

- 1) Student Name: Anthony Krenselewski
- 2) Faculty Mentor: Dr. Luis Fernandez-Torres
- 3) Project Title: Synthesis of Nanostructure Materials for Bulk Heterojunction Photovoltaic Devices
- 4) During my research I was trained in the use of the X-ray Photoelectron Spectroscopy and the Scanning Electron Microscope, which are both extremely useful tools in the characterization of unknown compounds.
- 5) My research has potential practical application in the fabrication of solar energy devices. If the materials we have synthesized possess useful conductive and photovoltaic properties they could be implemented in constructing more efficient solar panels.

Today's energy demands place significant strain on available resources. Solar energy holds promise for relieving this stress through its ability to produce energy from a practically limitless resource, sunlight. However, current technology is not efficient enough to be practical in today's global society. Our project focused on the novel syntheses of materials that could potentially be implemented as an electrode or electrolyte in the design of new, more efficient solar cells. Particular emphasis was placed on molecular structures on the nano scale, as well as syntheses performed under mild conditions, specifically atmospheric pressure, temperatures below 100° C, neutral pH, and in aqueous or ethanolic solutions.

In all of our investigations, our primary tool for characterization of undetermined compounds was the use of X-ray Photoelectron Spectroscopy (XPS). However, we also used a number of other methods in addition to this including Infrared, Ultraviolet, and Nuclear Magnetic Resonance Spectroscopies. We utilized the Scanning Electron Microscope for the imaging of the molecular structures.

Our initial investigations centered on reactions involving sulfur- and selenium-containing organic compounds. Our only real success in this area came about with a reaction involving a diiodothiophene and selenourea in a dimethyl sulfoxide solvent in the presence of a copper (II) oxide catalyst and slightly basic conditions. This yielded a poly(2,5-diselenothiophene) (see figure 1), which we believed might exhibit the conductive or photovoltaic characteristics we had hoped to develop. However, when we began to investigate the reactive properties of this molecule we obtained very poor results. We attempted to bond the poly(2,5-diselenothiophene) to a number of metal sulfides and selenides, several long carbon chain linking molecules, and Cadmium metal, but the XPS showed no successful bonding. This would of course make implementation of this molecule into a solar cell difficult unless some successful bonding method can be found.

We then moved on to try and develop and investigate metal sulfides and selenides, specifically those involving copper and mercury. We discovered that solutions of copper and mercury when reacted with thiourea, thioacetamide, and adamantanethiol, yielded their respective sulfides. The reaction of these solutions with selenourea yielded the selenide form. Our next important discovery came when we attempted to build a self-assembled monolayer of the copper sulfide. We discovered that by dipping a gold substrate in alternating solutions of

$\text{Cu}^{2+}$  and Thioacetamide repeatedly, we could obtain a layering of the copper sulfide, meaning that it would build upon itself.

Our final task was to investigate the electrical properties of metal sulfides and selenides. For this experiment we decided to use a cadmium selenide instead of the metal sulfides we had been working with previously. We assembled a small-scale dye sensitized solar cell by using two indium-doped tin oxide glass slides. One was coated with a layer of titanium oxide and then soaked in a solution of our cadmium selenide nanoparticles. This would serve as our electrode. The other slide was coated with a fine layer of graphite to serve as the counter-electrode, and a liquid solution of lithium iodide between the two would serve as our electrolyte. This was then attached to a voltmeter and exposed to different levels of light. It registered a consistent voltage difference of about 10 mV between normal light levels and darkness and a 70 mV difference between UV and normal light. This is opposed to our control cell, comprised of the same setup except for the soak in the cadmium selenide nanoparticles, which gave inconsistent voltage readings.

Though we are a long way from a full-scale solar cell, this research has been successful in confirming the possible synthesis of sulfur and selenium containing nanostructures via mild reaction conditions. It has shown these nanostructures have the capability to attach and layer on top of each other. Perhaps most importantly, it has shown that these particles, when implemented in a small-scale solar energy device, produce a measurable difference in output voltage. The next step would be to begin to optimize these particles for maximum voltage output and further investigation into the specific conductive and photovoltaic properties they contain.

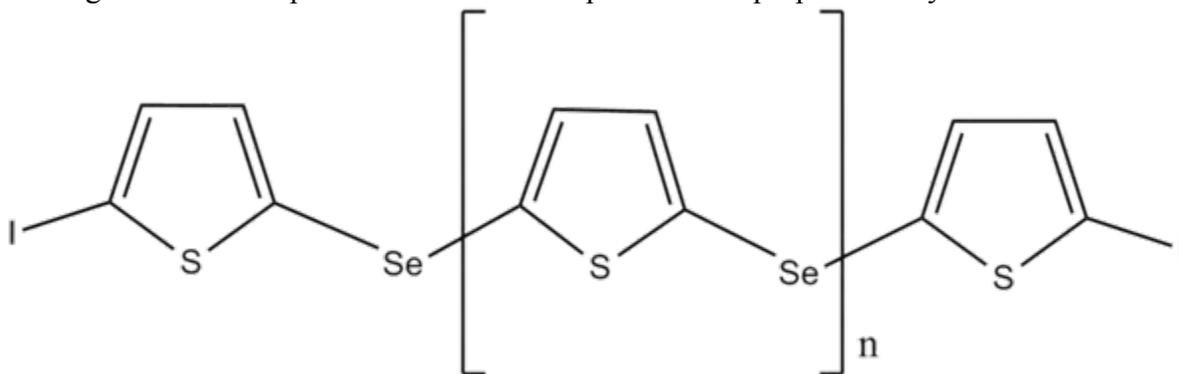


Figure 1: Structure of poly(2,5-diselenothiophene)

I also had the opportunity to participate in a poster presentation of this research during the 2012 Undergraduate Research Summer Symposium at Notre Dame. For a small scale copy of my poster please see the next page.

### Introduction

The project sought to synthesize nanostructure materials for bulk heterojunction photovoltaic devices under ambient temperatures and pressures which could potentially be used in developing solar energy harvesting devices. A particular interest was placed on the formation of metal sulfides and selenides and other sulfur- and selenium-containing organic compounds.

### Background

Today's energy demands place significant strain on available resources. Solar energy holds promise for relieving this stress through its ability to produce energy from a practically limitless resource, sunlight. However, current technology is not efficient enough to be practical in today's global society. Investigations into revealing more effective semi-conductors and electrolytes will be critical in resolving this problem.

### Results cont.

**Copper Sulfide and Copper Selenide**

- The reaction of  $Cu^{2+}$  with thiourea, thioacetamide, and adamantanethiol in a slightly basic solution all yielded copper sulfide, and  $Cu^{2+}$  and selenourea yielded the copper selenide. The XPS confirms the formation of these products.

### Results cont.

**Mercury Sulfide and Mercury Selenide**

The reaction of Mercuric Chloride with thiourea, thioacetamide, and adamantanethiol in a slightly basic solution all yielded Mercury sulfide, and Mercuric Chloride and selenourea yielded the Mercury selenide. This was also confirmed via XPS.

### Methods

- Compounds were dissolved in aqueous or ethanolic solutions and reacted
  - Atmospheric pressure
  - 70-80 C range
  - Neutral or slightly basic conditions
- Products were then characterized using the following:
  - X-ray Photoelectron Spectroscopy
  - Scanning Electron Microscope
  - Infrared Spectroscopy
  - Mass Spectrometry

### Results

#### Poly(2,5-dithienothiophene)

- The reaction of selenourea with 2,5-dithienothiophene in Dimethyl Sulfoxide solution using a Copper(I)oxide catalyst yielded a poly(2,5-dithienothiophene), PDSel.



Figure 1. Poly(2,5-dithienothiophene)

- Bonding experiments were then conducted to determine the bonding capabilities of PDSel. It was reacted with Cadmium, Zinc, and Lead Sulfide and Selenide nanoparticles as well as other linking molecules, but all attempts showed no successful bonding.



Figure 2. SEM and XPS of  $Cu^{2+}$  and Thiourea Reaction



Figure 3. SEM and XPS of  $Cu^{2+}$  and Thioacetamide Reaction



Figure 4. SEM and XPS of  $Cu^{2+}$  and Selenourea Reaction



Figure 5. SEM and XPS of  $Cu^{2+}$  and Adamantanethiol Reaction

- A Self-Assembled Monolayer (SAM) was then constructed on a gold substrate by repeated alternating dippings in a  $Cu^{2+}$  solution and a Thiocetamide solution. The formation of this structure is supported by XPS data.



Figure 6.  $Cu^{2+}$ /Thioacetamide SAM structure

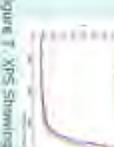


Figure 7. XPS Stacking Copper Layering

#### Dye Sensitized Solar Cell

- A dye Sensitized Solar Cell using CdSe nanoparticles was constructed by dipping Indium doped Tin Oxide Glass (ITO) coated with  $TiO_2$  in a CdSe solution to serve as the electrode. A LiI solution served as the electrolyte, and a graphite coated ITO served as the counter electrode. When attached to a voltmeter this assembly registered a 10mV difference between light and darkness, and a 70 mV difference between normal and UV light.

Figure 8. Diagram of Dye Sensitized Solar Cell Assembly

### Conclusions

This project has confirmed the possible synthesis of sulfur and selenium containing nanostructures via mild reaction conditions. It has also shown these nanostructures have the capability to attach one layer on top of each other. Perhaps most importantly, it has shown that these particles, when implemented in a small-scale solar energy device, produce a measurable difference in output voltage.

### References

- Reddy, V. P.; Kumar, A. V.; Bao, K. R. *J. Org. Chem.* **2011**, *75*, 8720
- Takachi, K.; Mutsaers, R.; Kamei, R. *Fabrication procedure of dye-sensitized solar cells*. Available from <http://www.nd.edu/~pkamat/ped/dsalc.html>. Accessed 18 July 2012.

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