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## **Introduction**

Our research involves the study and testing of a variety of semiconductor materials for the development of phosphor-based chemical sensors and the development of catalysts for the photoelectrolysis of water to produce hydrogen using sunlight. The second 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.

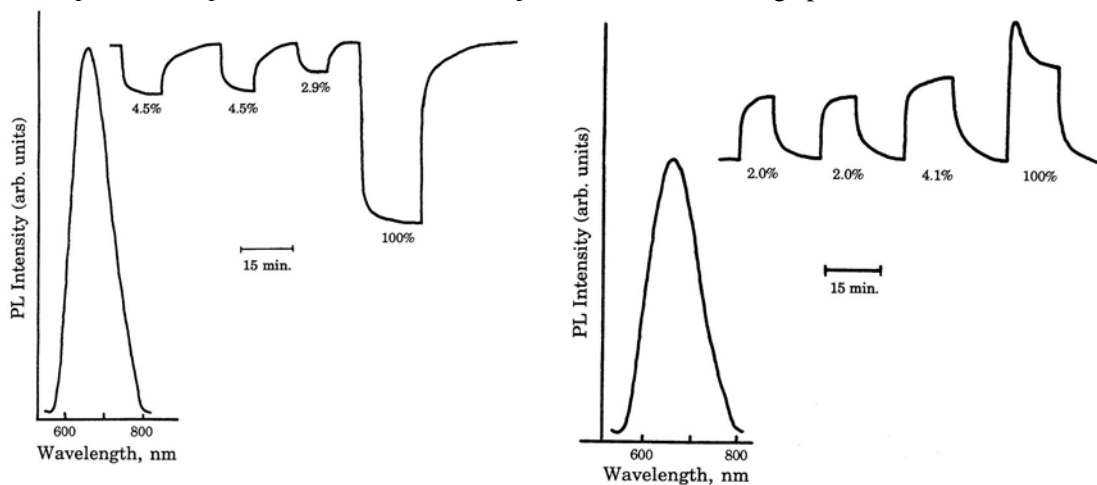
## **Chemical Sensor Project**

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.<sup>1,2</sup> and later CaS<sup>3</sup> 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 1a. 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 1b shows how pCdS:Te responds to ammonia. Again the PL response is both reversible and reproducible and the magnitude of the PL change is dependent on the concentration of ammonia. In this case, however, the PL increases upon exposure to ammonia as opposed to decreasing under sulfur dioxide exposure. Exposure to 100% ammonia produces an interesting spike.



**Figure 1** a) Exposure to sulfur dioxide

b) Exposure to ammonia

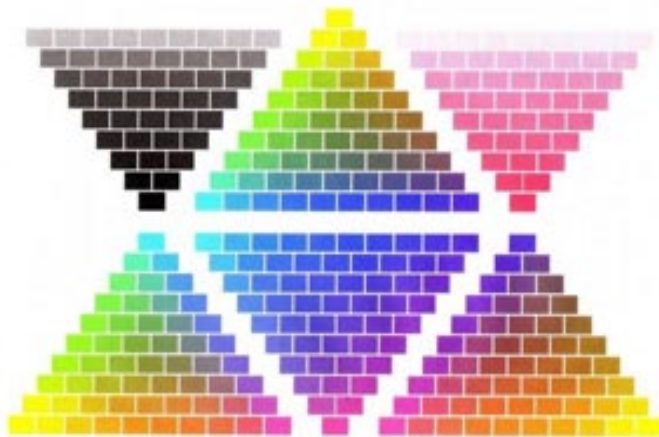
This summer I wish to focus on ZnO and ZnSiO<sub>4</sub> based phosphors. ZnO phosphors are easily prepared but only work as sensors at high temperature. In order to study the powdered ZnO samples they will need to be “glued” onto a temperature controlled immersion tube using a sol gel technique or thin films will need to be grown onto the immersion tube using the spray pyrolysis method described below. ZnSiO<sub>4</sub> doped with Mn is a well know green emitting phosphor that will be the next phosphor to synthesize and test as a chemical sensor.

### **Production of Hydrogen from Water and Sunlight**

Over 30 years ago TiO<sub>2</sub> electrodes produced hydrogen from water without decomposition under UV illumination.<sup>4</sup> The problem is that the absorption of light by TiO<sub>2</sub> does not overlap well with the solar spectrum. This project is very much a search for the “Holy Grail.” Looking through a wide range of mixed metal oxides for one that can use sunlight to convert water to hydrogen and oxygen without decomposition and fully utilizing the solar spectrum. 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.<sup>5</sup> 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 having smaller band gaps than TiO<sub>2</sub> and thus make better use of the solar spectrum.

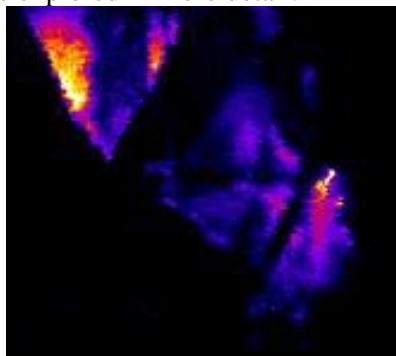
The experiment will involve the deposition of metal ion solutions onto conductive glass substrates by spray pyrolysis controlled by a Lego Mindstorms® apparatus. The films are then dried and fired at 500°C for 24 hours in air to form the oxides. The resulting films are tested as electrodes under illumination to see if they demonstrate any photocatalytic behavior. In order to

test a wide range of compositions efficiently, we will spray gradients of the metal ion solutions onto the substrate in which three elemental oxides will be mixed in ternary ratios.



In this way we can explore all the possible combinations of the three metal oxides; the single metal oxides in the corners (yellow, light blue, dark blue, 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.

The metal oxide films are tested as photocatalysts by placing them in an electrochemical cell containing 0.1M NaOH and then scanning a green laser over the surface under applied potential while monitoring any photocurrent using another Lego Mindstorms® based apparatus. An “image” of the sample highlights the photoelectrochemical active areas and thus promising metal oxide compositions that can be explored in more detail.



The Colored areas correspond to metal oxide compositions giving rise to photocurrent, the brighter, the greater the photocurrent.

### **Projects:**

1. Continue development of sensors that are composed of chemically different phosphor materials specifically  $\text{ZnSiO}_4\text{:Mn}$ .
2. Test and use a developed Sol Gel method to immobilize ZnO phosphor powders or use the spray pyrolysis method to grow thin ZnO films. Next test ZnO to explore and quantitate how well it will function as a high temperature sensor.
3. Produce and test a range of metal oxide films for their ability to photoelectrolyze water.

## References

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