Lee R. Sharpe. (b. 1960) Associate Professor. B.A., 1983, Ripon College; Ph.D., 1987, University of Wisconsin - Madison; Postdoctoral Fellow, 1987-1989, University of Cincinnati; Visiting Assistant Professor, 1995-1996, University of North Carolina - Chapel Hill; Visiting Research Fellow, University of Oregon, 2003. ANALYTICAL CHEMISTRY. Semiconductor based Chemical Sensors, Hydrogen Photocatalysts, and CE of inorganic ions. (641) 269-3008. sharpe@grinnell.edu

Introduction

Our research involves the study and testing of a variety of semiconductor materials for the development of catalysts for the photoelectrolysis of water to produce hydrogen using sunlight and the development of luminescent-based chemical sensors. The first project is a joint project with faculty and students from ~10 other institutions. Both areas of research are of national interest. The need for better environmental monitoring and sensing of chemical agents requires the development of better and more selective chemical sensors. The development of a hydrogen economy requires an efficient, sustainable method for producing hydrogen. The chemical sensor project is an ongoing project that has resulted in a couple papers with the latest work in preparation for publication. The Solar Hydrogen project was started two summers ago and my MAP students presented our results at the CCI Solar Annual Retreat in Huntington Beach, CA, January 29-31 and at the Regional ACS meeting in the fall. This summer's work will focus on the hydrogen project however if we produce any luminescent materials we will test their potential as chemical sensors as well.

Production of Hydrogen from Water and Sunlight

Over 30 years ago a TiO_2 electrode produced hydrogen from water without decomposition under UV illumination. The problem is that the absorption of light by TiO_2 does not overlap well with the solar spectrum. Other materials such as GaAs and CdSe have been found to slowly photocorrode under illumination in typical electrolytes. The only electrolytes that protect these materials are Se^{-2} and Te^{-2} which are too air sensitive to be practical. This project will involve looking through a wide range of mixed metal oxides for a composition that can use sunlight to convert water to hydrogen or oxygen without decomposition and fully utilize the solar spectrum. In some ways it is a search for the "Holy Grail." In comparison, the best high temperature superconductors are composed of up to 5 different metal oxides. As a result of the millions of possibilities, this is a combinatorial project. We will be working with several groups around the nation testing a range of mixed metal oxide compounds to identify ones that can oxidize water to oxygen and others that can reduce water to hydrogen. In effect we are looking for two "Holy Grails." The idea is to use two different materials; one for oxidation and the other for reduction, both having smaller band gaps than TiO_2 and thus make good use of the solar spectrum.

The experiment involves the deposition of metal ion solutions onto conductive glass substrates by spray pyrolysis using an airbrush and controlled by a Lego Mindstorms® apparatus, **Figure 1**. The films are then dried and fired at 500°C in air to form the oxides. The resulting films are tested by scanning a green Laser over the surface of substrate while the metal oxide coated substrate is hooked up in an electrochemical cell to see if any of the metal oxide mixtures demonstrate photocatalytic behavior. In order to test a wide range of compositions efficiently, we spray gradients of each metal ion solution onto the substrate in which three elemental oxides will be mixed in ternary ratios as shown in **Figure 2**.

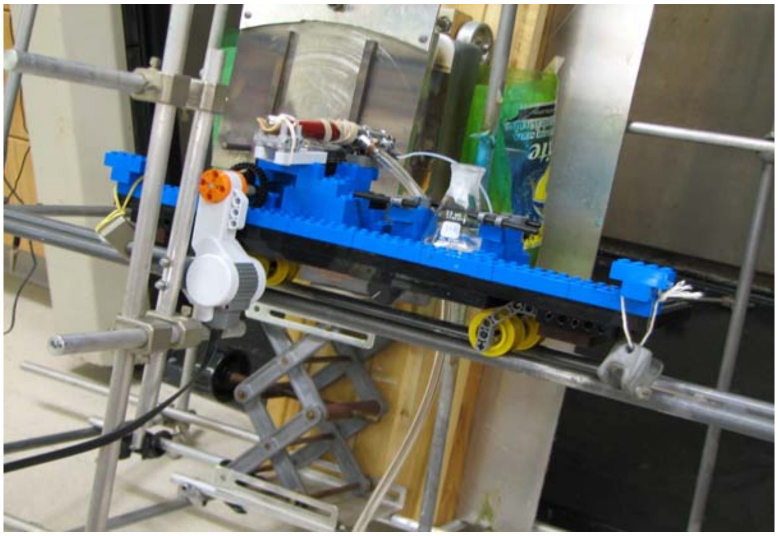

Figure 1

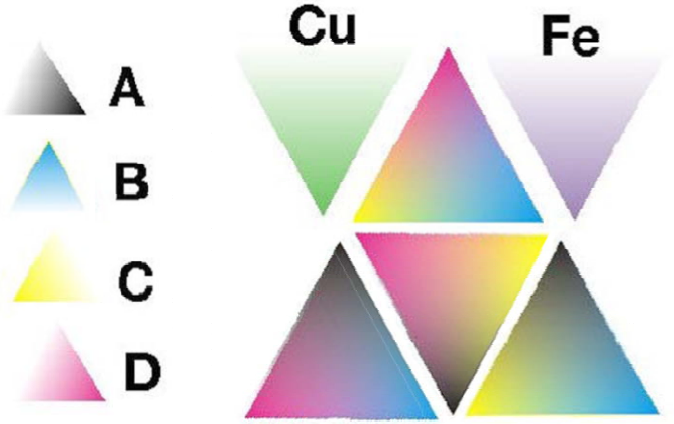

Figure 2

In this way we can explore all the possible combinations of three metal oxides; the single metal oxides in the corners (black, blue, yellow, and pink), the varying binary mixtures along the edges and the varying ternary mixtures in the middle. The pattern on the substrate has six triangles, four three metals at a time which will cover all the ternary combinations of four metal oxides and two reference material triangles at the top left and right. CuO is the hydrogen producing reference and Fe_2O_3 is the oxygen producing reference material. The performance of all our mixed metal oxides is compared to these two references.

The metal oxide films are tested as photocatalysts by placing them in an electrochemical cell containing 0.1M Na_2SO_4 and then scanning a green laser over the surface under applied potential while monitoring any photocurrent using the Lego Mindstorms® based apparatus in **Figure 3**.

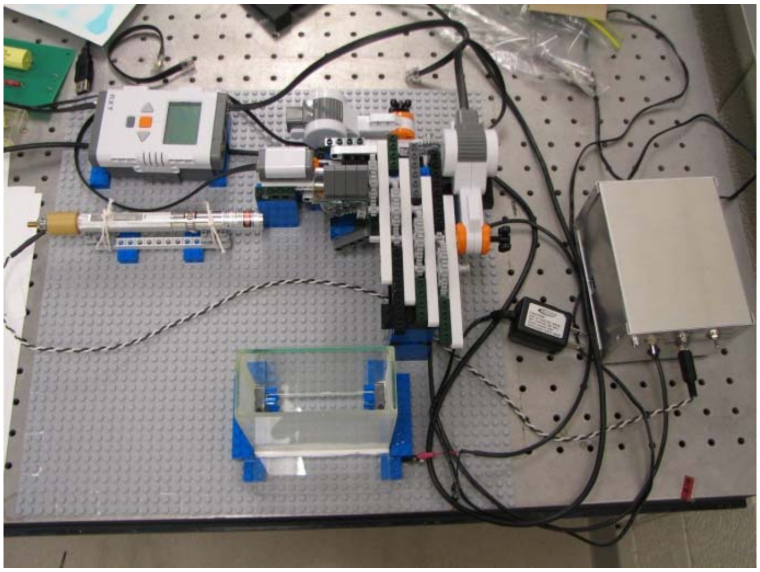

Figure 3

An “image” of the sample highlights the photoelectrochemical active areas and thus promising metal oxide compositions that can be explored in more detail. **Figure 4** is an example of data collected last summer for a positive scan which highlights materials that oxidizes water into oxygen.

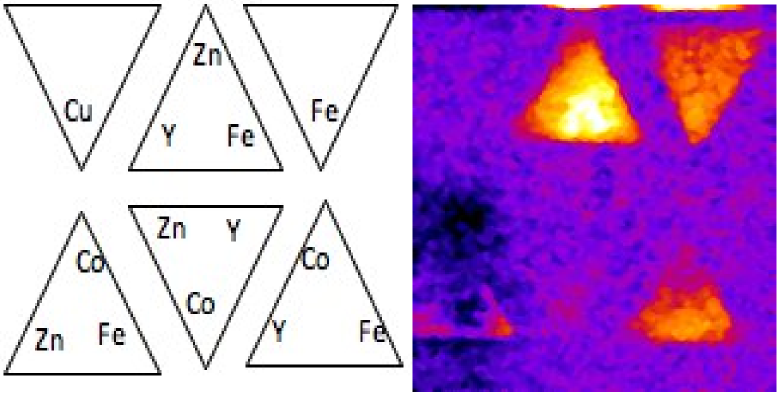

Figure 4

The “brighter” areas correspond to metal oxide compositions giving rise to photocurrent or in other words converting optical energy into chemical energy; the brighter the image, the larger the photocurrent being produced (the samples do not actually glow). One can see that the Zn, Y, Fe triangle is more photoelectrochemically active than the iron oxide triangle indicating a successful composition to be further investigated.

The next thing we do is go to Iowa State University to take a look of the sample under a Scanning Electron Microscope and to have the elemental compositions of the “hot” spots determined by Electron Microprobe. The results for the above sample showed that the “hot” spot is composed of mostly yttrium and iron with just a small amount of zinc. Then we refine the composition by preparing solutions straddling this composition and confirm the photoactivity.

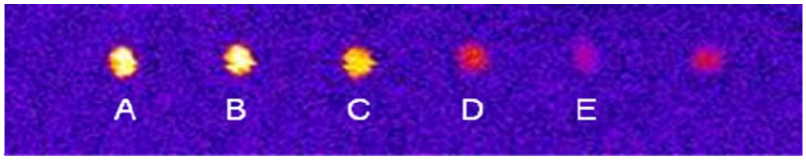

Figure 5

Figure 5 is the result of a grid template comparing Fe:Y ratios of 40:60, 45:55, 50:50, 55:45, and 60:40 in circles A, B, C, D, and E respectively. The last dot is the iron oxide reference.

The final step is to produce an electrode of the optimized material in both composition and thickness and photoelectrochemically characterize it for solar conversion efficiency.

Specific Projects for the Summer of 2010:

1. We have demonstrated that the spray pyrolysis method works so the first thing to do is to rebuild the cage that holds the spray apparatus to improve its stability and repair the damage done to it when I moved it into storage (sorry Clair and Stephanie).
2. Look further at the successful metal oxide combinations from last summer to evaluate them for commercial applications by further optimizing there compositions, thickness, and finally evaluate their solar conversion efficiency.
3. Continue to produce and test new metal oxide films for their ability to photoelectrolyze water.

References

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