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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 renewable energy infrastructure requires the ability to chemically store solar energy. 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 four summers ago and my MAP students have presented our results at both regional and national ACS meetings, the CCI Solar Annual Retreat, and most recently the Midstates Research Symposium. This summer I plan to have 2 students focus on the hydrogen project and one student work on the chemical sensor project.

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 glass sprayer 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**.

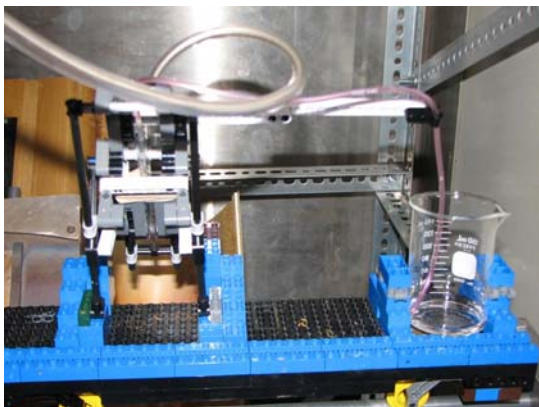


Figure 1

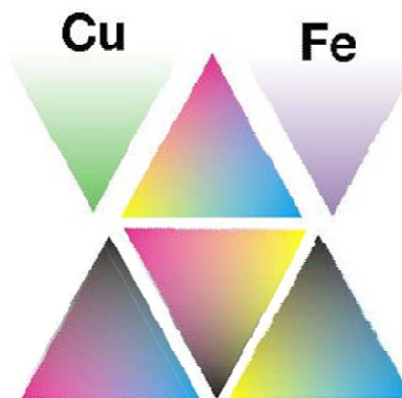


Figure 2

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 Fe₂O₃ 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 Na₂SO₄ 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**.

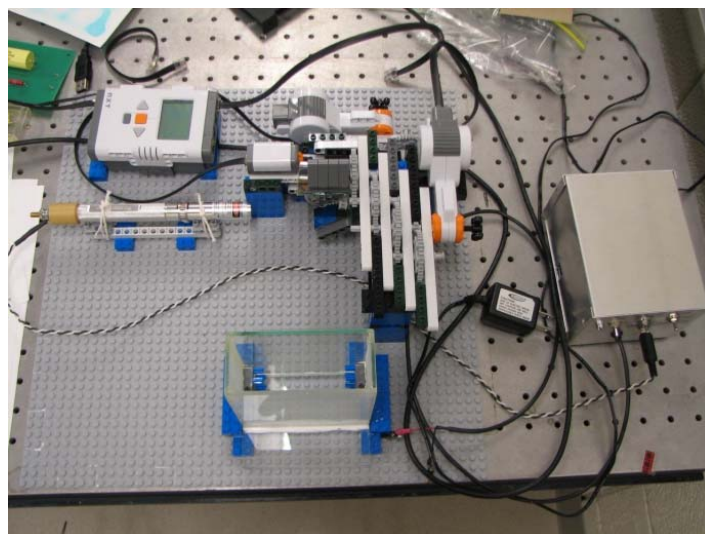


Figure 3

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 for a positive scan which highlights materials that oxidizes water into oxygen.

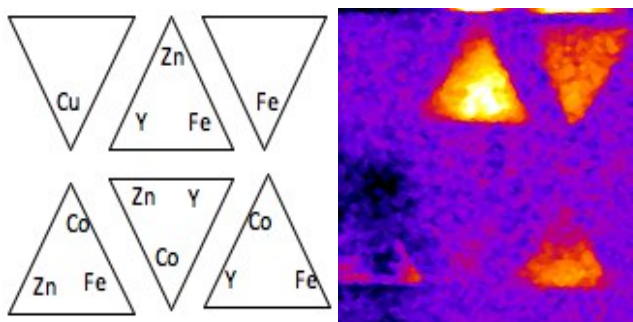


Figure 4

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.

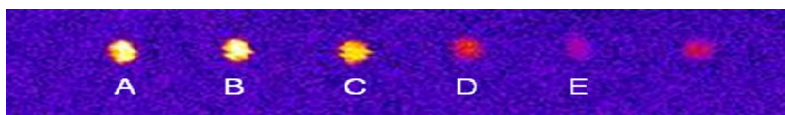


Figure 5

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. First we measure current voltage curves under illumination and in the dark. We then measure a photoaction spectrum which is a plot of photocurrent vs. wavelength. Capacitance as a function of voltage is also measured.

Chemical Sensor Project

Our sensors indicate the presence of a gas by changes in the photoluminescence, PL, intensity relative to nitrogen as a reference gas. We have been exploring a variety of powdered semiconductor phosphors primarily developed in the 1960’s and early 1970’s for use in lighting and colored television as candidates for optically coupled chemical sensors. Powdered phosphors

are relatively easy to prepare, stable, brightly emissive, and appear to be highly selective as chemical sensors. As a result, sensors can be developed that do not consist of single-crystal components or colloids and do not require laser excitation. In addition, a wide variety of chemically different phosphors with different impurities (added to increase the fluorescence) can be investigated in an effort to understand how the chemical make-up of the surface affects the sensor response. Our hope is the development of a family of chemical sensors based on these powdered phosphors that have both good sensitivity and complementary selectivity so that they may be used in gas sensor arrays. In the few powdered phosphors that we have investigated, we have found a significant difference in the response of the different phosphors to different gases. In addition, studying changes in PL upon exposure to various substances provides a novel means to explore the surface chemistry at the solid/gas interface.

Our work demonstrates that sensors based on the PL of semiconductor materials can be developed that are highly selective toward certain compounds and the selectivity can be varied by changing the composition of the semiconductor.

Completed Work and Findings: Our original success with this project was centered on the powdered tellurium doped CdS phosphor, pCdS:Te and later CaS based phosphors in addition to SrS, ZnS and more recently ZnO based phosphors. pCdS:Te is easily prepared and is brightly emissive having a emission maximum of 670 nm (red-orange in color). When exposed to sulfur dioxide, there is a distinct decrease in the PL intensity as shown in **Figure 6**. The wavelength of the emission does not change, just the PL intensity. On the left side is the PL spectrum of the pCdS:Te under a nitrogen atmosphere and then moving off to the right is the PL intensity at 670 nm resulting from alternating the exposure between nitrogen and various concentrations of sulfur dioxide. The PL response is both reversible and reproducible and the magnitude of the PL change is dependent on the concentration of the sulfur dioxide.

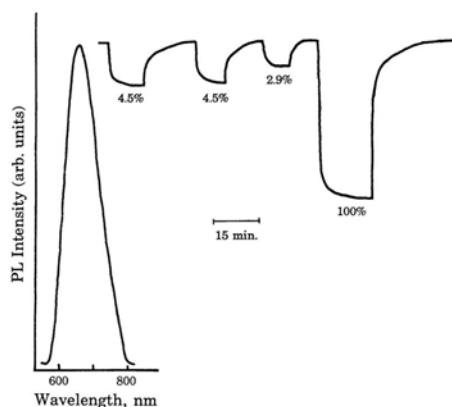


Figure 6 a) Exposure to sulfur dioxide

This summer I wish to focus on ZnO based phosphors. ZnO phosphors are easily prepared but only work as sensors at high temperature. In order to study the powdered ZnO samples they will need to be “glued” onto a temperature controlled immersion tube using a sol gel technique or thin films will need to be grown onto the immersion tube using the spray pyrolysis method.

Specific Projects for the Summer of 2012:

1. Explore electrolyte/surface equilibrium processes by capacitance measurements.
2. Continue to produce and test new metal oxide films combinations and evaluate their ability to produce solar fuels.
3. Get the chemical sensor project/equipment up and running again and investigate ZnO phosphors and/or ZnO thin films as high temperature chemical sensors.

References

Solar Fuel Project:

Project websites: <http://www.thesharkproject.org/> ; <http://www.ccisolar.caltech.edu/>

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CaS paper in preparation