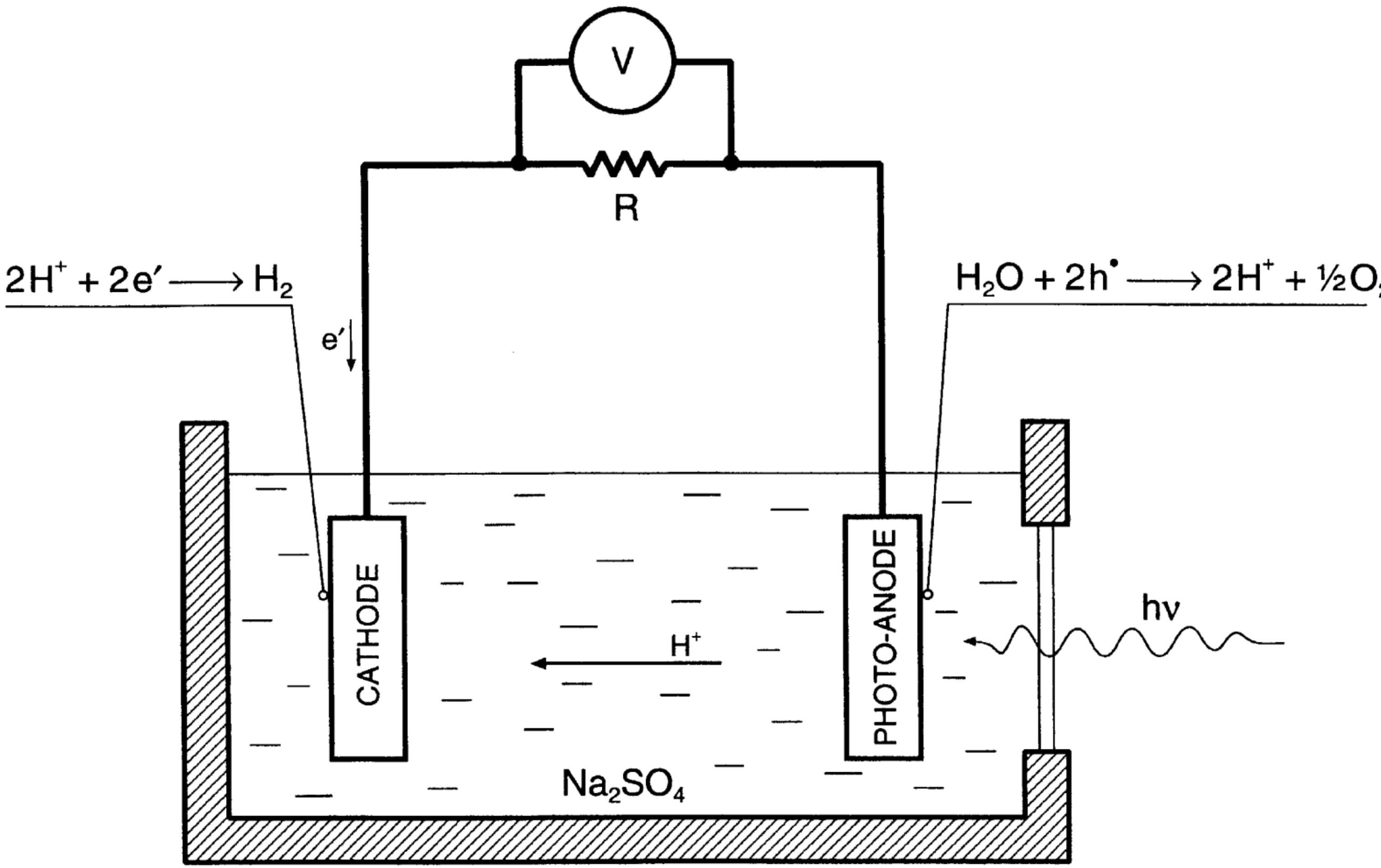
Hematite Photoelectrodes Review
&
Scope of Plasmonic Photoelectrodes for splitting water

Sarath Ramadurgam

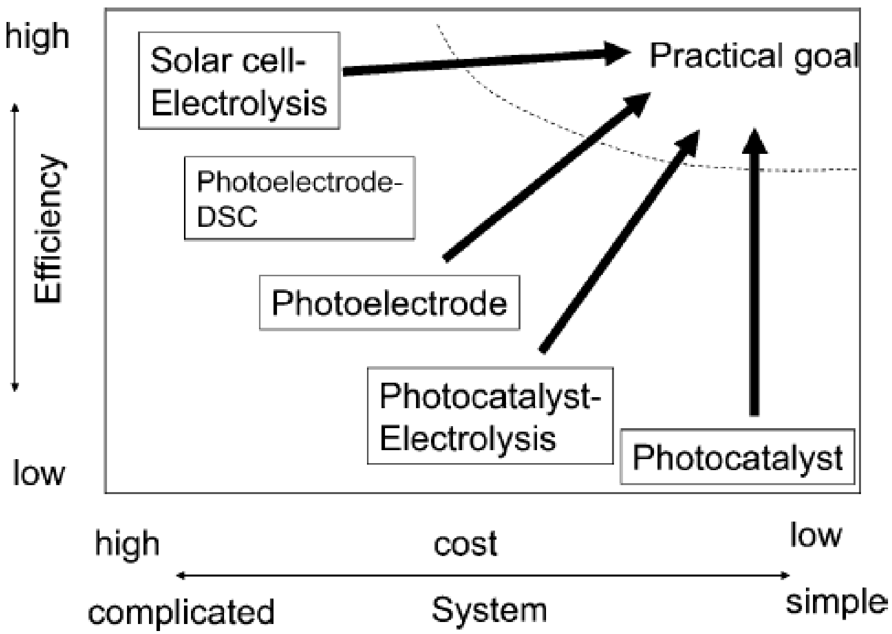
09/18/2013

Contents

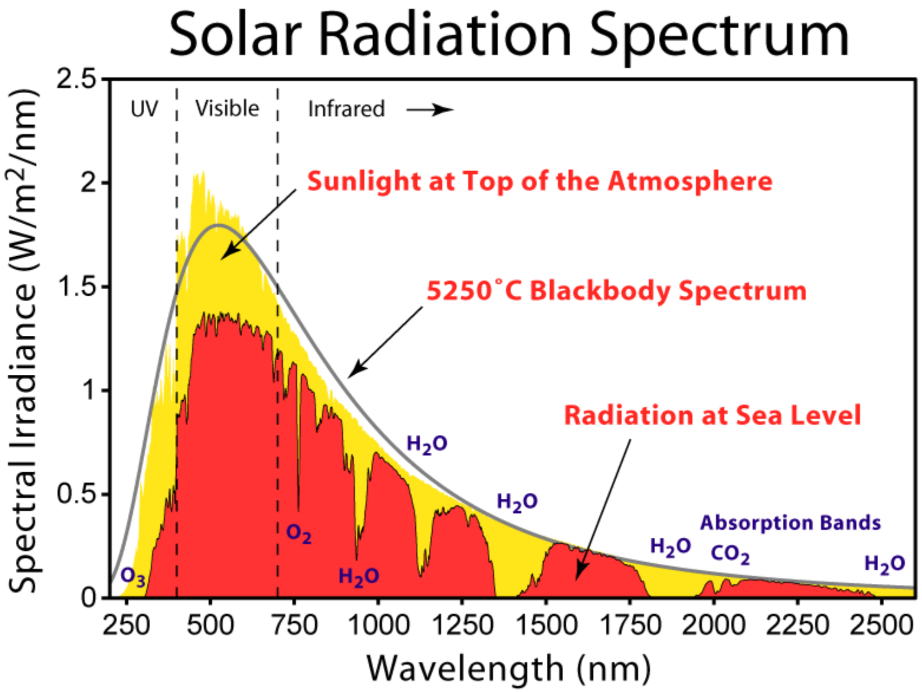
Photo-electrochemical Cell



Benchmark for photoelectrodes

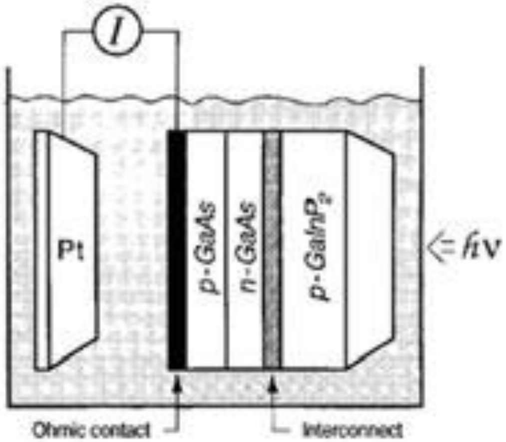
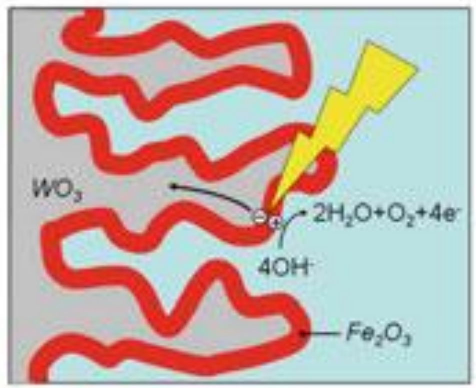
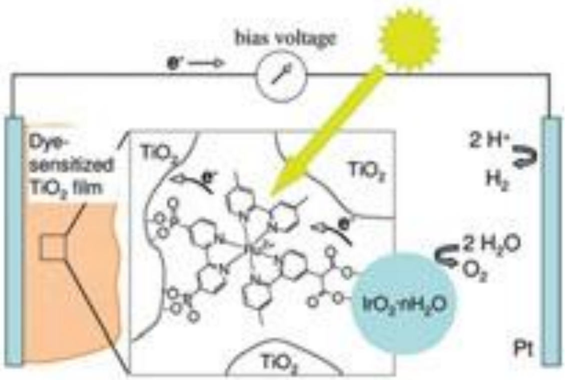


Krol, Gratzel, Springer, 2012



- Energy required for electrolysis of water ~ 1.23 eV which corresponds to 1006 nm.

Benchmark for photoelectrodes

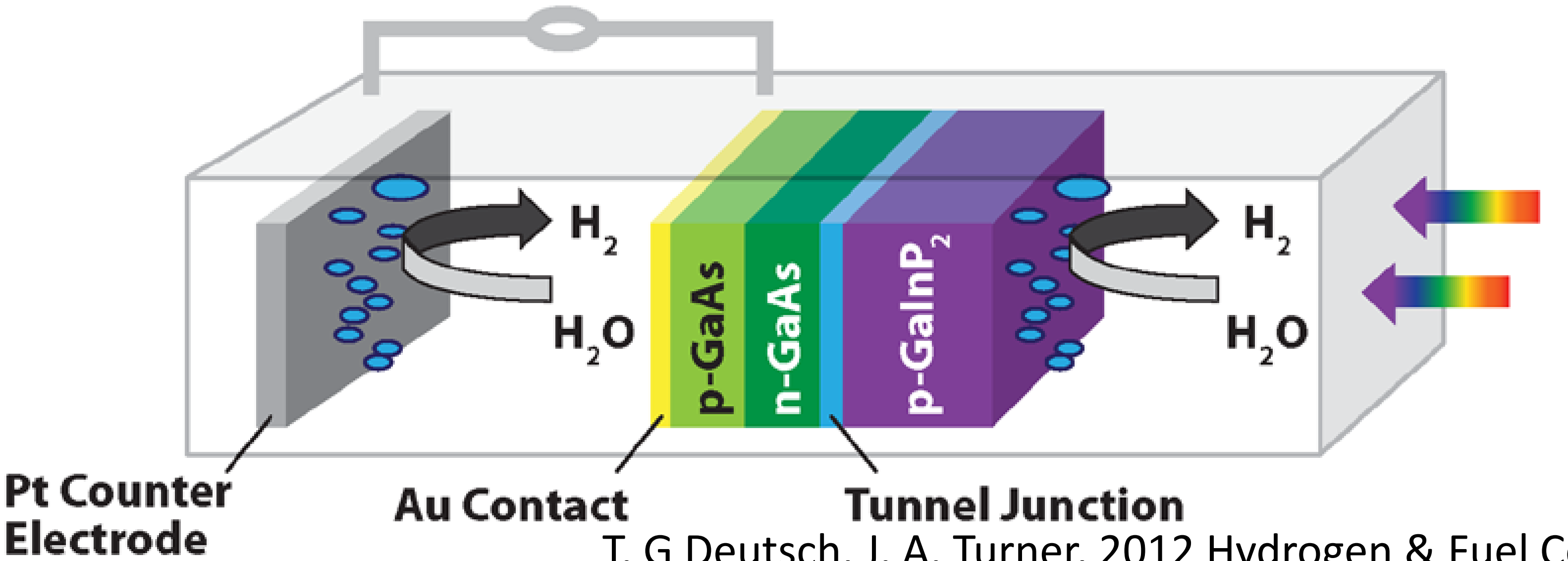
Monolithic PV+Electrolysis	Metal Oxide Photoelectrodes	Molecular/Hybrid Systems
		
10-15%	3-5%	< 1%

Krol, Gratzel, Springer, 2012

Proven efficiencies ←

Low cost →

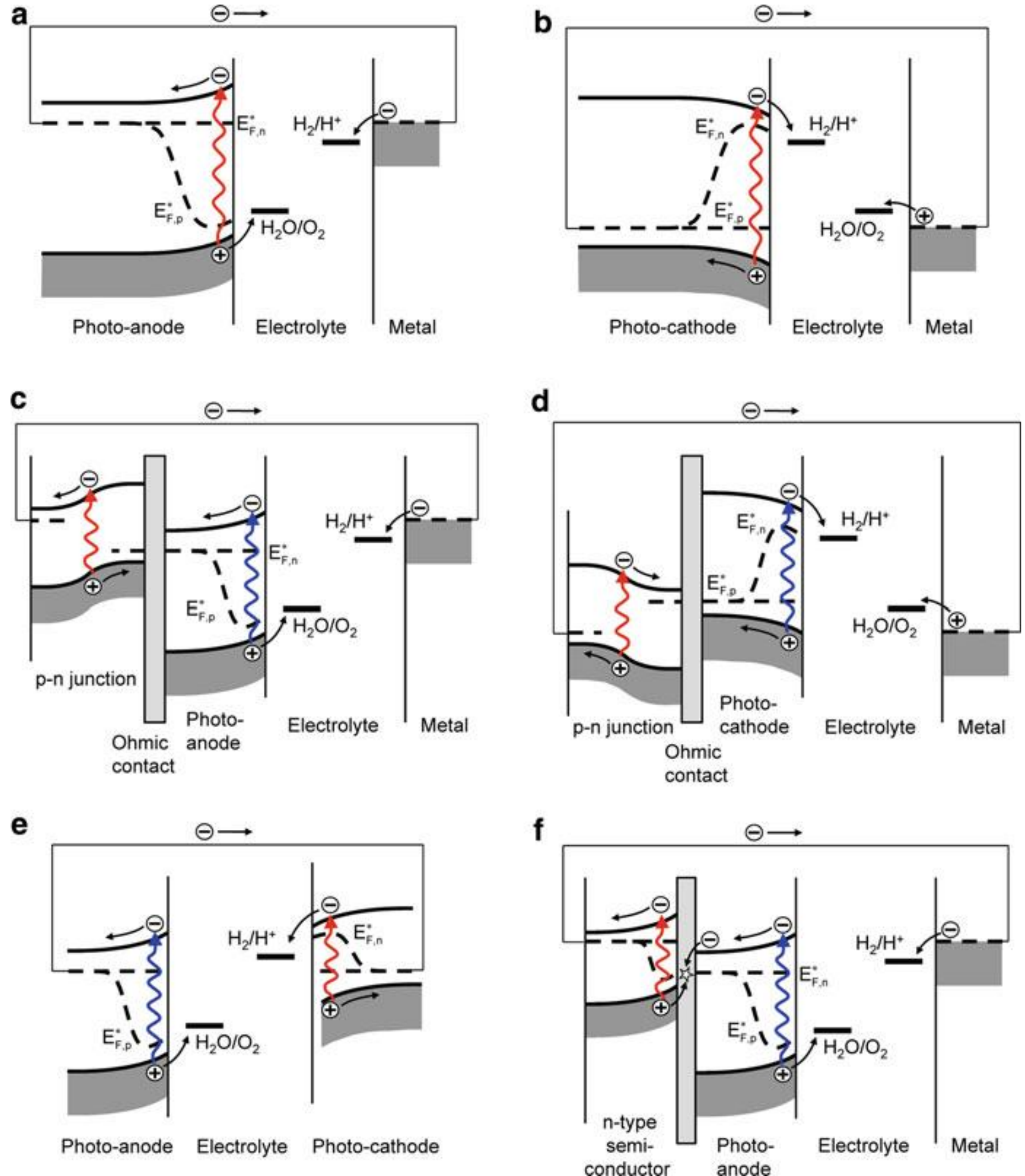
Benchmark for photoelectrodes



T. G Deutsch, J. A. Turner, 2012 Hydrogen & Fuel Cells Program review, NREL.

- Efficiency ~ 12.4%
- Nitride passivated surface achieved over 100+ hours of undamaged operation

Photo-electrochemical cell designs



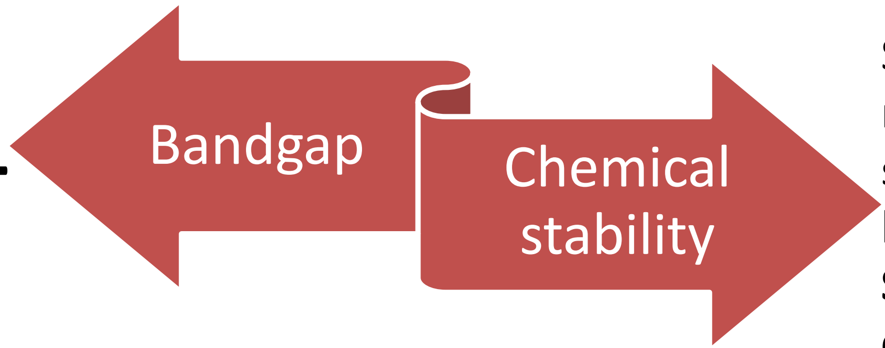
Krol, Gratzel, Springer, 2012

Photoelectrode requirements

Good visible light absorption	• 1.23 eV – minimum photon energy for splitting water • Bandgap – 1.9-3.1 eV
Chemical stability	• Stable in electrolyte • No Photo-corrosion
Band edge positions	• Band gap straddles the oxidation and reduction potentials for water.
Efficient charge transport	• Reduced recombination.
Low overpotential	• Lower implies lesser energy photons required
Low cost	

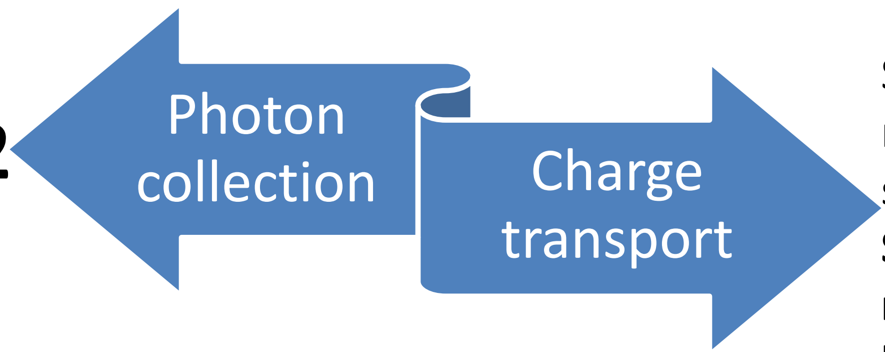
Photoelectrode trade-offs

Trade off 1



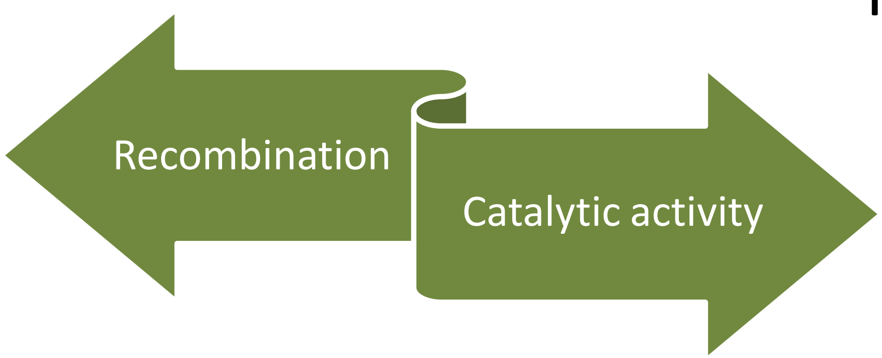
Small bandgap materials absorb more light but are more susceptible to corrosion. Ideal bandgap – 1.9-3.1 eV
Solution: Heterojunctions, doping

Trade off 2



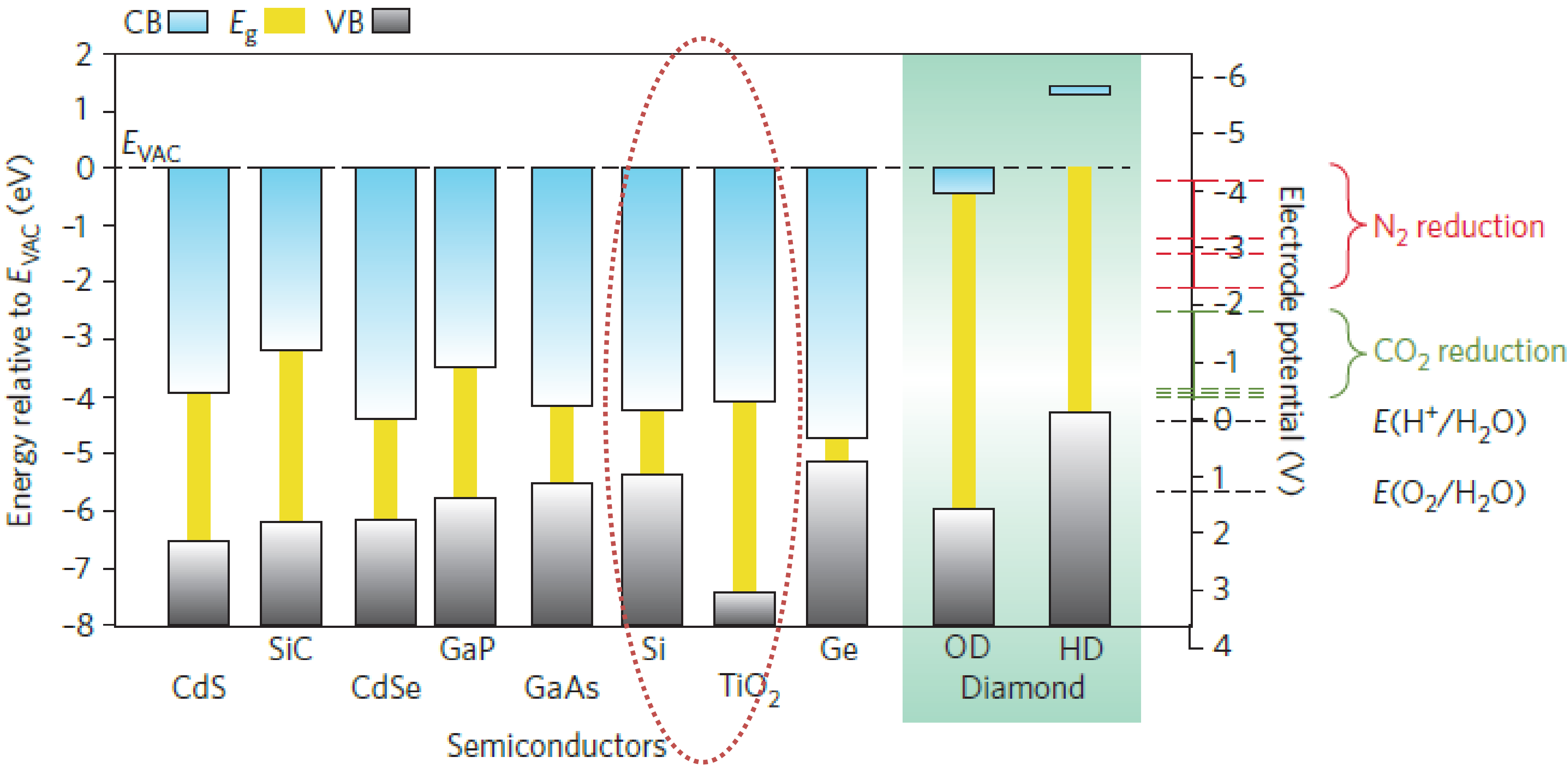
Small bandgap materials absorb more light but are more susceptible to corrosion.
Solution: Nanostructures, anti-reflection coating, Resonant light trapping, Plasmonics

Trade off 3



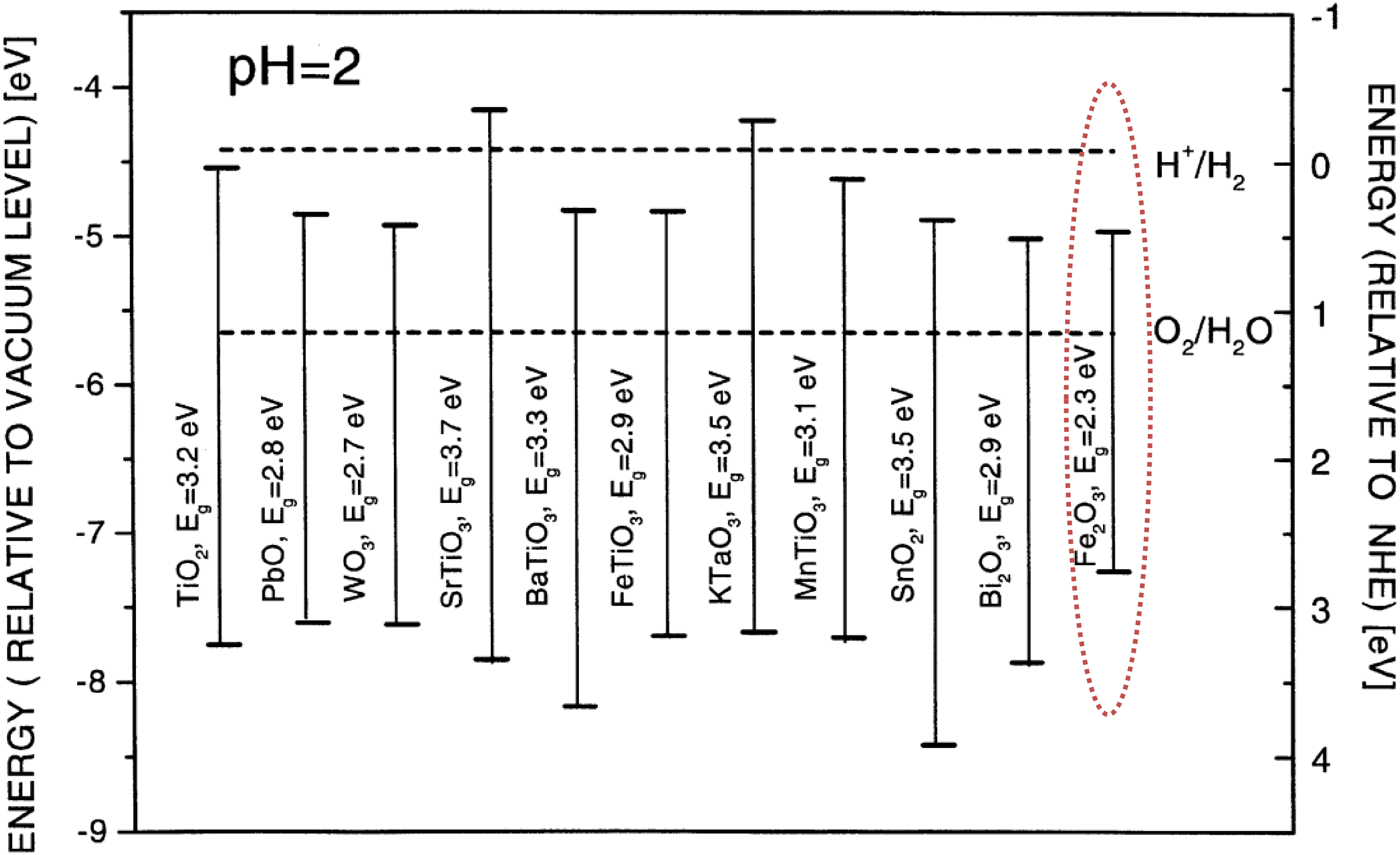
Surface sites that promote catalysis also promote recombination.
Solution: doping, co-catalysts

Bandgap vs. Chemical stability



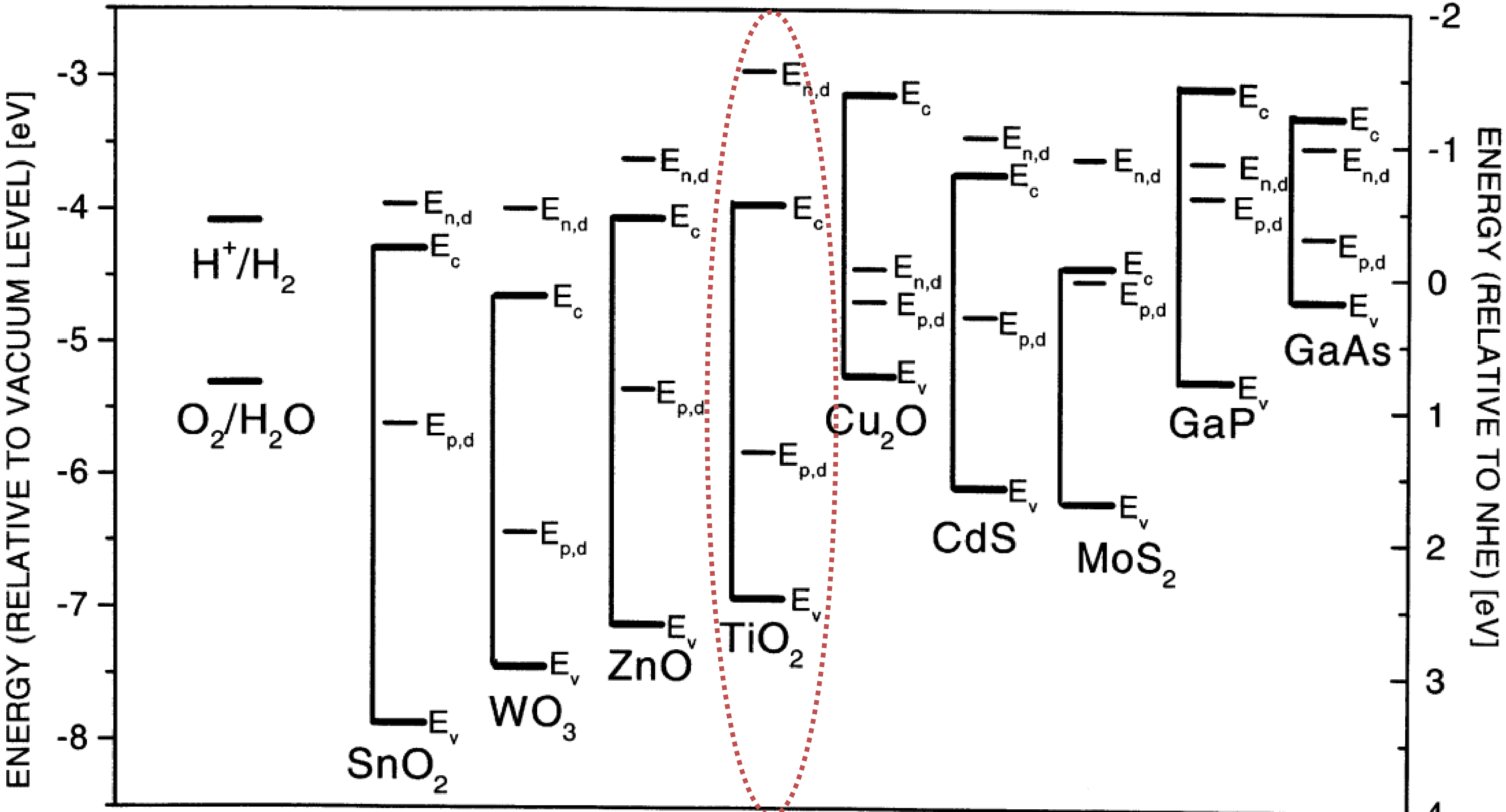
C. E. Nebel, Nature Mat., 2013

Bandgap vs. Chemical stability



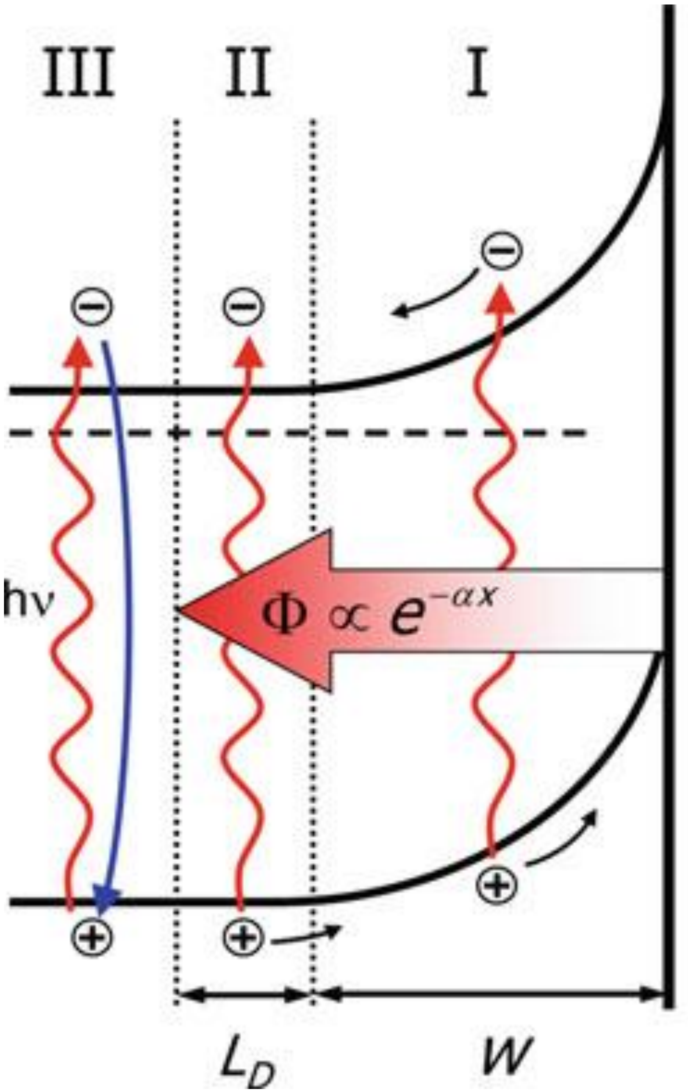
T. Bak, et. al., Int. J. Hyd. Energy, 2002

Bandgap vs. Chemical stability



T. Bak, et. al., Int. J. Hyd. Energy, 2002

Photon collection vs. Charge transport



Region I:

- Absorption
- Charge separation
- Field-assisted transport (drift)

Region II:

- Absorption
- Transport by diffusion
- Holes are able to reach region I before recombining

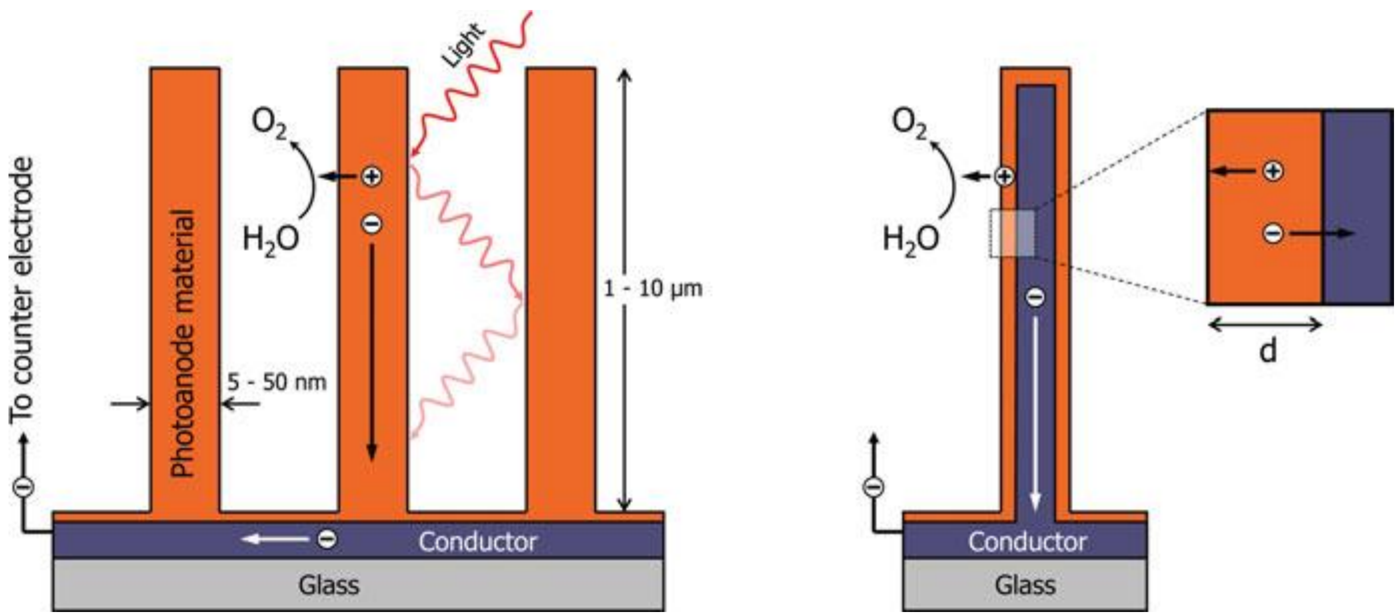
Region III:

- Absorption + recombination

Optimal film thickness: $d \approx \alpha^{-1} \approx W + L_D$

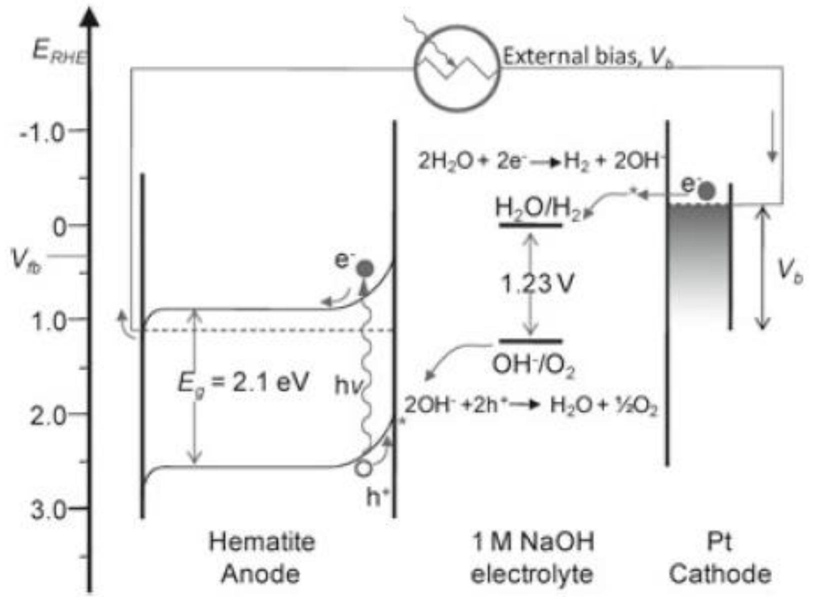
Krol, Gratzel, Springer, 2012

Photon collection vs. Charge transport: Nanostructures

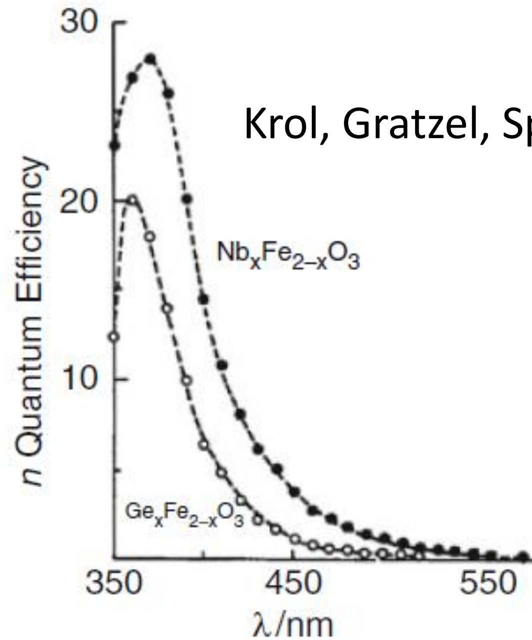


Krol, Gratzel, Springer, 2012

Hematite photoelectrodes for splitting water



Krol, Gratzel, Springer, 2012

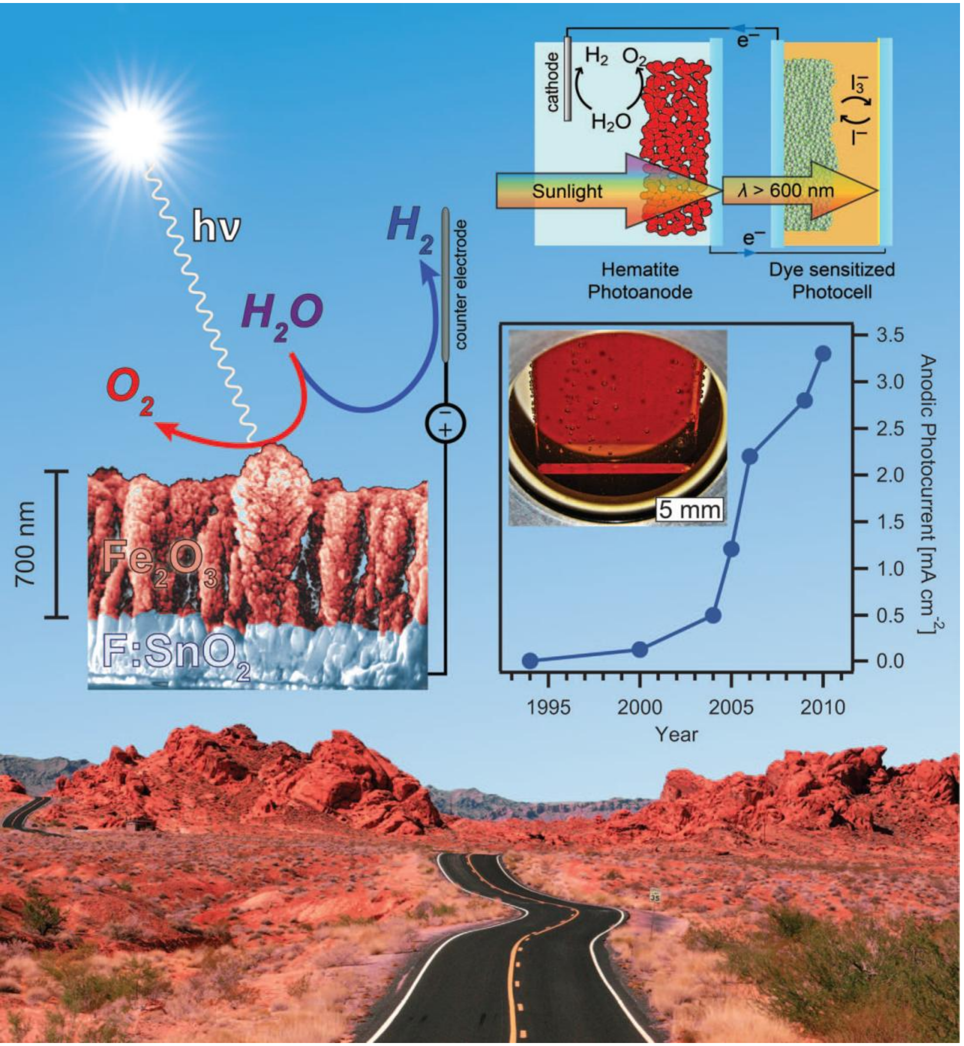


- Based on the bandgap, TiO_2 (anatase, Eg = 3.2 eV) and WO_3 (Eg = 2.6 eV) can at most convert **3.4%** and **10.2%**, respectively, of the sun's energy into hydrogen.
- Iron (III) oxide (Hematite - α-Fe2O3) can potentially convert **16.8%**.

Hematite photoelectrodes for splitting water

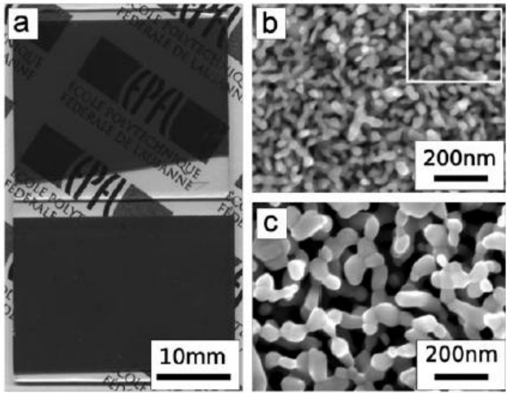
- Challenges - **Solutions**:
  - Flatband potential too low in energy for water reduction – **tandem cells, heterojunctions.**
  - Large overpotential and slow water oxidation kinetics – **co-catalysts like Co and Co-Pi.**
  - Low absorption coefficient, requiring relatively thick films – **nanostructures, plasmonics.**
  - Poor photogenerated majority carrier conductivity – **nanostructures.**
  - Short diffusion length of minority – **nanostructures.**

Hematite nanostructures

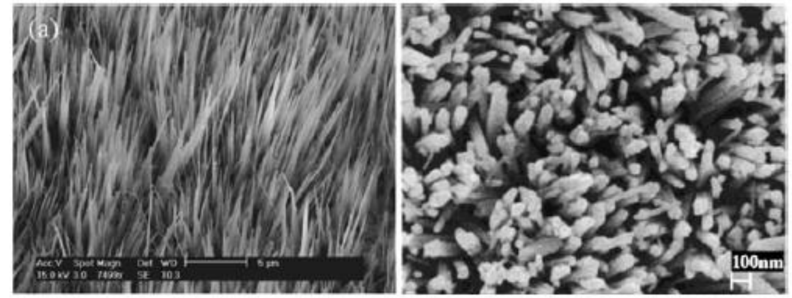


- Methods for preparing hematite nanostructures:
  - Porous thin films from solution based colloidal method.
  - Nanowires
  - Electrochemical anodization
  - Ultrasonic Spray pyrolysis
  - Atmospheric pressure CVD
  - Extremely thin absorbers

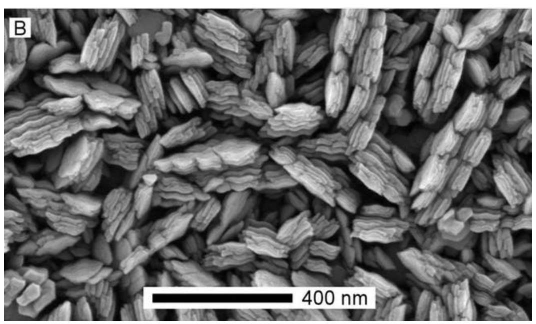
Hematite nanostructures



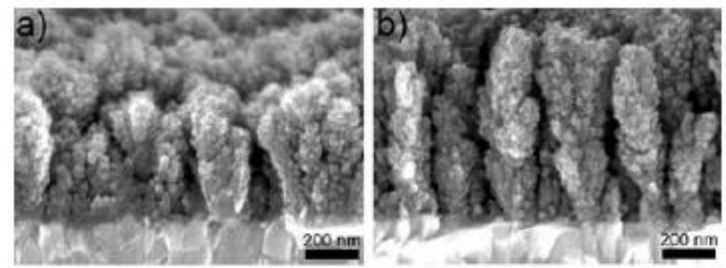
Porous thin films from solution based colloidal method



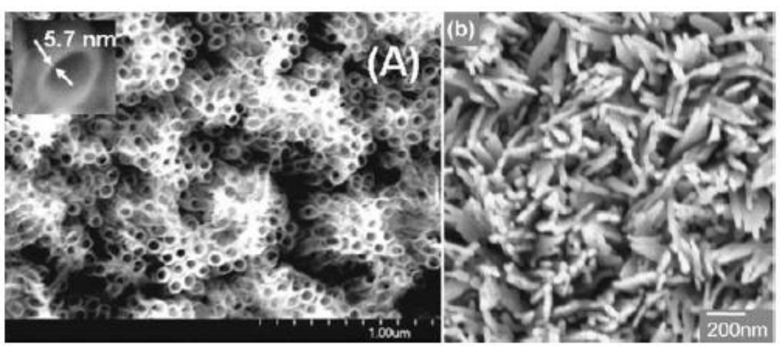
Nanowires



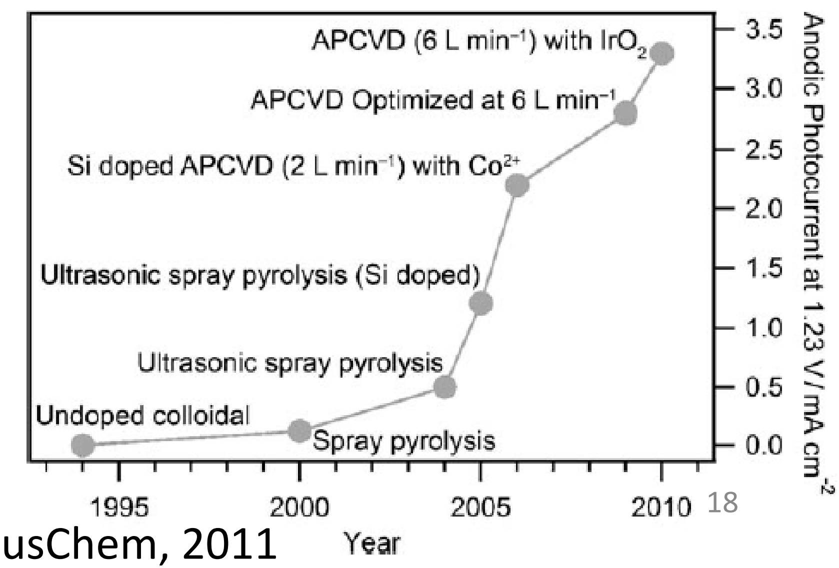
Ultrasonic spray pyrolysis



Atmospheric pressure CVD



Electrochemical anodization



K. Sivula, F Le Formal, M. Gratzel, ChemSusChem, 2011

Hematite nanosctructures

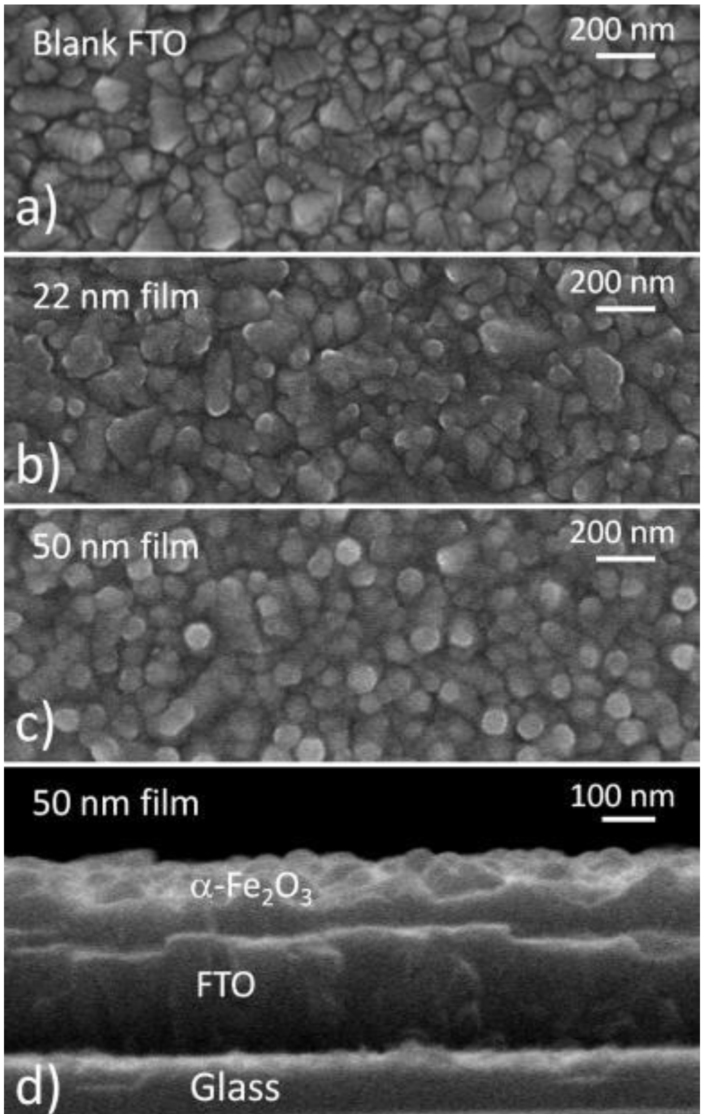
Table 1. Comparison of hematite photoanode structuring methods

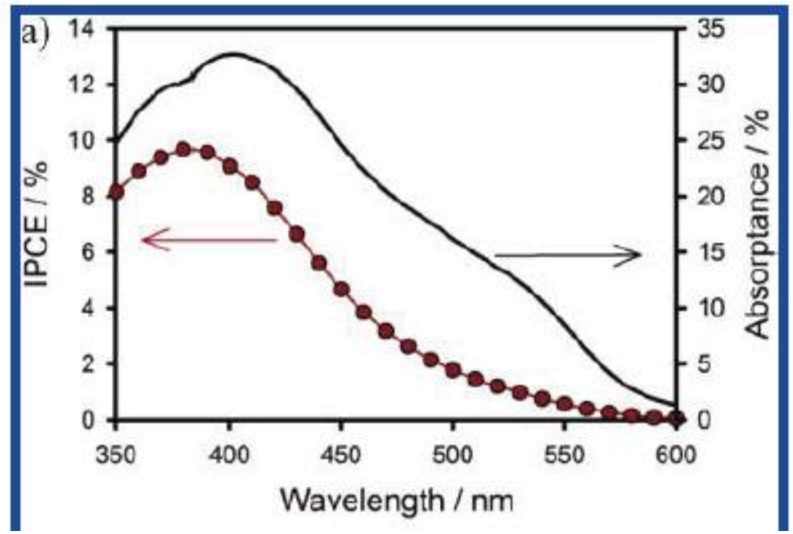
Technique	Feature size	Dopant	Performance
Single crystal[57]	micrometer	Nb	IPCE 37% at 370 nm and 1.23 V_{RHE}
Sintered polycrystalline disk[47]	micrometer	Si	IPCE 34% at 400 nm and 1.23 V_{RHE}
Colloidal deposition of porous films[88]	25 nm	Ti	2.34 mA cm^{-2} at 1.63 V_{RHE} and AM 1.5 (100 mW cm^{-2}) and IPCE 40% at 400 nm and 1.6 V_{RHE}
Solution-based nanowires[27]	50 nm × 500 nm	none	IPCE 7% at 400 nm and 0.9 V_{RHE} (in KI)
Potentiostatic anodization (nanotubes)[102]	6 nm × 1 μm	none	Before annealing: None reported After annealing:[a] 1.0 mA cm^{-2} at 1.23 V_{RHE} and AM 1.5 (87 mW cm^{-2})
Electro-deposition[28]	20–50 nm	Mo	IPCE 8% at 400 nm and 1.2 V_{RHE}
Ultrasonic spray pyrolysis[66,114]	10 nm × 300 nm	Si	1.5 mA cm^{-2} at 1.23 V_{RHE} and AM 1.5 (100 mW cm^{-2}) and IPCE 14% at 400 nm and 1.23 V_{RHE}
Atmospheric pressure CVD[77]	5 nm × 800 nm	Si	3.3 mA cm^{-2} at 1.23 V_{RHE} and AM 1.5 (100 mW cm^{-2}) and IPCE 39% at 400 nm (50% at 325 nm and 16% at 550 nm) and 1.23 V_{RHE}
Extremely thin absorber[123]	50 nm film	Si	1.3 mA cm^{-2} at 1.23 V_{RHE} and AM 1.5 (100 mW cm^{-2}) and IPCE 26% at 400 nm and 1.43 V_{RHE}

[a] Feature size not reported after annealing.

K. Sivula, F Le Formal, M. Gratzel, ChemSusChem, 2011

Hematite Photoelectrodes: Thin films from ALD

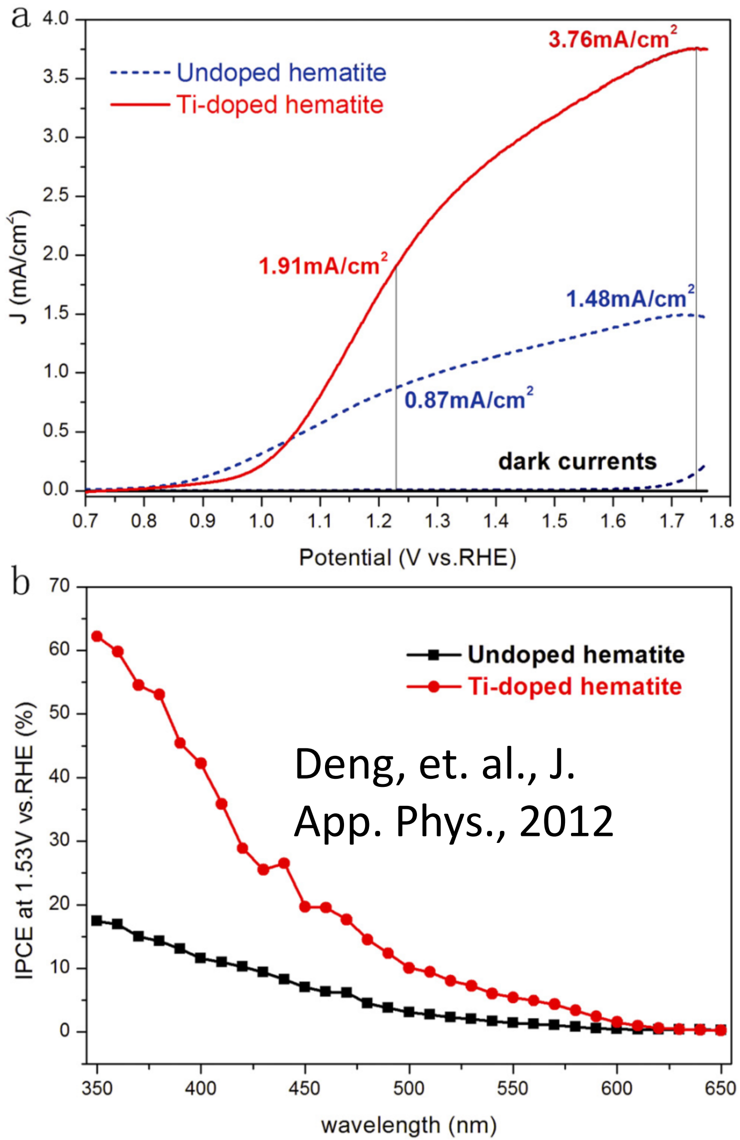




- Optimal thickness was found to be 20 nm.
- Efficiency is low due to mid-gap traps and low hole mobility.

Klahr, et. al., Langmuir, 2011

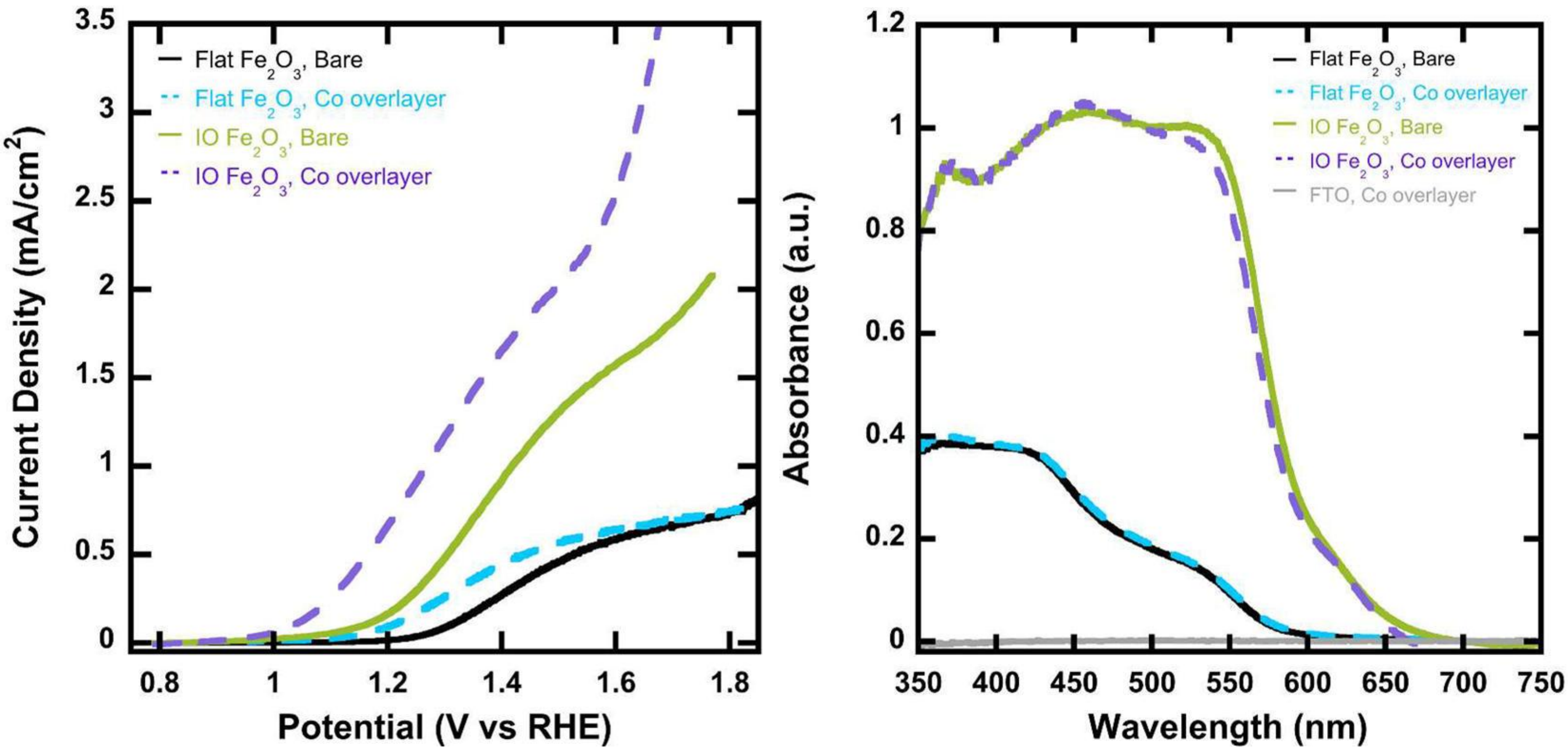
Hematite Photoelectrodes: Doped Hematite thin films



Deng, et. al., J. App. Phys., 2012

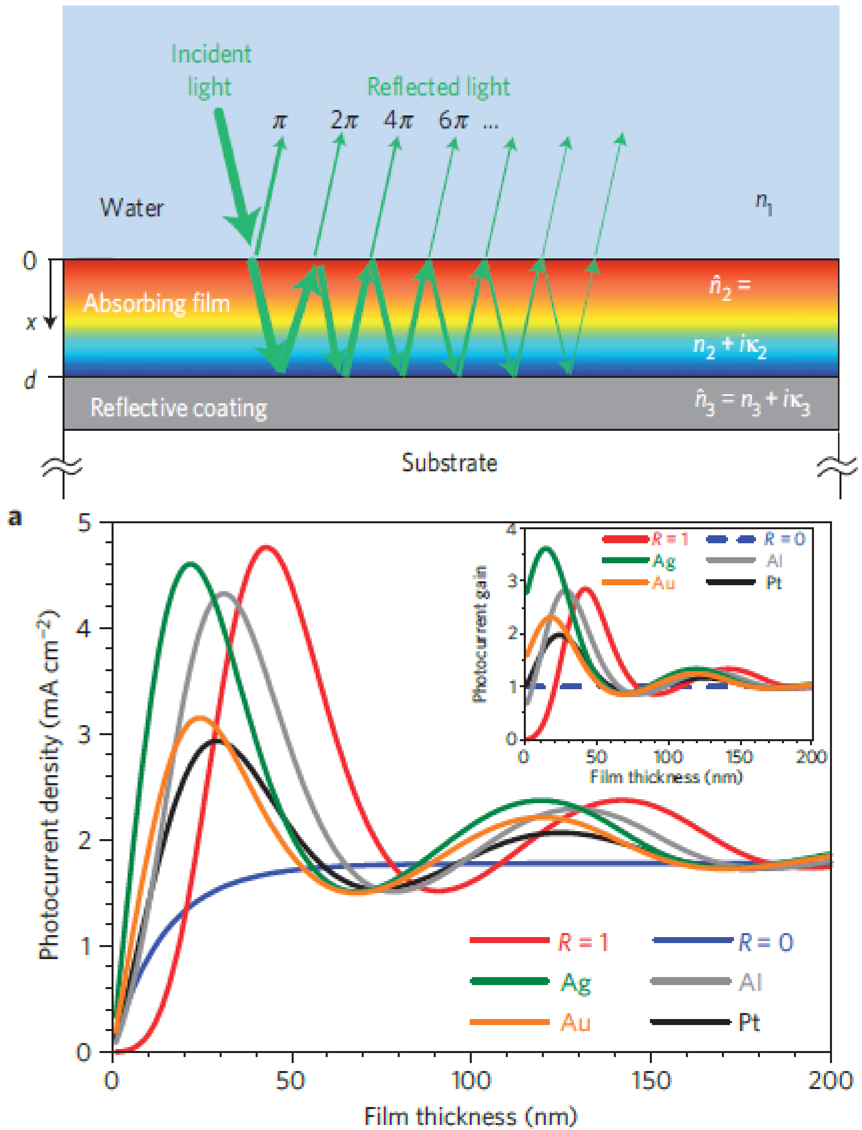
- Si, Ti and Zr doping have been shown to improve the photocurrent density.

Hematite photoelectrodes: Co-catalyst and nano-scaffolds



Riha, et. al., ACS Nano, 2013

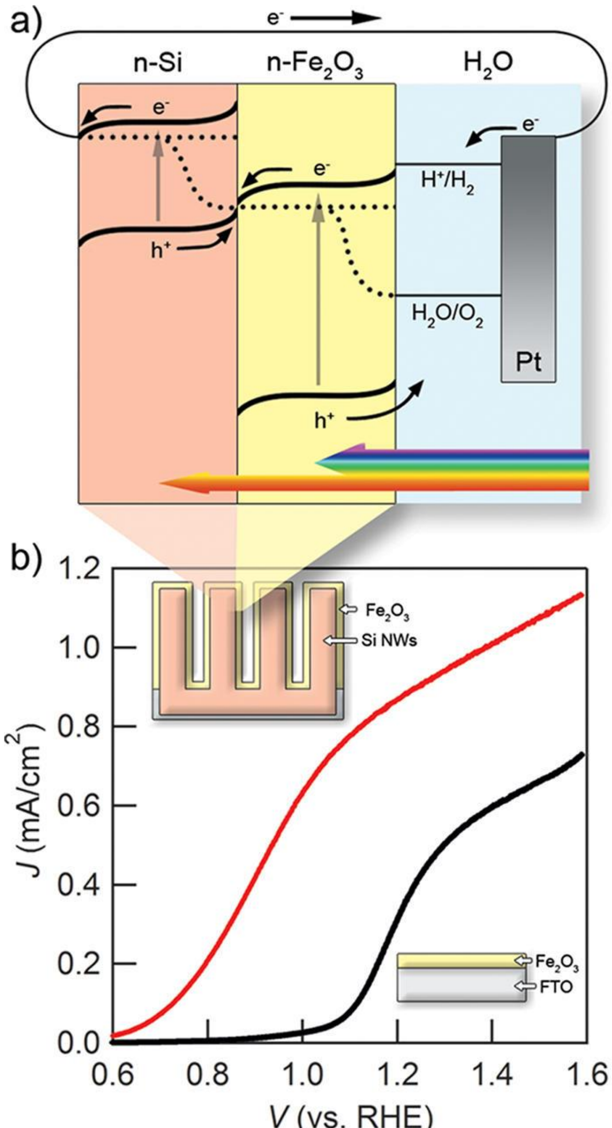
Hematite photoelectrodes: Resonant light trapping



- Charge separation and collection yield of photogenerated holes in Ti doped hematite increases with decreasing thickness.
- Absorption decreases with decreasing thickness. Solution – optical cavity.

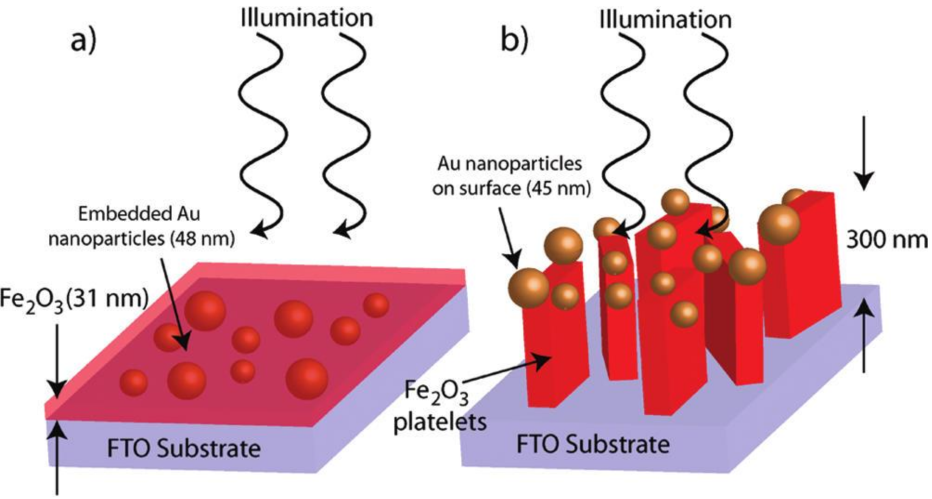
Dotan, et. al., Nature Mat., 2012

Hematite photoelectrodes: Heterojunctions

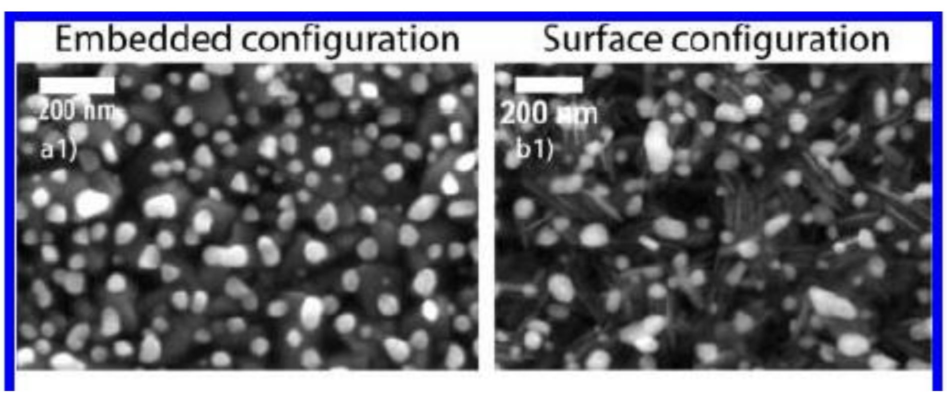


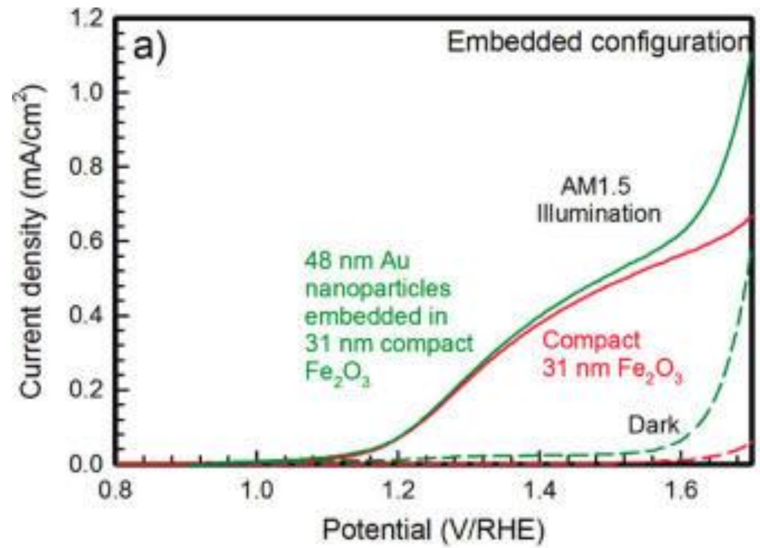
- Onset potential is 0.6 V_{RHE}
- Fig b - Red – nanowire; Black – planar

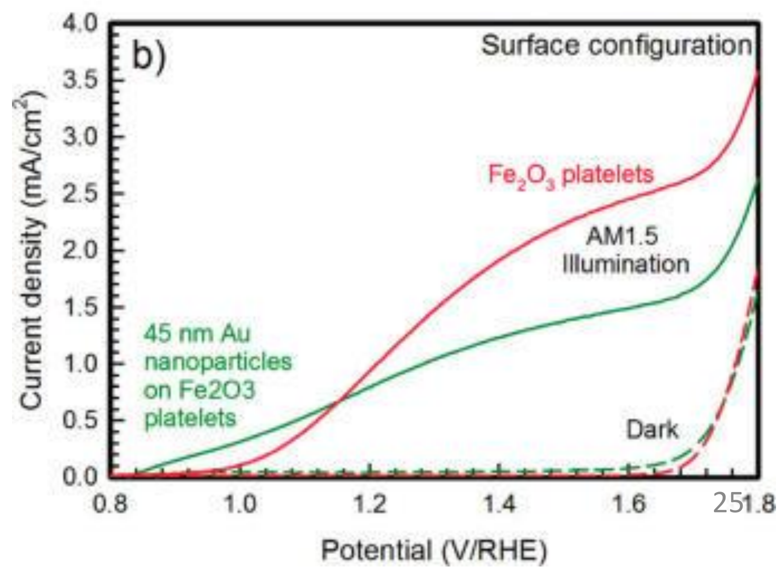
Plasmonic Photoelectrodes: Au-Hematite



Embedded configuration Surface configuration

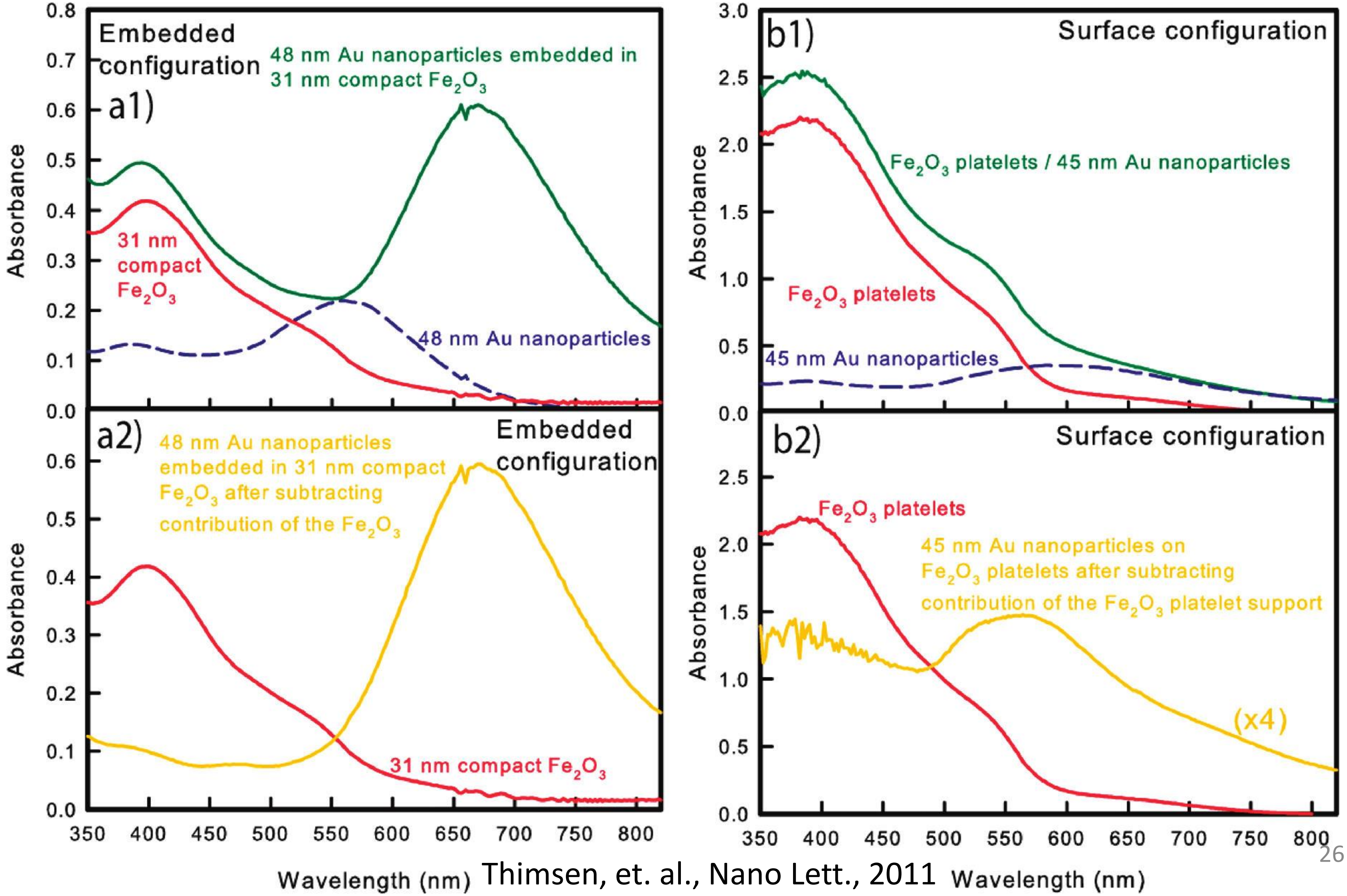






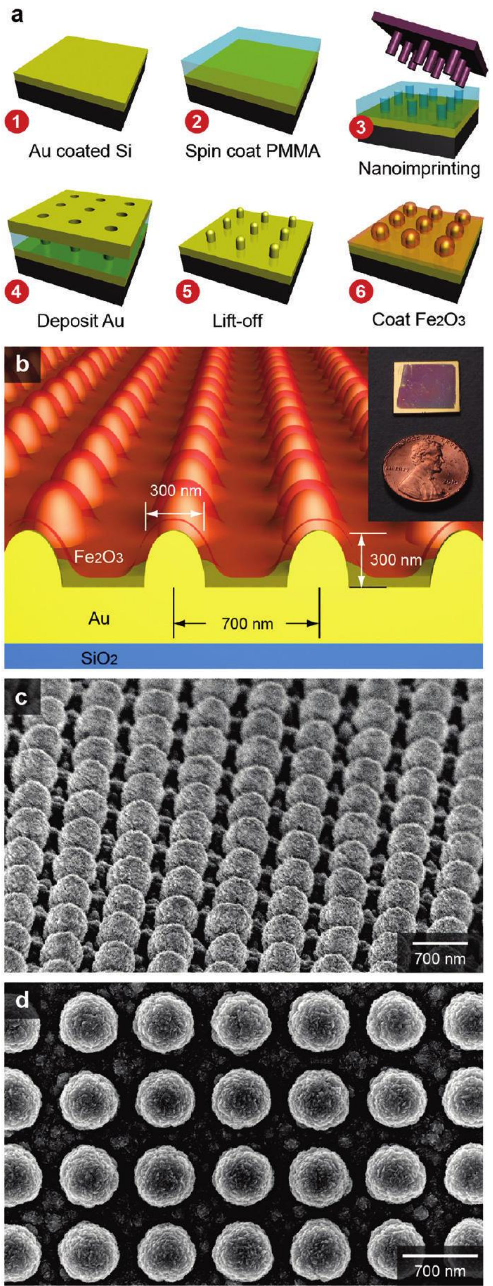
Thimsen, et. al., Nano Lett., 2011

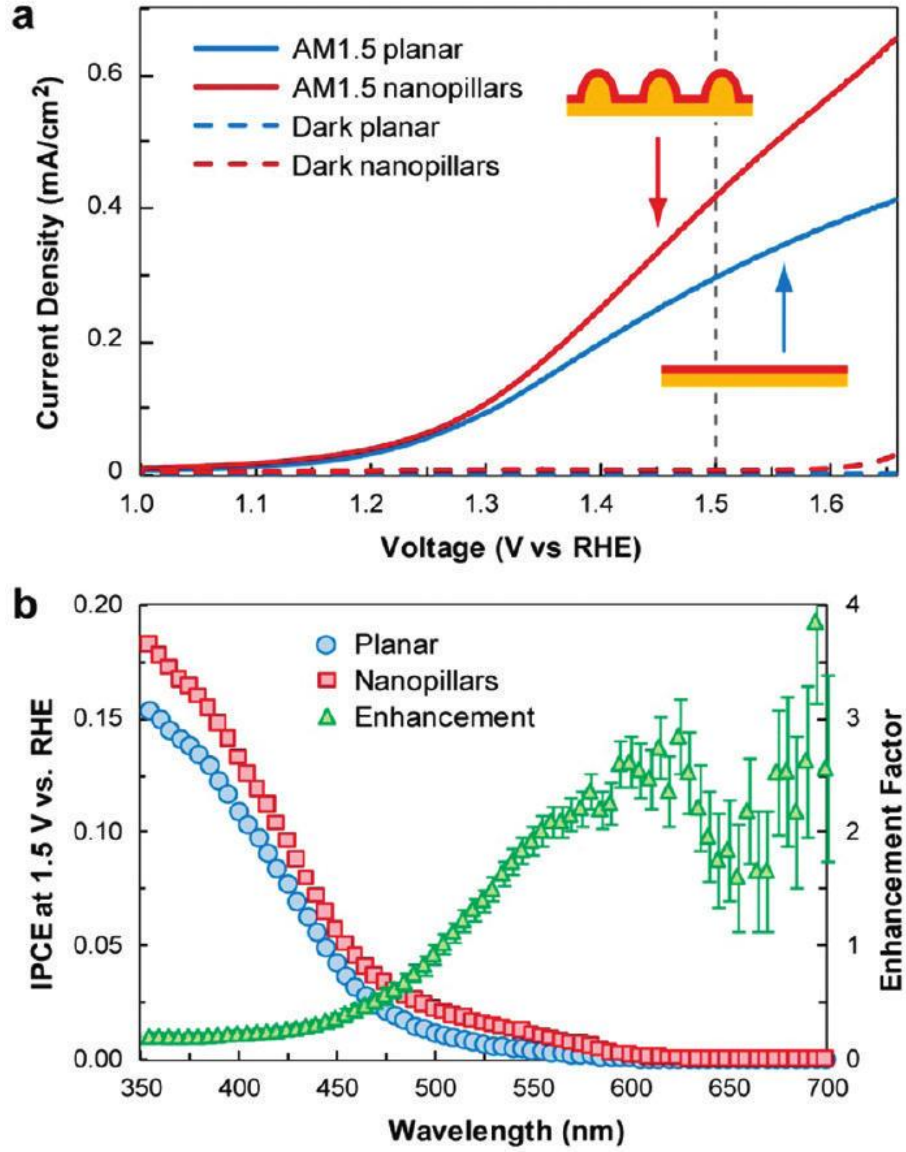
Plasmonic Photoelectrodes: Au-Hematite



Thimsen, et. al., Nano Lett., 2011

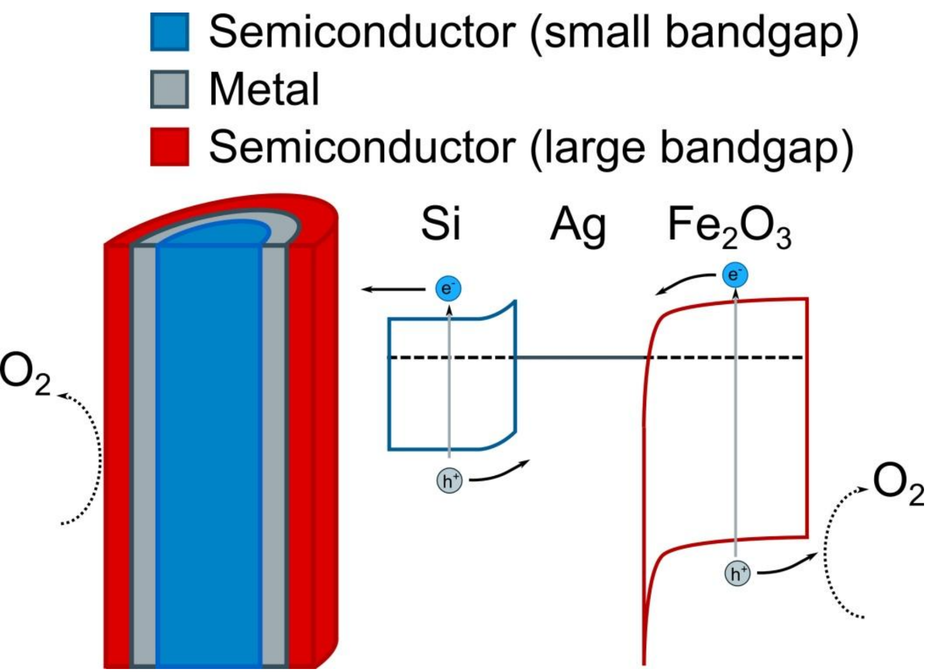
Plasmonic Photoelectrodes: Au-Hematite





Gao, et. al., ACS Nano, 2012.

Plasmonic Photoelectrodes: Core-multishell nanowires



- Flatband potential too low in energy for water reduction – **Si core provides the required increase in energy.**
- Large overpotential and slow water oxidation kinetics – **Hot electrons from the metal inner shell could potentially help.**
- Low absorption coefficient, requiring relatively thick films – **Si core, plasmonic resonances and nanowire geometry.**
- Poor photogenerated majority carrier conductivity – **metal shell, thin hematite shells.**
- Short diffusion length of minority – **nanowire geometry, metal inner shell.**

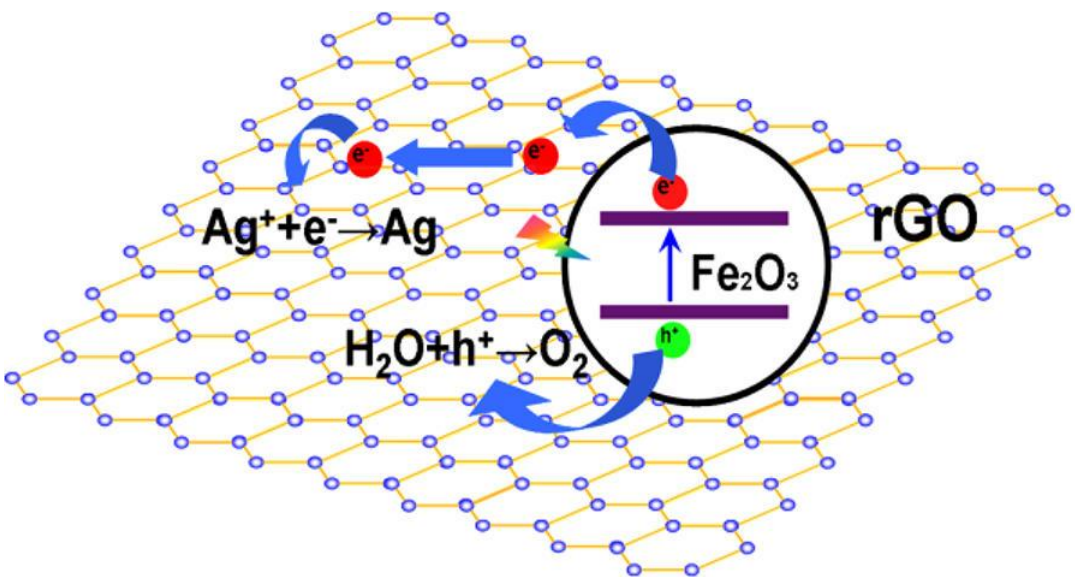
Conclusion

- Hematite is chemically stable in electrolytes and has the right bandgap to function as a photoelectrode with a potential maximum efficiency of 16.8%.
- Poor absorption, high recombination, low conductivity limits it's performance
- Many nanostructures, doping, co-catalysts and growth methodologies have been studied to improve material quality and efficiency.
- More recently, plasmonic enhancement of hematite photoelectrodes has been explored. These studies indicate that carefully designed plasmonic photoelectrodes could lead to higher efficiency.
- In this regard, core-multishell nanowire structures could lead to significantly improved efficiencies.

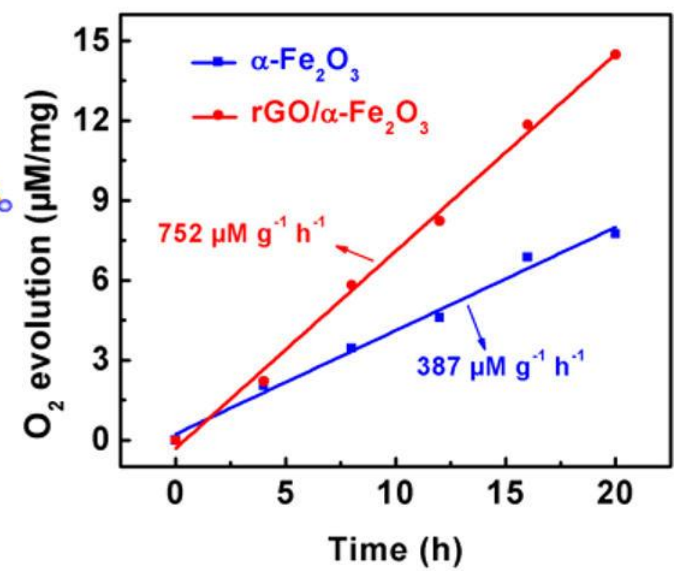
Thank you!

Questions?

Appendix



e⁻
Ag⁺+e⁻→Ag
Fe2O3
rGO
h⁺
H2O+h⁺→O2



α-Fe2O3
rGO/α-Fe2O3
752 μM g-1 h-1
387 μM g-1 h-1
O2 evolution (μM/mg)
Time (h)
0
3
6
9
12
15
0
5
10
15
20