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

Solar Energy Potential
US energy consumption ~ $3 \times 10^{12}$ Watts
200 W/m$^2$ @10% efficiency → 390 km x 390 km area
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 \( \text{H}_2 \) Economics

\[
\sim 1000 \text{ W/m}^2 \text{ available for harvesting.}
\]

“useful flux” \( \sim 10^{21} \) photons/m\(^2\)-s day averaged \( \theta > 1.5 \text{ eV} \)

Hydrogen

\[ \@ 2e^- / \text{H}_2 \rightarrow 50e^- (\text{kg H}_2/\text{m}^2\text{-year}) \]

\[ \text{To compete with } $2-5/\text{kg H}_2 \text{ with an e } \sim 10\% \text{ system} \]

\[ \text{ANY photocatalysis system cost (material+reactor) } < $20/\text{m}^2\text{-year} \]

\[ \text{Compared to presently available 10Y-life Si solar panel } \sim $80/\text{m}^2\text{-year} \]
Oil $\rightarrow$ 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

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

PV + EC → Fuels

\[ \text{hv} \]

\[ \text{hv} \]

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

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**Nocera**

The ONLY sustainable and renewable H₂ source is solar and water

http://www.premioitalgas.it/premio/bin/pdf/nocera.pdf

Maybe?

\[ \text{PEC} + 2\text{H}_2\text{O} \]

\[ 2\text{H}_2 + \text{O}_2 \]

2.9 eV (20,200 cm⁻¹)
(58 kcal mol⁻¹)
(23.3 kJ mol⁻¹)
Process Alternatives: \( C_nH_mO_z \rightarrow H_2 + CO_2 \)

Biomass → Treatment → Separation → X-ols → Reactor → Catalyst → Regeneration → Separation → H_2 → CO_2

Following Nature's example – but much faster!

1 year → 24 hours

Energy source – The sun

PEC ???

400 million years
Photo-electrochemical hydrogen production from Glucose oxidation

\[ 4\text{OH}^- + 4\text{h}^+ \rightarrow \text{O}_2 + 2\text{H}_2\text{O} \quad >1.23\text{V vs NHE} \]

\[ \text{OH}^- + \text{Glucose} + \text{h}^+ \rightarrow \text{Gluconate} + \text{H}_2\text{O} \quad 0.8\text{V vs NHE} \]
Electro-oxidation of Hydrocarbons

- CH$_3$CH$_2$OH
  \[
  \text{CH}_3\text{COOH} + 4 \text{H}^+ + 4 \text{e}^- \rightarrow \text{CH}_3\text{CHO} + 2 \text{H}_2\text{O} + 2 \text{e}^- 
  \]

- HOCH$_2$CH$_2$OH

- Glucose

$\text{Au} + \text{H}_2\text{O} \rightarrow \text{AuOH}^{3+} + \text{H}^+ + \text{e}^-$


Electrochimica Acta, 37, 367, 1992

$15/\text{bbl oil}$

at $75/\text{bbl oil}$ ??
Process Alternatives: \( \text{HBr} \rightarrow \text{H}_2 + \text{Br}_2 \)

*Integrated System*

```
Coal/Biomass

Br_2

\( \text{HC Products} \)

\[ \text{HBr} + \text{H}_2\text{O} \rightarrow \text{Reactant Regeneration} \]

\[ \text{Catalyst} \]

\[ \text{Reactor} \]

\[ \text{Separation} \]

\[ \text{H}_2 \]

\[ \text{Br}_2 \]
```

**CSTR (Continuously Stirred Tub Reactor)**

- \( \text{HBr} \rightarrow \text{Br}_2 + \text{H}_2 \) = 1.07 V
- \( \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2 \) = 1.2 V

- \( \text{Br}\text{⁻} \) uninhibited oxidation
- \( \text{Br}_2 \) is valuable

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

- Silicon ??
- \( E_g = 1.1 \text{ eV} \)

```
HBr \rightarrow \text{Br}_2(\text{g}) + \text{H}_2 = 1.07 \text{ V}
\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2 = 1.2 \text{ V}
```

- \( p = 3.11 \)
- solubility = 1% v/v

```
Colloidal PEC Silicon particles

\( \text{HBr in} \)

\( \text{Br}_2 \text{ out} \)

\( \text{H}_2 \text{ gas out} \)

\( \text{Insoluble liquid} \)
```

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11
HBr $\rightarrow$ Br$_2$  

H$_2$S + 2 OH$^-$ = S$^{2-}$ + 2 H$_2$O  
(or H$_2$S + OH$^-$ = HS$^-$ + H$_2$O)  

2 e$^-$ + 2 H$_2$O = H$_2$ + 2 OH$^-$  

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

H$_2$S = H$_2$ + S$^0$
PEC Materials “Issues”

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

Inexpensive and Durable Semiconductor Materials

@1 µm x 400 km x 400 km \(\Rightarrow \sim 10^6 \text{ m}^3\) + Lots of it!

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

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

\(\rightarrow\) particulates

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Si, C, O, N, H, P,
No theory can predict a material with adequate absorbance (bandgap/surface states), conductivity, bandedge locations, stability.

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
  Sawatzky and Kay, IBM Report
- 1995 Xiang et al Science
- 1997 Symyx, 2000 HTE, etc.

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

HighThroughput Methodology

Science 279, 837-839 (1998)
### Generalized Electrosynthesis Chemistries

<table>
<thead>
<tr>
<th>Metal deposition/Oxidation</th>
<th>Metal Oxide Deposition</th>
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</thead>
<tbody>
<tr>
<td>( M^+ \rightarrow M \rightarrow MO )</td>
<td>( Aqueous: M^+ \rightarrow MOH \rightarrow MO )</td>
</tr>
</tbody>
</table>

#### 1. Metal Electrodeposition
\( M^{n+} + ne^- \rightarrow M^0 \) (Cathodic)

#### 2. Anodization/Anneal
\( M^0 + H_2O \rightarrow MO + 2 H^+ + 2 e^- \)
\( M^0 + O_2 \rightarrow MO \)

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

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### Metal Oxide Deposition
- **Aqueous:**
  \( M^+ \rightarrow MOH \rightarrow MO \)

#### 1. MO Deposition
- electrode: \( 2 H_2O + 2 e^- \rightarrow H_2 + 2(OH^-)_{sur} \)
- \([M^{n+}(ligand)] + n(OH^-)_{sur} \rightarrow M(OH)^n_{ligands} \)
- **ligands** (acidic) = peroxide
  (basic) = lactate, citrate, ethylene glycol, acetate

#### 2. Dehydration/Anneal
\( M(OH)_n \rightarrow MO_{n+2} + \frac{n}{2} H_2O \)

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### Non-Aqueous:
\( M^+ + O_2 \rightarrow MO \)

#### 1. Direct MO Deposition
\( xM^{n+} + \frac{y}{2}O_2 + ne^- \rightarrow M_xO_y \)
In DMSO etc

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### Parallel Synthesis

- **substrate**
- **library**
- **counter-electrode array**
- **potentiostat/power supply**
Rapid Serial Synthesis

Automated Electrodeposition of Thin Films
**Automated Pyrolysis System**

Fe$_2$O$_3$ Library

**Photocatalyst Screening**

Zero-bias photocurrent as a function of time
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

Glass Substrate (1/8” thick)

$\text{WO}_x$ (500 nm)

Pd (20 nm)

$\text{N}_2$ only

Injection of $\text{H}_2$

“Regeneration” with $\text{O}_2$

Electrocatalytic H₂ Production

Expected trends are validated, as materials containing Ni, Pd, and Pt were the most effective H₂-producers while materials consisting of Ti or Ge performed poorly. The Al/Pt mixture was clearly the best electrocatalyst of those studied.

Library of Hydrogen Evolution Electro catalysts

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 H₂-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

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.

**Electrodeposition of ZnO in DMSO**
- Plating solution
  - 0.2M ZnCl₂ or Zn(NO₃)₂ + dissolved O₂
  - Zn²⁺ + 0.5O₂ +2e⁻ → 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

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<th>0%</th>
<th>1%</th>
<th>2%</th>
<th>5%</th>
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200mM ZnCl₂ in DMSO (saturated O₂)
-1.16V vs. Ag pseudo-reference (-1.0 vs. Ag/AgCl)
85 deg. C 15min deposition onto ITO-coated glass

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

### Ternary ZnO Materials

- **(AₓZn₁₋ₓO₂)**
- 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

<table>
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### Zn<sub>1-x</sub>Co<sub>x</sub>O Library Design

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Rapid Serial Electrochemical Deposition System (RSEDS)
- 120 samples (10x12 array). 27 different Zn:Co ratios with 4 replicates each.
- 100mM ZnCl<sub>2</sub> & 60mM LiNO<sub>3</sub> in DMSO with varying concentrations of Co(NO<sub>3</sub>)<sub>2</sub>.
- 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 TPC-15™ Fluorine-doped Tin Oxide (FTO) coated on glass
- 60 second deposition @ 105°C (Total time for library synthesis: 4 hrs)
- Calcined 500°C for 8 hrs.

### Zn<sub>1-x</sub>Co<sub>x</sub>O: Morphology by SEM

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$_x$O: 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\(_x\)O: 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\(_3\)O\(_4\) was observed, indicating that an atomically mixed Zn\(_{1-x}\)Co\(_x\)O (wurtzite) was synthesized for all values of x investigated.

Zn\(_{1-x}\)Co\(_x\)O: Cobalt oxidation state by XPS

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\(_x\)O, 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 Co_3O_4 or ZnCo_2O_4.
- 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.
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 $\sim$2.8eV

Compositional Dependencies in Metal Oxide Photocatalysts

Electrodeposition and Processing of WO$_3$

- Deposition via peroxide, calcine in air
- Methanol Electrooxidation
- Zero Bias Photocurrent!
- Electrodeposition $\Rightarrow$ increased n-type doping
  PROCESSING MATTERS!
WO$_3$ libraries doped with transition metals


Tungsten-Molybdenum Mixed Oxide Library

JACS Comm. 2004

EDS
Tungsten-Molybdenum Mixed Oxides

Cyclic Voltammograms in 0.5M KNO₃ for K⁺ Intercalation

- WO₃
- WₓMoₓO₃
- WₓMo₂O₃

Photocurrent

- WₓMoₓO₃
- MoO₃

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 WO₃ by pulsed deposition

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
Fe₂O₃ Nanorods

Sample 1 - FeCl₃
Sample 2 - FeCl₃-doped Ti
95 °C, 22hr growth

FeCl₃-Doped Ti was unsuccessful

Can we use electrochemistry and self assembly Methods together??

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$_2$O$_3$ materials synthesized by ASPDS

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

[Graph showing photocurrent vs. time under different light conditions]

Photocurrent from iron oxide doped with Zn (30%) deposited by spray pyrolysis (~ 1 W/cm$^2$ illumination)

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

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**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

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

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$\text{Ti}_x\text{Fe}_{2-x}\text{O}_3$ (PO sol gel)

- Optical Characterization

- Surface Morphology and Topology

Films thicker than 500nm show cracks after thermal treatment.

- X-ray Diffraction of $\alpha$-$\text{Fe}_2\text{O}_3$

- Photoelectrochemical Performance

$0.5\text{M K}_2\text{SO}_4 \text{ ph 4.5}$

$10\% \text{ Ti doping}$
Al$_x$Fe$_{2-x}$O$_3$ (PO sol gel)

- Optical Characterization

- Surface Morphology and Topology

Hematite is the only phase observed

-Photoelectrochemical Performance

Al$_x$Fe$_{2-x}$O$_3$ (PO sol gel)
Iron Oxides by PO Sol Gel

<table>
<thead>
<tr>
<th>Type</th>
<th>Type</th>
<th>Improved</th>
<th>Improved</th>
<th>Best</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dopant</td>
<td>Expected</td>
<td>Obtained</td>
<td>C.T.1</td>
<td>PC.2</td>
</tr>
<tr>
<td>Ti</td>
<td>N</td>
<td>N</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Al</td>
<td>N</td>
<td>N</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Ca</td>
<td>P</td>
<td>N-</td>
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<td>No</td>
</tr>
<tr>
<td>Li</td>
<td>P</td>
<td>N-</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Cu</td>
<td>P</td>
<td>N-</td>
<td>No</td>
<td>No</td>
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<tr>
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<td>P</td>
<td>N-</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Mg</td>
<td>P</td>
<td>N-</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>

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 500°C. Weak magnetic behavior is observed for the powder calcined below 350°C.

2% Al doped sample shows less crystallinity below 900°C. Due to poor crystallinity, the Magnetite phase is also diminished. No Al₂O₃ was present in the XRD.

Processing Temperature
(poly vinyl pyridine sol gel)

Samples calcined at 700°C have the best performance, samples calcined at 900°C show Fe₃Ti₃O₁₀, which renders the photoanode inactive.
IPCE of Samples PVP-Fe$_2$O$_3$: NaOH

![Graph showing IPCE of Samples PVP-Fe$_2$O$_3$: NaOH](image)

\[ \text{QE} = \frac{\text{# electrons}}{\text{# photons}} \times \frac{j_e(\lambda)}{eI_0(\lambda)} \times 100 \]

\[ \text{Efficiency} = \frac{j_e(1.23 - E_{app})}{I_d} \times 100 \]

Hydrogen Production From Glycerol On $\alpha$-Fe$_2$O$_3$ (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.

![Graph showing Hydrogen Production From Glycerol On $\alpha$-Fe$_2$O$_3$](image)

http://www.treeoilsindia.com
Silicon ???

1) Methyl terminated Si wafer passivation*
   - H-terminated Si
   - Cl-terminated via. PCl₅ + hv → radical chlorination
   - Methyl-terminated via. CH₃Li
   - Subsequent Pt deposition
     - Electrochemically
     - is limited to defects in CH₃ termination
     - BHF / Pt⁺ soln.
     - Should also be confined to defects
     - Pt deposition first, followed by methylation

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

   * Lewis, N., Weinberg, H., et. al.
   **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.

H₂O → H₂ + O₂
H₂C₂O₄ → H₂ + CO₂
HBr → H₂ + Br₂
HₙXₘ → H₂ + Y ????
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UCSB
College of Engineering
DOE

Questions?