

### **IV.F.3 Photoelectrochemical Hydrogen Production Using New Combinatorial Chemistry Derived Materials**

*Eric W. McFarland (Primary Contact), Thomas F. Jaramillo, Sung-Hyeon Baeck, Alan Kleiman-Shwarcstein, and Scott M. Roney*

*University of California*

*Dept. of Chemical Engineering*

*Santa Barbara, CA 93106-5080*

*Phone: (805) 893-4343; Fax: (805) 893-4731; E-mail: mcfar@engineering.ucsb.edu*

*DOE Technology Development Manager: Roxanne Garland*

*Phone: (202) 586-7260; Fax: (202) 586-9811; E-mail: Roxanne.Garland@ee.doe.gov*

*DOE Project Officer: Jill Gruber*

*Phone: (303) 275-4961; Fax: (303) 275-4753; E-mail: Jill.Gruber@go.doe.gov*

*Contract Number: DE-FG36-05GO15040*

*Start Date: September 1, 2004*

*Projected End Date: May 31, 2008*

#### **Objectives**

- 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 Hydrogen Implementing Agreement on photoelectrolytic hydrogen production.

#### **Technical Barriers**

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- AP. Materials Efficiency
- AQ. Materials Durability
- AS. Device Configuration Designs
- AT. Systems Design and Evaluation

## Technical Targets

McFarland Group Progress Toward Meeting DOE Photoelectrochemical Hydrogen Production Targets

Characteristic	Units	2003 Prog. Status	2010 Target	2005 Status of Combinatorial Chemistry Derived Materials
Usable Semiconductor Band gap	eV	2.8	2.3	2.75
Chemical Conversion Process Efficiency	%	4	10	1%
Plant Durability	hr	NA	1000	(see below)

Although we have not directly measured the lifetime of our materials in photoelectrochemical systems, photocurrent stability under UV illumination (over 15 minutes or longer) is one of the key screening parameters used to identify promising material systems. Work on ZnO/Cu<sub>2</sub>O systems and doped ZnO is partially aimed at improving the stability of these systems.

## Approach

- Systems Development
  - Continue synthesis & high-throughput screening system upgrades.
    - More samples/higher throughput
    - Increased reproducibility
  - Develop an automated spray pyrolysis deposition system.
  - Develop a combinatorial slurry reactor for the production of hydrogen.
- Combinatorial Library Synthesis and Screening
  - Using new and existing high-throughput synthesis and screening technology, create and screen suitable new mixed 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 band-edges of the identified semiconductor materials as required.
  - Synthesize, using conventional routes, selected materials identified in libraries for detailed morphological, spectroscopic and photo-electrochemical analysis.
  - Determine if existing photovoltaic device structures could be easily modified to effect the direct splitting of water.

## Accomplishments

- Development of combinatorial slurry reactor system for hydrogen production from colloidal photocatalysts (80% complete).
- Applied automated spray pyrolysis deposition system (ASPDS) to synthesize libraries of transition-metal doped Fe<sub>2</sub>O<sub>3</sub> and high-throughput photoelectrochemical screening system (HTPSS) to characterize these libraries.
- Demonstrated synthesis of ZnO/Cu<sub>2</sub>O heterojunctions, using spray pyrolysis, and the improved resistance of these materials to photocathodic corrosion.
- Determined optimal particle size of nanoparticulate Au on TiO<sub>2</sub> for surface photoelectrocatalysis.

- Elucidated effect of nitrogen incorporation in photoelectrochemically-active  $\text{TiO}_{2-x}\text{N}_x$  thin films, in collaboration with researchers at Uppsala University in Sweden.
- Developed synthesis routes for co-electrodeposition of ZnO and  $\text{C}_{60}$  derivatives to improve the visible light absorption of wide-band gap semiconductor materials.

### Future Directions

- Synthesize libraries of transition-metal doped  $\text{Fe}_2\text{O}_3$  using both ASPDS and sol-gel methods; screen for optical bandgap and determine the photoelectrochemical performance of such materials.
- Explore ternary and quaternary zinc oxides of the form  $\text{Zn}_{1-x}\text{Co}_x\text{O}_y\text{A}_y\text{B}_z$  ( $0.03 < x < 0.05$ ), where A and B are typically inexpensive transition metals or non-metal dopants such as S, N, or O.
- Synthesize and screen libraries of wide-band gap semiconductors doped with  $\text{C}_{60}$  by electrochemical co-deposition; study carbon-doping by calcination of these materials above the thermal stability limit of fullerene derivatives.
- Complete development of combinatorial reactor for colloidal photocatalyst screening and apply to libraries based upon sol-gel derived  $\text{CeO}_2$ , beginning with  $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$  and  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ .
- Evaluate heterojunction device structures such as  $\text{ZnO}/\text{Cu}_2\text{O}$ ,  $\text{ZnS}/\text{Cu}_2\text{O}$ ,  $\text{WO}_3/\text{Cu}_2\text{O}$ ,  $\text{WO}_3/\text{Fe}_2\text{O}_3$ ,  $\text{ZnO}/\text{Fe}_2\text{O}_3$ , etc.
- Investigate the use of alternative regenerable oxidants in catalytic cycles to reduce the overpotential required for hydrogen production.
- Participate in development and maintenance of a central database of photoelectrochemical materials, in collaboration with the National Renewable Energy Laboratory in Golden, CO.

### Introduction

The overall project objective is to discover and optimize an efficient, practical, and economically sustainable material for photoelectrochemical production of bulk hydrogen from water – a clean, renewable route to hydrogen energy. The properties of the semiconductors investigated for this application, which are similar to those in photovoltaic devices, must satisfy conditions in several areas if cost-effective hydrogen production is to be realized: (1) efficient solar absorption, (2) effective charge separation/transport, (3) appropriate conduction band/valence band energies relative to  $\text{H}_2$  and  $\text{O}_2$  redox potentials, (4) facile interfacial charge transfer, (5) long-term stability, and (6) low cost. A material which satisfies all the above conditions simultaneously could provide clean hydrogen in bulk and at low cost; unfortunately, no such material or system has been discovered or developed to date. The DOE has identified the following future targets for solar-to-hydrogen efficiency and durability: 2010, 8% and 1,000 hours; 2015, 10% and 5,000 hours.

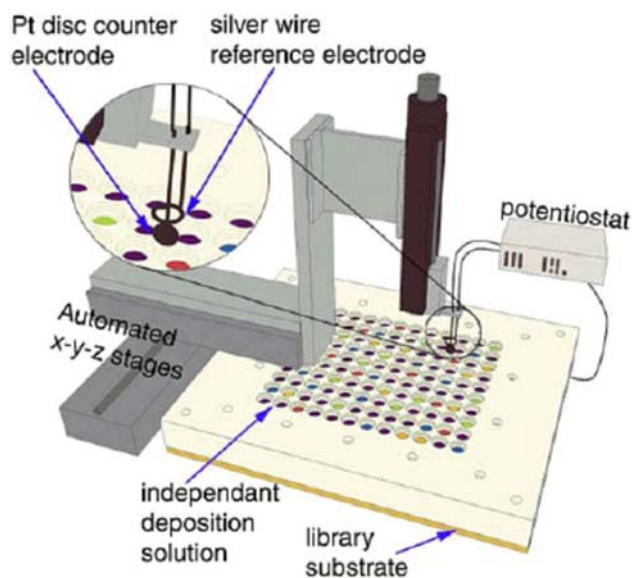
### Approach

This project involves the application of combinatorial chemistry methods to discover and optimize photoelectrochemical materials and systems for cost effective hydrogen production. Our research paradigm features systematic and high-speed exploration of new metal-oxide based solid-state materials. By investigating large arrays of diverse materials, we are working to improve understanding of the fundamental mechanisms and composition-structure-property relationships within these systems while discovering new and useful energy producing photocatalysts. It should also be noted that our approach focuses on the investigation of semiconductor materials that are inherently inexpensive, such as ZnO,  $\text{WO}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Cu}_2\text{O}$ . Although more expensive systems (e.g., GaAs, InP, etc.) have generally demonstrated greater efficiency, cost and/or natural abundance, they could be problematic on a large scale; thus we are applying combinatorial techniques toward inexpensive host photocatalysts with the aim of significantly improving their properties while negligibly affecting cost.

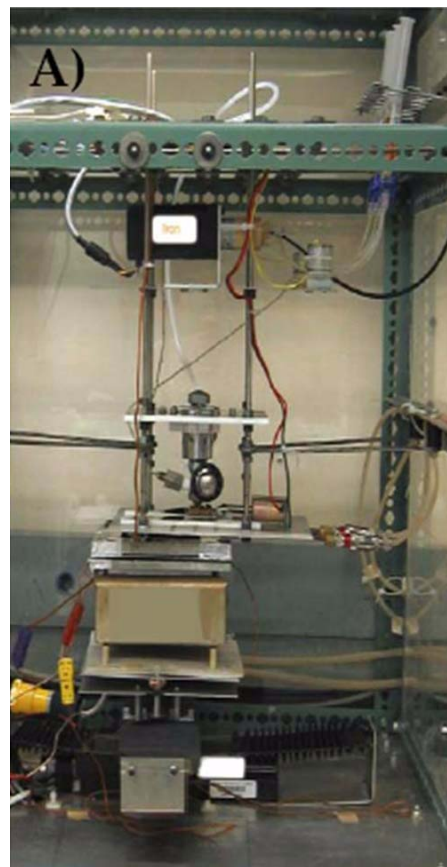
## Results

We have designed and constructed automated electrochemical synthesis (Figure 1) and photoelectrochemical screening systems (HTPSS – not shown) for a variety of new materials and we have focused primarily on ZnO, Fe<sub>2</sub>O<sub>3</sub>, and Cu<sub>2</sub>O hosts, investigating libraries of variable composition and morphology. We have developed a pulsed-electrodeposition scheme for depositing nanoparticulate pure metals (Pt, Au, Pd), alloys (Pt-Au, Pt-Ru) and metal oxides (WO<sub>3</sub>) which we have incorporated into our automated synthesis and screening systems. We have also developed an automated spray pyrolysis deposition system (ASPDS – Figures 2a, 2b, and 2c) for synthesis of Fe<sub>2</sub>O<sub>3</sub> and ZnO libraries.

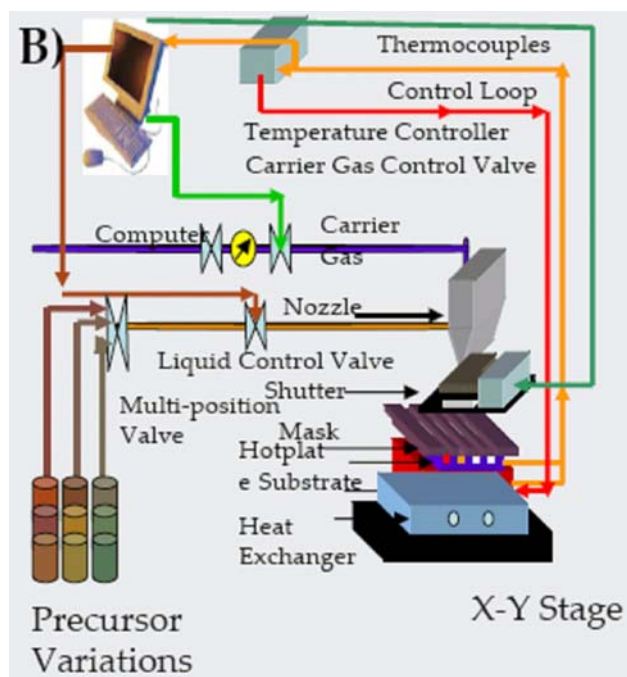
Spray pyrolysis-derived Fe<sub>2</sub>O<sub>3</sub> films have been synthesized un-doped and with 7 different dopants (Al, Co, Cu, Mn, Ni, Zn, Pt) using the ASPDS with 10 mM chloride salt precursors. We explored the effect of water content in the ethanol/water solvent and found that 60% water gave the most desirable and reproducible morphology as observed by Scanning Electron Microscopy (Figure 3). X-ray photoelectron spectroscopy (XPS) (see Table 1)



**Figure 1.** Automated Electrochemical Synthesis Based on Rapid-Serial Deposition: 120 Independent Electrochemical Cells are Sealed upon a Single 14 cm x 16 cm Conductive Substrate



**Figure 2a.** Photo of the ASPDS



**Figure 2b.** ASPDS Schematic Diagram

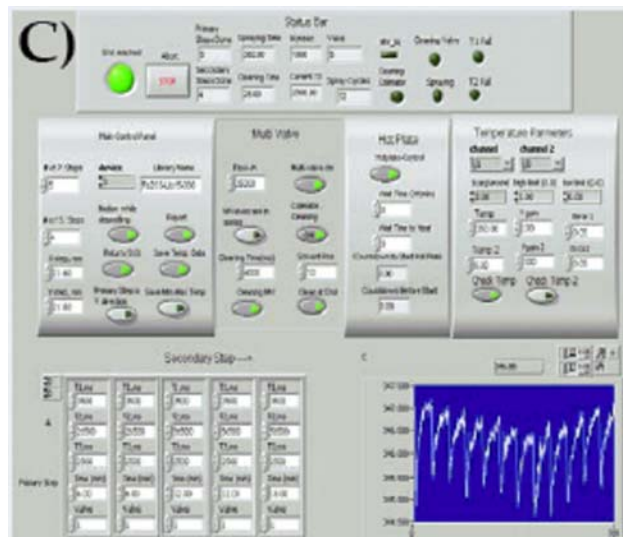


Figure 2c. User Interface of ASPDS

Table 1. XPS Analysis of Spray Pyrolysis  $\text{Fe}_2\text{O}_3$  Films

	Molar% Dopant by EDX	Molar % Dopant by XPS	XPS Line (eV)	Oxidation State
Al	2.04	20.754	Al-2p / 73.8	$\text{Al}^{3+}$
Cu	11.75	25.573	Cu-2p(3/2) / 934.2	$\text{Cu}^{2+}$
Zn	16.68	13.751	Zn-2p(3/2) / 1021.3	$\text{Zn}^{2+}$
Ni	12.11	7.413	Ni: Ni-2p(3/2) / 854.7, 856.2	$\text{Ni}^{2+} / 3+$
Co	10.68	8.502	Co-2p(3/2) / 780.5	$\text{Co}^{3+}$
Mn	8.02	16.434	Mn-2p(3/2) / 642	$\text{Mn}^{3+} / 4+$
Pt	10.53	12.517	Pt-4f(7/2) / 74.6	$\text{Pt}^{4+}$

verified that all samples contained  $\text{Fe}^{3+}$  and allowed quantification of the doping level for each material; some dopants were observed to segregate to the surface while others concentrated in the bulk of the film. The resulting materials were then screened for photoelectrochemical hydrogen production; current work is aimed at finding the most promising dopant for in-depth study.

We applied our automated electrochemical synthesis system to the study of ZnO thin films.

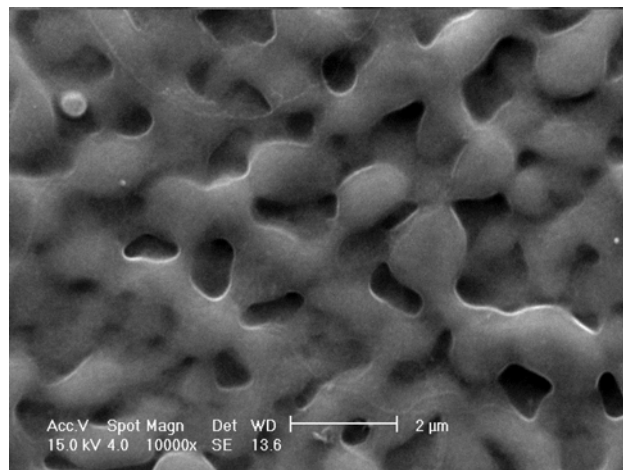


Figure 3A

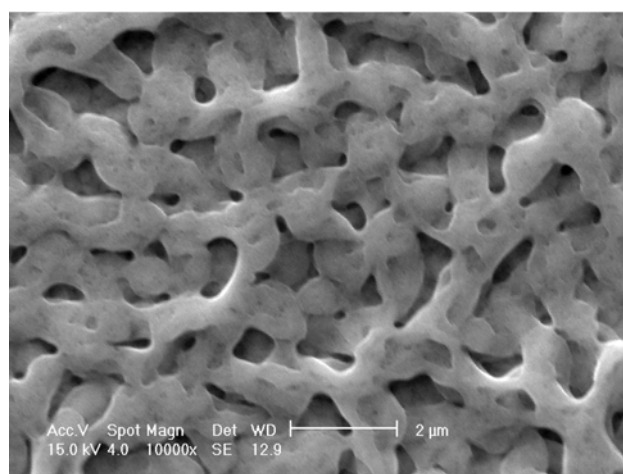
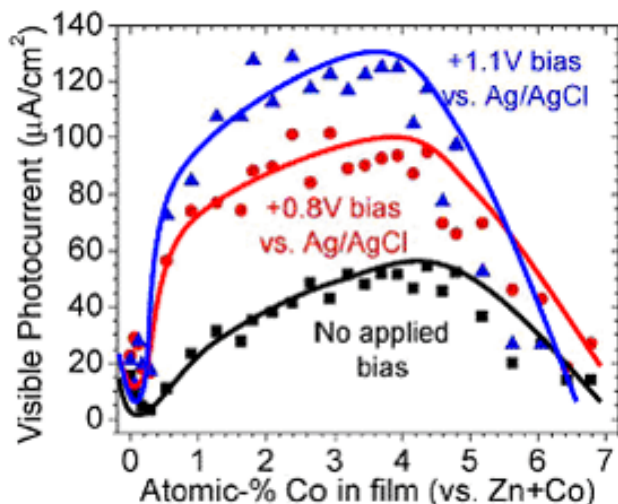


Figure 3B

Figure 3. Scanning Electron Microscopy of Spray Pyrolysis  $\text{Fe}_2\text{O}_3$  Doped with Cu (3A) and Zn (3B)

On the basis of an initial screening of 24 different dopants, Co-doped ZnO was chosen for in-depth study with the aim of increasing visible-light absorption and photocurrent. A 120-member library was synthesized to explore 27 Co dopant concentrations up to 7%. XPS reveals that  $\text{Co}^{2+}$  is the predominant oxidation state of cobalt, while XRD confirms that the wurtzite structure (typical of pure ZnO) is maintained. Figure 4 exhibits results from photoelectrochemical screening. When a UV cut-off filter is used to emulate the solar spectrum, photocurrent decreases with low cobalt concentrations ( $< 1\%$ ), but then increases to a maximum at 4.4% cobalt, where photocurrent is 4 times that of pure ZnO. Action spectra and incident photon conversion efficiency measurements (not



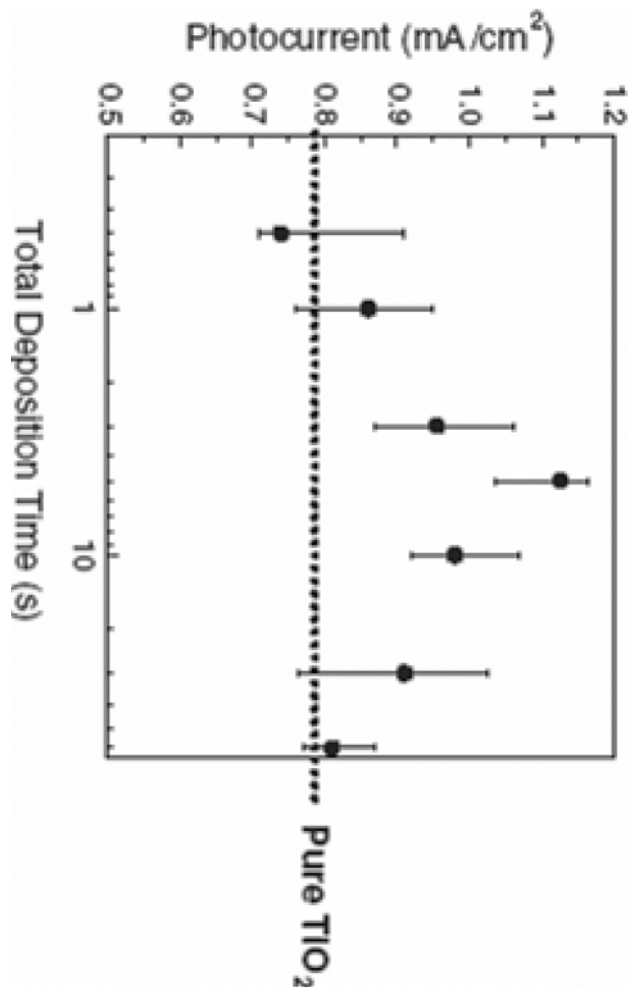
**Figure 4.** Effect of Atomic% Co Incorporation in  $Zn_{1-x}Co_xO$  on Visible-Light Photocurrent, as a Function of Applied Bias

shown) reveal that the increased photoelectrochemical activity is due to improved visible absorption.

We applied our automated high-throughput electrochemical synthesis and photoelectrochemical screening systems to the study of Au nanoclusters electrodeposited on oxidized titanium substrates. Pulsed electrodeposition was used to nucleate nano-sized Au clusters, and the total deposition time was varied across the library to create a range of cluster sizes. The resulting library was screened for both photoelectrochemical water splitting and electrocatalytic CO oxidation. As shown in Figure 5, Au films synthesized using 5 ms pulses with a total deposition time between 3 and 10 s of total deposition time demonstrated the greatest activity for photodecomposition of water (20–40% greater than pure  $TiO_2$ ), due to the resulting optimal size of the Au clusters.

### **Conclusions**

- The methodology of combinatorial material science has been applied to expedite the discovery of improved photocatalytic materials for hydrogen production.
- ASPDS can reliably and reproducibly synthesize  $Fe_2O_3$  thin films doped with various transition metals.



**Figure 5.** Effect of Pulsed Electrodeposition Time on Photocurrent of Nanoparticulate Au on  $TiO_2$

- Cobalt-doped ZnO samples were explored in depth with  $Zn_{0.956}Co_{0.044}O$  exhibiting optimal performance—a visible-light photocurrent efficiency four times that of pure ZnO.
- Au nanocluster libraries electrodeposited on  $TiO_2$  were screened for photoelectrochemical hydrogen production; those deposited for 5 s using 5 ms pulses showed 40% improvement over pure  $TiO_2$ .
- Low-voltage electrodeposition of thin films of  $C_{60}$  derivatives has been demonstrated.

### **FY 2005 Publications/Presentations**

1. J. M. Mwabora, T. Lindgren, E. Avendaño, T.F. Jaramillo, J. Lu, S.-E. Lindquist, and C.-G. Granqvist, "Structure, Composition, and Morphology of Photoelectrochemically Active  $TiO_{2-x}N_x$  Thin

- Films Deposited by Reactive DC Magnetron Sputtering,” *Journal of Physical Chemistry B* 108 (2004) 20193 – 20198.
2. S.-H. Baeck, T.F. Jaramillo, A. Kleiman-Shwarscstein, E.W. McFarland, “Automated Electrochemical Synthesis and Characterization of TiO<sub>2</sub> Supported Au Nanoparticle Electrocatalysts,” *Measurement Science and Technology* 16 (2005) 54-59.
  3. T.F. Jaramillo, S.-H. Baeck, A. Kleiman-Shwarscstein, K.-S. Choi, G.D. Stucky, E.W. McFarland, “Automated Electrochemical Synthesis and Photoelectrochemical Characterization of Zn<sub>1-x</sub>Co<sub>x</sub>O Thin Films for Solar Hydrogen Production,” *Journal of Combinatorial Chemistry* 7 (2005) 264-271.
  4. X. Liu, T.F. Jaramillo, A. Kolmakov, S.-H. Baeck, M. Moskovits, G.D. Stucky, E.W. McFarland, “Synthesis of Au Nanoclusters Supported Upon a TiO<sub>2</sub> Nanotube Array,” *Journal of Materials Research* 20 (2005) 1093-1096.
  5. A. Kleiman-Shwarscstein, “Automated Spray Pyrolysis System for Hematite Synthesis as a Photocatalyst for Hydrogen Production”, Poster, 227 American Chemical Society (ACS) National Meeting, Anaheim, California, March 2004.
  6. T.F. Jaramillo, “Optimized Materials for Photoelectrochemical Hydrogen Production,” University of California—Santa Barbara Chemical Engineering Department, June 2004.
  7. T.F. Jaramillo, “High-Throughput Methods for the Investigation of Photoelectrochemical Hydrogen Production from Zn<sub>1-x</sub>Co<sub>x</sub>O Thin Films,” Presentation, 206th Meeting of The Electrochemical Society, Honolulu, HI, October 2004
  8. S.M. Roney, “ZnO/Cu<sub>2</sub>O Heterojunctions for Photoelectrochemical Hydrogen Production,” Poster, Gordon Research Conference on Electrochemistry, Ventura, CA, February 2005.
  9. T.F. Jaramillo, “High throughput investigation of new materials for the photoelectrochemical production of hydrogen,” Invited Talk, National Renewable Energy Laboratory, Golden, CO, February 2005.
  10. T.F. Jaramillo, “Combinatorial Discovery: New Materials for Photoelectrochemical Hydrogen Production,” KAIST-UCSB “Partners Across the Globe” Symposium, Santa Barbara, CA, February 2005.
  11. T.F. Jaramillo, “Doped Semiconductors and Mixed-metal Nanoparticles: New Materials for Energy Conversion Reactions,” Invited Talk, University of California—Los Angeles Chemical Engineering Department, Los Angeles, CA, April 2005.
  12. T.F. Jaramillo, “New Materials for Energy Conversion Reactions: Photoelectrochemical Hydrogen Production and Electrocatalytic Methanol Oxidation,” Invited Talk, Technical University of Denmark Department of Physics, Lyngby, Denmark, April 2005.
  13. T.F. Jaramillo, “New Materials for Photoelectrochemical Hydrogen Production: A High-Throughput Investigation,” Invited Talk, Stanford University Chemical Engineering Department, Stanford, CA, March 2005.