

## II.K.18 Combinatorial methods for the Improvement of Semiconductor Metal Oxide Photoelectrodes

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### Objectives

The main problem with photoelectrochemical water splitting is that no semiconducting materials are known that satisfy all the requirements necessary to construct an efficient and stable solar photoelectrolysis system. Metal oxide semiconductors can satisfy the stringent requirement that a photoelectrode will be stable in an electrolyte under full or concentrated sunlight for many years. However no stable metal oxide semiconductors with the proper band gap and band positions are known. Therefore we have developed a combinatorial search strategy to quickly and efficiently produce many thousands of metal oxides and screen them for photoelectrolysis activity.

### Technical Barriers

- A metal oxide semiconductor that can meet stability and efficiency requirements will probably contain at least three different metals, greatly increasing the number of potential materials to be produced and screened.
- Once several promising materials are identified it will take considerable effort to optimize the electronic properties and nanostructured morphology to final have a few materials to construct a practical and efficient photoelectrode for a solar water splitting system.

### Abstract

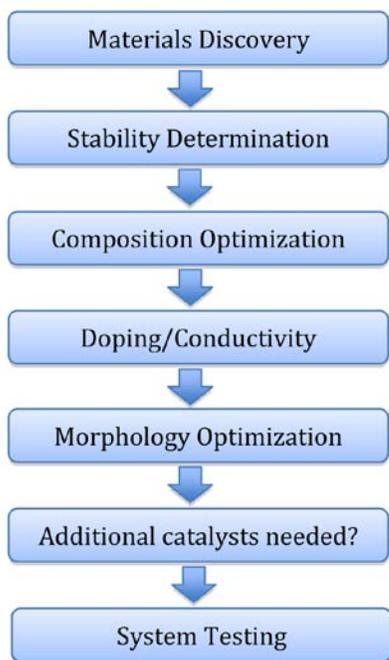
A combinatorial method to produce and screen for efficient photoelectrolysis activity was developed. The method employs high-throughput ink-jet printing of patterns of multiple oxide precursors onto conductive glass substrates. Subsequent pyrolysis yields a library of oxide electrodes that are screened for photoelectrolysis activity by immersing in an electrolyte and scanning a laser over the electrodes to map the photocurrent response.

Iron oxide is a d-band semiconductor that serves as a prototype for a future material that may be useful in a photoelectrolysis device. Therefore it is useful to explore how to optimize the photoactivity of this material. Since there are literature reports that “doping” small amounts of impurities could greatly influence the properties of  $\alpha\text{-Fe}_2\text{O}_3$ , we investigated the effect of adding small amounts of Ti, Si, and Al on the photoelectrochemical activity of  $\alpha\text{-Fe}_2\text{O}_3$  was investigated using our combinatorial protocols. When Si and Al are individually added to iron oxide at the levels we studied, the photoelectrolysis activity decreased whereas low levels of Ti addition enhanced the photocurrents. Synergistic effects were observed resulting in enhanced photocurrents when multiple impurities were added to  $\alpha\text{-Fe}_2\text{O}_3$ .

It was also found that the photoelectrolysis activity of the Bi-V oxides could be improved by the addition of various levels of W, Cu, Fe, Mg and Mn to Bi-V binary oxides. Some Bi-V-W ternary oxides had improved photoresponse of up to 18 times of that of the well-known  $\text{BiVO}_4$  phase whereas Bi-V-Mo ternary oxides had very little photoresponse. However, when elements like Fe, Cr and Mg were introduced to the Bi-V-Mo oxides, their photoresponse could be increased.

### Progress Report

With DOE Hydrogen Program support we have been pursuing a novel high throughput combinatorial search strategy for the identification of multicomponent metal oxide materials with suitable band gaps and band positions for water photoelectrolysis operating as either a photoanode or a photocathode. Our combinatorial search strategy uses ink jet printing of overlapping patterns of metal oxide precursors on to conductive glass substrates. Metal nitrates, one class of simple oxide precursors that we use, decompose to form metal oxides, oxygen and  $\text{NO}_2$  by heating at relatively low temperatures (500 °C). Scanning a laser over the printed and fired electrodes while it is in an electrolyte produces a false color map of photocurrent response that can be related to the printed compositions. It is desirable for many groups to help with this search since it is easy to calculate the numbers of combinations that may have to be produced and screened. If we prepare all possible ternary oxides, mixing N materials three at a time there are  $N!/3!(N-3)!$  combinations if we only consider 1:1:1 stoichiometries. Since there are ~60 possible candidate metals in the periodic table this results in >34,000 combinations to be produced and tested with only this simple stoichiometry. If a quaternary material is needed then there are  $N!/4!(N-4)! > 480,000$  possible combinations. Again these numbers do not consider producing and screening the many possible stoichiometries. It is also possible that a ternary or quaternary material



**FIGURE 1.** A flow chart illustrating the steps from a combinatorial discovery process through composition and conductivity optimization and progressing through configuring the materials for high device efficiencies.

will require small amounts of an additional element that acts as an electrical dopant to optimize its conductivity. These small amounts can often exist as impurities in the metal oxide precursors or may have to be discovered by additional combinatorial screening (discussed later in this chapter) greatly multiplying the number of experiments that must be done. However, some combinations could be excluded because it would not make sense to, for example, mix only large band gap oxide materials (i.e. Ti-Zr-Si-Y oxides) and expect visible light absorption. It is clear that given the large number of possible mixtures that need to be produced, a “high throughput” approach is needed as well as multidimensional experimental design to explore the parameter space more rapidly. And while it may not be reasonable to produce and test ALL of the possible combinations, it is certainly imperative that the throughput of materials screening be rapid relative to the serial approaches previously used.

### Future Directions

New metal oxide semiconductors will be produced and screened for photoelectrolysis activity. Also we will be following up on “hits” obtained by the SHaRK (Solar Hydrogen Activity research Kit), our outreach program that provides the tools to undergraduate and high school students to join the search for the “holy grail” of

photoelectrochemistry. Currently we have over 40 sites participating. We will also support the efforts of DOE’s newly funded Solar Hub at Caltech who have taken our idea and will expand it to an automated robotic high throughput screening.

### Publication list (including patents) acknowledging the DOE grant or contract

1. Michael Woodhouse and B.A. Parkinson, “Combinatorial Approaches for the Identification and Optimization of Oxide Semiconductors for Efficient Solar Photoelectrolysis”, *Chemical Society Reviews*, 38(1), 197-210, (2009)
2. Michael Woodhouse and B.A. Parkinson, “Combinatorial Discovery and Optimization of a Complex Oxide with Water Photoelectrolysis Activity”, *Chemistry of Materials*, 20(7), 2495-2502, (2008)
3. B.A. Parkinson, “Distributed Research: A New Paradigm for Undergraduate Research and Global Problem Solving”, *Energy & Environmental Science*, 3, 509-511, (2010)
4. Aron Walsh, Su-Huai Wei, Yanfa Yan, M.M. Al-Jassim, John A. Turner, Michael Woodhouse, and B.A. Parkinson, “Structural, magnetic, and electronic properties of the Co-Fe-Al oxide spinel system”, *Phys. Rev. B*, 76, 165119, (2007)
5. B.A. Parkinson and M. Woodhouse, “A Digital Method for the Identification of Photoelectrolysis Catalysts for Water”, *Digital Fabrication*, R. Mills, Ed., The Society for Imaging Science and Technology: Baltimore, MD, p190-193, (2005)
6. Michael Woodhouse, G.S. Herman and B.A. Parkinson, “A Combinatorial Approach to Identification of Catalysts for the Photoelectrolysis of Water”, *Chemistry of Materials*, 17, 4318-4324, (2005)
7. Jianghua He and B. A. Parkinson, “A Combinatorial Investigation of the Effects of the Incorporation of Ti, Si, and Al on the Performance of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Photoanodes”, *ACS Combinatorial Science*, in revision
8. Chunping Jiang, Ruilin Wang and B.A. Parkinson, “A Combinatorial Approach to Improve Photoelectrodes Based on BiVO<sub>4</sub>”, in preparation
9. In addition Frank Osterloh and B.A. Parkinson were guest editors for a special issue of the Materials Research Society Bulletin in January 2011 focused on Solar Hydrogen Production.