

# **Photoelectrochemical Hydrogen Production Using New Combinatorial Chemistry Derived Materials**

**Thomas F. Jaramillo<sup>1</sup>, Sung-Hyeon Baeck<sup>1</sup>, Alan Kleiman-Shwarsctein<sup>1</sup>,  
Galen D. Stucky (PI)<sup>2</sup>, Eric W. McFarland (PI)<sup>1</sup>,**

<sup>1</sup> Dept. of Chemical Engineering, <sup>2</sup> Dept. of Chemistry & Biochemistry,  
University of California, Santa Barbara

DOE Hydrogen Program DE-FC36-01GO11092

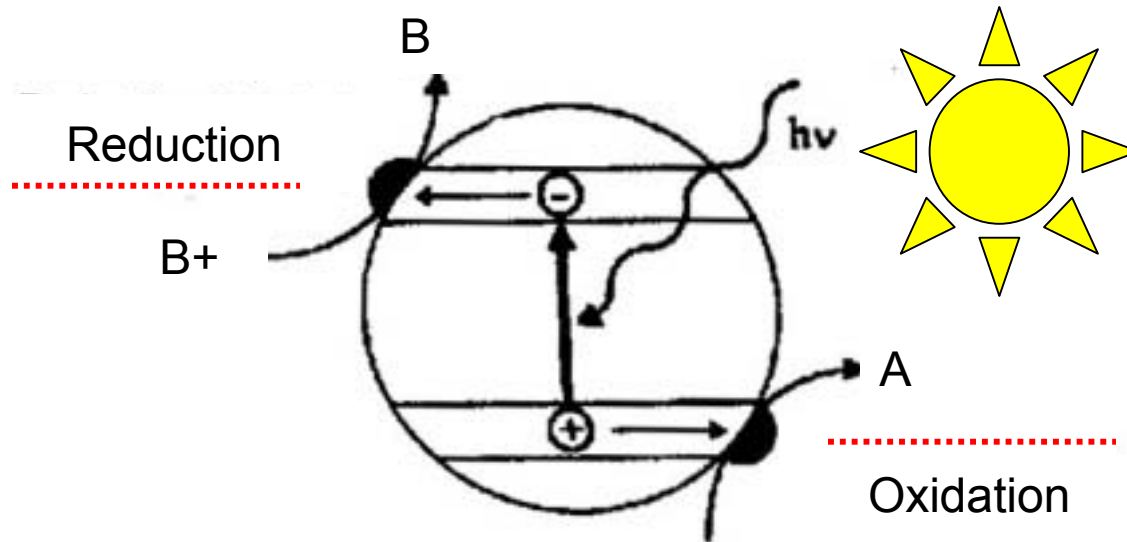
(September 2001 – April 2004)

This presentation does not contain any proprietary or confidential information.

# Project Objectives: Year 3

- Continue synthesis and screening of libraries designed in previous years and follow promising (lead) materials as they are identified.
- Explore the composition-function relationship of dopants in ZnO hosts.
- Investigate metal oxide libraries for electrocatalytic hydrogen production and expand our high-throughput screening to include electrocatalytic overpotential as a routine screen.
- Develop a high-throughput optical screening system to measure the effective bandgap of metal oxides in libraries.
- Synthesize and screen model libraries optically for bandgap as a primary screen; create secondary libraries of compositions with solar spectrum adsorption and subsequently screen the derivative libraries for appropriate redox/flatband levels and finally for H<sub>2</sub> production.
- Continue to expand our investigations of nanoporous materials with the emphasis on ZnO, WO<sub>3</sub> and TiO<sub>2</sub>.
- Participate as a member of the USA Annex-14 Expert Group in the International Energy Agency's (IEA's) Hydrogen Implementing Agreement on photoelectrolytic hydrogen production.

# Photoelectrocatalysis



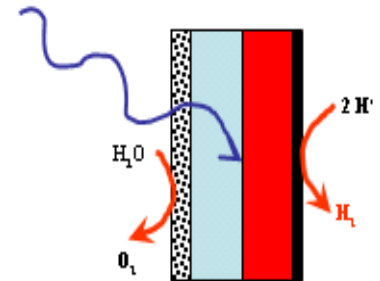
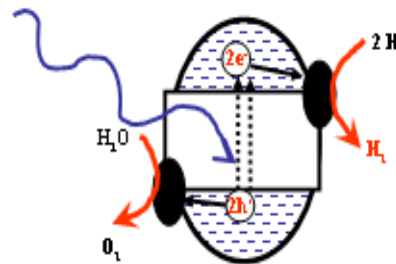
## Materials “Issues”

- ❖ Absorbance
- ❖ Charge Transport ( $e^-/h^+$ )
- ❖ Surface States
- ❖ Surface Electrocatalysis
- ❖ Band Structure Energetics
- ❖ **Stability and Cost**

A-

**Bulk  
Particulates**

**Structural  
Photoelectrodes**

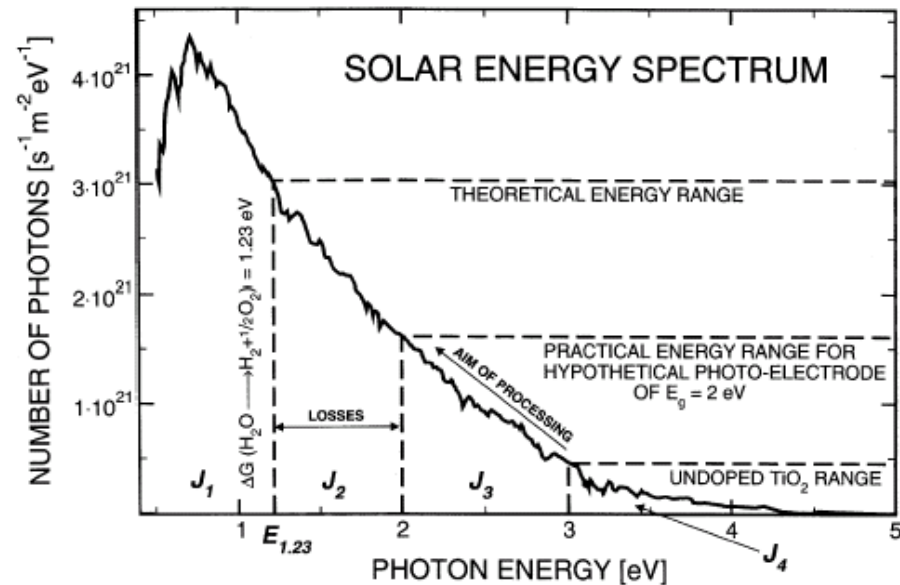


**No presently known materials are suitable**

# Photoelectrochemical H<sub>2</sub> Economics

~ 1000 W/m<sup>2</sup> available for harvesting.

“useful flux” ~ 10<sup>21</sup> photons/m<sup>2</sup>-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 for example

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

# Budget

- Project Funding From DOE for Total 3 Year Program (\$624k)
  - Direct Costs \$446k
  - Overhead \$178k
- Year 3 Funding
  - Direct Costs \$152k
  - Overhead \$ 66k

# Technical Barriers

This project addresses the following technical barriers from the Multi-Year Research, Development and Demonstration Plan Planned activities for 2003-2015 (Draft 6/3/03).

- ❖ **M. Material Durability**
- ❖ **N. Material and System Engineering**
- ❖ **O. Photoelectrochemical Efficiencies**

## DOE Technical Targets

Technical Targets	2003	2005	2010	2015
Solar-to-hydrogen Efficiency	7 %	7.5 %	9 %	14 %
Durability (hrs)	100	1,000	10,000	20,000
Cost \$/Kg	N/A	360	22	5

# Approach

## (1) System Development

- ✓ Continuing synthesis & high throughput screening system upgrades
  - More samples / higher throughput
  - Faster measurements
  - Increased reproducibility
- ✓ Develop Automated Spray Pyrolysis Deposition System (ASPDS)
- ✓ Develop combinatorial slurry reactor for the production of hydrogen

## Library Synthesis and Screening

- ✓ Using new and existing high-throughput synthesis and screening technology, create and screen suitable new mixed metal oxide materials for electrochemical/photoelectrochemical hydrogen production.
- ✓ Improve and expand the chemical synthesis routes developed for automated high-throughput experimentation.
- ✓ Catalyze the surfaces and engineer the bandedges of the identified semiconductor materials as required.
- ✓ Synthesize, using conventional routes, selected materials identified in libraries for detailed structure-electronic analysis.
- ✓ Determine if existing photovoltaic (PV) device structures could be easily modified to effect the direct splitting of water.

# Project Safety

- No accidents or injuries have been reported at anytime during the project (Sept 01- April 04).
- All laboratory members are required to take a 4 hour course in laboratory safety, provided by UCSB EH&S.
- UCSB EH&S routinely inspects the laboratory for safety to ensure compliance to federal, state, and county laws. Our laboratory has passed every inspection
- As new equipment is installed and/or developed, the primary scientist responsible for that equipment is also responsible for:
  - Assessing safe operation protocol
  - Training other group members for safe operation of the equipment
- No individual is permitted to operate equipment without consent of the primary scientist responsible for that equipment.
- Hydrogen safety is inherent within this project because in combinatorial chemistry, only small amounts of each catalyst ( $\ll 1\text{mg}$ ) are tested. Small amounts of catalyst yield low hydrogen/oxygen production rates well below flammable or explosive quantities in air or  $\text{N}_2$ .



# Project Timeline

9/01 – 08/02

9/02 – 08/03

9/03 – 08/04

Phase I

Phase II

Phase III

NS IP C

I	System Development	<ol style="list-style-type: none"> <li>1. Development of Automated Electrochemical Synthesis Systems (Rapid Serial Electrochemical Deposition System (<b>RSEDS</b>) and Parallel Electrochemical Deposition System (<b>PEDS</b>))</li> <li>2. Development of High Throughput Photoelectrochemical Screening System (<b>HTPESS</b>)</li> <li>3. Chemo-Optical High Throughput Hydrogen Screening System</li> </ol>			✓
	Library Synthesis & Characterization	<ol style="list-style-type: none"> <li>1. Tungsten oxide based libraries</li> <li>2. Cu<sub>2</sub>O based libraries</li> <li>3. Cu<sub>2</sub>O/TiO<sub>2</sub> heterojunction photoelectrode</li> </ol>			✓ ✓ ✓
II	System Development	<ol style="list-style-type: none"> <li>1. Development of Automated Spray Pyrolysis Deposition System (<b>ASPDS</b>)</li> </ol>		✓	
	Library Synthesis & Characterization	<ol style="list-style-type: none"> <li>1. Combinatorial synthesis of mesostructured metal / metal oxide libraries (WO<sub>3</sub>, ZnO, TiO<sub>2</sub>, Pt)</li> <li>2. Cobalt doped ZnO libraries for the improvement of visible light absorption</li> <li>3. Electroless deposition of metal oxide libraries (WO<sub>3</sub>, MoO<sub>3</sub>)</li> </ol>			✓ ✓ ✓
III	System Development	<ol style="list-style-type: none"> <li>1. Development of Automated UV-VIS Spectroscopy</li> <li>2. Development of slurry reactor for quantified hydrogen production from colloidal suspension powder photocatalyst</li> </ol>		✓ ✓	
	Library Synthesis & Characterization	<ol style="list-style-type: none"> <li>1. Continued synthesis &amp; screening of ZnO based libraries</li> <li>2. Fe<sub>2</sub>O<sub>3</sub> based libraries by <b>ASPDS</b></li> <li>3. Tungsten-molybdenum mixed oxide libraries (W<sub>x</sub>Mo<sub>1-x</sub>O<sub>3</sub>)</li> <li>4. Electrocatalytic nanoparticulate Au libraries</li> </ol>		✓ ✓	✓ ✓

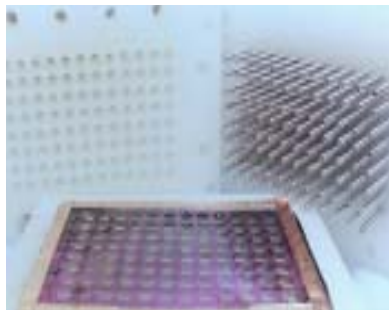
\* **NS**: Not Started, **IP** : *In* Progress, **C** : Completed

# Significant Achievements To Date

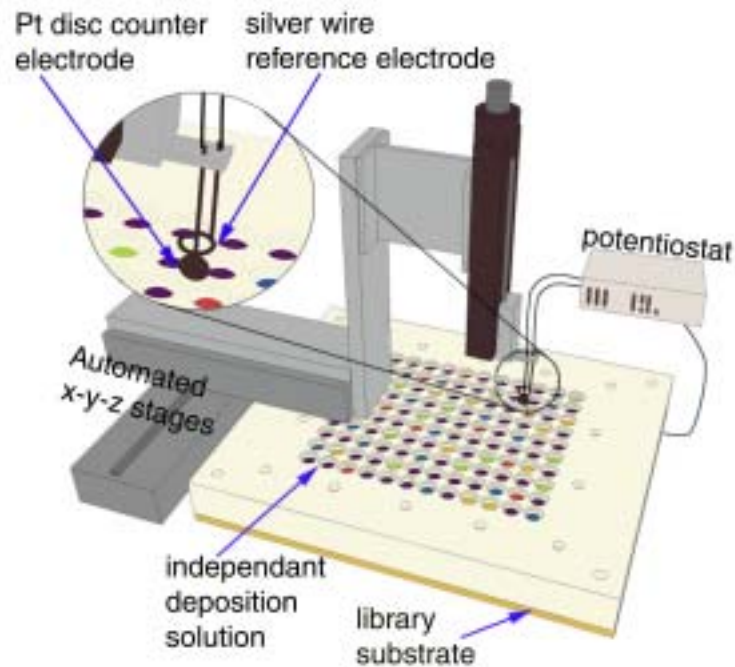
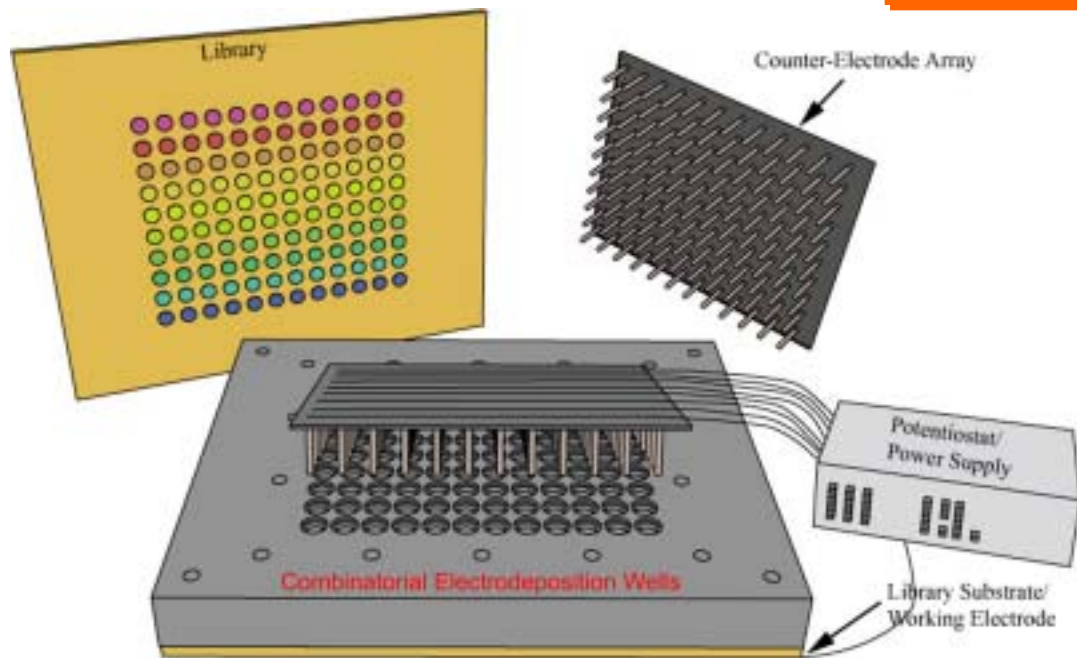
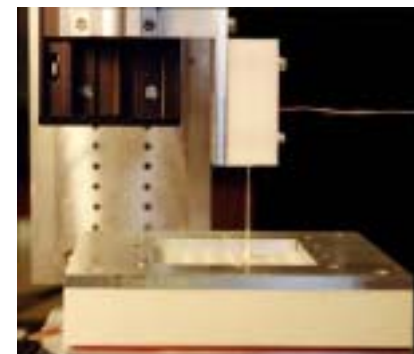
<p>1. Combinatorial System Development for Automated, High-speed Synthesis &amp; Screening</p>	<ul style="list-style-type: none"> <li>❖ Parallel Electrochemical Deposition System (PEDS)</li> <li>❖ Rapid Serial Electrochemical Deposition System (RSEDS)</li> <li>❖ Automated Spray Pyrolysis Deposition System (ASPDS)</li> </ul>
<p>2. Combinatorial Synthesis and Screening of Mixed Metal Oxides &amp; Metal doped Oxides</p>	<ul style="list-style-type: none"> <li>❖ Photocurrent screening</li> <li>❖ Bandgap &amp; bandedge measurement</li> <li>❖ Measurement of electrocatalytic properties</li> </ul>
<p>3. Combinatorial Synthesis and Screening of Mixed Metal Oxides &amp; Metal doped Oxides</p>	<ul style="list-style-type: none"> <li>❖ Tungsten-Molybdenum mixed metal oxides</li> <li>❖ Binary zinc oxides – <b>significant</b> (~ <b>4X</b>) improvement of visible photocurrent in <math>Zn_{1-x}Co_xO</math> materials (<math>0.03 &lt; x &lt; 0.05</math>)</li> <li>❖ Metal doped oxides (<math>WO_3</math>, <math>TiO_2</math>, <math>ZnO</math>, <math>Cu_2O</math>)</li> </ul>
<p>4. Combinatorial Electrochemical Synthesis of Mesostructured Materials</p>	<ul style="list-style-type: none"> <li>❖ Mesostructured <math>ZnO</math> &amp; <math>WO_3</math> with Lamellar Phase</li> <li>❖ Mesostructured <math>TiO_2</math> and Pt with Hexagonal Phase</li> </ul>
<p>5. Investigation of high activity for Au nanocluster electrocatalysts.</p>	<ul style="list-style-type: none"> <li>❖ Fabrication of Nanoparticulate <math>WO_3</math></li> <li>❖ Fabrication of nanoparticulate Pt/<math>WO_3</math> for DMFC's</li> <li>❖ Fabrication of nanoparticulate Au, Pt</li> </ul>
<p>5. Investigation of high activity for Au nanocluster electrocatalysts.</p>	<ul style="list-style-type: none"> <li>❖ Synthesis of nanoparticulate Au, Ir, and Pt by block copolymer micelle encapsulation</li> <li>❖ Electrocatalysis &amp; gas phase catalysis</li> </ul>

# Automated (Combinatorial) Electrodeposition Systems

Parallel Electrochemical Deposition System (**PEDS**)



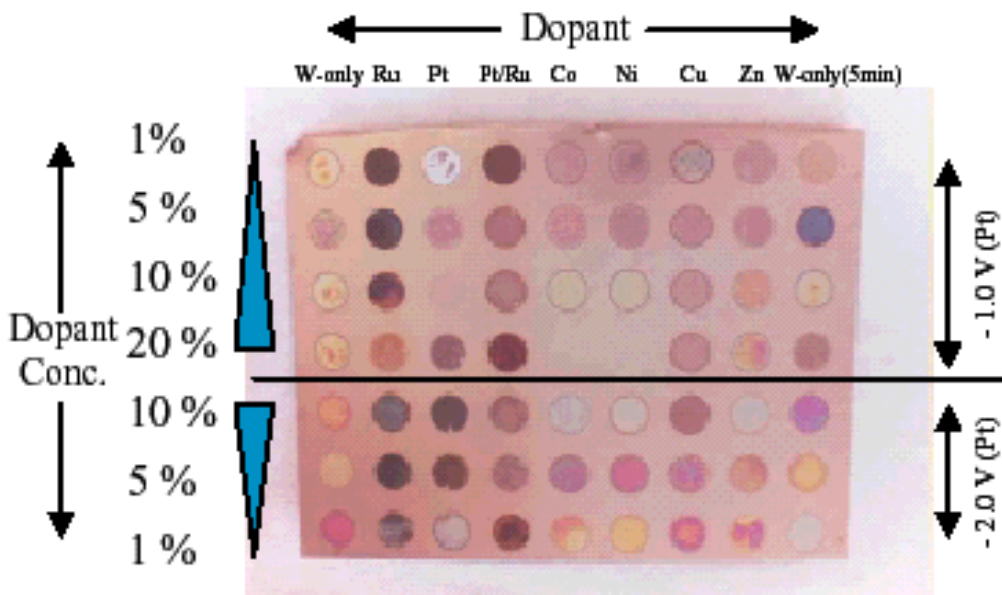
Rapid Serial Electrochemical Deposition System (**RSEDS**)



# Photocatalyst Discovery is Well Suited to Combinatorial Chemistry

- ❖ Large interdependent parameter space to explore
- ❖ Limited theoretical understanding to predict optimal composition / structure
- ❖ Feasible to rapidly create and screen solid-state libraries
- ❖ Much to be learned about composition-structure-function relationships in photocatalytic materials
- ❖ There has been no suitable material found to date

## Combinatorial Electrochemical Synthesis & Screening



### Diversity in...

#### Synthesis Parameters

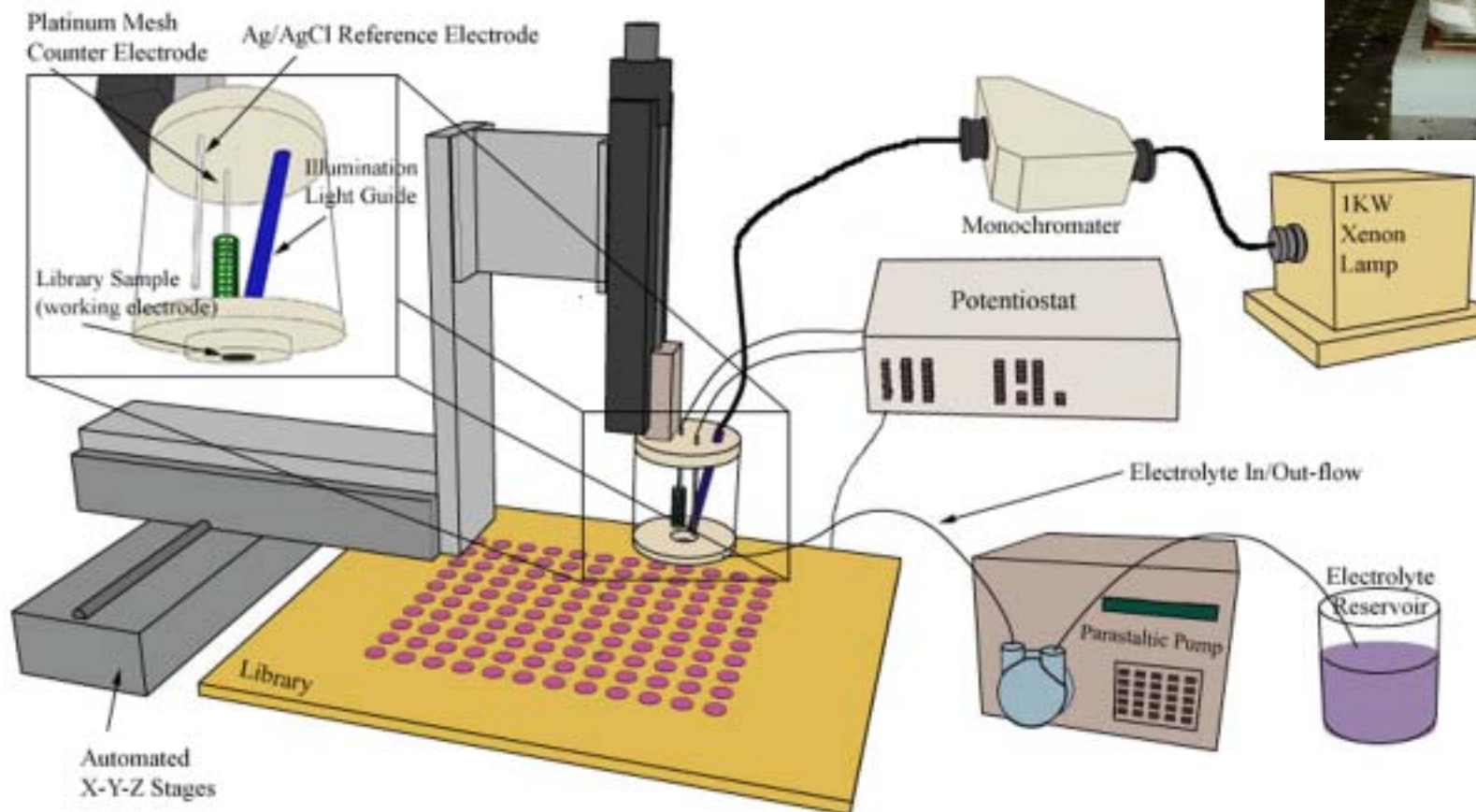
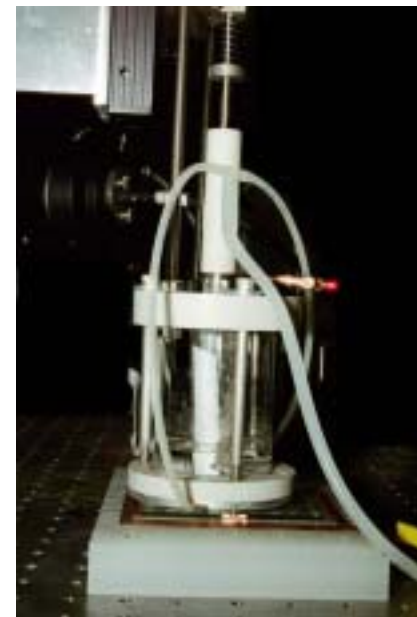
- solvent
- electrolyte composition
- ligands
- surfactant additives
- temperature
- pH
- voltage
- current
- time

#### Synthesized Materials

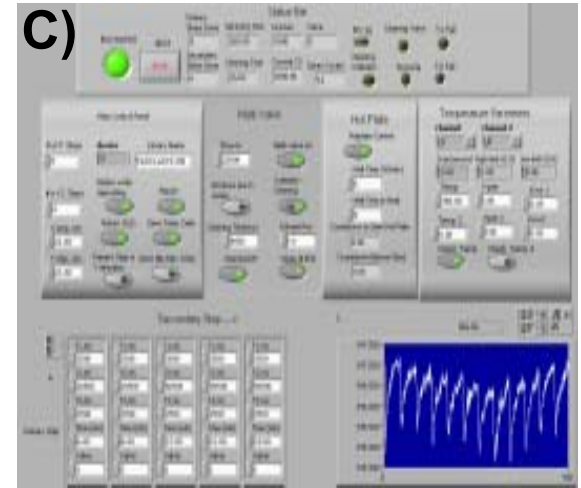
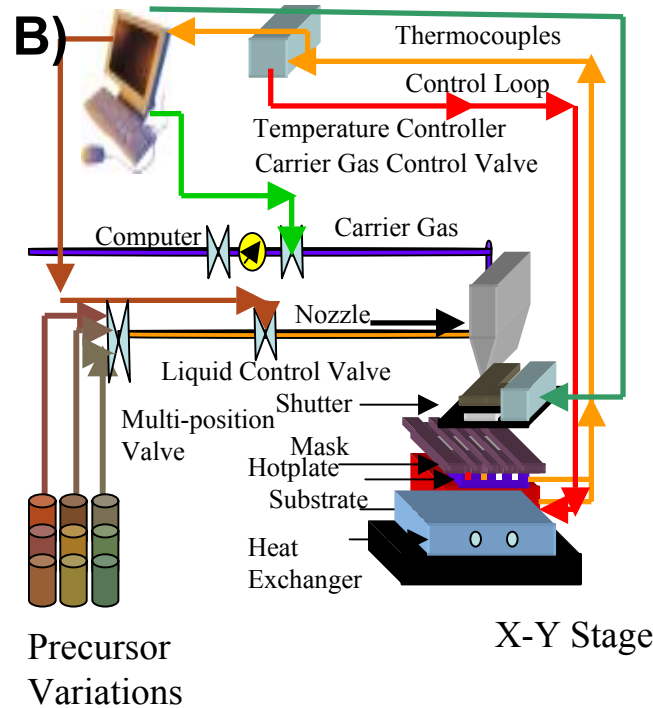
- composition
- structure
- thickness
- crystallinity
- surface states
- morphology

# 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.

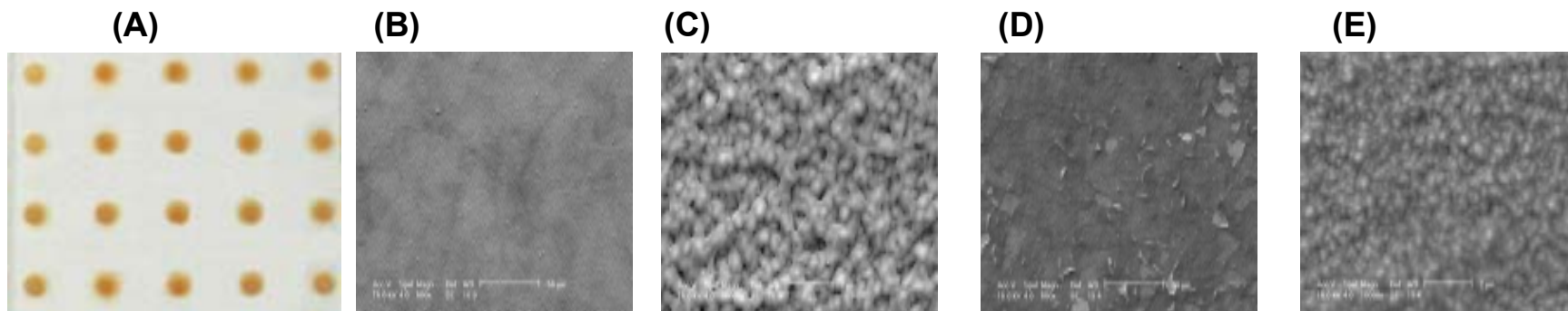


# Automated Spray Pyrolysis Deposition System (ASPDS)



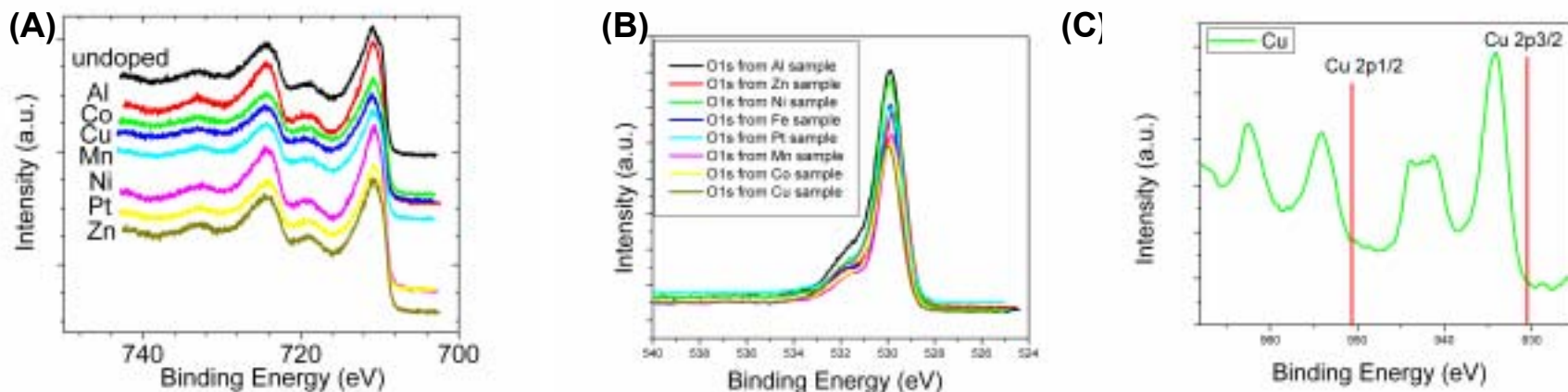
**A)** Photograph and **B)** Schematic diagram of ASPDS system; **C)** User interface

# 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.

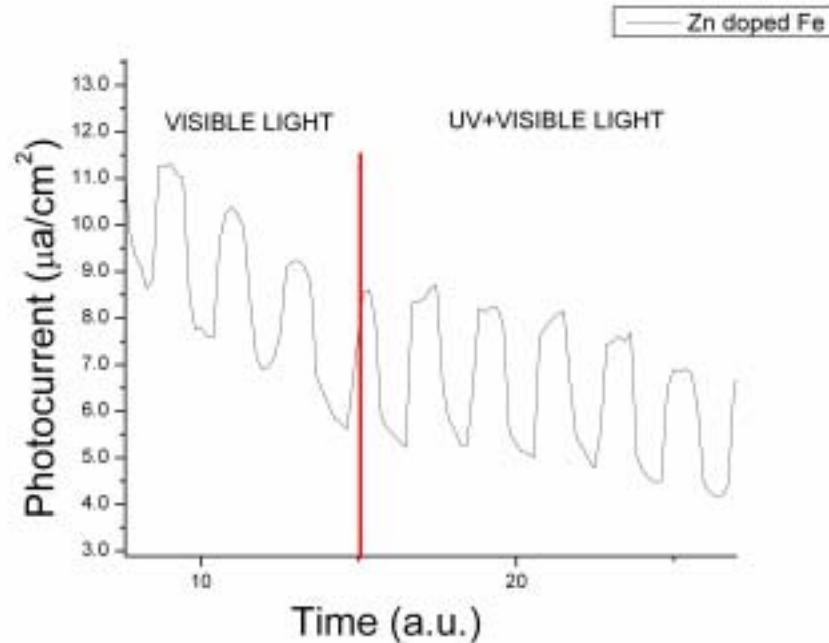
## Film Characterization by XPS



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 $\text{Fe}_2\text{O}_3$ materials synthesized by ASPDS

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



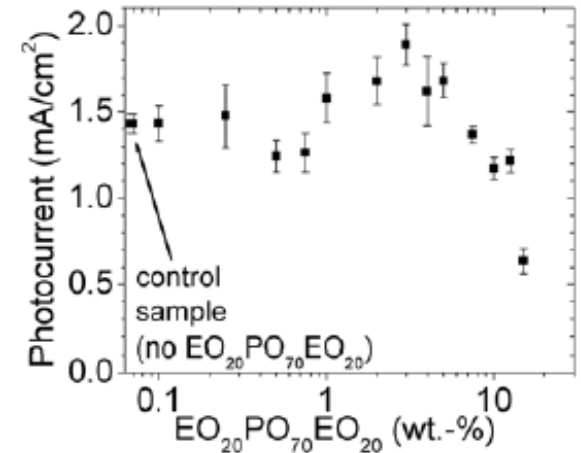
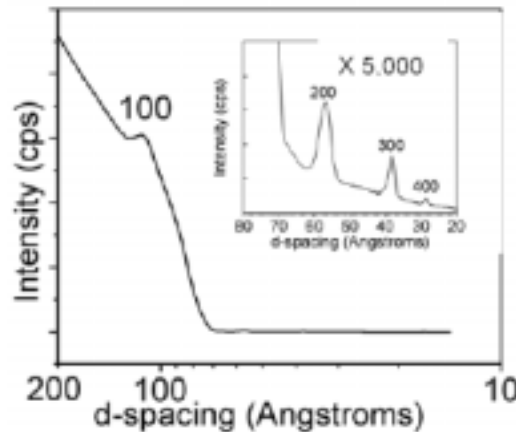
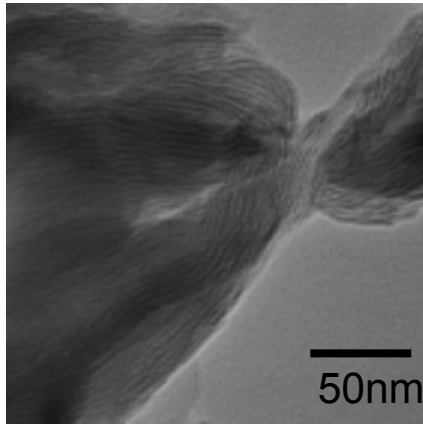
Photocurrent from iron oxide doped with Zn (30%) deposited by spray pyrolysis ( $\sim 1 \text{ W}/\text{cm}^2$  illumination)

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

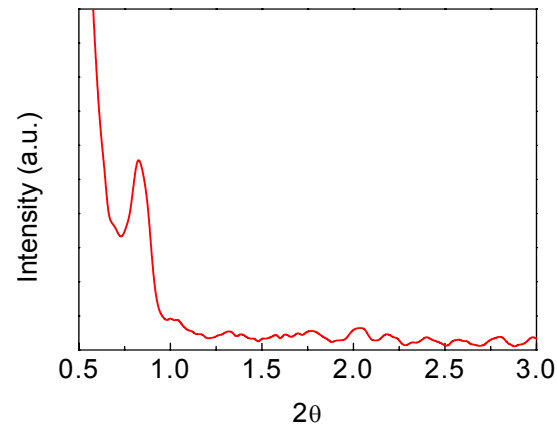
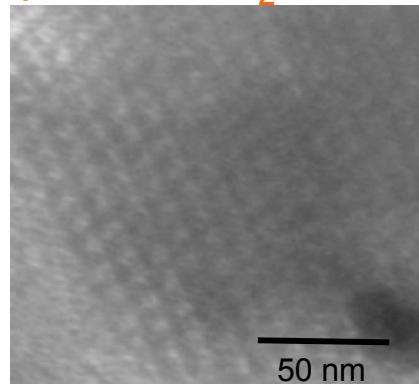
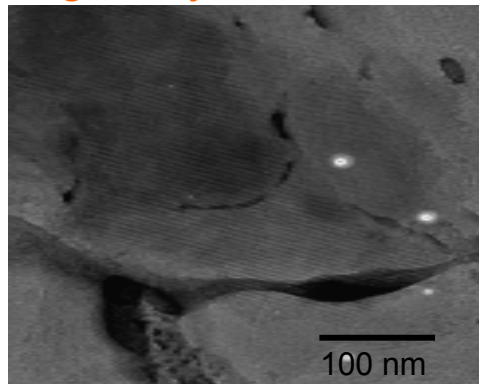


# Electrochemical Synthesis of Mesostructured Materials

## Lamellar ZnO

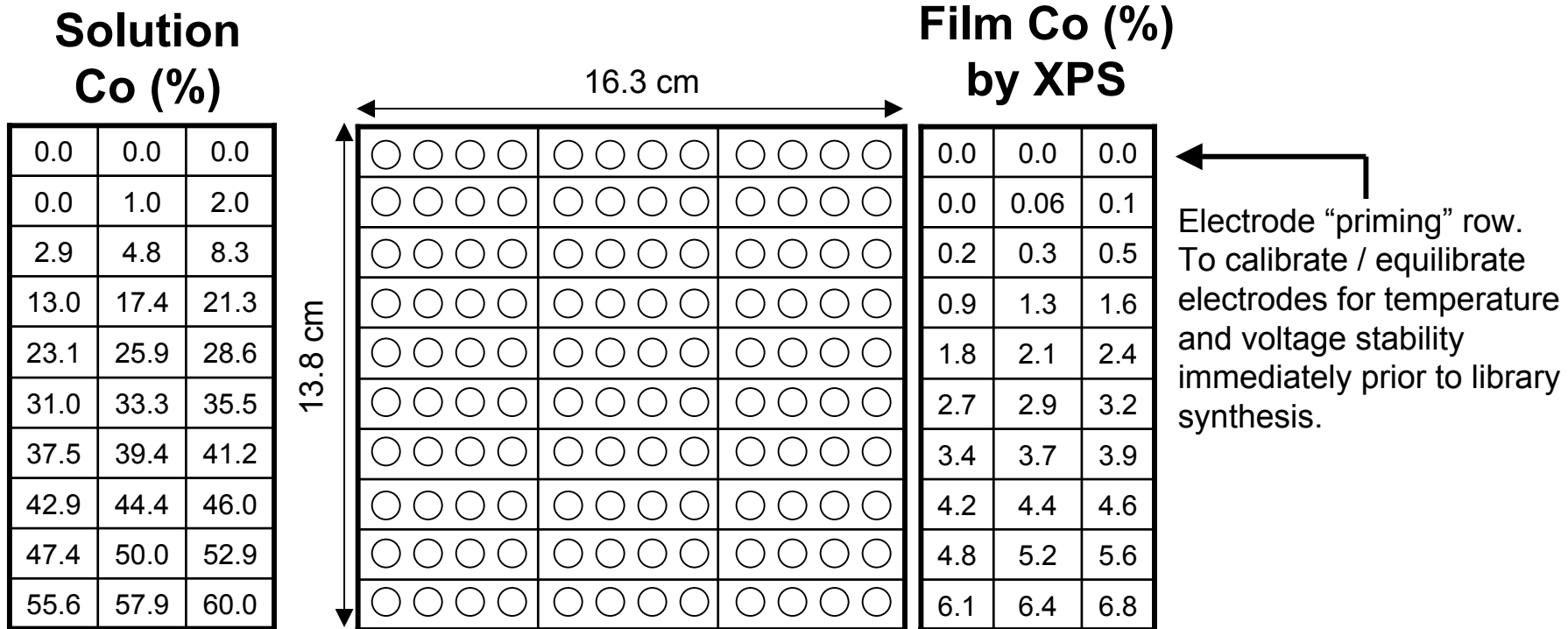


## Hexagonally ordered Mesoporous TiO<sub>2</sub>



Mesostructured ZnO and TiO<sub>2</sub> were fabricated by surfactant-templated electrodeposition. (a) Lamellar-structured ZnO was observed by TEM, whose long range order was evidenced by XRD (b). (c) A library of mesostructured ZnO was photoelectrochemically screened and optimum concentration of the structure-directing agent (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) was identified. Hexagonally ordered TiO<sub>2</sub> was also achieved (d,e,f).

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

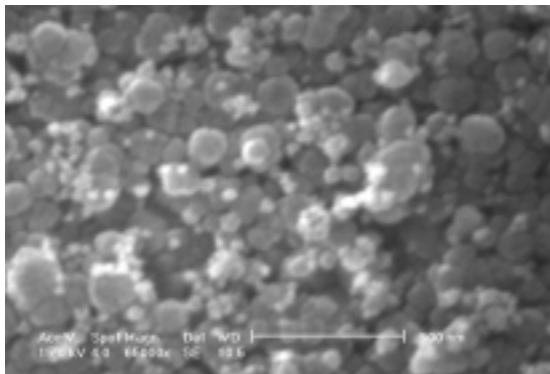
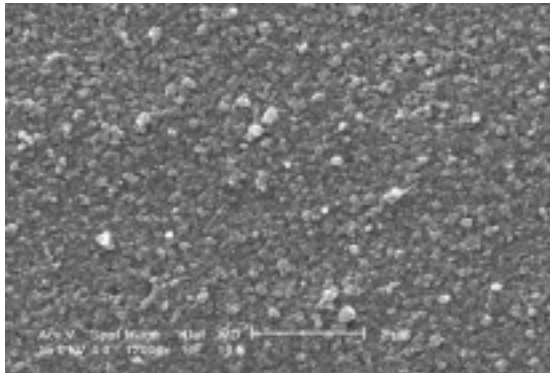


## Rapid Serial Electrochemical Deposition System (RSEDS)

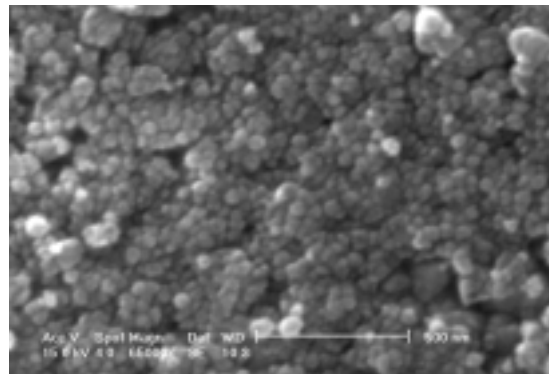
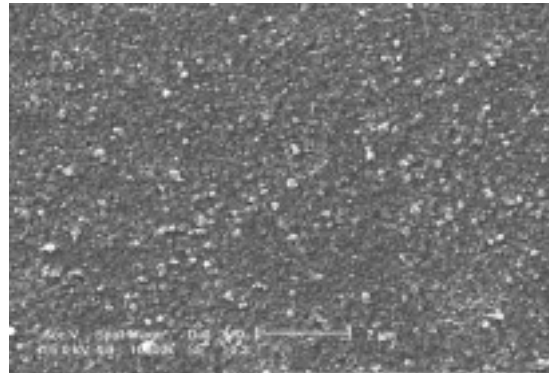
- Motivation: to increase absorption of visible photons within ZnO by cobalt-doping
- 120 samples (10x12 array). 27 different Zn:Co ratios with 4 replicates each.
- 100mM ZnCl<sub>2</sub> & 60mM LiNO<sub>3</sub> in DMSO with varying concentrations of Co(NO<sub>3</sub>)<sub>2</sub>.
- 1.5mL of electrolyte 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 TEC-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

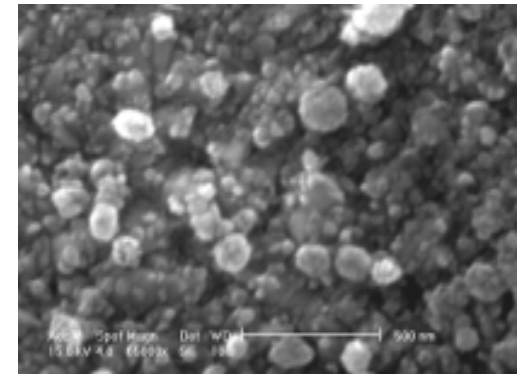
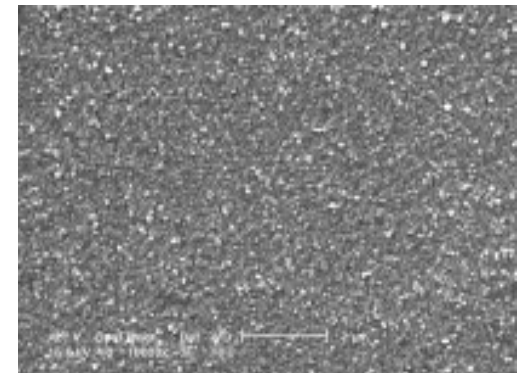
ZnO



Zn<sub>0.979</sub>Co<sub>0.021</sub>O

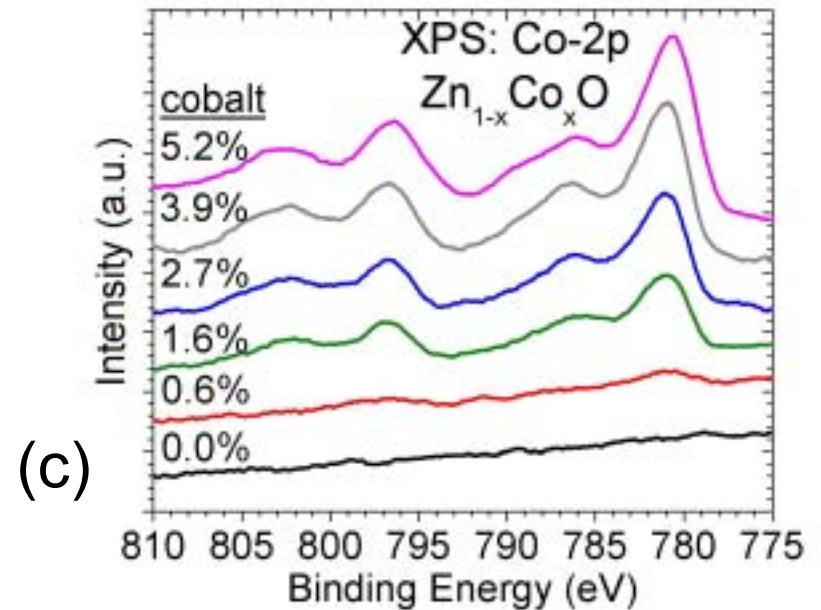
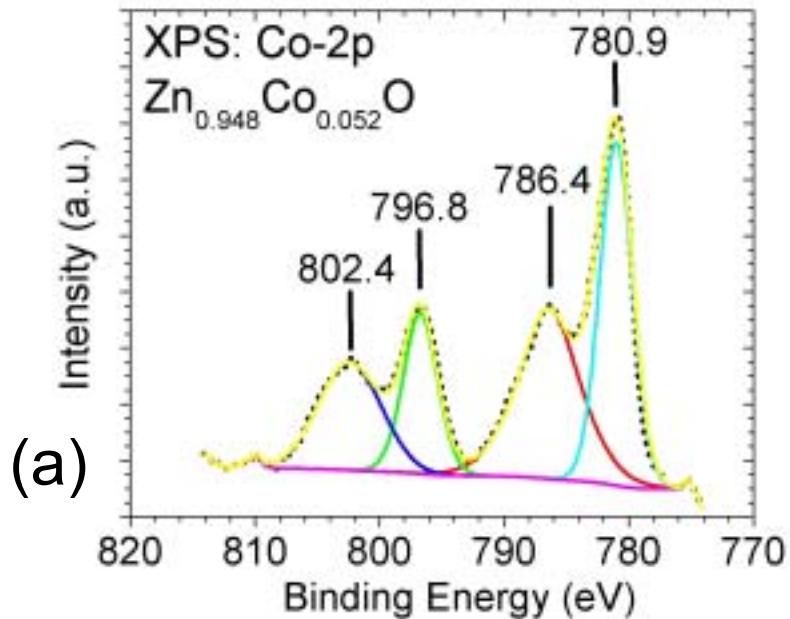


Zn<sub>0.948</sub>Co<sub>0.052</sub>O



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<sub>1-x</sub>Co<sub>x</sub>O: Cobalt oxidation state by XPS

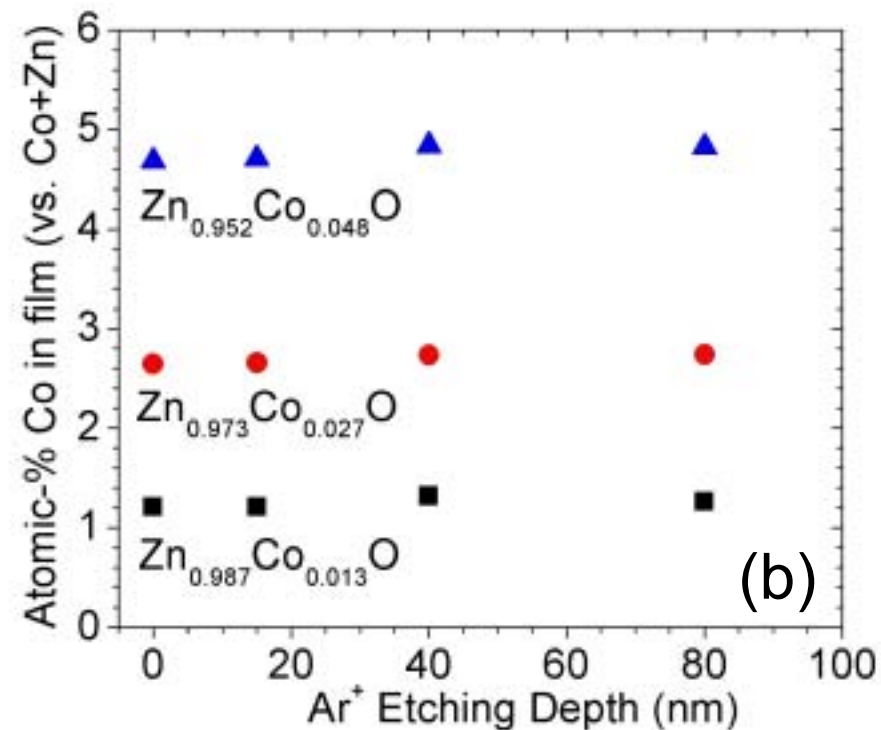
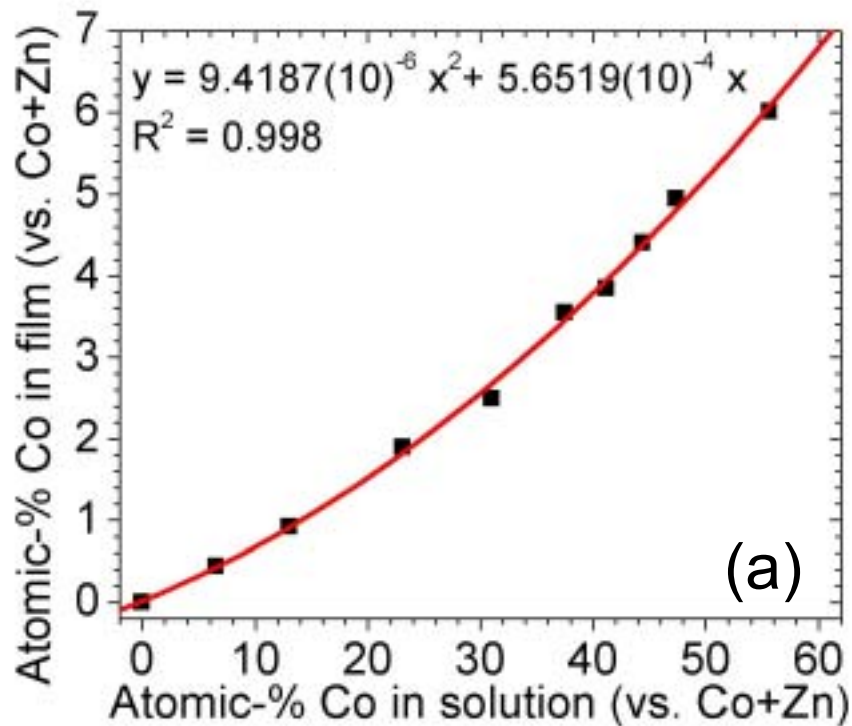


(b)

Spectral Region	Binding Energy & FWHM	Assignments
Co-2p <sub>3/2</sub>	780.9 eV (3.1)	Co <sup>2+</sup> multiplet splitting
	786.4 eV (5.7)	Co <sup>2+</sup> shake-up satellite
Co-2p <sub>1/2</sub>	796.8 eV (3.2)	Co <sup>2+</sup> multiplet splitting
	802.4 eV (5.9)	Co <sup>2+</sup> shake-up satellite

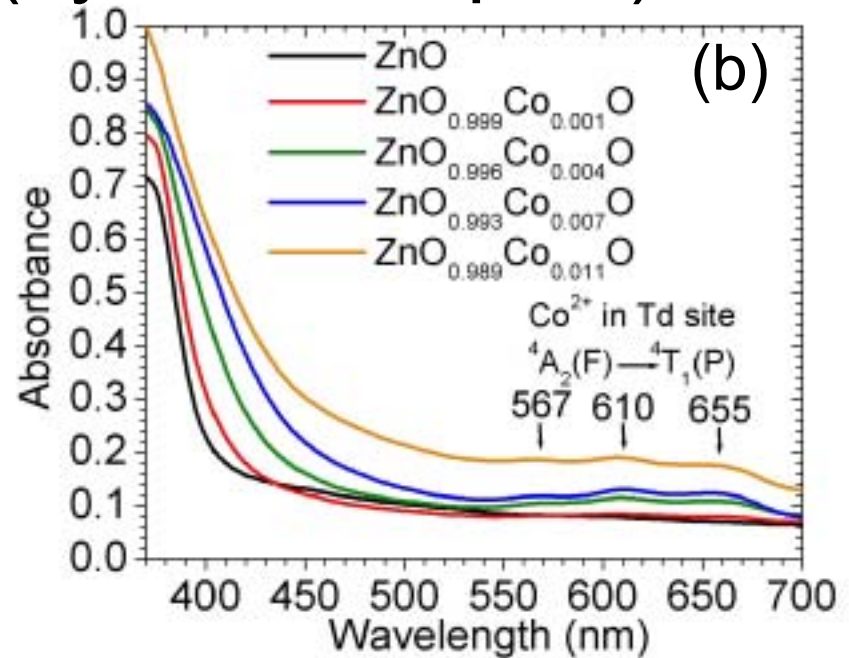
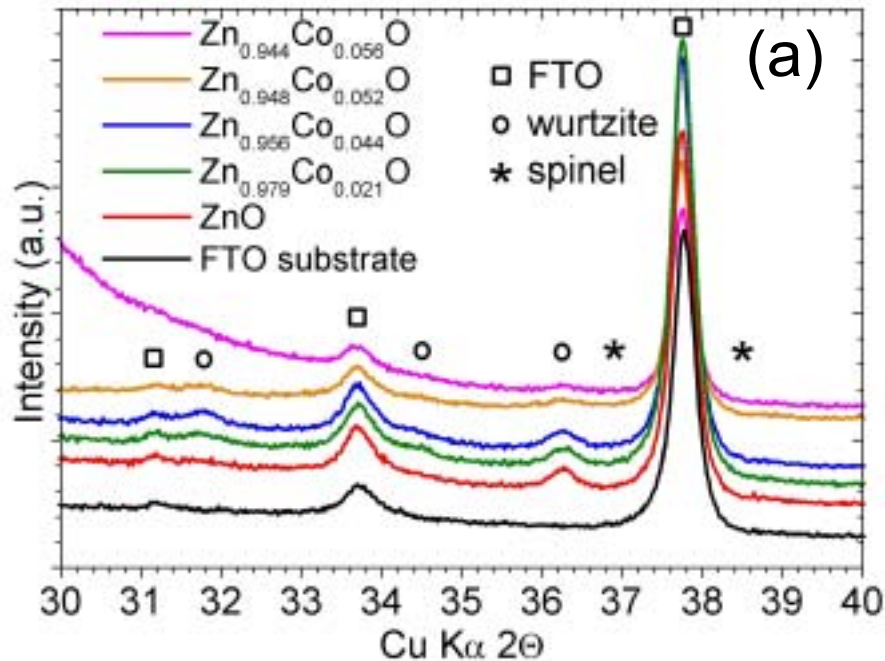
XPS was conducted on selected samples to determine Zn:Co stoichiometry as well as the oxidation state of cobalt. Graph (a) reveals the deconvoluted Co-2p spectrum of Zn<sub>0.948</sub>Co<sub>0.052</sub>O, in which all four cobalt peaks are assigned to Co<sup>2+</sup>, as indicated in Table (b). Graph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

# Zn<sub>1-x</sub>Co<sub>x</sub>O: Stoichiometry by XPS



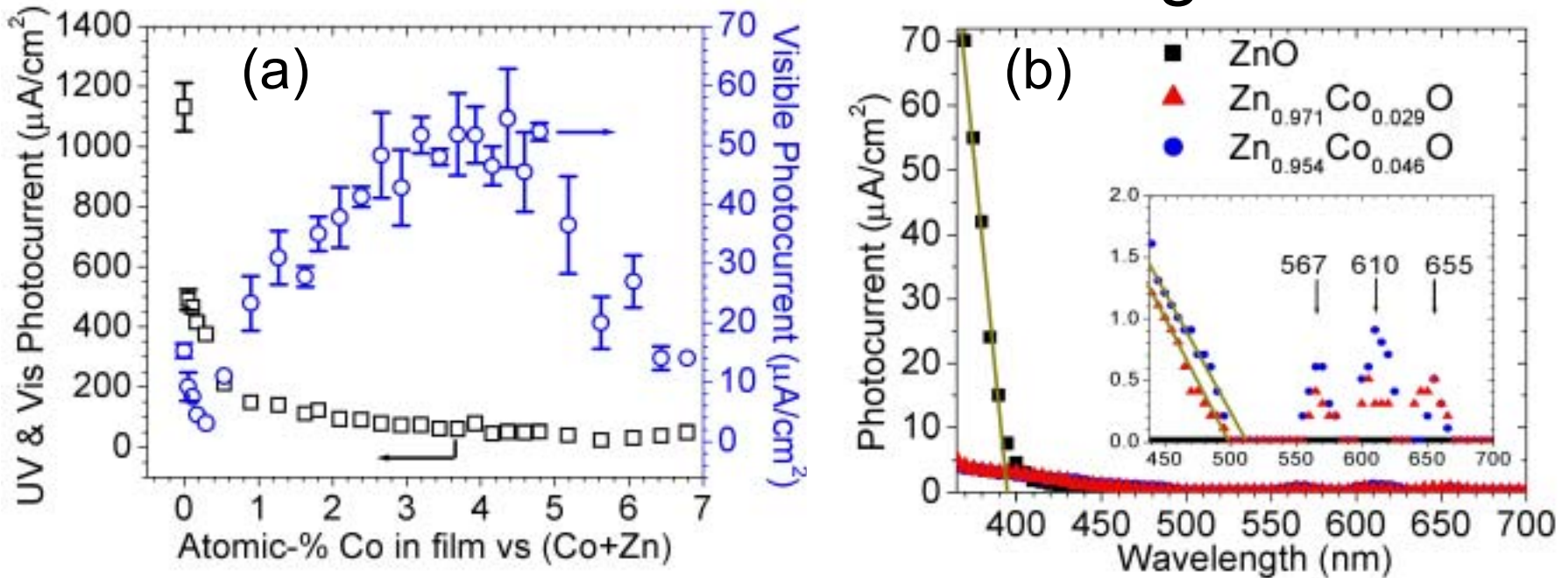
Zn:Co stoichiometry was determined by the ratio of integrated peak areas assigned to Co-2p<sub>3/2</sub> vs. Zn-2p<sub>3/2</sub>, after normalizing areas with Scofield sensitivity factors. Graph (a) correlates Zn:Co stoichiometry in the films to Zn:Co ratios in the electrochemical deposition baths. A 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<sup>+</sup> etching (4kV, 1.6 $\mu$ A, ~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<sub>1-x</sub>Co<sub>x</sub>O: Crystal structure (by XRD) & Optical absorption (by UV-Vis spec.)



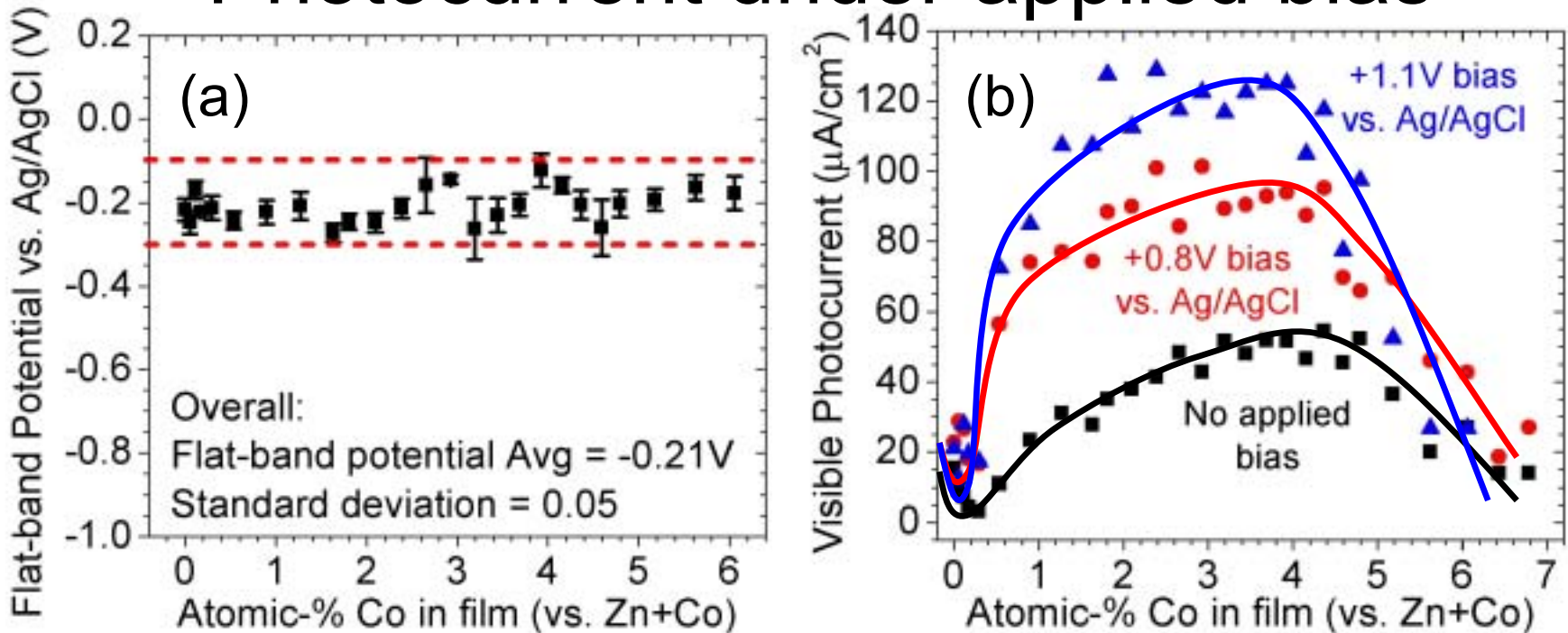
(a) XRD was performed on selected samples for the purpose of identifying crystal structure of the mixed oxide. All compositions revealed a wurtzite structure typical of pure ZnO. No phase separation of CoO (rocksalt) nor spinel  $\text{Co}_3\text{O}_4$  was observed, indicating that an atomically mixed  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  (wurtzite) was synthesized for all values of  $x$  investigated. (b) UV-vis spectroscopy was conducted on several  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  compositions, and even at low concentrations of Co, two trends emerge. First, the bandgap of  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  decreases with increasing Co concentration, and secondly, peaks at 567nm, 610nm, 655nm are clearly present – characteristic  $d-d$  transitions of  $\text{Co}^{2+}$  within a tetrahedral site (consistent with the wurtzite structure). Increased visible absorption of ZnO by mixing with cobalt is promising for photoelectrochemical and photocatalytic applications.

# Zn<sub>1-x</sub>Co<sub>x</sub>O: High-throughput Photocurrent Screening



(a) The high throughput photoelectrochemical screening system was used to measure photocurrent (with no applied bias) under two conditions – first, with a UV-filter in the light path (“visible photocurrent”), and then without the filter in place (UV & Vis photocurrent). Under UV & Vis illumination, photocurrent drops sharply even with low concentrations of cobalt, and then decreases asymptotically (towards  $\sim 60 \mu\text{A}/\text{cm}^2$ ) with larger concentrations of cobalt in the film. Photocurrent under visible illumination reveals a very different trend. Initially, the visible photocurrent drops (with very low Co  $< 0.5\%$ ), but the photocurrent increases steadily until a maximum is reached at 4.4% –  $55 \mu\text{A}/\text{cm}^2$  – nearly a four-fold improvement over pure ZnO ( $15 \mu\text{A}/\text{cm}^2$ ). (b) Monochromated light was subsequently used for further high-throughput photoelectrochemical characterization. The action spectra of three selected samples are shown in Figure (b). Not surprisingly, the pure ZnO showed high photoactivity with illumination  $< 400\text{nm}$ , consistent with a ZnO bandgap of approx. 3.2eV. The inset shows a magnification of the 450nm – 700nm region, where clearly, the cobalt-doped samples exhibit strong photoactivity. Increased photocurrent in this region is derived from two sources – first, a decrease in the bandgap of these Zn<sub>1-x</sub>Co<sub>x</sub>O materials, and secondly from characteristic *d-d* transitions at 567nm, 610nm, and 655nm observed for tetrahedrally coordinated Co<sup>2+</sup>.

# Zn<sub>1-x</sub>Co<sub>x</sub>O: Flat band potential & Photocurrent under applied bias



The high throughput screening system was used to take two cyclic voltammograms of each sample of the library under chopped illumination (first with and then without a UV-filter in place) in a 0.2M KNO<sub>3</sub> aq. electrolyte. This allows for measurement of flat-band potential (a) as well as photocurrent under applied bias (b). Clearly, flat-band potential changes negligibly as a function of composition, approximately  $-0.21\text{V} \pm 0.05\text{V}$  vs. a Ag/AgCl reference electrode. This agrees with the notion that Co<sup>2+</sup> substitutes Zn<sup>2+</sup> in the ZnO lattice, as interstitial doping would have more likely increased the Fermi level of the material. Figure (b) shows, as expected, how photocurrent increases with increased applied bias. The shape of the curve is nearly identical in all three cases. Although a three-fold improvement is observed under a +1.1V applied bias (vs. Ag/AgCl), the energy input required does not justify its use for an industrial application. Nevertheless, the relatively small increase in photocurrent under such a large applied bias as compared to no applied bias indicates that charge separation is not a significant problem in either case.



# Publications resulting from DOE H<sub>2</sub> Program support (1 of 2)

## Phase I (9/2001 ~ 8/2002)

1. C. Brandli, T.F. Jaramillo, A. Ivanovskaya, and E.W. McFarland, "Automated Synthesis and Characterization of Diverse Libraries of Macroporous Alumina," *Electrochimica Acta* **47 (4)** 553-557 (2001).
2. T.F. Jaramillo, A. Ivanovskaya, and E.W. McFarland, "High-Throughput Screening System for Catalytic Hydrogen-Producing Materials," *J. Combinatorial Chem.* **4 (1)** 17-22 (2002).
3. S.-H. Baeck, T.F. Jaramillo, C. Brandli, and E. McFarland, "Combinatorial Electrochemical Synthesis and Characterization of Tungsten-based Mixed Metal Oxides," *J. Combinatorial Chemistry* **4 (6)**, 563-568 (2002).
4. S.-H. Baeck and E.W. McFarland, "Combinatorial Electrochemical Synthesis and Characterization of Tungsten-Molybdenum Mixed Oxides," *Korean J. Chem. Eng.* **19 (4)**, 593-596 (2002).
5. S.-H. Baeck, T.F. Jaramillo, G.D. Stucky, and E. McFarland, "Controlled Electrodeposition of Nanoparticulate Tungsten Oxide," *Nano Letters* **2 (8)** 831-834 (2002).
6. S.-H. Baeck, T.F. Jaramillo, and E.W. McFarland, "Influence of composition and morphology on photo and electrocatalytic activity of electrodeposited Pt/WO<sub>3</sub>," *Am. Chem. Soc., Abs. Pap.* **224: 062-FUEL Part 1** (2002).

## Phase II (9/2002 ~ 8/2003)

7. K.-S. Choi, H. Lichtenegger, G.D. Stucky, and E.W. McFarland, "Electrochemical Synthesis of Nanostructured ZnO films Utilizing Self Assembly of Surfactant Molecules at Solid-Liquid Interfaces," *J. Am. Chem. Soc.* **124(42)** 12402-12403 (2002).
8. W. Siripala, A. Ivanovskaya, T.F. Jaramillo, S.-H. Baeck, and E.W. McFarland, "A Cu<sub>2</sub>O/TiO<sub>2</sub> Heterojunction Thin Film Cathode for Photoelectrocatalysis," *Sol. Ener. Mat. & Sol. Cells.* **77(3)** 229-237 (2003).
9. K.-S. Choi, E.W. McFarland, and G.D. Stucky, "Electrocatalytic Properties of Thin Mesoporous Platinum Films Synthesized Utilizing Potential-Controlled Surfactant Assembly," *Adv. Materials.* **15 (23)** 2018-2021 (2003).

# Publications resulting from DOE H<sub>2</sub> Program support (2 of 2)

## Phase II continued (9/2002 ~ 8/2003)

10. T.F. Jaramillo, S.-H. Baeck, B.R. Cuenya, and E.W. McFarland, "Catalytic Activity of Supported Au Nanoparticles Deposited from Block Copolymer Micelles," *J. Am. Chem. Soc.* **125(24)** 7148-7149 (2003).
11. B. Roldan Cuenya, S.-H. Baeck, T.F. Jaramillo, E.W. McFarland, "Size and Support Dependent Electronic and Catalytic Properties of Au<sup>0</sup>/Au<sup>3+</sup> Nanoparticles Synthesized From Block Co-polymer Micelles," *J. Am. Chem. Soc.*, **125(42)**; 12928-12934 (2003).
12. S.-H. Baeck, T.F. Jaramillo, G.D. Stucky, and E.W. McFarland, "Synthesis of Tungsten Oxide on Copper Surfaces by Electroless Deposition," *Chem. Mater.* **15(18)** 3411-3413 (2003).
13. S.-H. Baeck, K.-S. Choi, T.F. Jaramillo, G.D. Stucky, and E.W. McFarland, "Enhancement of Photocatalytic and Electrochromic Properties of Electrochemically Fabricated Mesoporous WO<sub>3</sub> Thin Films," *Advanced Materials* **15(15)** 1269-1273 (2003).

## Phase III (9/2003 ~ 8/2004)

14. T.F. Jaramillo, S.-H. Baeck, A. Kleiman-Shwarsstein, and E.W. McFarland, "Combinatorial Electrochemical Synthesis and Screening of Mesoporous ZnO for Photocatalysis," *Macromol. Rapid Commun.* **25**, 297-301 (2004).
15. S.-H. Baeck, T.F. Jaramillo, D.H. Jeong, E.W. McFarland, "Parallel synthesis and characterization of photoelectrochemically and electrochromically active tungsten molybdenum oxides", *Chem. Comm.*, **390-391** (2004).
16. S.-H. Baeck, T.F. Jaramillo, A. Kleiman-Shwarsstein, and E.W. McFarland, "Automated Electrochemical Synthesis and Characterization of TiO<sub>2</sub> Supported Au Nanoparticle Electrocatalysts", *Meas. Sci. Tech.*, **Submitted** (2004).
17. T.F. Jaramillo and E.W. McFarland, "Combinatorial investigation of Zn<sub>1-x</sub>Co<sub>x</sub>O for photoelectrochemical hydrogen production" (in preparation, to be submitted May 2004)

# Interactions and Collaborations

- Private and Public
  - Uppsala University, Sweden: collaboration on N-doped TiO<sub>2</sub> photocatalysts.
  - Intematix Inc.: Characterization of PVD deposited film libraries, other planned collaboration outlined in newly submitted proposal.
  - International Energy Agency: Participated in IEA Annex-14 Expert Group in the Hydrogen Implementing Agreement on photoelectrolytic hydrogen production.
  - Mitsubishi Chemical: C60 activated metal oxide photocatalysts.
  - General Electric: Seminar at CR+D, other planned collaboration outlined in newly submitted proposal.

# Responses to Previous Year Reviewers Comments

- Comment: Scale-up needs more emphasis
- Response: A scale-up photocatalytic reactor system has been developed using gas chromatography for quantitative measurement of H<sub>2</sub> & O<sub>2</sub> production on larger-scale samples (~ 1-20 grams).
  - Scale-up plans are greatly emphasized in the new proposal to DOE for FY 2005-2008 funding.
- Comment: Needs more focused direction
- Response: Of the many mixed oxide systems we have investigated, we have focused on one promising host to pursue further studies and optimization. With Zn<sub>1-x</sub>Co<sub>x</sub>O (0.03 < x < 0.05) catalysts established as improved visible light photocatalysts, future work will focus on ternary and quaternary materials derived from this Zn:Co composition regime.

# Work to be completed by the end of Phase III (September 2004)

- Continue C-60 doping of oxide materials for visible light absorption.
- Transition metal doped  $\text{Fe}_2\text{O}_3$
- Ternary and quaternary derivatives of  $\text{Zn}_x\text{Co}_{1-x}\text{O}$ 
  - For improved corrosion resistance
  - For improved catalytic redox activity
- Single-sample slurry reactor for quantitative  $\text{H}_2$  analysis
- Quantitative efficiencies for best materials found to date
- Preliminary reactor concepts and economics for best materials