

Christy Lewis

Professor: Kim Gray

Photo-oxidation reactions by functionalized TiO₂ catalysts with visible response

Introduction

The energy portfolio of the future will rely heavily on technologies that harvest the sun's energy. Yet, great advances first have to be made in converting this radiative energy into high density chemicals which are easy to store. Among these technologies TiO₂-based materials are good candidates due to their stability and good electron conduction properties. Their light absorption capability is limited to the UV part of the spectrum, and can consequently only harvest 5% of the sun's energy. This project will investigate the use of small molecules (catechol and salicylate derivatives) as TiO₂ sensitizers that extend the light absorption into the visible range, and drive an oxidation reaction so that CO₂ can be converted to a fuel.

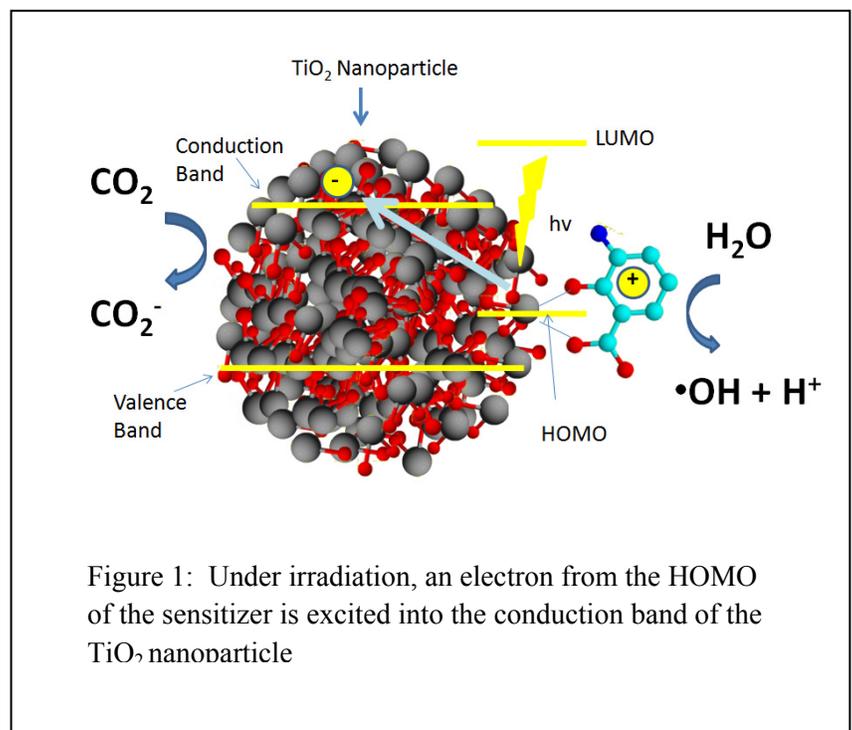
Background

TiO₂ materials have been widely investigated across photocatalytic applications, from solar energy fuel production such as water splitting and carbon dioxide reduction, to energy remediation purposes in the photodegradation of organic pollutants.¹ A strong limitation is their weak absorbance of the solar spectrum region (~5%) which has pushed researchers to extend the photoresponse both by the introduction of dopants or by the use of organic dyes and sensitizers.²

Work in the Gray group and the Rajh group at Argonne has shown that the adsorption of certain sensitizers onto the surface of TiO₂ can shift the photoexcitation response into the visible region, and therefore enhance the photocatalytic capability of the TiO₂ surface.³ The experiments show that an electron is promoted from the highest molecular orbital of the sensitizer to the conduction band of TiO₂ (seen in Figure 1).

These differ from dye-sensitized solar cells² in that the injection occurs directly into the conduction band, indicated a much tighter coupling between adsorbate and

semiconductor. The hole remaining on the sensitizer has drastically different properties than a hole in the valence band of TiO₂ which would be the case upon UV irradiation of the bare semiconductor. While TiO₂ has been shown to reduce CO₂ to various fuels,⁴ for the successful application of these sensitized TiO₂ systems for photocatalysis, the sensitizer cation radical needs to drive the oxidation that was taking place at the valence band of bare TiO₂. (Fig. 1). This project will first investigate the redox properties of the cation radical resulting from charge injection into the semiconductor in order to fully understand its potential reactivity. Different approaches have been used using metallo-organic catalysts,^{5,6} however this family of materials has not been investigated before for this type of oxidation reaction and could result in a very simple, inexpensive catalyst for solar fuel production.



Christy Lewis

Professor: Kim Gray

Photo-oxidation reactions by functionalized TiO₂ catalysts with visible response

Research Questions

Although research has shown that the electron in the conduction band of TiO₂ can be used to reduce different molecules, there has yet to be any research surrounding the oxidation potential of the cation radical. In this case, a number of crucial questions remain unanswered. What is the redox potential of sensitizer molecules when adsorbed on the semiconductor surface? Do these vary as a function of metal oxide? Can they produce OH radicals?

The first task will be to determine the redox potential of candidate sensitizer molecules when they are adsorbed on the semi-conductor surface. Using cyclic voltammetry, I will determine the redox potential of these molecules and their corresponding capacity to generate OH radicals.⁷ Target molecules will include amine derivatives which can also serve as proton shuttles. During my previous research work in this lab, I showed that the amino group actively participates in the charge transfer process and that it also responds to environmental perturbations such as metal ion concentration, justifying further investigation into its interaction with substrates of interest in photochemical transformations. After the best molecules are selected, I will proceed to test them in a photocatalytic cycle to determine intermediates and products using a reactor equipped with a quartz window and a GC equipped with an FID and TCD detectors. I will begin the exploration of synthetic modifications to the adsorbate to tune its oxidation potential. This will involve spectroscopic techniques such as Raman, NMR, and IR along with organic synthesis procedures.

Preparation

To realize this research, I have immersed myself in science and engineering courses for the past 3 years. Through the Environmental Engineering curriculum, I was exposed to chemistry and quickly developed a strong interest. In fall of my sophomore year, I decided to pursue a minor in Chemistry. In the winter of my sophomore year, I began research with Daniel Finkelstein-Shapiro of Kimberly Gray's lab. During my 4 quarters of independent and guided research, I investigated photocatalytic systems of TiO₂ and various adsorbates using IR, NMR, and Raman. Through this research I have been able to develop my ability to plan, execute, and analyze experiments involving synthesis and spectroscopy. After working with these experiments for several quarters, I discovered that within the realm of chemistry, my interests are largely associated quantum level electronic processes and spectroscopy. In order to fully understand the electron transfer processes that I have been researching, I completed coursework in Quantum Mechanics and Spectroscopy and Organic Chemistry. These classes, along with the background in science classes I have gained through the basic engineering requirements, have enabled me to understand the fundamental concepts involved in this research, and have given me the tools to expand my knowledge in chemistry through running and analyzing experiments.

I decided to pursue a summer research opportunity for several reasons. First, I have developed a very strong interest in photocatalysis on TiO₂ and the related processes, and I am excited to apply the knowledge I gained in my recent coursework. I will be starting this project in spring quarter using my work study money to fund the research. Continuing into next year, I intend to continue this project during the school year. I think the experience of full-time research will be extremely valuable for my future, and will provide me with the knowledge I need to pursue a graduate degree in Chemistry.

Christy Lewis

Professor: Kim Gray

Photo-oxidation reactions by functionalized TiO₂ catalysts with visible response

References

- (1) Fujishima, A.; Zhang, X.; Tryk, D. A. *Surface Science Reports* **2008**, *63*, 515.
- (2) Michael, G. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **2003**, *4*, 145.
- (3) Finkelstein-Shapiro, D.; Hurst, S. J.; Gosztola, D.; Dimitrijevic, N.; Gray, K.; Rajh, T.; Pilarisetty, T.; Mujica, V. *In preparation*.
- (4) Dimitrijevic, N. M.; Vijayan, B. K.; Poluektov, O. G.; Rajh, T.; Gray, K. A.; He, H.; Zapol, P. *Journal of the American Chemical Society* **2011**, *133*, 3964.
- (5) Kanan, M. W.; Surendranath, Y.; Nocera, D. G. *Chemical Society Reviews* **2009**, *38*.
- (6) Hull, J. F.; Balcells, D.; Blakemore, J. D.; Incarvito, C. D.; Eisenstein, O.; Brudvig, G. W.; Crabtree, R. H. *Journal of the American Chemical Society* **2009**, *131*, 8730.
- (7) Ishibashi, K.-i.; Fujishima, A.; Watanabe, T.; Hashimoto, K. *Journal of Photochemistry and Photobiology A: Chemistry* **2000**, *134*, 139.