

II.E.4 Photoelectrochemical Hydrogen Production Using New Combinatorial Chemistry Derived Materials

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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 absorption and subsequently screen the derivative libraries for appropriate redox/flatband levels and finally for H₂ production.
- Continue to expand our investigations of nanoporous materials with the emphasis on ZnO, WO₃ and TiO₂.
- 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.

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:

- M. Material Durability
- N. Materials and System Engineering
- O. Photoelectrochemical Efficiency

Approach

Systems development

- Continue synthesis & high-throughput screening system upgrades.
 - More samples/higher throughput
 - Faster measurements
 - 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 structure-electronic analysis.
- Determine if existing photovoltaic (PV) device structures could be easily modified to effect the direct splitting of water.

Accomplishments

- Developed automated systems for material synthesis by electrochemical deposition (rapid-serial and parallel) and by spray pyrolysis.
- Developed automated systems for optical (Ultra-Violet – Visual [UV-Vis] spectroscopy), electrochemical, and photoelectrochemical (photocurrent, photovoltage, flat-band potential, action spectra, incident photon conversion to electrons [IPCE]) characterization.
- Explored $\text{WO}_3\text{-MoO}_3$ mixed oxides/solid solutions, and found 50:50 W:Mo to be optimal for electrochromic and photoelectrochemical applications.
- Investigated mesostructured ZnO synthesized by block co-polymer templating, and improved upon hydrogen production by 30%.
- Explored cobalt-doped ZnO solid solutions and found 4.4% cobalt to improve visible photocurrent (H_2 production) by a factor of 4 compared to pure ZnO.

Future Directions

- Ternary and quaternary derivatives of $\text{Zn}_{1-x}\text{Co}_x\text{O}$.
 - For improved corrosion resistance
 - For improved catalytic redox activity
- Continued C-60 doping of oxide materials for visible light absorption.
- Transition metal doped Fe_2O_3 .
- Single-sample slurry reactor for quantitative H_2 analysis.
- Quantitative efficiencies for best materials found to date.
- Preliminary reactor concepts and economics for best materials.

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 H_2 and O_2 redox potentials (“band matching”), (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: 2005, 7.5% and 1,000 hours; 2010, 9% and 10,000 hours; 2015, 14% and 20,000 hours.

Approach

The approach of this project involves the application of combinatorial chemistry methods to discover and optimize photoelectrochemical materials and systems for cost-effective hydrogen production. This represents a shift in the research paradigm from conventional chemical research in that a combinatorial approach 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 the 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 upon the investigation of semiconductor materials that are inherently inexpensive, such as ZnO, WO₃, and Cu₂O. Although more expensive systems (eg. GaAs, InP, etc.) have generally demonstrated greater efficiency, cost and/or natural abundance could be problematic on a large scale; thus, we are applying combinatorial techniques toward inexpensive host photocatalysts with the aim of improving their properties significantly while negligibly affecting cost.

Results

We have designed and developed automated electrochemical synthesis and photoelectrochemical screening systems, Figures 1 and 2, for a variety of new materials, and we have focused primarily on WO₃ and ZnO hosts, investigating libraries of variable composition and morphology. We have also developed a general method for the production of high surface area nanostructured films (WO₃, ZnO, TiO₂, Pt) by utilizing electrochemically driven self-assembly of surfactants and a pulsed-electrodeposition scheme for depositing nanoparticulate pure metals (Pt, Au, Pd), alloys (Pt-Au, Pt-Ru) and metal oxides (WO₃) which we

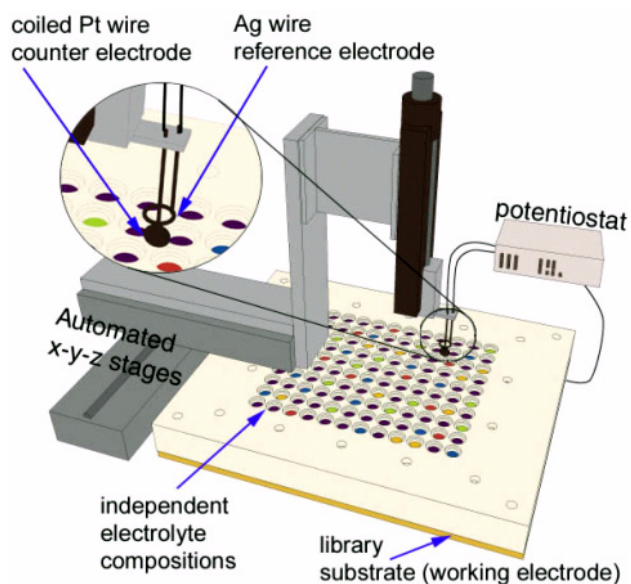


Figure 1. Automated Electrochemical Synthesis Based on Rapid-Serial Deposition (120 independent electrochemical cells are sealed upon a single 14 cm x 16 cm conductive substrate)

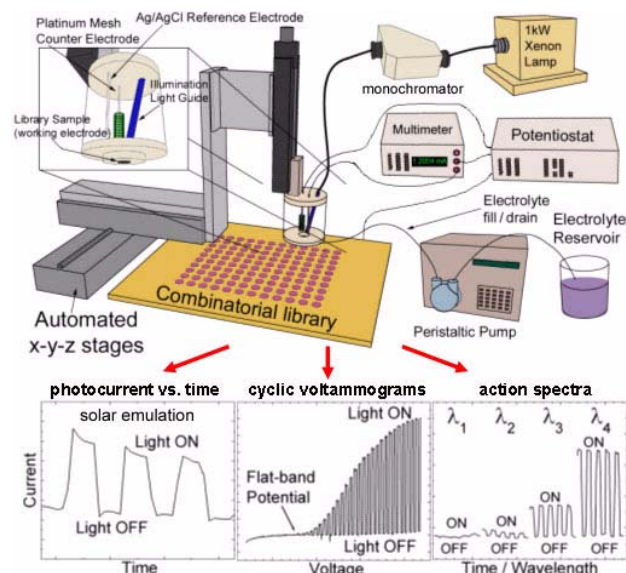


Figure 2. Automated Photoelectrochemical Screening (A unique photoelectrochemical probe is stepped across the library, analyzing one sample at a time in automated fashion, measuring photocurrent, photovoltage, cyclic voltammograms, action spectra, etc.)

have incorporated into our automated synthesis and screening systems. By virtue of a mesostructured morphology (features 2-50 nm in size), transport

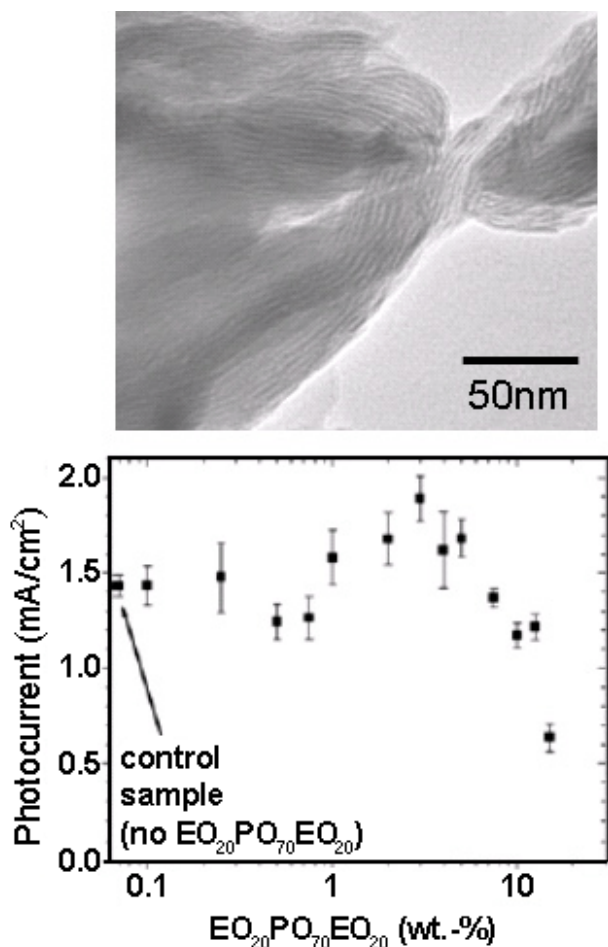


Figure 3. TEM Image of Mesostructured ZnO and Results of Zero-Bias Photocurrent Screening (3 wt.-% of the SDA gave rise to a 30% improvement in photocurrent.)

distances for charge carriers (electrons and electron vacancies) are decreased dramatically – thus, recombination can be mitigated, resulting in greater photoelectrochemical efficiency.

Mesostructured ZnO was synthesized by the addition of a block copolymer (EO₂₀PO₇₀EO₂₀) structure directing agent (SDA) during electrochemical synthesis. A 56-member library explored a range of the SDA from 0 to 15 wt.-%. Transmission electron microscopy (TEM) images, as shown in Figure 3, reveal lamellar planes, which were observed on all samples. Disordered mesopores were also observed (not shown). The high-throughput photoelectrochemical screening system was then used to characterize the samples. Figure 4 illustrates the trend of zero-bias

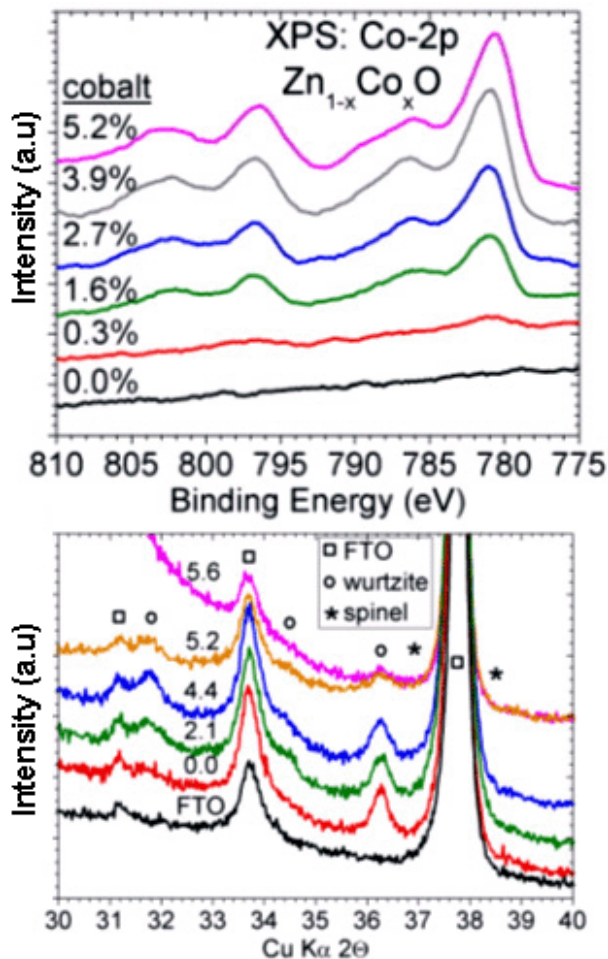


Figure 4. XPS (top) and XRD (bottom) of Zn_{1-x}Co_xO Library Samples (XPS reveals Co²⁺ as the predominant oxidation state, XRD shows the wurtzite structure is maintained regardless of composition.)

photocurrent for the samples as a function of the SDA concentration used during synthesis. Samples synthesized with low concentrations (< 1 wt.-%) of the SDA exhibited similar performance to the control ZnO sample; however, samples synthesized with 2 < [SDA] < 5 wt.-% showed improved performance, with a maximum at 3 wt.-%, where films demonstrated a 30% improvement over the control ZnO. Films deposited with high concentrations of the SDA (> 5%) performed poorly with respect to the control samples, presumably because of poor wall crystallinity.

Several hundred samples of different ZnO-based materials, exploring 24 different dopants, have been synthesized from a dimethyl sulfoxide (DMSO)-

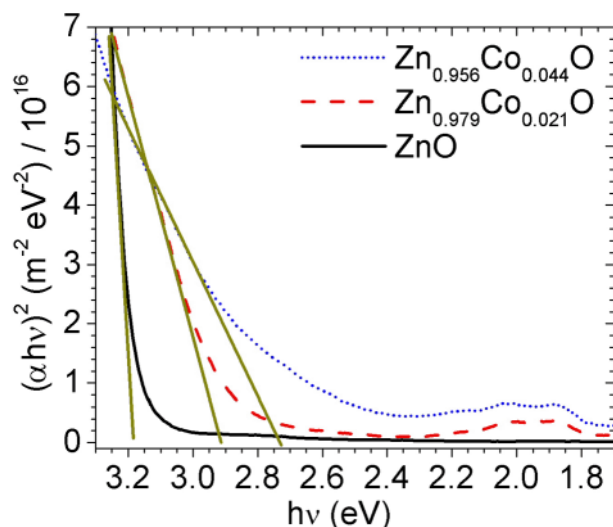


Figure 5. UV-Vis Spectroscopy of $Zn_{1-x}Co_xO$ Library Samples (Bandgap decreases with increasing cobalt, and characteristic Co^{2+} $d-d$ transitions are observed. Clearly, cobalt doping of ZnO gives rise to increased visible photon absorption.)

based electrodeposition bath and screened photoelectrochemically with the aim of improving visible photon absorption and photoelectrochemical efficiency. We have shown significantly increased visible band absorption of ZnO through substitutional doping with Co, and a 120-member library was synthesized to explore 27 Co dopant concentrations up to 7%. X-ray photoelectron spectroscopy (XPS) reveals that Co^{2+} is the predominant oxidation state of cobalt, and x-ray diffraction (XRD) confirms that the wurtzite structure (typical of pure ZnO) is maintained. Figure 5 illustrates a decrease in bandgap with increasing cobalt content, as well as Co^{2+} $d-d$ transitions in the 550-650 nm range, both of which represent increased visible photon absorption for cobalt-doped samples. Figure 6 exhibits results from photoelectrochemical screening. Under full illumination of the Xe lamp (which includes both UV and Vis radiation), photocurrent decreases as a function of increasing cobalt. When a UV cut-off filter is used to emulate the solar spectrum, however, a different trend emerges – photocurrent decreases with low cobalt concentrations (< 1%), but then climbs dramatically, reaching a maximum at 4.4% cobalt, where photocurrent is four times that of pure ZnO. After this point, photocurrent drops sharply, presumably due to increased defect-related

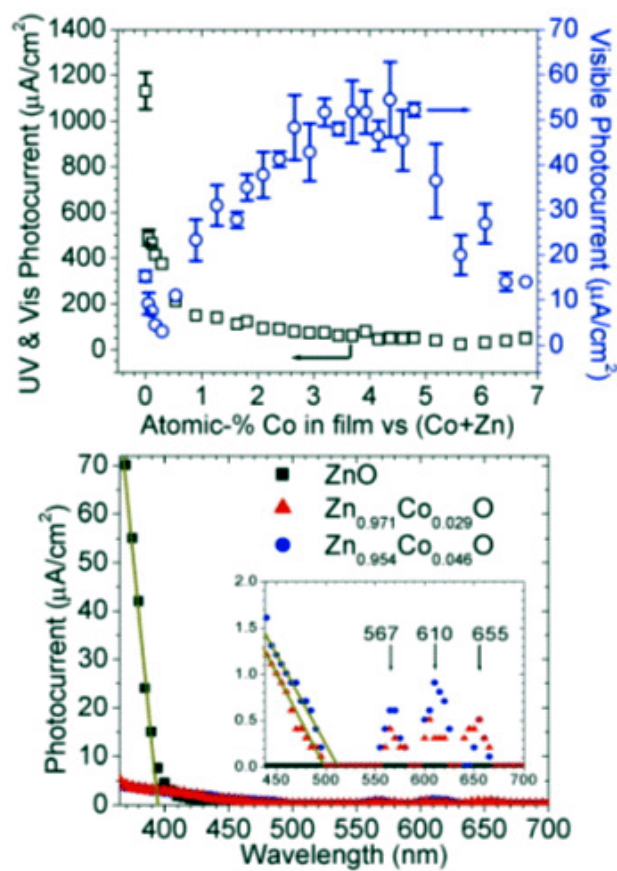


Figure 6. Zero-Bias Photocurrent Screening (top) and IPCE (bottom) of $Zn_{1-x}Co_xO$ Library Samples (Under solar-spectrum emulated irradiation, the photocurrent of $Zn_{0.956}Co_{0.044}O$ was 4 times that of pure ZnO. IPCE shows that the increased visible absorption observed in Figure 5 are responsible for the increased photoelectrochemical activity.)

recombination of charge carriers. Action spectra and IPCE were measured on select samples, revealing that the increased visible photon absorptions observed in Figure 5 give rise to increased photoelectrochemical activity.

Conclusions

- The methodology of combinatorial material science has been applied to expedite the discovery of improved photocatalytic materials for hydrogen production.
- WO_3 and ZnO host materials have been investigated extensively.

- Mesoporous ZnO demonstrated a 30% improvement in efficiency over a morphologically dense ZnO.
 - Cobalt-doped ZnO samples were explored in depth, with $\text{Zn}_{0.956}\text{Co}_{0.044}\text{O}$ exhibiting optimal performance, an efficiency four times that of pure ZnO.
5. E. McFarland, “*Fundamentals of electrocatalysis and photoelectrocatalysis in hydrogen production*” and “*Combinatorial methods for discovery and optimization of catalysts for hydrogen production*”, Presented at the International Summer School “Towards a Hydrogen-based Society”, Lyngby, Denmark, August 2003.

FY 2004 Publications/Presentations

1. 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 Comm.*, **2004**, 25, 297.
2. 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.*, **2004**, 4, 390.
3. S.-H. Baeck, T.F. Jaramillo, A. Kleiman-Shwarsstein, and E.W. McFarland, “Automated electrochemical synthesis and characterization of TiO_2 supported Au nanoparticle electrocatalysts”, *Meas. Sci. Tech.*, submitted (May 2004).
4. T.F. Jaramillo, S.-H. Baeck, A. Kleiman, K.-S. Choi, G.D. Stucky, E.W. McFarland, “Automated electrochemical synthesis and photoelectrochemical characterization of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ thin films for solar hydrogen production” in preparation (June 2004).
6. E. McFarland, “*High-throughput discovery of new and optimized metal oxide photocatalysts*”, Invited talk, Gordon Research Conference on Future Directions in Combinatorial Materials Science, January 2003.
7. E. McFarland, “*Combinatorial electrochemistry for the discovery of new and improved mixed metal oxide photoelectrocatalysts*”, Invited talk, General Electric, Corporate R+D Center, September 2003.
8. A. Kleiman-Shwarsstein, “*Automated spray pyrolysis system for hematite synthesis as a photocatalyst for hydrogen production*”, Poster, Presented at 227th American Chemical Society National Meeting, Anaheim, California, March 2004.
9. T.F. Jaramillo, “*Optimized materials for photoelectrochemical hydrogen production*”, Thesis defense, Dept. Chemical Engineering, University of California, Santa Barbara, June 2004.

