August 2006 ICMR Symposium on
Materials Issues in Hydrogen Production and Storage

New Materials for Photoelectrocatalytic Production of Hydrogen From Sunlight

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Predicting the future is easy.
It's trying to figure out what's going on now that's hard.

~ Fritz R. S. Dressler ~

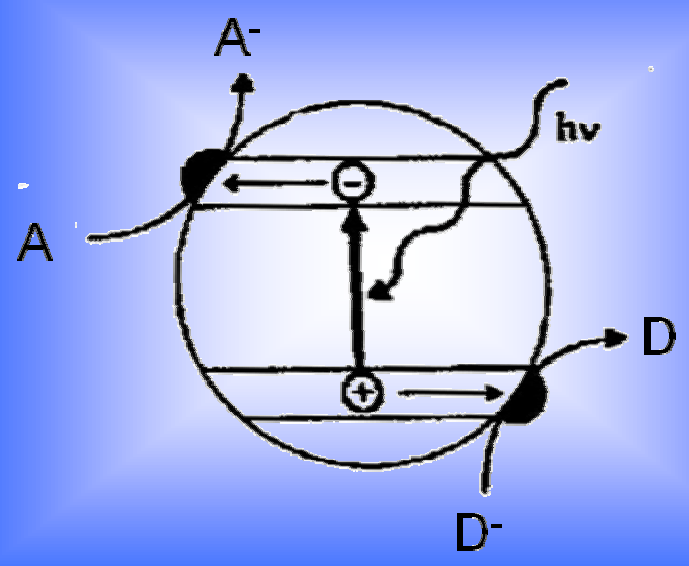
Outline

- **Motivation and Background**
- **Materials Issues in Photoelectrocatalysis.**
- **High Throughput Photocatalyst Synthesis and Screening**
- **Observed Compositional And Morphological Dependencies in Metal Oxide Photocatalysts.**

Motivation: It's Important

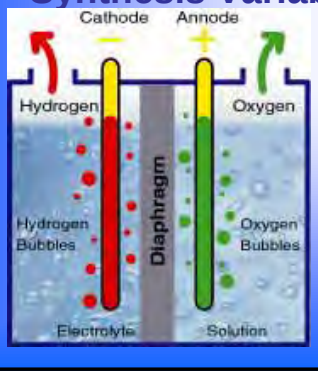
Motivation: It's Imaginable

Motivation: It's Interesting



It's Just Solar Powered Electrosynthesis of Chemicals

- **Low Temperature**
- **Selective**
- **Wide Range of Synthesis Variables**



- **Art and "Magic"**
- **Relatively slow**
- **Electricity Cost**
- **Electrode Stability**

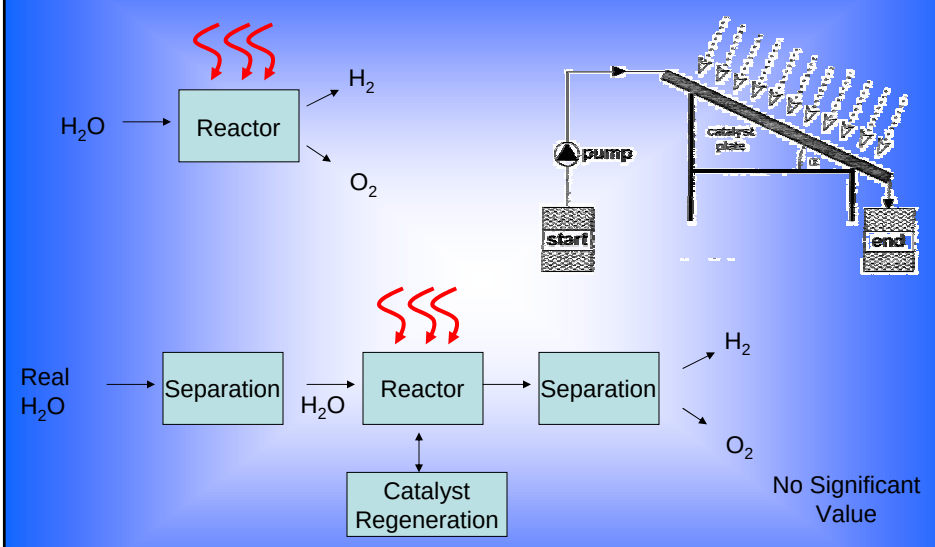
Photoelectrochemical Synthesis

- Low Temperature
- Selective
- Same Chemistries as Electrosynthesis

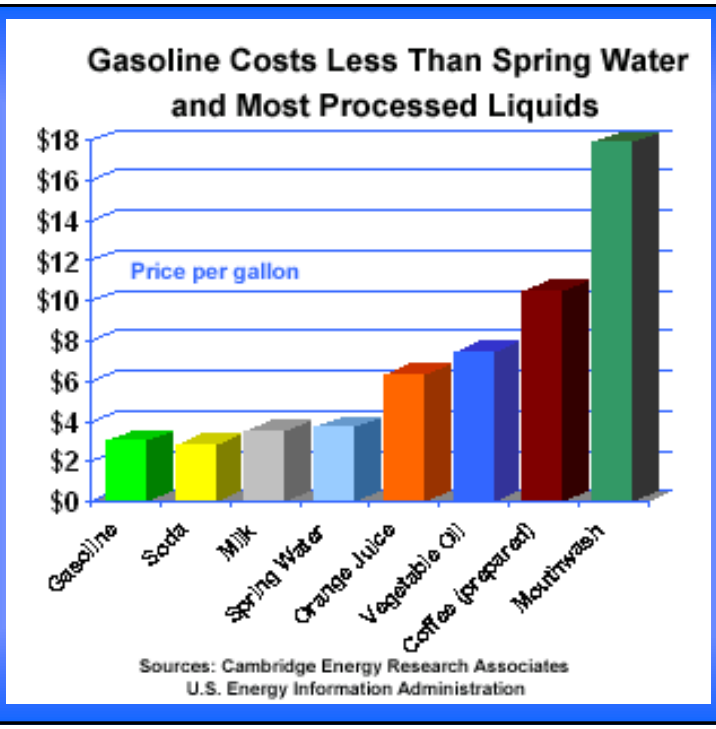
- **Art and "Magic"**
- Relatively slow
- Photon Costs
- Photon-Electron Conversion
- Material Stability

We're Making Low Value Fuel

The Engineering Process Realities



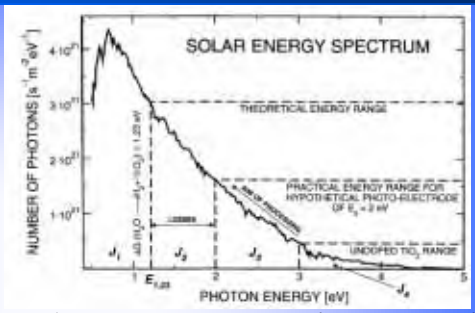
Industrial Chemistry Is Only Possible through Engineering



Photoelectrochemical H_2 Economics

~ 1000 W/m² available for harvesting.

"useful flux" ~ 10^{21} photons/m²-s day averaged @ > 1.5 eV



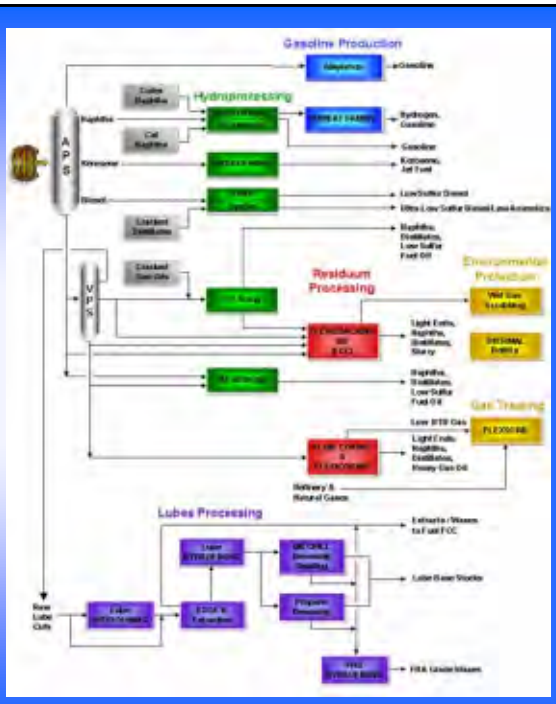
Solar Energy Spectrum (AM of 1.5) In Terms of Number of Photons vs Photon Energy

T. Bak, et al. *Int. J. Hydrogen Energy* **27** (2002) 991-1022.

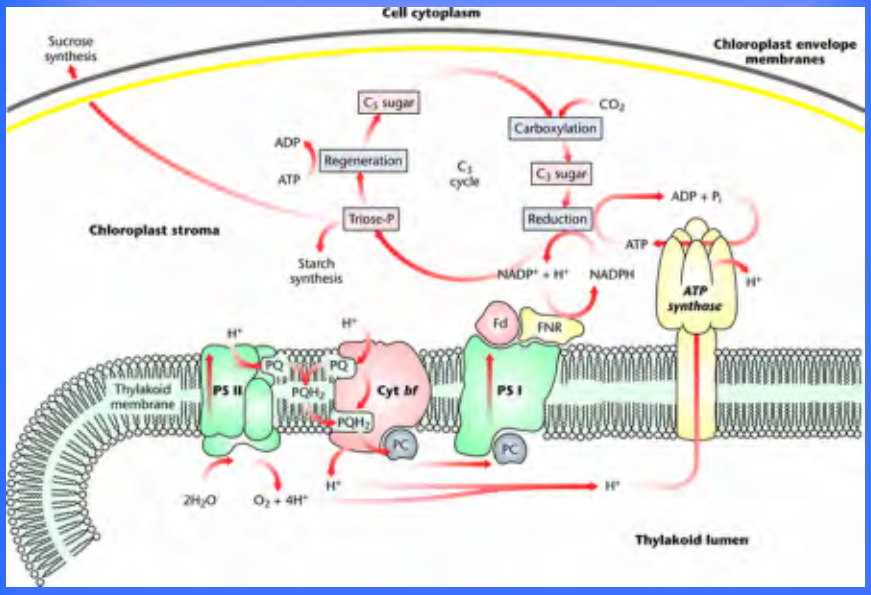
Hydrogen

- **@ $2e^- / H_2$ -> 50e (kg H_2/m²-year)**
- **To compete with \$2-5/kg H_2 with an e ~10% system**
- **ANY photocatalysis system cost (material+reactor) < \$20/m²-year**
- **Compared to presently available 10Y-life Si solar panel ~ \$80/m²-year**

Oil → Gasoline is cheap because it is simple and can be integrated



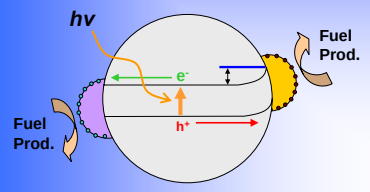
Process Integration



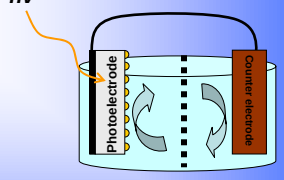
Options for PEC:

- Limitations of thin film PV's no not apply
- Fabrication, processability, carrier transport, epitaxy, etc.
- Intrinsically high surface area devices
- No external hardware required
- More materials with appropriate Eg

Colloidal PEC → Fuels

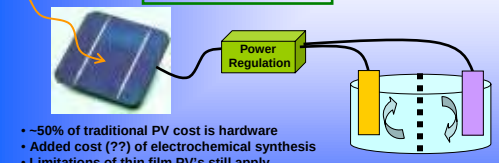


PEC → Fuels



- Limitations of thin film PV's still apply
- High surface area devices necessary
  - mass transport issues
- External hardware required

PV + EC → Fuels



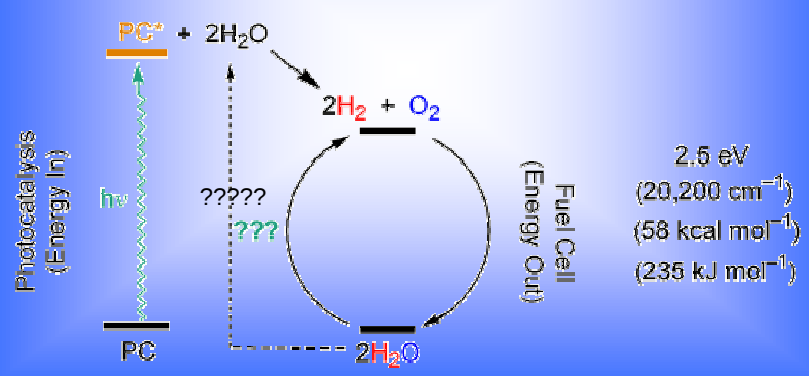
- ~50% of traditional PV cost is hardware
- Added cost (??) of electrochemical synthesis
- Limitations of thin film PV's still apply
  - Viable materials: E_g, epitaxy,
  - Fabrication, processability
  - Carrier transport, lifetimes
- Complex production facility

"

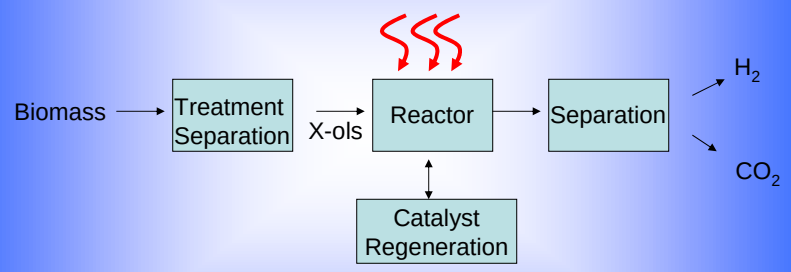
Nocera

The ONLY sustainable and renewable H_2 source is solar and water
http://www.premioitalgas.it/premio/bin/pdf/nocera.pdf

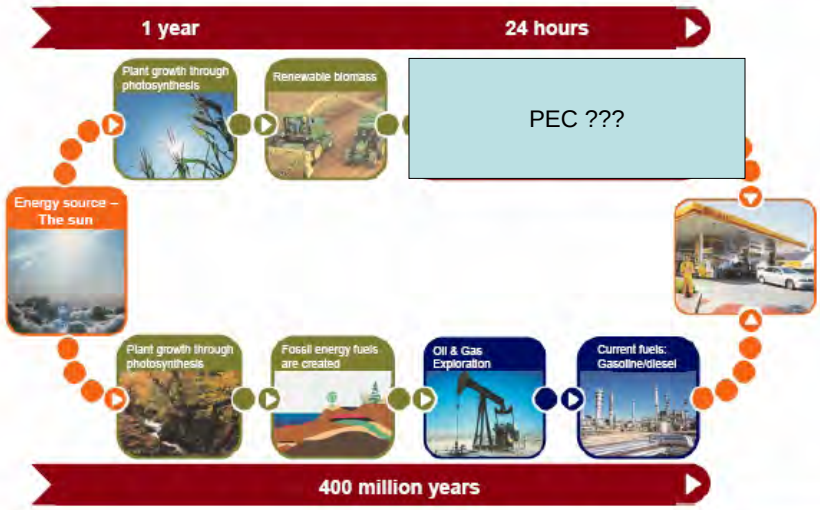
Maybe ?



Process Alternatives: $C_nH_mO_z \rightarrow H_2 + CO_2$



Following Nature's example – but much faster!



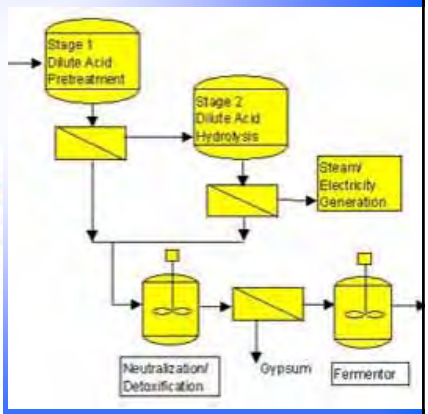
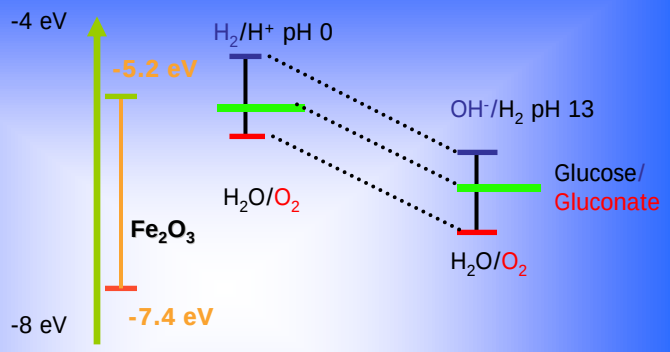
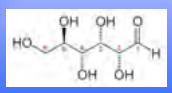


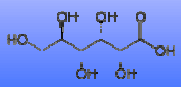
Photo-electrochemical hydrogen production from Glucose oxidation



$4OH^- + 4h^+ \rightarrow O_2 + 2H_2O$ >1.23V vs NHE

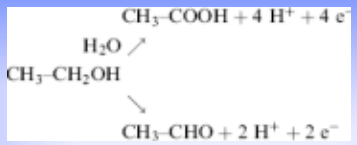
$OH^- + \text{Glucose} + h^+ \rightarrow \text{Gluconate} + H_2O$ 0.8V vs NHE



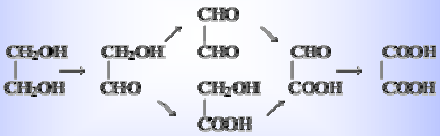


Electro-oxidation of Hydrocarbons

- CH_3CH_2OH

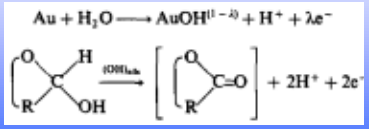


- $HOCH_2CH_2OH$

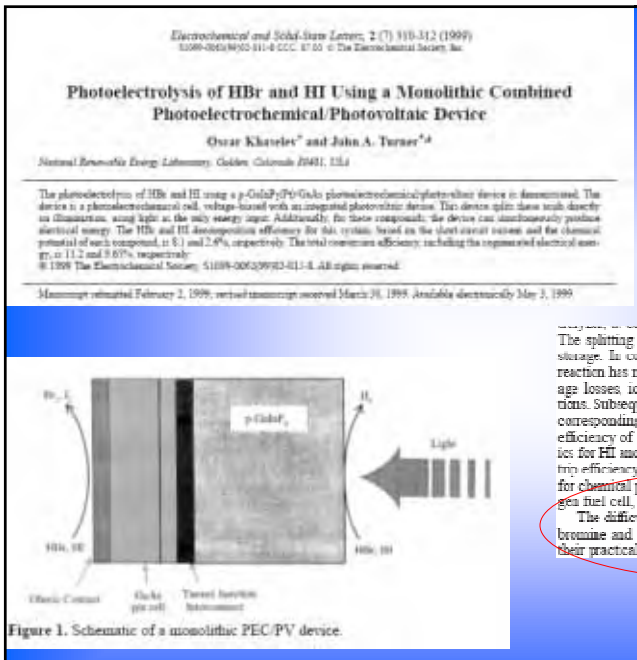


Journal of Applied Electrochemistry, 31, 799, 2001

- Glucose



Electrochimica Acta, 37, 357, 1992



Electrochemical and Solid-State Letters, 2 (7) 310-312 (1999)

Photoelectrolysis of HBr and HI Using a Monolithic Combined Photoelectrochemical/Photovoltaic Device

Oscar Khaselev* and John A. Turner*,z

National Renewable Energy Laboratory, Golden, Colorado 80401, USA

The photoelectrolysis of HBr and HI using a p-GaInP$_2$(Pt)/GaAs photoelectrochemical/photovoltaic device is demonstrated. The device is a photoelectrochemical cell, voltage-biased with an integrated photovoltaic device. The device splits these acids directly on illumination, using light as the only energy input. Additionally, for these compounds, the device can simultaneously produce electrical energy. The HBr and HI decomposition efficiency for this system, based on the short circuit current and the chemical potential of each compound, is 8.1 and 2.6%, respectively. The total conversion efficiency, including the generated electrical energy, is 11.2 and 9.61%, respectively.

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Manuscript submitted February 2, 1999; revised manuscript received March 31, 1999. Available electronically May 3, 1999.

Figure 1. Schematic of a monolithic PEC/PV device.

$15/bbl oil

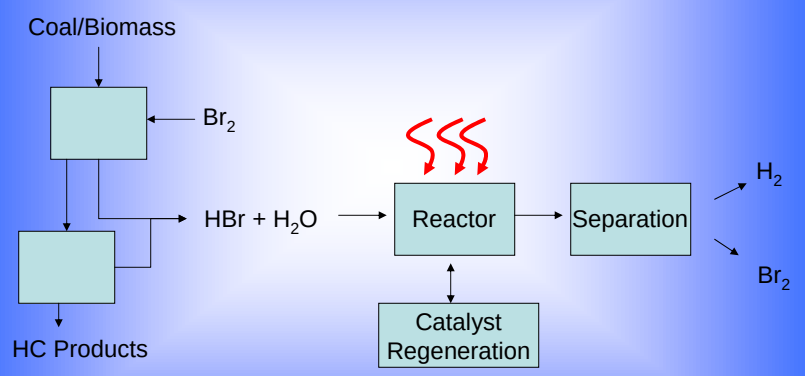
The splitting of HI and HBr is another possibility for solar energy storage. In contrast to water splitting, where the oxygen evolution reaction has multiple electron steps and consequently high overvoltage losses, iodide and bromide have rapid kinetics for their reactions. Subsequently, a much lower overvoltage is required, leading to correspondingly lower energy losses. If one considers the round-trip efficiency of the electrolysis-fuel cell combination, the rapid kinetics for HI and HBr as compared to water give them a higher round-trip efficiency. Additionally, if the bromine and iodine could be used for chemical processing, then the hydrogen could be used in an oxygen fuel cell, greatly increasing the overall efficiency of the system.

The difficulty of dealing with highly corrosive materials such as bromine and iodine is an important matter. That will certainly limit their practical application to any energy storage system.

at $75/bbl oil ??

Process Alternatives: HBr → H_2 + Br_2

Integrated System



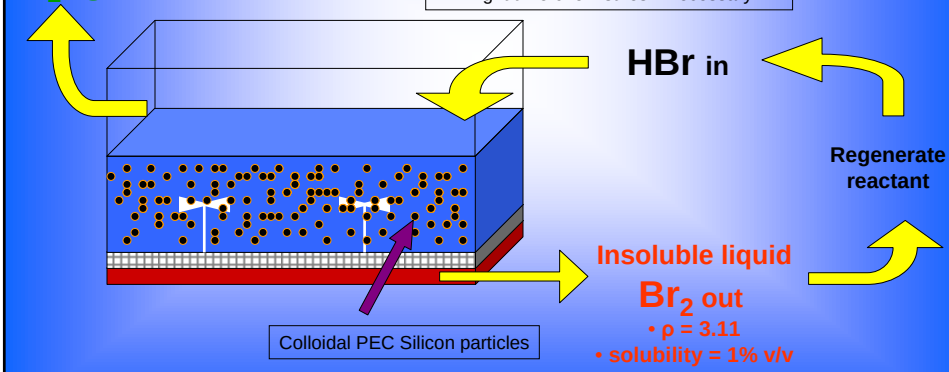
CSTR (Continuously Stirred Tub Reactor)

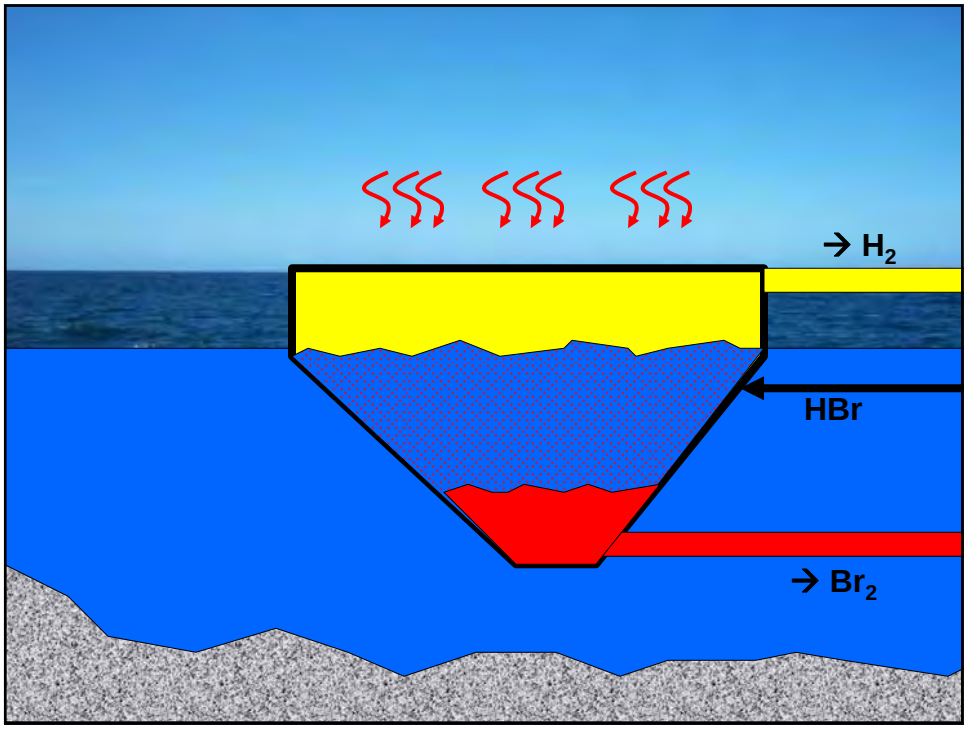
HBr → $Br_{2\,(l)}$ + H_2 = 1.07 V
H_2O → H_2 + O_2 = 1.2 V

Silicon ??
E_g = 1.1 eV

- Br- uninhibited oxidation
- Br_2 is valuable

- Simple, low cost and easily modeled
- *Night time chemistries if necessary*





$$H_2S + 2\,OH^- = S^{2-} + 2\,H_2O$$

$$(\text{or } H_2S + OH^- = HS^- + H_2O)$$

$$2\,e^- + 2\,H_2O = H_2 + 2\,OH^-$$

$$S^{2-} = S^0 + 2\,e^-$$

$$H_2S = H_2 + S^0$$

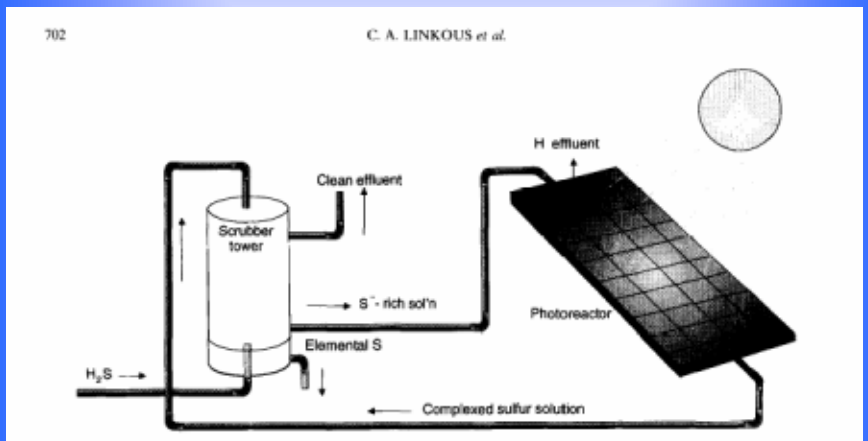
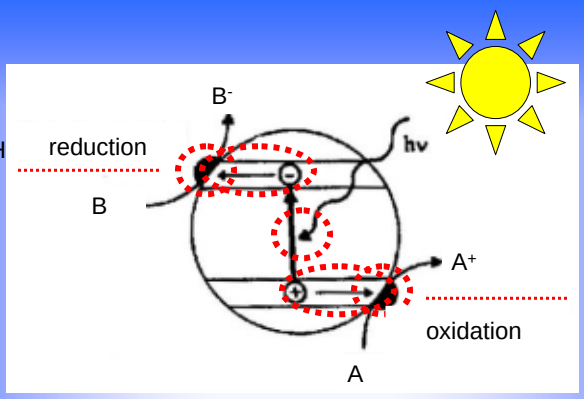


Fig. 1. Schematic of generalized scheme for light-driven H_2S decomposition using an immobilized photocatalyst.

B → B-
$CO_2 \rightarrow CH_3OH$
$CO_2 \rightarrow CH_2OOH$
$CO_2 \rightarrow CH_4$
$H^+ \rightarrow H_2$

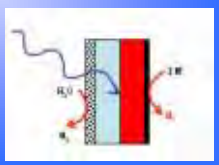


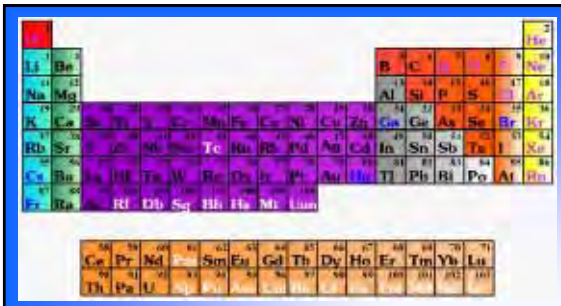
A → A+
$CH_3OH \rightarrow CO_2 + H^+$
$CH_n \rightarrow CO_2 + H^+$
$H_2O \rightarrow O_2 + 2H^+$
$OH \rightarrow O_2 + 2H^+$
$2X^- \rightarrow X_2$

PEC Materials "Issues"

- **Absorbance**
- **Transport e-/h+**
- **Surface States**
- **Surface Electrocatalysis**
- **Band Structure Energetics**
- **Stability and Cost**

Bulk Particulates ~ **Structural Photoelectrodes**





Inexpensive and Durable Semiconductor Materials

@1 μm x 400 km x 400 km => ~ 10^6 m^3 + Lots of it!

#1) Host materials must be inexpensive to buy/use -> ROCKS (metal oxides)

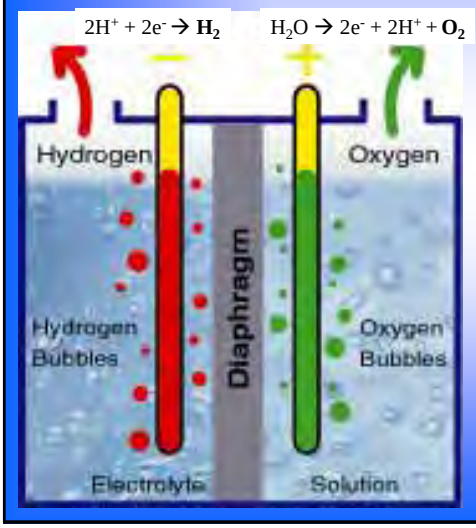
#2) Structure/reactor/materials must be inexpensive < $20/m2-y

-> particulates

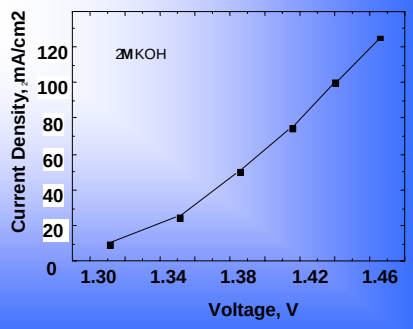
		$/kg
	Al	1.5
*	Cu	1.6
*	Pb	0.4
	Ni	6.8
	Sn	4.8
*	Zn	0.9
	Au	8700
	Ag	140
	Pt	18300
*	TiO2	1.9
	Ti	26
*	W	0.4
*	Fe	0.3

Si, C, O, N, H, P,

Electrolytic Potential

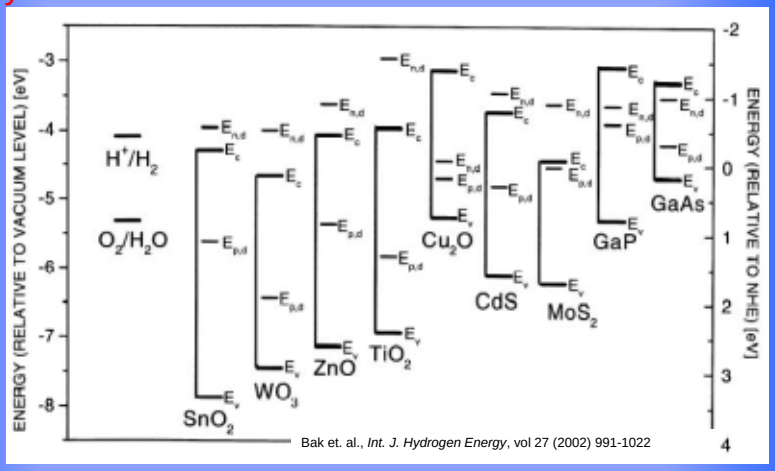


j ~ H_2 production rate



J. Turner NREL

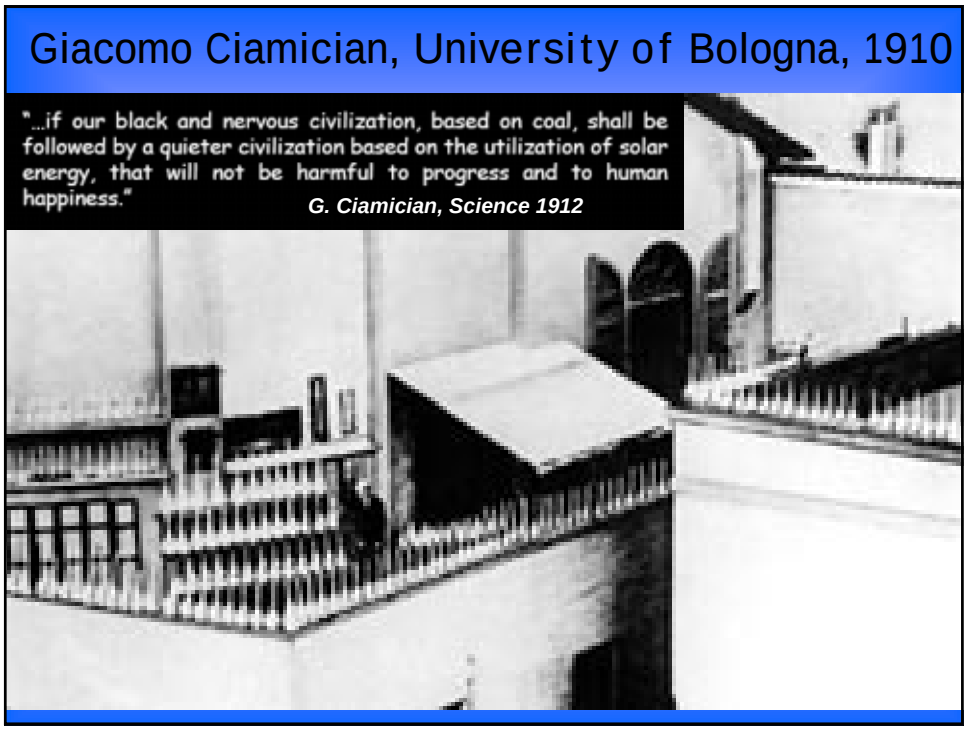
No theory can predict a material with adequate absorbance (bandgap/surface states), conductivity, bandedge locations, stability.



Bak et. al., *Int. J. Hydrogen Energy*, vol 27 (2002) 991-1022

No presently known material is suitable.


Inductive Approaches to Materials Discovery and Optimization
Countless Unseen Details Are Often the Difference Between Mediocre and Magnificent

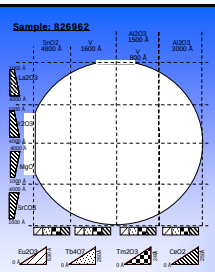

Giacomo Ciamician, University of Bologna, 1910
"...if our black and nervous civilization, based on coal, shall be followed by a quieter civilization based on the utilization of solar energy, that will not be harmful to progress and to human happiness."
G. Ciamician, Science 1912

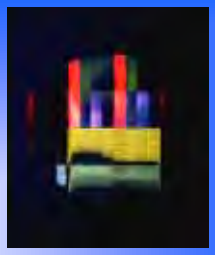
Parallel ("combinatorial") Experimentation

An Old Methodology NOT a New Field

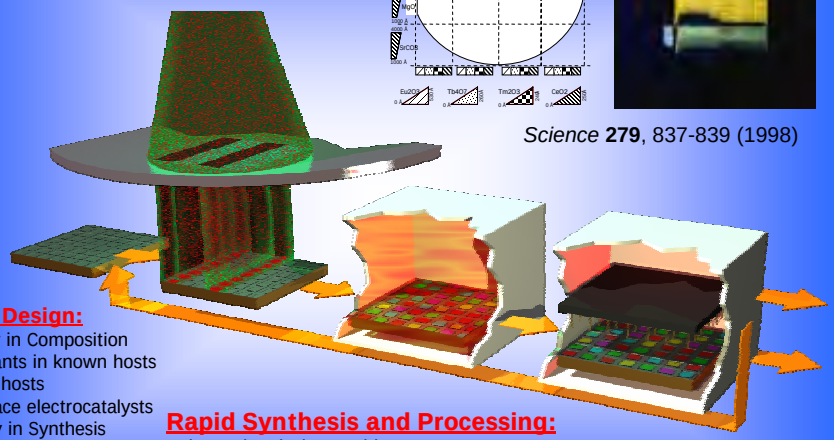
- ~ 400 bce Plato, Socrates - Induction
- ~ 1600 Sir Francis Bacon
- ~ 1840's Thomas Edison (G.E.)
- ~ 1900 Ciamician (photocatalysis)
- ~ 1960's Dupont, IBM, and Sarnoff Labs
- 1969 Joe Hanak Phys. Lett. 30A 201-202
  Sawatzky and Kay, IBM Report
- 1995 Xiang et al Science
- 1997 Symyx, 2000 HTE, etc.

HighThroughput Methodology





Science **279**, 837-839 (1998)



Library Design:
Diversity in Composition
- dopants in known hosts
- new hosts
- surface electrocatalysts

Diversity in Synthesis
- structure variability
- surfactant templates

Rapid Synthesis and Processing:
Electrochemical Deposition
Electroless Deposition
Parallel Reactor Blocks
Rapid Serial Scanning Cells

High-Throughput Screening:
Photoelectrochemical
Chemo-Optical

Generalized Electrosynthesis Chemistries

Metal deposition/Oxidation

$M^+ \rightarrow M \rightarrow MO$

1. Metal Electrodeposition

$M^{n+} + n\,e^- \rightarrow M^o$ (Cathodic)

2. Anodization/Anneal

$M^o + H_2O \rightarrow MO + 2\,H^+ + 2\,e^-$

$M^o + O_2 \rightarrow MO$

Electrochemical Deposition

- Voltage, Current Density
- Electrolyte, Electrode, Dopants
- Time, Temperature, pH, Concentration

Metal Oxide Deposition

Aqueous: $M^+ \rightarrow MOH \rightarrow MO$

1. MO Deposition

electrode: $2\,H_2O + 2\,e^- \rightarrow H_2 + 2(OH^-)_{sur}$

$[M^{n+}(\text{ligand})] + n(OH^-)_{sur} \rightarrow M(OH)_n$

ligands (acidic) = peroxide

(basic) = lactate, citrate, ethylene glycol, acetate

2. Dehydration/Anneal

$M(OH)_n \rightarrow MO_{n/2} + {}^n/_2\,H_2O$

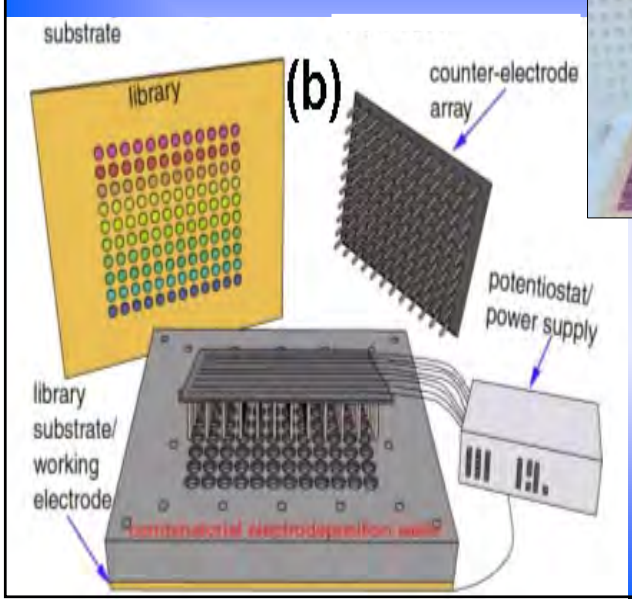
Non-Aqueous: $M^+ + O_2 \rightarrow MO$

1. Direct MO Deposition

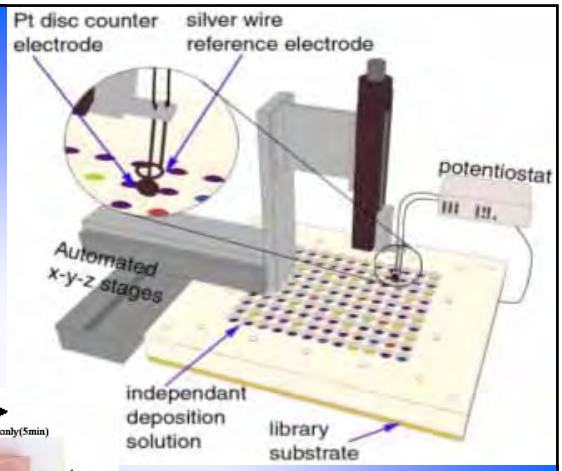
$xM^{n+} + {}^y/_2O_2 + ne- \rightarrow M_xO_y$

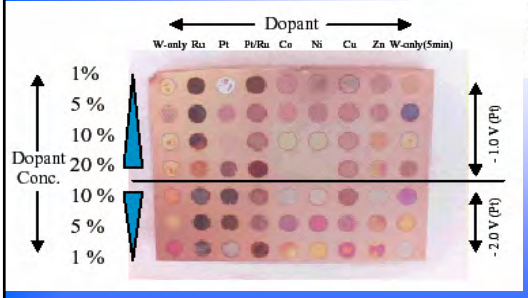
In DMSO etc

Parallel Synthesis



Rapid Serial Synthesis

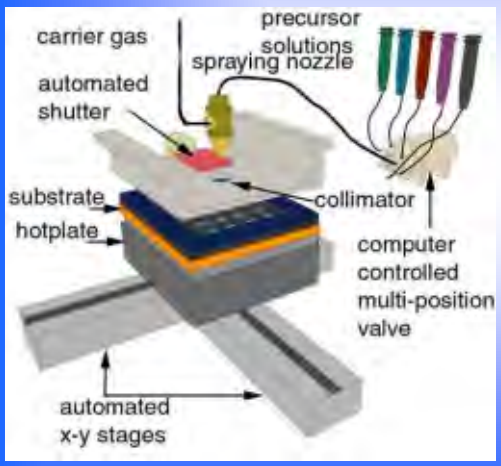




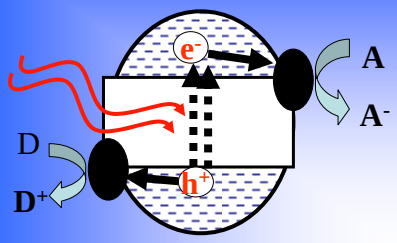
Automated Electrodeposition of Thin Films

Automated Pyrolysis System

Fe_2O_3 Library



Photocatalyst Screening



Zero-bias photocurrent as a function of time

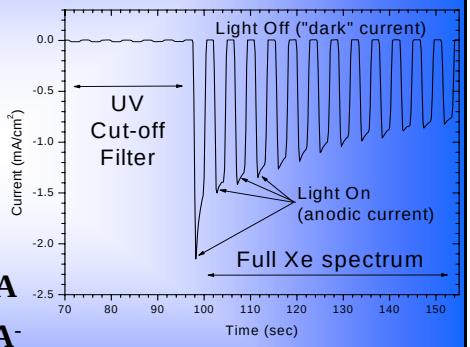
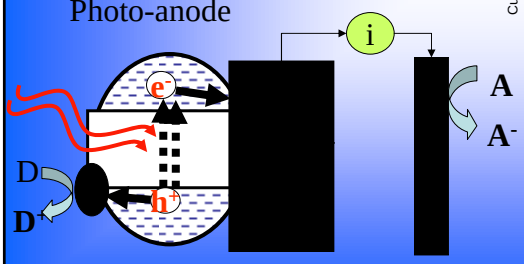
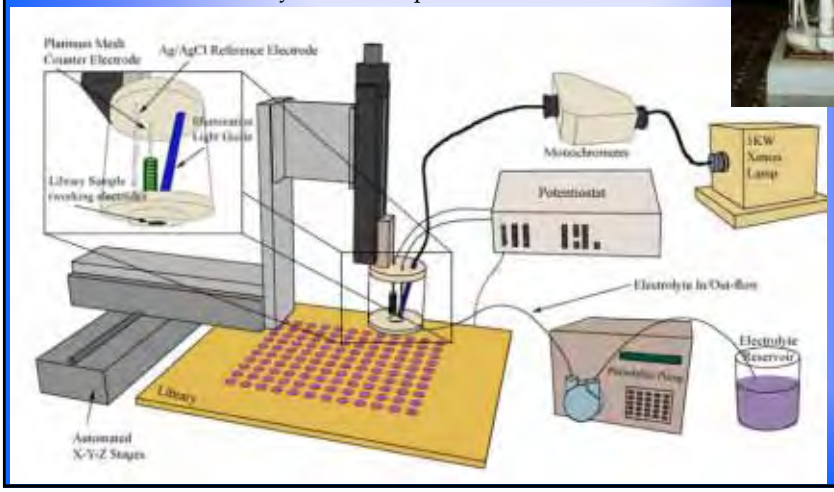


Photo-anode

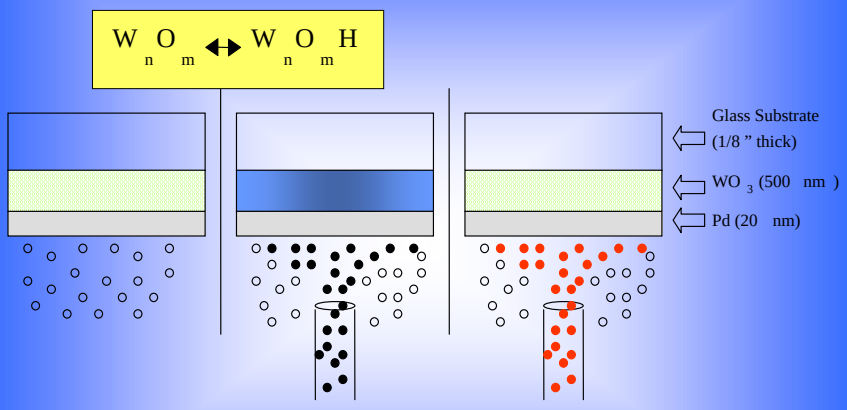


High-Throughput Photoelectrochemical Screening System (HTPESS)

The photoelectrochemical probe (magnified) is symmetrically stepped across the library surface to allow complete photoelectrochemical characterization of each material in the library under computer control.



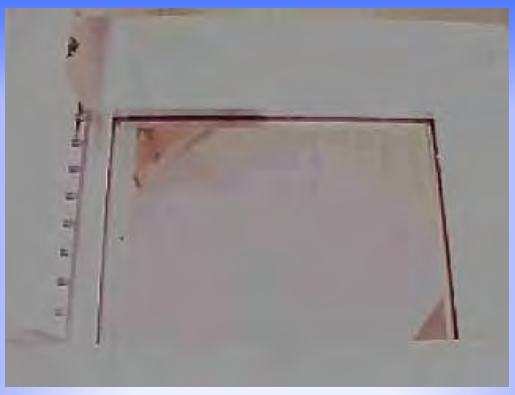
Chemo-Optical Hydrogen Sensor



N_2 only | Injection of H_2 | "Regeneration" with O_2

Ito, K., and Ohgami, T., ***Appl. Phys. Lett****. 60, 8, 938-940 (1992).*

Electrocatalytic H_2 Production



Au	Au/Ge	Ni/Ge	Ag/Au	Al/Au
Ge	Ti/Ag	Ni/Ag	Ag/Ni	Al/Ni
Ni	Ti/Al	Ni/Al	Ag/Pt	Al/Pt
Ag	Ti/Pd	Ni/Pd	Ag/Ti	Al/Ti
Pt				
Al				
Ti				
Pd				

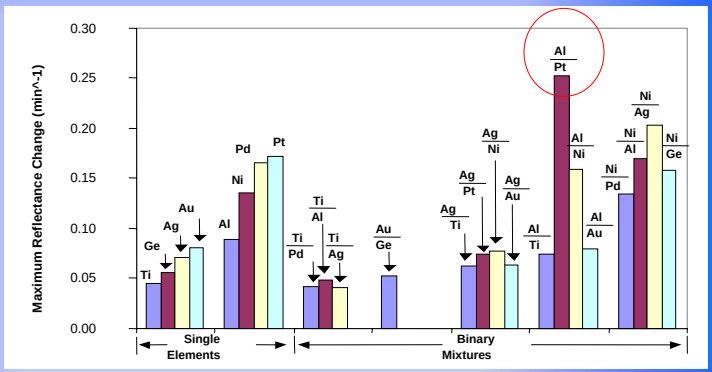
All binaries are 80/20 except for Au/Ge which is 50/50.

J. Combi. Chem. Vol. 4, No. 1 2002

Library of Hydrogen Evolution Electrocatalysts

	A	B	C	D
1	Ti	Pt	Ni	Au
2	Pd	Al	Ag	Ge
3	Ti/Pd	Ti/Al	Ti/Ag	Au/Ge
4	Ni/Pd	Ni/Al	Ni/Ag	Ni/Ge
5	Ag/Ti	Ag/Pt	Ag/Ni	Ag/Au
6	Al/Ti	Al/Pt	Al/Ni	Al/Au

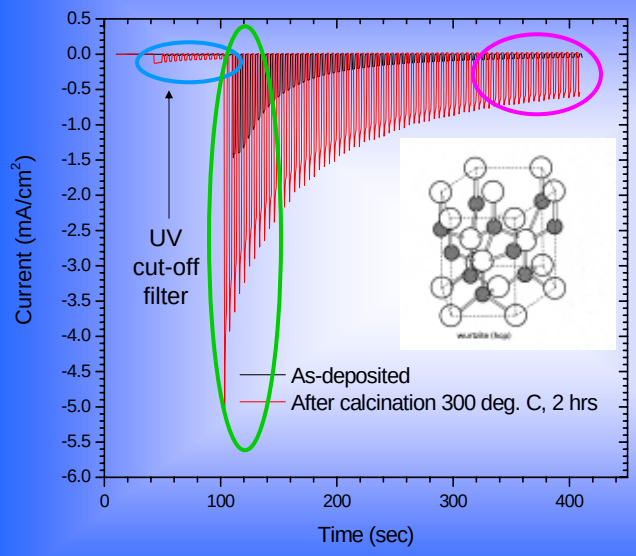
All binaries are 80/20 except for Au/Ge which is 50/50.



2-D bar graph representing the maximum change in reflectance for each material. Expected trends are validated, as materials containing Ni, Pd, and Pt were the most effective H_2-producers while materials consisting of Ti or Ge performed poorly. The Al/Pt mixture was clearly the best electrocatalyst of those studied.

Zinc Oxide Photocatalyst Host

Inexpensive in bulk
High conductivity
High Dopant Solubility



Promising
Photocatalytically active (in the UV)

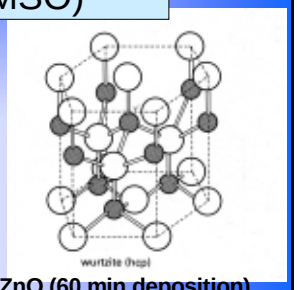
Unfortunate
3 eV Bandgap, minimal visible light photocurrent

Unacceptable
Photocurrent decay from photoanodic corrosion

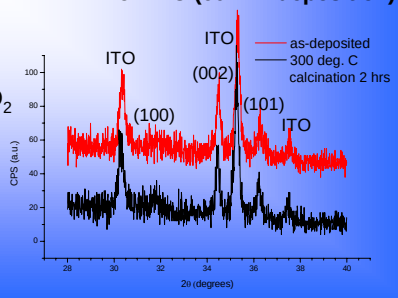
Electrochemically Deposited ZnO from Non-aqueous Solution (DMSO)

Advantages over aqueous routes

- Deposition of metal hydroxide does not take place.
- Higher deposition temperature → improved crystallinity. (e.g. Dimethylsulfoxide (DMSO) boils at 189°C)
- Optically more transparent films with very low concentration of defects.



XRD of ZnO (60 min deposition)



Electrodeposition of ZnO in DMSO

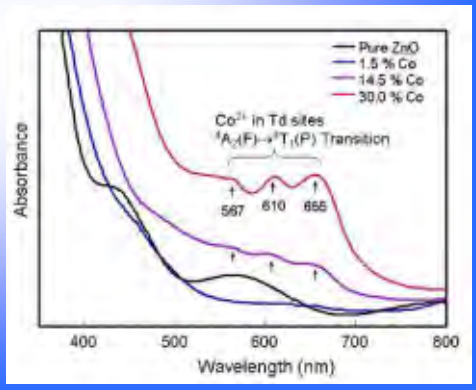
- Plating solution
  - 0.2M $ZnCl_2$ or $Zn(NO_3)_2$ + dissolved O_2
- $Zn^{2+} + 0.5O_2 + 2e^- \rightarrow ZnO$
- V = -1.0V vs. Ag/AgCl reference
- 15 min
- 60°C - 80°C

Problem #1: Improve visible band absorption (doping)

ZnO → Co

A	B	C	D	E	F	G
0%	1%	2%	5%	10%	15%	20%

200mM $ZnCl_2$ in DMSO (saturated O_2)
-1.16V vs. Ag pseudo-reference (-1.0 vs. Ag/AgCl)
85 deg. C 15min deposition onto ITO-coated glass



Ternary ZnO Materials ($A_xZn_yO_z$)

- 24 different dopants
- 8-12 concentrations (typically 0-20mM or 0-50mM in solution)
- 2-4 replicates
- 500 - 800 ZnO-based films
- Synthesis by
  - "single-sample"
  - "diversity" libraries

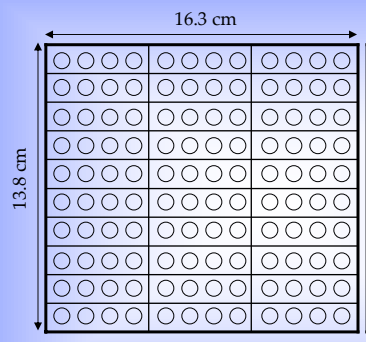
Cobalt-doped ZnO showed the most promise for visible absorption. Thus, the next step was to explore this system more deeply.

Dopant	Vis PC	UV PC	Stability in KNO_3 (aq.)
Ag	Poor	Poor	Average
Al	Good	Average	Good
Au	Poor	Poor	Average
Ce	Average	Average	Excellent
Cd	Poor	Poor	Average
Co	Excellent	Poor	Good
Cr	Poor	Poor	Average
Cu	Poor	Poor	Average
Eu	Poor	Poor	Average
Fe	Good	Good	Average
Mn	Average	Average	Good
Mo	Poor	Poor	Poor
Ni	Excellent	Excellent	Average
Nb	Poor	Average	Good
Pd	Very Poor	Very Poor	N/A
Pt	Poor	Poor	Poor
Rh	Poor	Poor	Aveage
Ru	Excellent	Excellent	Average
Sb	Poor	Poor	Average
Sn	Average	Average	Good
Ti	Very Poor	Very Poor	N/A
V	Poor	Poor	Average
W	precipitated	precipitated	precipitated
Zr	Average	Average	Good

$Zn_{1-x}Co_xO$ Library Design

Solution Co (%)

0.0	0.0	0.0
0.0	1.0	2.0
2.9	4.8	8.3
13.0	17.4	21.3
23.1	25.9	28.6
31.0	33.3	35.5
37.5	39.4	41.2
42.9	44.4	46.0
47.4	50.0	52.9
55.6	57.9	60.0



Film Co (%) by XPS

0.0	0.0	0.0
0.0	0.06	0.1
0.2	0.3	0.5
0.9	1.3	1.6
1.8	2.1	2.4
2.7	2.9	3.2
3.4	3.7	3.9
4.2	4.4	4.6
4.8	5.2	5.6
6.1	6.4	6.8

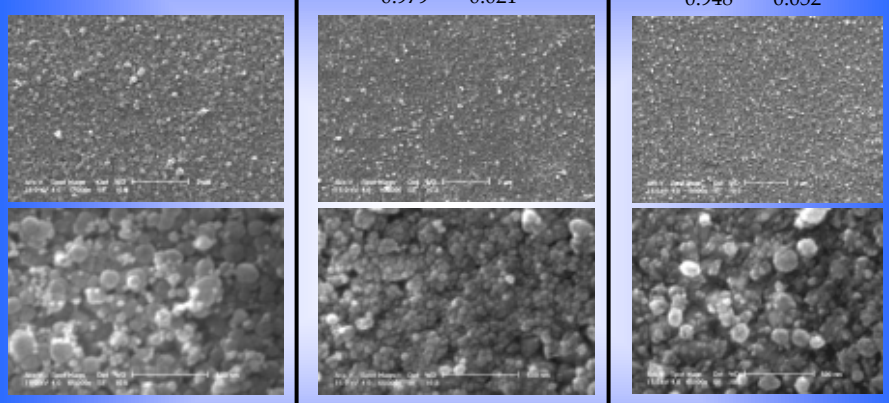
Electrode "priming" row. To calibrate / equilibrate electrodes for temperature and voltage stability immediately prior to library synthesis.

Rapid Serial Electrochemical Deposition System (RSEDS)

- 120 samples (10x12 array). 27 different Zn:Co ratios with 4 replicates each.
- 100mM $ZnCl_2$ & 60mM $LiNO_3$ in DMSO with varying concentrations of $Co(NO_3)_2$.
- 1.5mL of electrolyte solution. Sample size ~ 8mm diameter.
- Potentiostatic deposition @ -1.15V vs. Ag-wire (-1.0V vs. Ag/AgCl) reference
- Coiled Pt wire counter electrode
- Substrate: Pilkington TEC-15™ Fluorine-doped Tin Oxide (FTO) coated on glass
- 60 second deposition @ 105 ºC (Total time for library synthesis: 4 hrs)
- Calcined 500 ºC for 8 hrs.

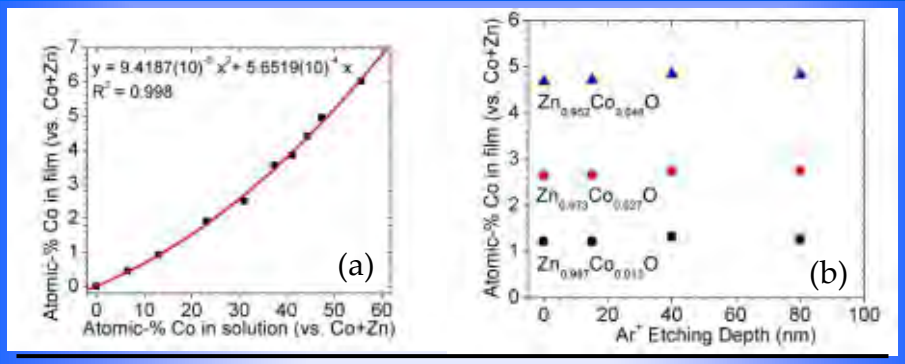
$Zn_{1-x}Co_xO$: Morphology by SEM

ZnO | $Zn_{0.979}Co_{0.021}O$ | $Zn_{0.948}Co_{0.052}O$

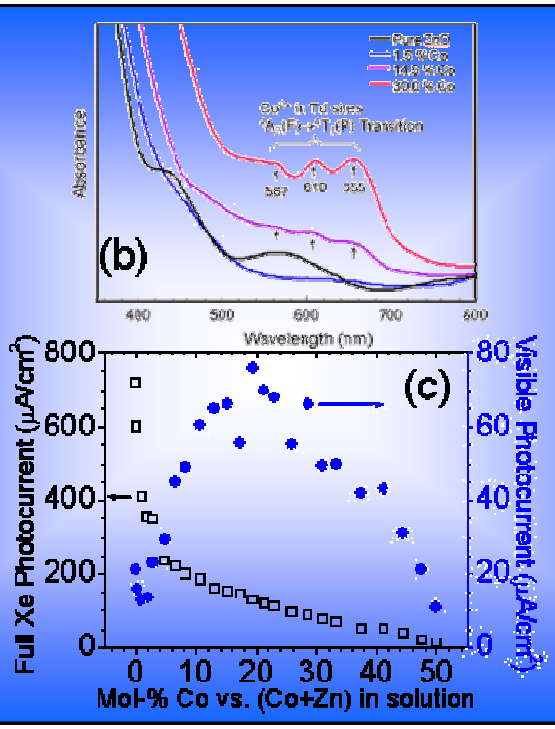


SEM was conducted on 12 selected samples from the library. Film morphology for all samples, regardless of composition, resembled that of pure ZnO. Densely packed particles of 20-200 nm, shaped either as spheres or as platelets, were observed.

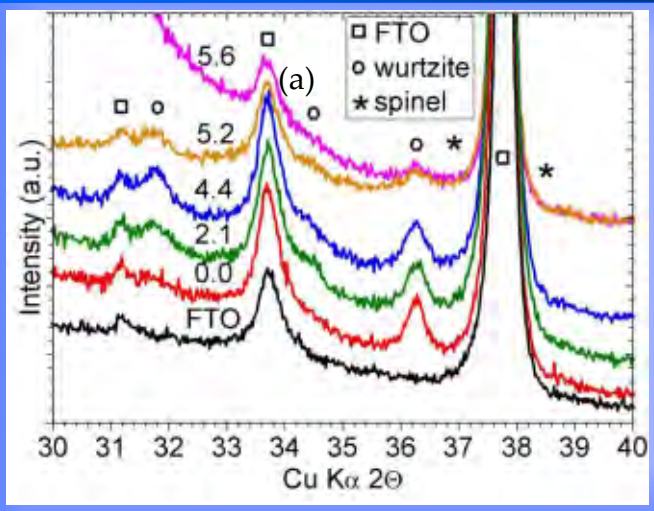
$Zn_{1-x}Co_xO$: Stoichiometry by XPS



Zn:Co stoichiometry was determined by the ratio of integrated peak areas assigned to Co-$2p_{3/2}$ vs. Zn-$2p_{3/2}$, after normalizing areas with Scofield sensitivity factors. Graph (a) correlates Zn:Co stoichiometry in the films to Zn:Co ratios in the electrochemical deposition baths. A second-order polynomial was used to fit the data and a relationship was established (R^2 = 0.998). The fitted data was used to predict all film compositions within the library (see library design). Graph (b) shows film composition as a function of depth by Ar^+ etching (4kV, 1.6mA, ~ 5nm/min). Although ion-etching is known to affect surface stoichiometry by selective etching, Zn:Co ratios in the film were found to be fairly consistent at all depths investigated.

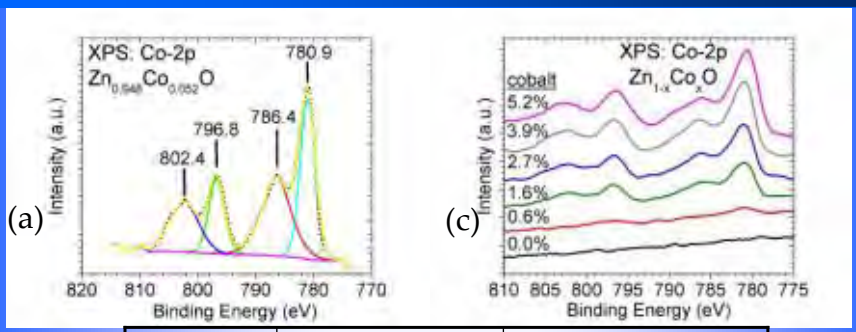


$Zn_{1-x}Co_xO$: Crystal structure (by XRD)



XRD was performed on selected samples for the purpose of identifying crystal structure of the mixed oxide. All compositions revealed a wurtzite structure typical of pure ZnO. No phase separation of CoO (rocksalt) nor spinel Co_3O_4 was observed, indicating that an atomically mixed $Zn_{1-x}Co_xO$ (wurtzite) was synthesized for all values of x investigated.

$Zn_{1-x}Co_xO$: Cobalt oxidation state by XPS

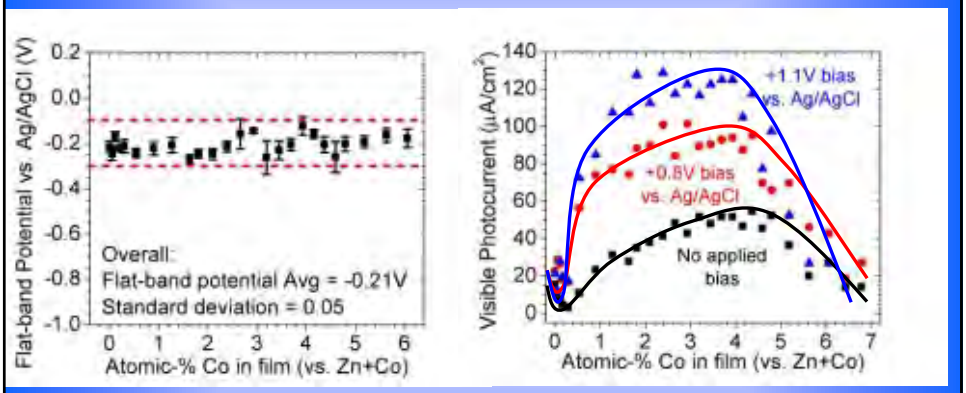


(b)

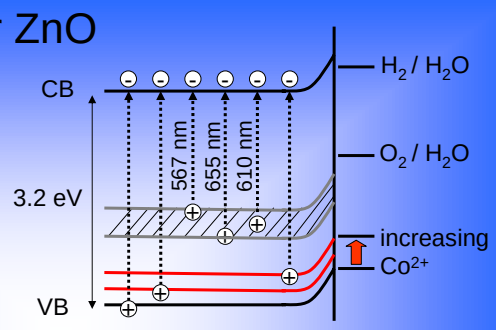
Spectral Region	Binding Energy & FWHM	Assignments
Co-2p$_{3/2}$	780.9 eV (3.1) 786.4 eV (5.7)	Co^{2+} multiplet splitting Co^{2+} shake-up satellite
Co-2p$_{1/2}$	796.8 eV (3.2) 802.4 eV (5.9)	Co^{2+} multiplet splitting Co^{2+} shake-up satellite

XPS was conducted on selected samples to determine Zn:Co stoichiometry as well as the oxidation state of cobalt. Graph (a) reveals the deconvoluted Co-2p spectrum of $Zn_{0.948}Co_{0.052}O$, in which all four cobalt peaks are assigned to Co^{2+}, as indicated in Table (b). Graph (c) compares Co-2p spectra for several different compositions of $Zn_{1-x}Co_xO$, illustrating that Co^{2+} was the predominant species encountered for all samples.

$Zn_{1-x}Co_xO$: Flat band potential & Photocurrent under applied bias



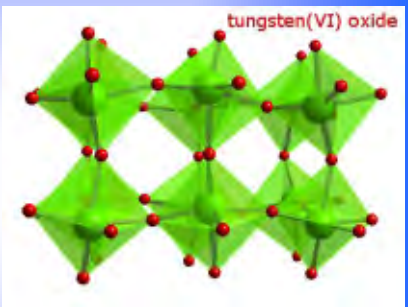
Putting it together for ZnO



- **Zn:Co film stoichiometries are well-controlled with Co mol-% < 7 %.**
- **Co(II) is the predominant valency of cobalt**
- **Only the Wurtzite structure is observed by XRD: No evidence of Rocksalt CoO, Spinel Co3O4 or ZnCo2O4**
- **A solid solution is formed, with Co(II) most-likely substituting Zn(II).**
- **The conduction band edge changes negligibly as a function of composition (for the cobalt range under exploration (< 7%).**
- **A Co(II) "defect band" emerges within the ZnO bandgap approximately 2 eV below the conduction band.**
- **The valence band is systematically raised by several tenths of an eV as cobalt concentrations increase.**

Compositional Dependencies in Metal Oxide Photocatalysts

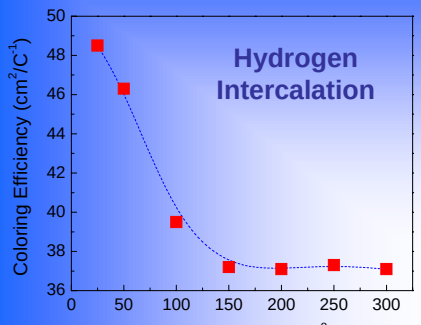
Electrodeposition of WO_3 Based Libraries

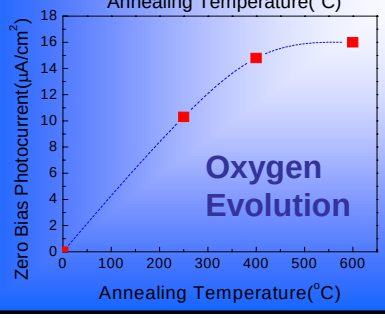


- WO_3
  - Stable in electrolytes
  - Inexpensive
  - Good host for dopants
  - Electrochromic ([Cat+])

- **BUT**
  - **Low CBM**
    - **Previously no ZBPC**
  - **Bandgap ~2.8eV**

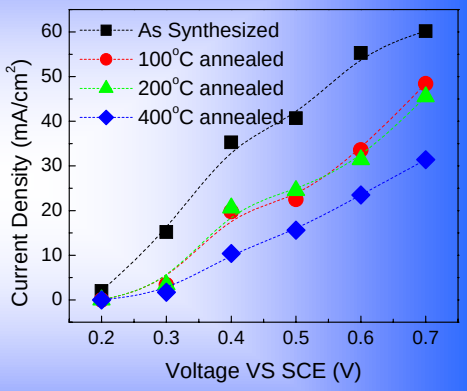
Electrodeposition and Processing of WO_3





Deposition via peroxide, calcine in air

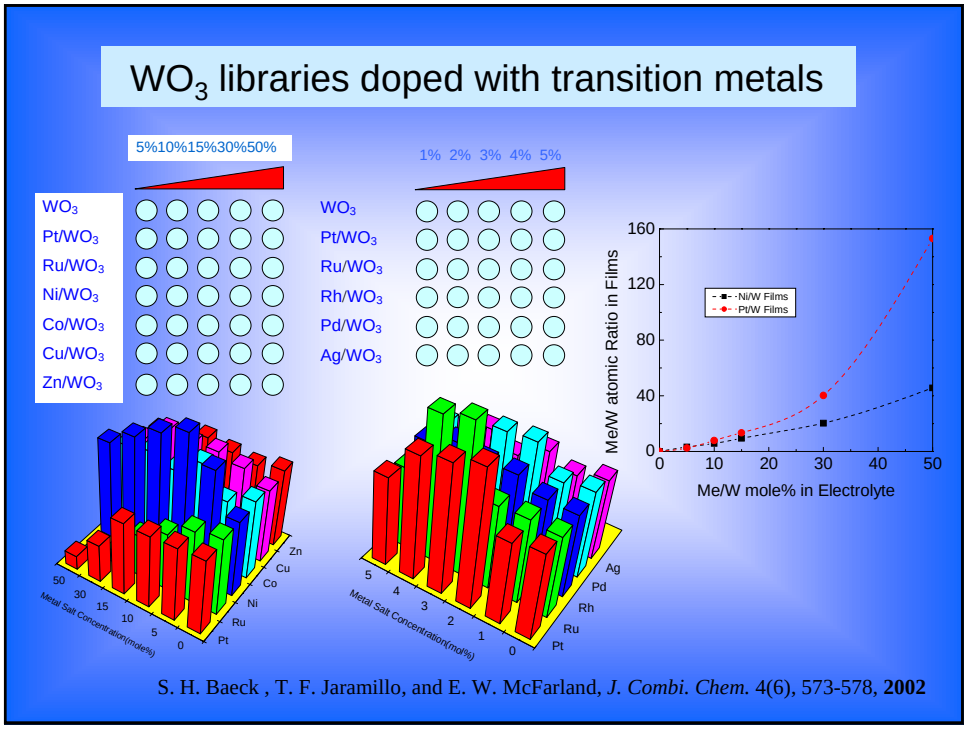
Methanol Electroxidation

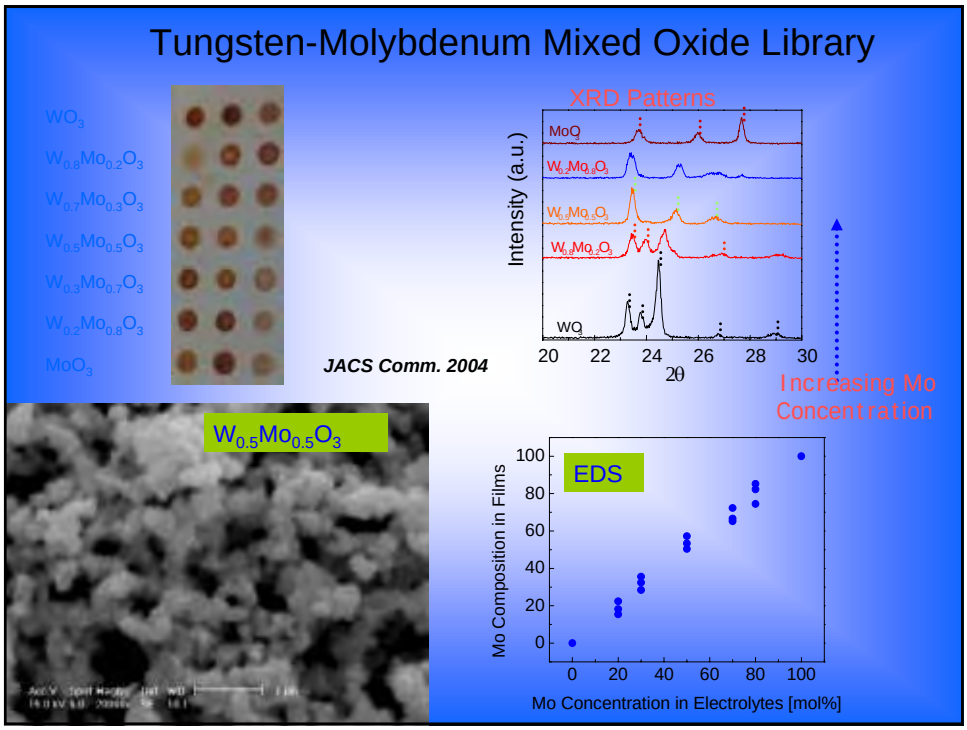


Zero Bias Photocurrent !

Electrodeposition => increased n-type doping

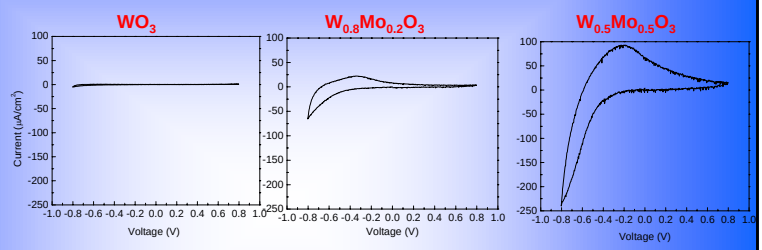
PROCESSING MATTERS !

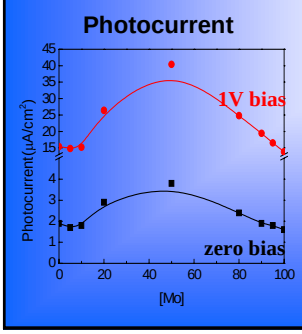

WO3 libraries doped with transition metals
5%10%15%30%50%
1% 2% 3% 4% 5%
WO3
Pt/WO3
Ru/WO3
Ni/WO3
Co/WO3
Cu/WO3
Zn/WO3
Rh/WO3
Pd/WO3
Ag/WO3
Metal Salt Concentration(mole%)
Metal Salt Concentration(mol%)
Me/W atomic Ratio in Films
Me/W mole% in Electrolyte
Ni/W Films
Pt/W Films
S. H. Baeck , T. F. Jaramillo, and E. W. McFarland, J. Combi. Chem. 4(6), 573-578, 2002

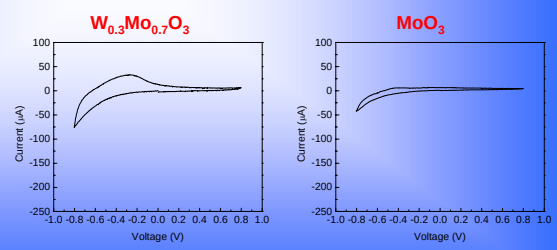

Tungsten-Molybdenum Mixed Oxide Library
WO3
W0.8Mo0.2O3
W0.7Mo0.3O3
W0.5Mo0.5O3
W0.3Mo0.7O3
W0.2Mo0.8O3
MoO3
JACS Comm. 2004
XRD Patterns
Intensity (a.u.)
MoO3
WO3
2θ
Increasing Mo Concentration
W0.5Mo0.5O3
EDS
Mo Composition in Films
Mo Concentration in Electrolytes [mol%]

Tungsten-Molybdenum Mixed Oxides

Cyclic Voltammograms in 0.5M KNO_3 for K^+ Intercalation

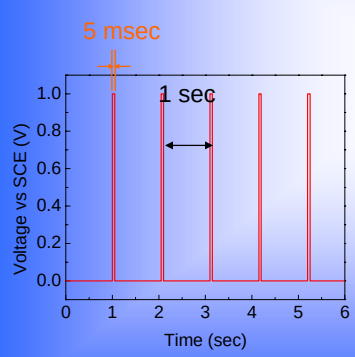


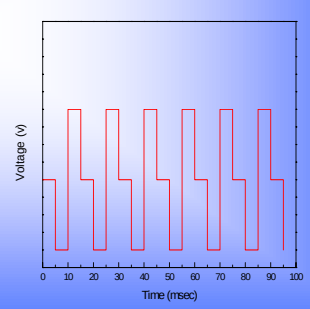




➢ Pulse Electrodeposition

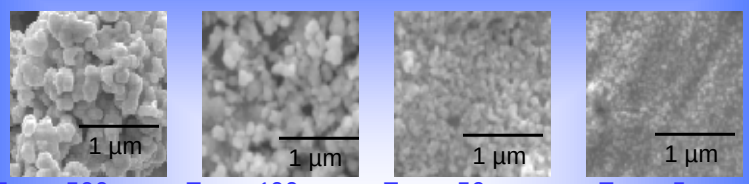
1. Formation of isolated nuclei
2. Growth to larger particles
3. Coalescence of larger particles
4. Formation of a linked network
5. Formation of a continuous deposit



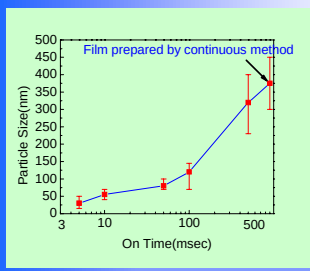


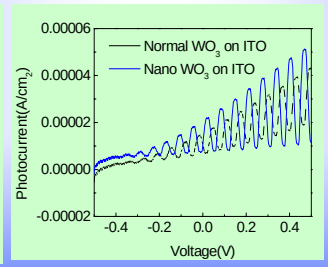
❖ Pulse Parameters : Pulse time, Pulse V, Off time (toff), Total deposition time

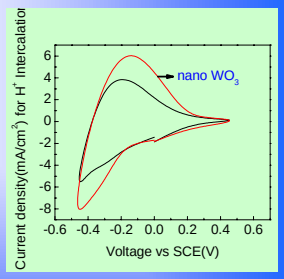
Electrodeposition of nanocrystalline WO_3 by pulsed deposition



T_{pulse} =500msec T_{pulse} =100msec T_{pulse} =50msec T_{pulse} =5msec

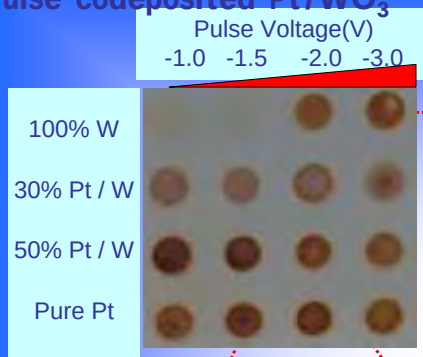


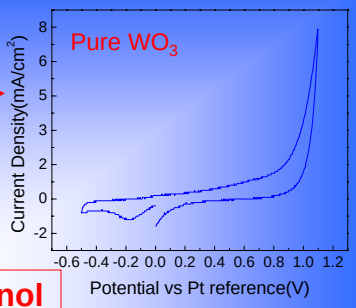




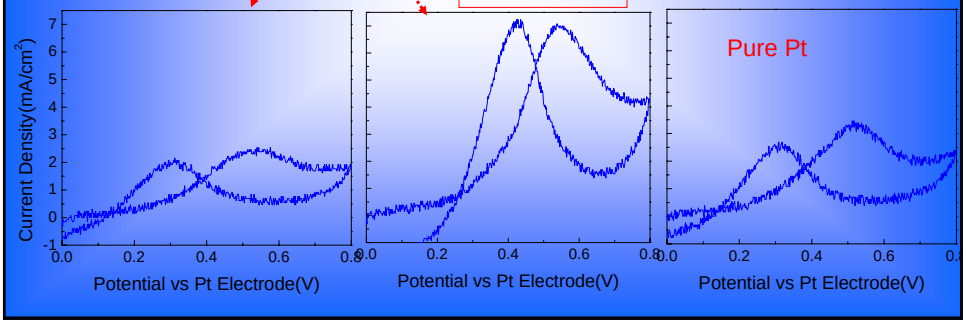
- S.H.Baeck, T. Jaramillo, G.D.Stucky, and E.W.McFarland, ***Nano Letters***, 2(8), 831(2002).

Pulse codeposited Pt/WO_3





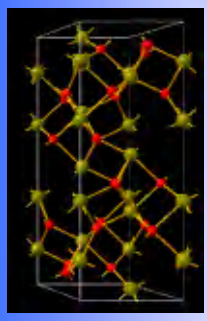
Methanol Oxidation



Points

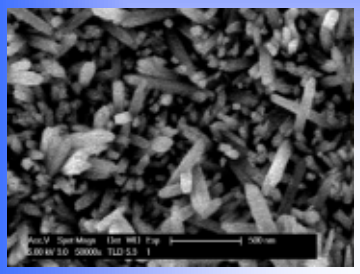
- Successful electrosynthesis of WO_3, and substituted/doped WO_3 from peroxo complex
  - Electrodeposited Mo substitution preserves unstable monoclinic phase to high concentrations
    => metastable materials are useful.
  - ZBPC !
  - Increased cation intercalation
  - No success as yet at decreasing effective gap.

Iron Oxide as a PEC material



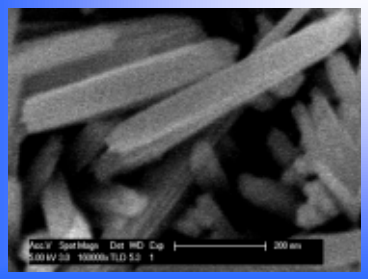
R -3 c (167) – trigonal
a=5.0380 Å c=13.7720 Å

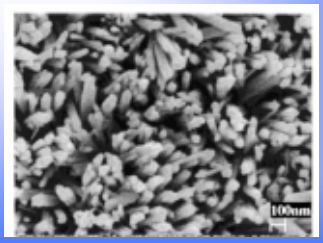
Fe_2O_3 Nanorods



Sample 1- FeCl3
Sample 2-FeCl3-doped Ti
95 ^{0}C, 22hr growth

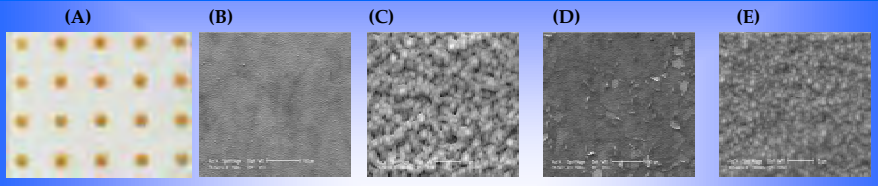
$FeCl_3$-Doped Ti was unsuccessful
→Can we use electrochemistry and self assembly Methods together??





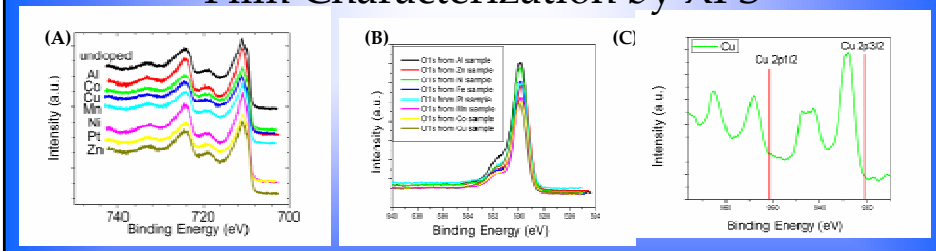
Lionel Vayssieres et al. *Chem. Mater., Vol. 13, No. 2, 2001*

Iron Oxide Deposited by ASPDS



(A) Photograph of a 5x4 library (spacing = 0.125 in.) **(B,C)** SEM images of a film with 62.5% water **(D,E)** SEM images of a film with 52.5% water. Changes in morphology are observed as a function of water content in the electrolyte.

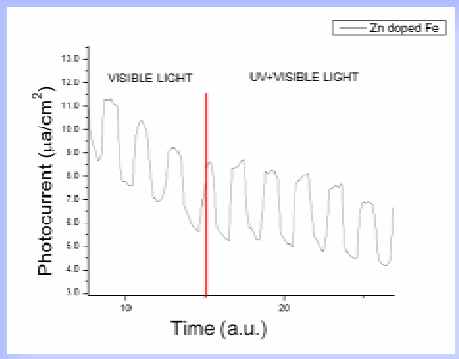
Film Characterization by XPS



XPS data of iron oxide samples deposited by ASPDS **(A)** XPS data of Fe-2p on different doped iron oxide materials **(B)** XPS data of O-1s **(C)** XPS data of Cu-2p on the Cu-doped sample

Photoelectrochemical Screening of Fe_2O_3 materials synthesized by ASPDS

Zero bias photocurrent was measured under UV-vis and vis-only radiation.



Photocurrent from iron oxide doped with Zn (30%) deposited by spray pyrolysis (~ 1 W/cm² illumination)

Preliminary Conclusions: The ASPDS can reliably and reproducibly synthesize samples; several steps are being taken to improve the crystallinity of iron oxides.

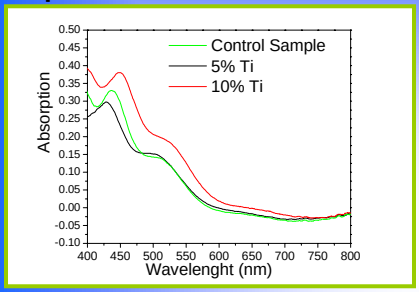
Sol Gel Synthesis

- Sol Gel Synthesis
  - Single sample technique amenable for combinatorial synthesis
  - Complex chemistry
  - High degree of control based on kinetics and solvent evaporation
  - Thickness limitations (>1 um) on a single processing step
  - Soft chemistry method
  - Inexpensive compared to other methods
  - Requires minimal investment

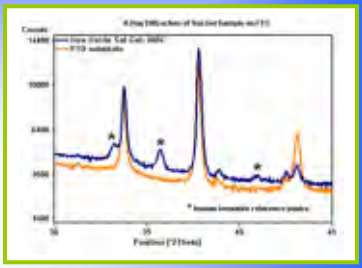
PO-Sol Gel	PVP- Sol Gel
Pros -Amenable for powders -Solubility of most precursors	Pros -High stability of sol gel -Viscosity is determined by the polymer
Cons -Complex gelling due to kinetics -Thickness variation -Limited stability of gel	Cons -Limited solubility of precursors -Use of polymers and metal organics

$Ti_xFe_{2-x}O_3$ (PO sol gel)

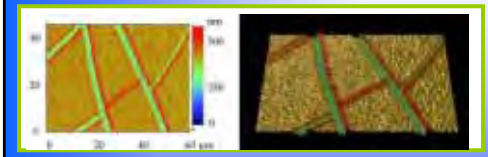
-Optical Characterization

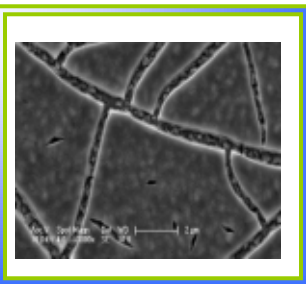


-X-ray Diffraction of α-Fe_2O_3



-Surface Morphology and Topology

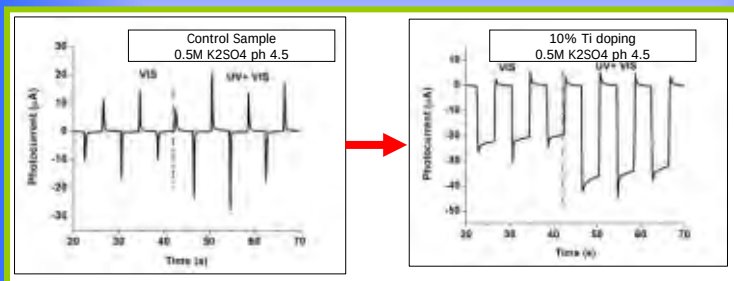


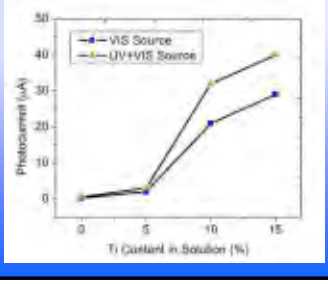


Films thicker than 500nm show cracks after thermal treatment.

$Ti_xFe_{2-x}O_3$ (PO sol gel)

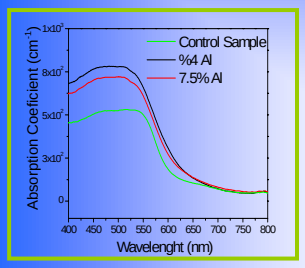
-Photoelectrochemical Performance

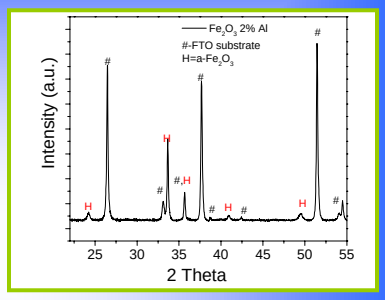




$Al_xFe_{2-x}O_3$ (PO sol gel)

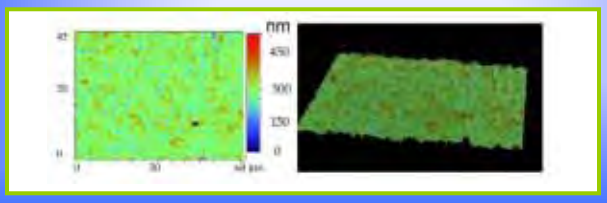
-Optical Characterization





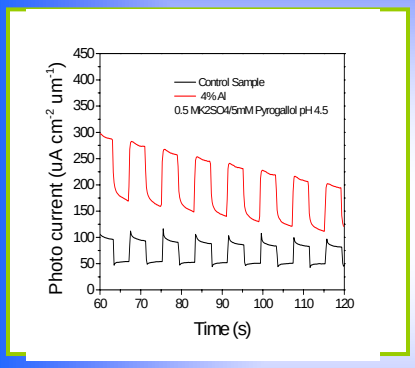
-Surface Morphology and Topology

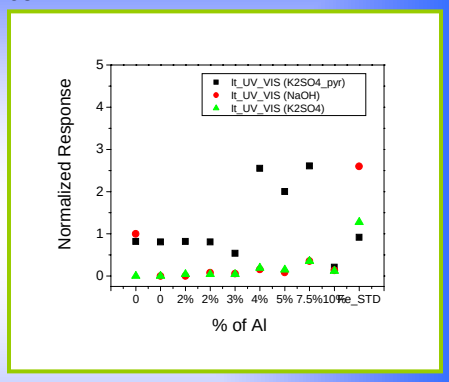
Hematite is the only phase observed



$Al_xFe_{2-x}O_3$ (PO sol gel)

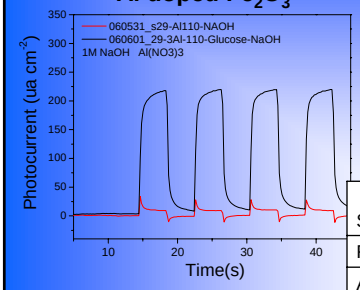
-Photoelectrochemical Performance



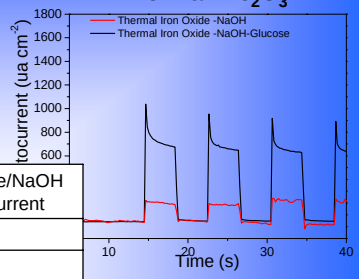


Glucose Oxidation with Doped Fe_2O_3 (PO sol gel)

Al doped Fe_2O_3

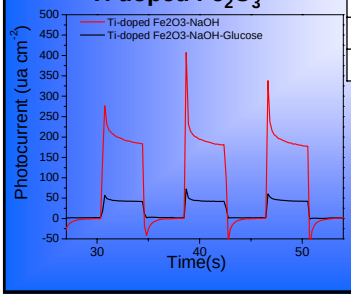


Thermal Fe_2O_3

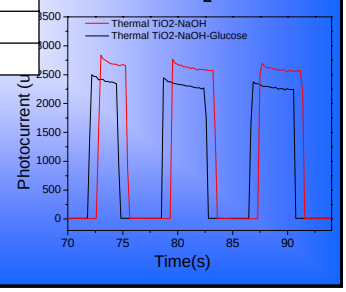


Sample	Glucose/NaOH Photocurrent
Fe_2O_3	~3-7
Al doped Fe_2O_3	~12-34
W doped Fe_2O_3	~6
Ti doped Fe_2O_3	~2-4
TiO2	<1

Ti doped Fe_2O_3



Thermal TiO_2 λ >400nm



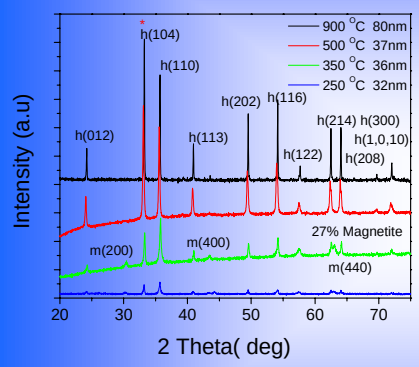
Iron Oxides by PO Sol Gel

Dopant	Type Expected	Type Obtained	Improved C.T [1]	Improved PC[2]	Best Comp.
Ti	N	N	Yes	Yes	X=0.05-0.09
Al	N	N	Yes	Yes	X=0.04-0.075
Ca	P	N-	No	No	
Li	P	N-	No	No	
Cu	P	N-	No	No	
Ni	P	N-	No	No	
Ag	P	N-	No	??	
Mg	P	N-	No	No	

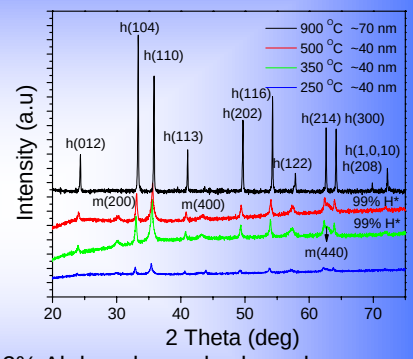
Other dopant materials that will be used: Zn, W, In, V, Cr, Mn

C.T.[1]=Charge Transport, P.C.[2]=Photocurrent

XRD of Hematite Powders



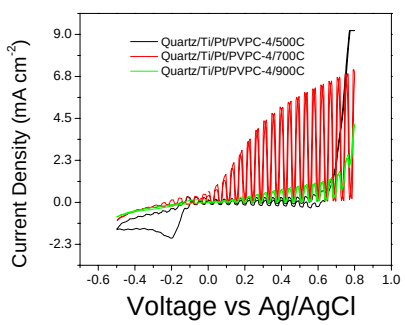
Undoped powder is crystalline at 500C. Weak magnetic behavior is observed for the powder calicined below 350 ^{O}C.



2% Al doped sample shows less crystalinity bellow 900 ^{O}C. Due to poor crystalinity the Magnetite phase is also diminished. No Al_2O_3 was present in the XRD.

Processing Temperature

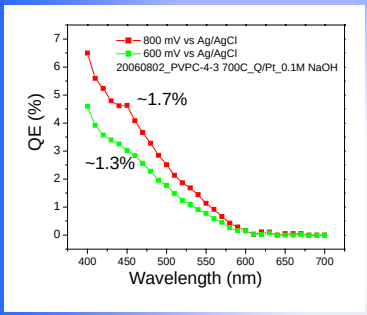
(poly vinyl pyridine sol gel)

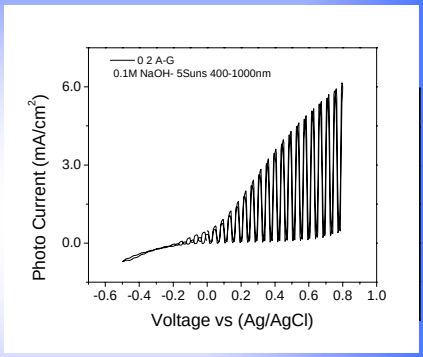


0.5M NaOH 400nm-1000nm 500 mW/cm^2

Samples calcined at 700 ^{0}C have the best performance, samples calcined at 900 ^{0}C show $Fe_3Ti_3O_{10}$, which renders the photoanode inactive.

IPCE of Samples PVP-Fe_2O_3: NaOH



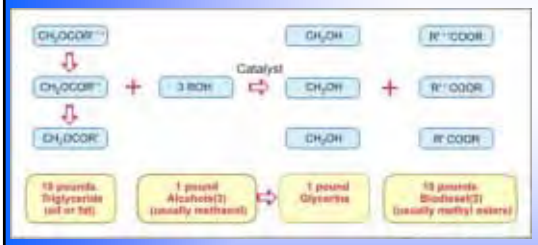


$$QE(\%) = \frac{\#electrons}{\#\,photons} = \frac{j_p(\lambda)}{e_0 I_0(\lambda)} * 100$$

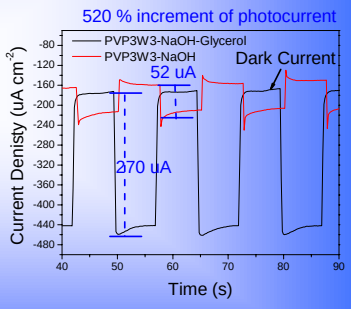
$$Efficiency(\%) = \frac{j_p(1.23 - Eapp)}{I_0} * 100$$

Hydrogen Production From Glycerol On α-Fe_2O_3 (PVP sol gel)

This photo-induced oxidation is not restricted to glucose. The rate of oxidation of fructose, sorbitol and glycine was observed to be much higher under illumination conditions



http://www.treeoilsindia.com

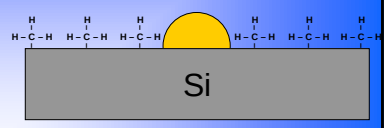


Silicon ???

1) Methyl terminated Si wafer passivation*

- H-terminated Si
- Cl-terminated via. PCl_5 + hv → radical chlorination
- Methyl-terminated via. CH_3Li

- **Subsequent Pt deposition**
  - Electrochemically
    - is limited to defects in CH_3 termination#
  - BHF / Pt^{4+} soln.
    - Should also be confined to defects
    - Pt deposition first, followed by methylation

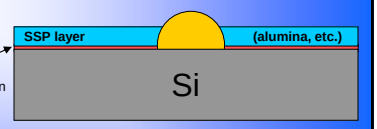


Active NP sites remain exposed

2) Metal oxide Si wafer passivation

- Surface Sol-gel Process (SSP)**
  - Deposition of virtually any metal oxide with monolayer control
    - Requires OH – terminated surface
    - Selective deposition on Si vs. NP surface
  - Purely inorganic passivation layer for long term stability
  - Electrical passivation

OH-termination

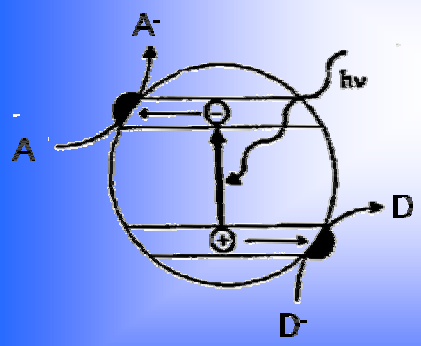


• Either method works well with planar electrodes and is easily amenable to powders

* Lewis, N., Weinberg, H., *et. al.*
# Nakato, Y., *et. al.* J. Electrochem. Soc., **153** (2) E38-E43 (2006)
**Chem. Mater. 1997, 9, 1296-1298

Summary

- Development of new photoelectrocatalytic materials is a multifactorial chemical, materials and engineering problem.
- Economics will determine the eventual success of PEC in the energy sector.
- As yet, no suitable materials or forms have been identified.



$H_20 \rightarrow H_2 + O_2$

$H_nC_mO_l \rightarrow H_2 + CO_2$

$HBr \rightarrow H_2 + Br_2$

$H_nX_m \rightarrow H_2 + Y$?????

Acknowledgements

S.H.-Baeck, T.F. Jaramillo,
A.Kleiman, A. Forman,
W. Tang, G. Stucky

$$ Funding $$
UCSB
College of Engineering
DOE

Questions ?