tafel slope =
$$b = 60 \text{ mV} / (n'+\alpha)$$

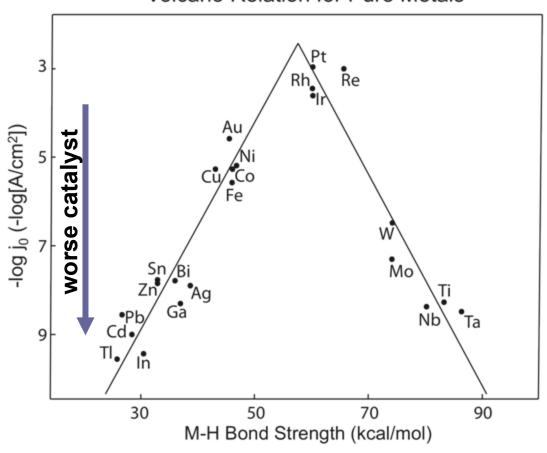
n' is the number of electrons transferred prior to the rate determining step.

Tafel slope gives mechanistic information (in principle!)



Hydrogen Evolution Reaction

Volcano Relation for Pure Metals



$$HA + e^{-*} \longrightarrow H^{\bullet *} + A^{-}$$

$$HA + H^{\bullet *} + e^{-*} \longrightarrow H_{2} + A^{-}$$

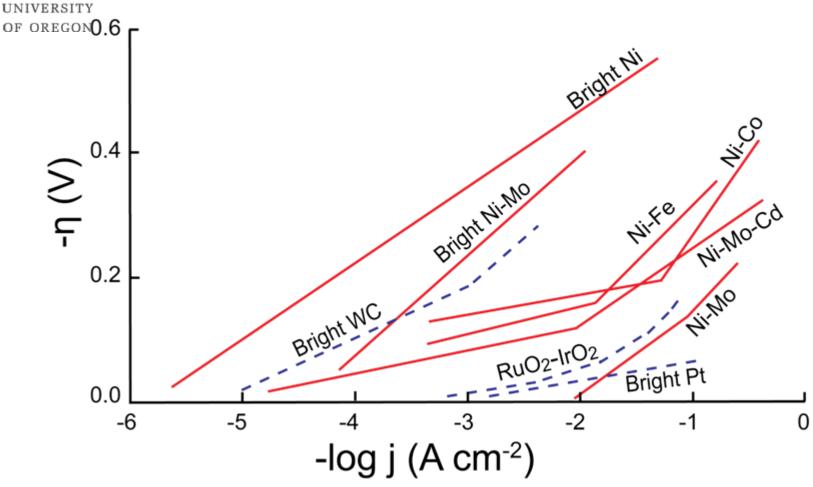
$$2H^{\bullet *} \longrightarrow H_{2}$$

"Goldilocks" principle; intermediate absorption energy (here M-H) is not too strong or too weak.

Trasatti, S. J. Electroanal. Chem. 1972, 39, 163.



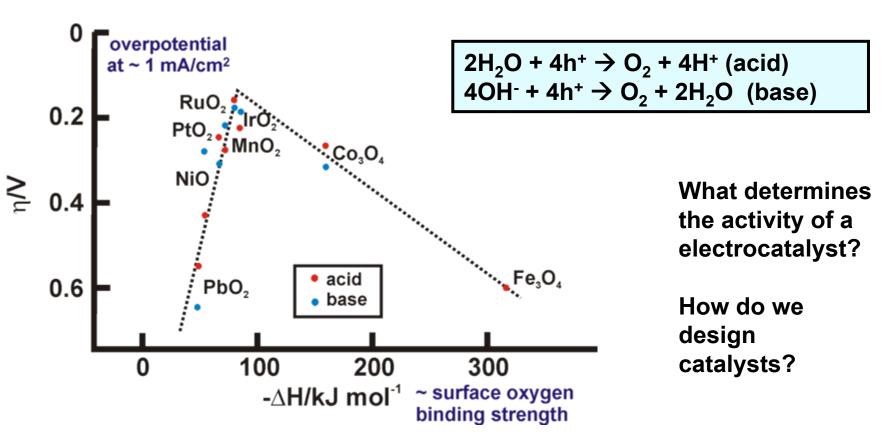
HER Overpotentials



- Pt is a phenomenally fast catalyst for HER.
- Much effort is applied to develop alternative catalysts to replace Pt.
- Different surface areas of materials makes comparison difficult.



Large loss for driving water oxidation reaction kinetics



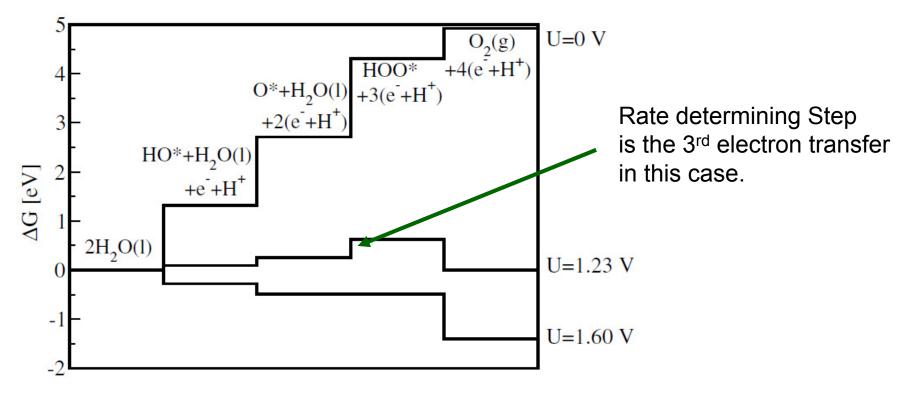
Complicated 4-step reaction!

$$H_2O \rightarrow *OH \rightarrow O* + H_2O \rightarrow *OOH \rightarrow O_2$$
* Indicates bonded to the surface

Trasatti. *Electrochim. Acta* **29** (11), 1503 (1984). Norskov et. al. *J. Electroanal. Chem.* **607** (1-2), 83 (2007). Suntivich, J.; et. al *Science* **2011**, *334*, 1383-1385.



Theory: electrocatalysis requires the stabilization of intermediates



 $H_2O \rightarrow *OH \rightarrow O* + H_2O \rightarrow *OOH \rightarrow O_2$

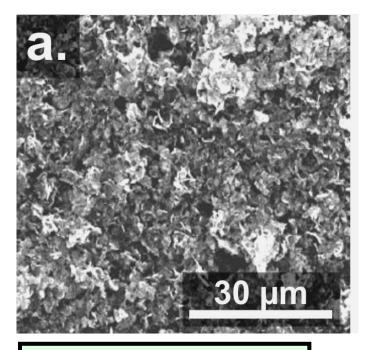
* Indicates bonded to the surface

(note: other reaction mechanisms can be drawn; for example requiring the recombination of two surface bound intermediates)

Rossmeisl, J.; Qu. Z.-W.; Zhu, H.; Kroas, G.-J.; **Nørskov, J.K.** *J. Electroanal. Chem.* **2007**, *607*, 83 – 89.



Optimization vs. Design



SEM of typical "thick" film electrocatalyst¹...

- High-surface area thick film
- Designed for maximum current per geometric area
- Dark colored poorly suited for PEC

Role of composition, conductivity, and porosity?

What is the actual active component? Complicated!

⁽¹⁾ Wang et. al., *Electrochimica Acta* 50 (2005) 2059–2064

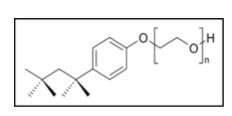
⁽²⁾ Norskov, J. K.; Rossmeisl, J. Oxygen Evolution Electrocatalysis on Oxide Surfaces. ChemCatChem 2011, 3, 1159-1165.



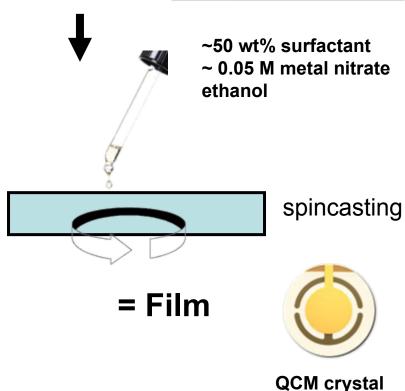
Solution-processed ultra-thin film catalysts

Advantages for fundamental study:

- Catalyst conductivity irrelevant
- Film composition controlled exactly by precursor solution
- Mass known
- Surface area controlled
- Facile gas and ion transport



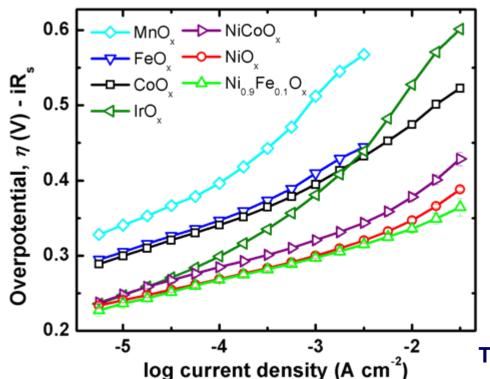






Thin Film OER Quantitative Comparison

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sample	η @ J = 1 mA cm ⁻² (mV)	loading μg cm ⁻²	at η =	300 mV TOF (sec ⁻¹)
MnO _x	512	1.2	1.3	0.0003
FeO _x	409	1.7	4.5	0.0009
CoO _x	395	1.3	7.6	0.0016
IrO _x	381	4.2	24.2	0.014
Ni _{0.5} Co _{0.5} O _x	321	1.1	273	0.056
NiO _x	300	1.3	773	0.15
Fe:NiO _x	297	1.2	1009	0.20

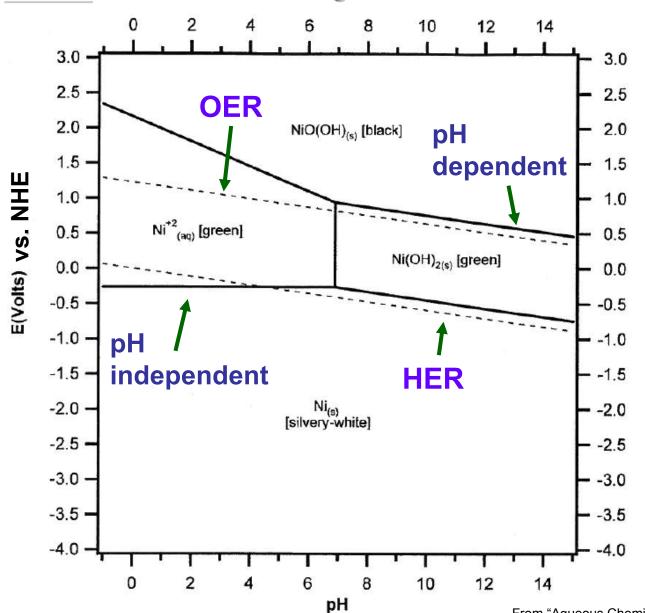
TOF = $\# O_2$ produced per metal per second

Fe:NiO_x >10x more active an IrO₂ and >100x more active than CoO_x Why?

Trotochaud et. al. Submitted 2012.



Stability: Pourbaix Diagrams



Ni

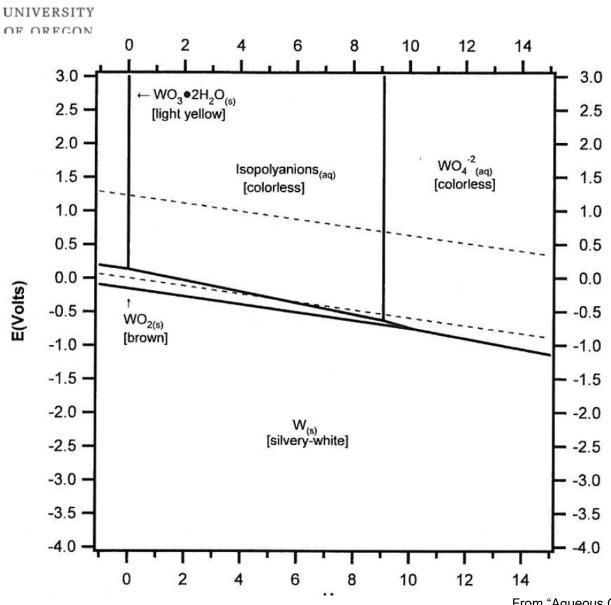
Based on freeenergies of formation; potential-pH "predominance-area diagram"

When can NiO be used as a electrocatalyst for OER?

From "Aqueous Chemistry of the Elements" Schweitzer and Pesterfield.



Stability: Pourbaix Diagrams



W

Under what conditions can tungsten oxide (WO₃) be used as a photocatalyst?

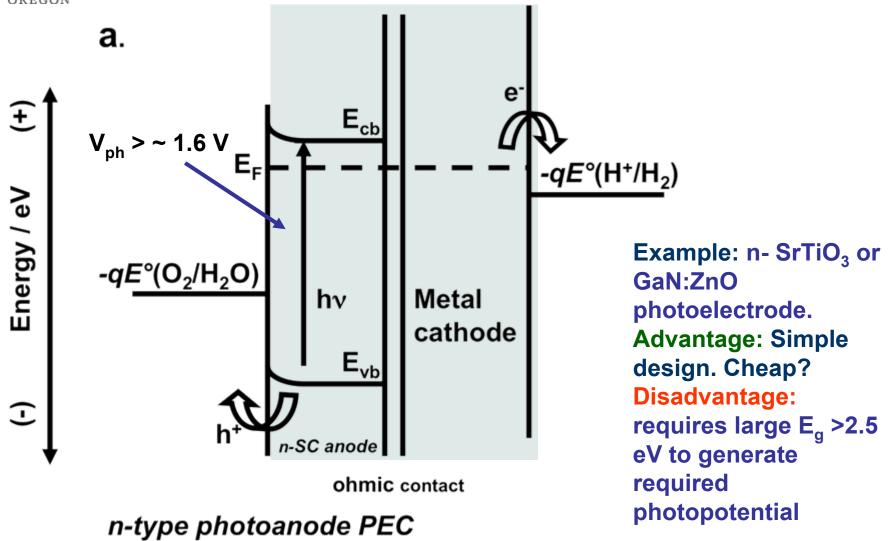
From "Aqueous Chemistry of the Elements" Schweitzer and Pesterfield.



Part III: Examples of integrated devices and some literature examples.

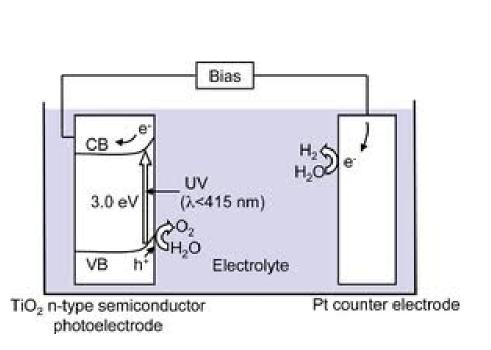


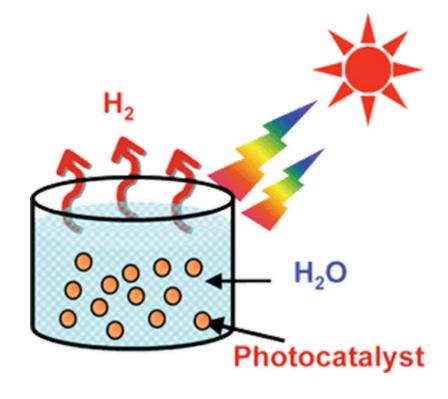
Energy Diagrams for Solar Water Splitting Devices: n-type photoanode





Wide Band Gap Photocatalysts





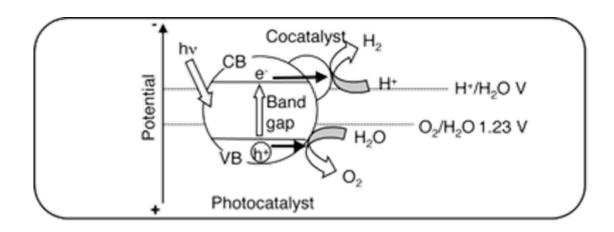
Photoelectrodes ("Fujishima – Honda Effect")

Dispersed nano/micropowders

- 1. Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, 238, 37-38.
- 2. Kumar, A.; Santangelo, P. G.; Lewis, N. S. Electrolysis of Water at SrTio3 Photoelectrodes Distinguishing between the Statistical and Stochastic Formalisms for Electron-Transfer Processes in Fuel-Forming Photoelectrochemical Systems. *J. Phys. Chem.* **1992**, 96, 834-842.
- 3. Kudo, A.; Miseki, Y. Heterogeneous photocatalyst materials for water splitting. *Chem. Soc. Rev.* **2009**, *38*, 253-278.



Powdered Photocatalysts



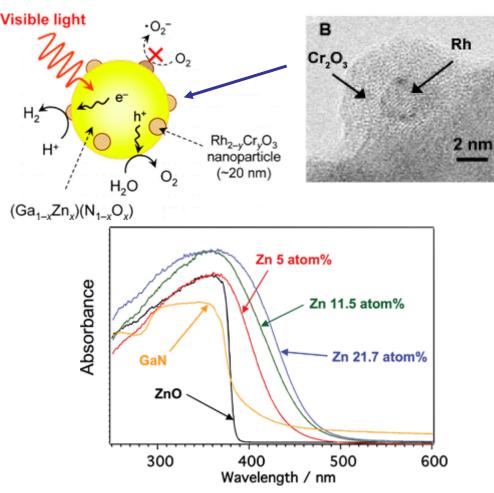
Advantage: No support, high surface area, easy to scale-up.

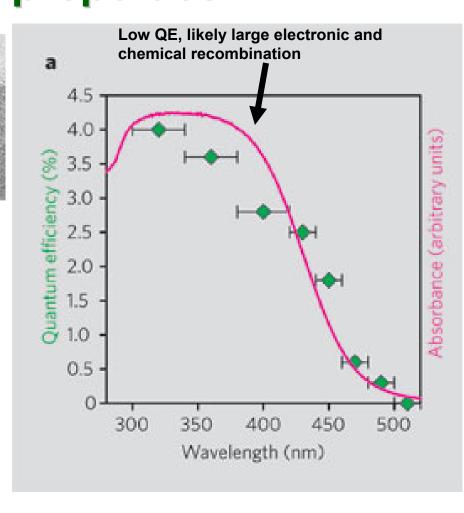
Disadvantage: 1. Single junction cell requires large $E_g > 2.5$ eV to generate required photopotential; fundamentally inefficient with solar spectrum. 2. Separation of H_2 and O_2 flammable mixture difficult. How to prevent reverse electrochemical reaction?



Example: Visible light activity via tuning materials properties

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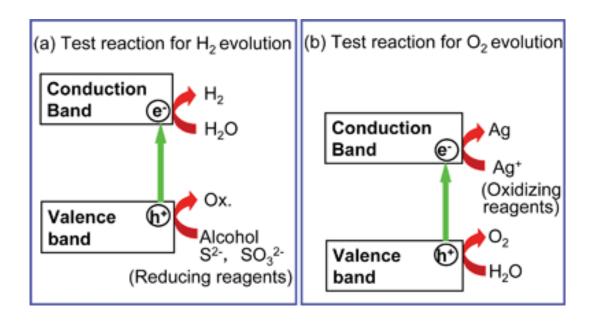


- (1) Kudo, A.; Miseki, Y. Heterogeneous photocatalyst materials for water splitting. Chem. Soc. Rev. 2009, 38, 253-278.
- (2) Maeda, K.; Teramura, K.; Lu, D. L.; Takata, T.; Saito, N.; Inoue, Y.; Domen, K. Photocatalyst releasing hydrogen from water Enhancing catalytic performance holds promise for hydrogen production by water splitting in sunlight. *Nature* **2006**, *440*, 295-295.
- (3) Maeda, K.; Domen, K. New Non-Oxide Photocatalysts Designed for Overall Water Splitting under Visible Light. J. Phys. Chem. C 2007, 111, 7851-7861.



Particle PEC and Sacrificial Reagents

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Often used to interrogate half-reactions individually.

However: Overall reaction can be energetically neutral or even downhill. Hard to test semiconductor photovoltage generation, which is important to split water.

$$Ag^+ + e^- \rightarrow Ag$$
 $E^\circ = 0.8 \text{ V vs. NHE}$ $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$ $E^\circ = 1.23 \text{ V vs. NHE}$

$$4Ag^+ + 2H_2O \rightarrow O_2 + 4H^+ + 4Ag$$
 $E^\circ = -.43 \text{ V} \longrightarrow \Delta G = -nFE$

Kudo, A.; Miseki, Y. Heterogeneous photocatalyst materials for water splitting. Chem. Soc. Rev. 2009, 38, 253-278.

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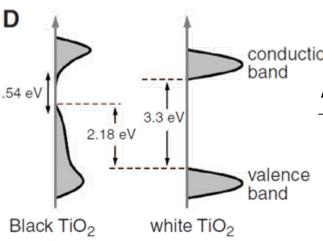
Example: TiO₂ based black photocatalysts

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"The energy conversion efficiency for solar hydrogen production, defined as the ratio between the energy of solar-produced hydrogen and the energy of the incident sunlight, reached 24% for disorderengineered black TiO₂ nanocrystals."

But a sacrificial agent was used:



Total Reaction: $CH_3OH \rightarrow H_2 + HCHO E^\circ = -.13 V$

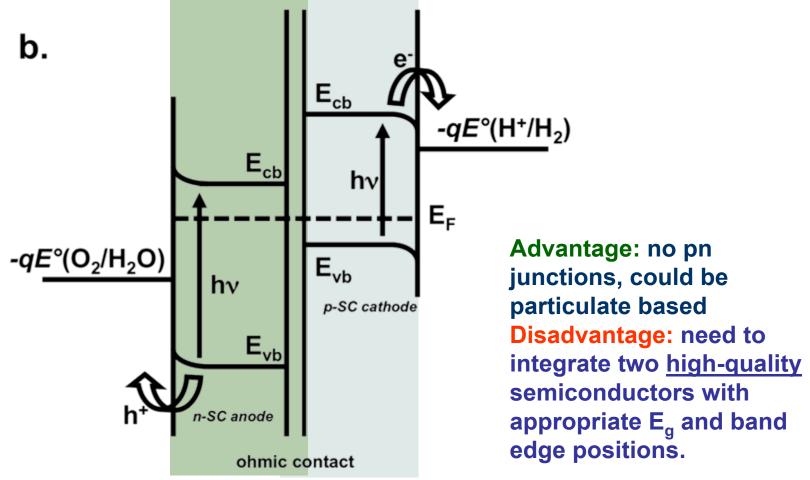
Almost zero net energy storage in this system.

Could map photovoltage generation using a series of sacrificial reagents with different chemical potentials.

Chen, X.; Liu, L.; Yu, P. Y.; Mao, S. S. Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals. *Science* **2011**, *331*, 746-750.



Energy Diagrams for Solar Water Splitting Devices – p/n PEC z-scheme



p/n-PEC (photoanode/cathode cell)



Individual component testing using a 3electrode potentiostat

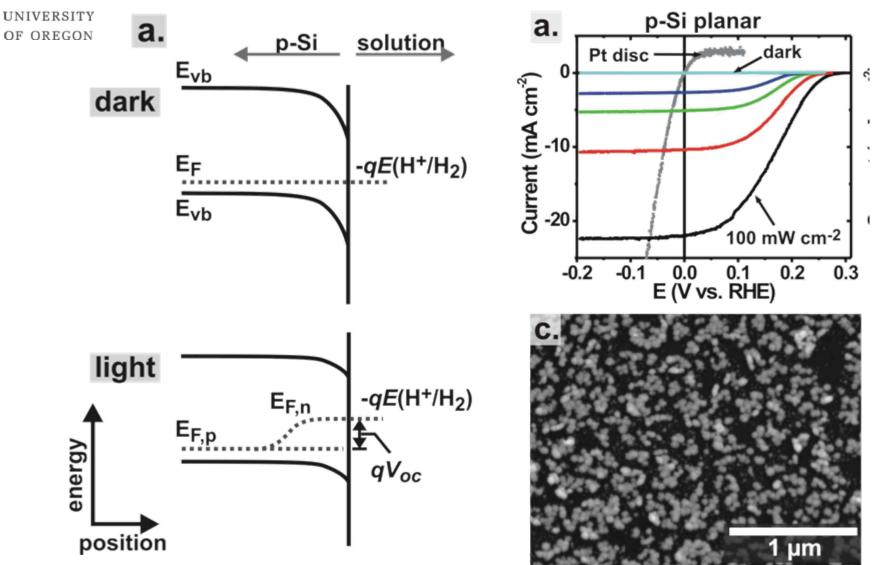
Reference electrode (RE) used to measure applied voltage versus absolute reference. Double Vessel Cell CE Pt mesh Typically bubble O₂ or H₂ through solution to maintain well-defined Epoxy resin **Nernstian potential** Grease joint Counter electrode (CE) used to complete circuit, potential required to Circulation Circulation pass current at CE usually not system I measured. system Separator Illumination Semiconductor working electrode (WE) control majority carrier Fermi level versus the reference electrode and measure current.

Chen, Z. B.; Jaramillo, T. F.; et. al. J. Mater. Res. 2010, 25, 3-16.

Magnetic stirrer



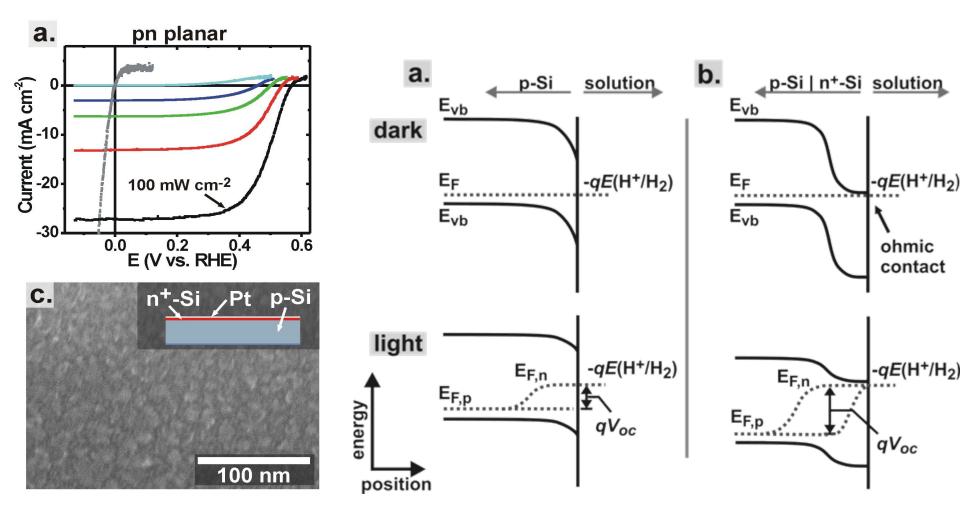
p-Si Photocathode Example



Boettcher, S. W.; Warren, E. L.; Putnam, M. C.; Santori, E. A.; Turner-Evans, D.; Kelzenberg, M. D.; Walter, M. G.; McKone, J. R.; Brunschwig, B. S.; Atwater, H. A.; Lewis, N. S. Photoelectrochemical Hydrogen Evolution Using Si Microwire Arrays. *J. Am. Chem. Soc.* **2011**, *133*, 1216-1219.



pn⁺ Si photocathode

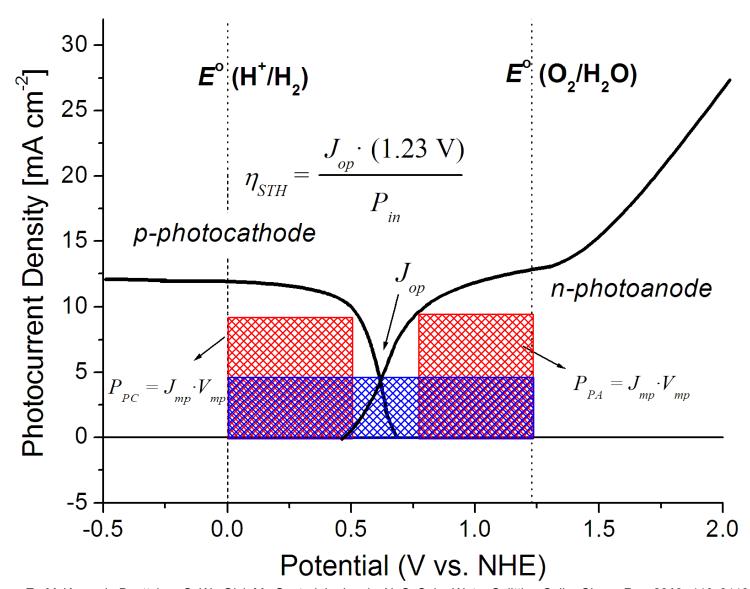


Boettcher, S. W.; Warren, E. L.; Putnam, M. C.; Santori, E. A.; Turner-Evans, D.; Kelzenberg, M. D.; Walter, M. G.; McKone, J. R.; Brunschwig, B. S.; Atwater, H. A.; Lewis, N. S. Photoelectrochemical Hydrogen Evolution Using Si Microwire Arrays. *J. Am. Chem. Soc.* **2011**, *133*, 1216-1219.



Overlaid J-E behavior System Performance

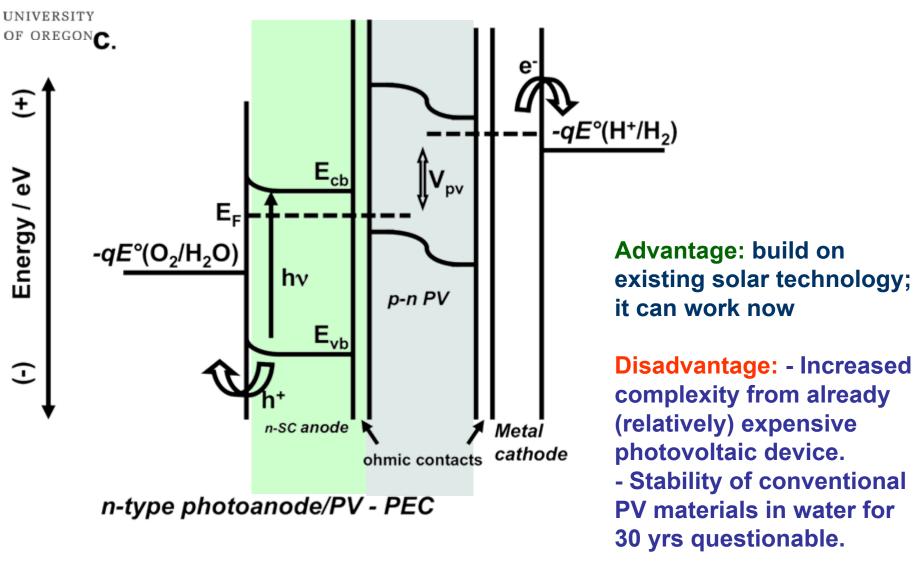
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Walter, M.; Warren, E.; McKone, J.; Boettcher, S. W.; Qixi, M.; Santori, L.; Lewis, N. S. Solar Water Splitting Cells. Chem. Rev. 2010, 110, 6446-6473.



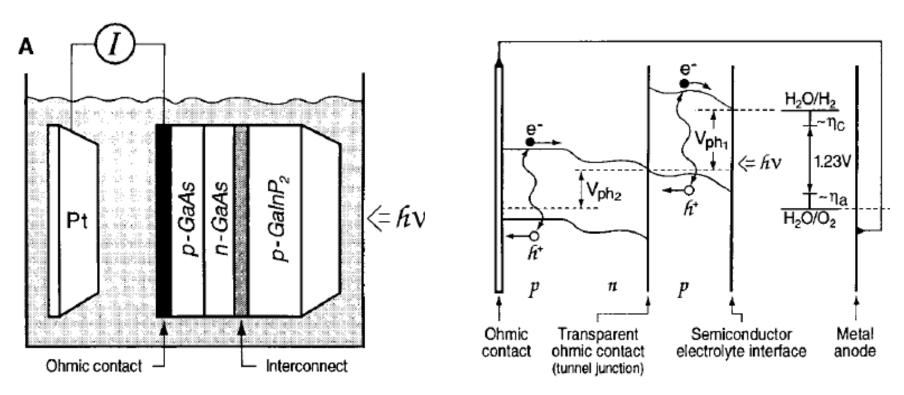
Cells with integrated PV/PEC junctions





Ex. "Turner" NREL Water Splitting Cell

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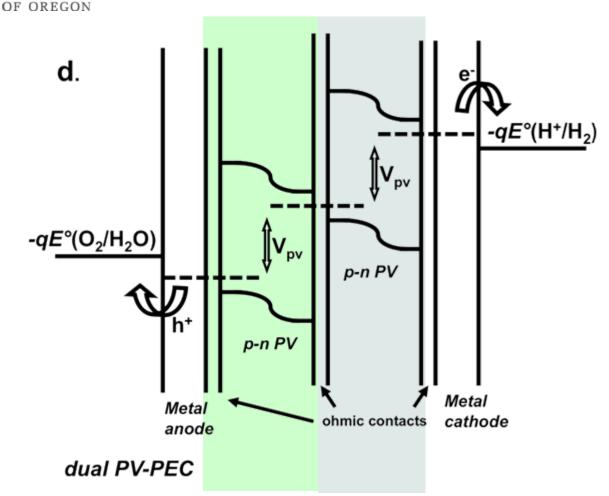


12.4% efficiency (STH) with a cost of ~\$10,000 m⁻² and limited stability

Khaselev, O.; Turner, J. A. A Monolithic Photovoltaic-Photoelectrochemical Device for Hydrogen Production via Water Splitting. *Science* **1998**, *280*, 425-427.



Buried PV-electrolyzer combination



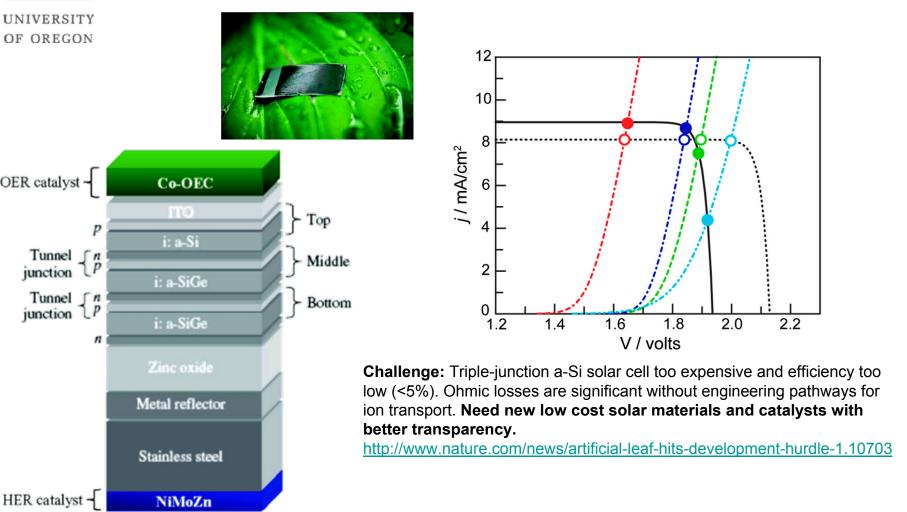
Advantage: build on existing solar technology, wireless design reduces cost relative to separate PV + electrolyzer?

Disadvantage:

Multijunction solar cells are expensive (III-V) or inefficient (a-Si), protection of surface needed, catalyst integration.

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Integrated PV-Electrolysis "Artificial Leaf"



⁽¹⁾ Rocheleau, R. E.; Miller, E. L.; Misra, A. High-efficiency photoelectrochemical hydrogen production using multijunction amorphous silicon photoelectrodes. *Energy Fuels* **1998**, *12*, 3-10.

⁽²⁾ Reece, S. Y.; Hamel, J. A.; Sung, K.; Jarvi, T. D.; Esswein, A. J.; Pijpers, J. J. H.; Nocera, D. G. Wireless Solar Water Splitting Using Silicon-Based Semiconductors and Earth-Abundant Catalysts. *Science* **2011**, 334, 645-648.

⁽³⁾ Nocera, D. G. The Artificial Leaf. Acc. Chem. Res. 2012, 45, 767-776.



Calculation of Overall Efficiencies

Based on total measured Hydrogen output:

$$STH = \left[\frac{(mmol\,H_2/s) \times (237\;kJ/mol)}{P_{total}(mW/cm^2) \times Area\;(cm^2)} \right]_{AM\;1.5\;G}$$

Based on measured current (in 2-electrode configuration)

ased on measured current (in 2-electrode configuration)
$$STH = \begin{bmatrix} \left|j_{SC}(mA/cm^2)\right| \times (1.23V) \times \eta_F \\ P_{total}(mW/cm^2) \end{bmatrix}_{AM\ 1.5\ G}$$
 STH = solar-to-hydrogen efficiency

Chen, Z. B.; Jaramillo, T. F.; et. al. *J. Mater. Res.* **2010**, *25*, 3-16.



Acknowledgements

To all the mentors and co-workers!

"If I have seen further, it is by standing on the shoulders of giants" - Isaac Newton.



Lena Trotochaud



Basic Energy Science Solar Photochemistry



Young Professor Program







Center for Sustainable Materials Chemistry

