

Session E – Chemistry (Alphabetical)

The Ionization of Strontium and Its Reaction with Oriented Molecules

Marissa Barrientos

Mentor: Philip Brooks, Rice University

Previous work focused on cross-beam reactions of potassium and various oriented molecules in order to understand how electron transfer is affected by molecule orientation. To ascertain how a second electron would affect electron transfer, preparations were made to begin performing oriented molecule experiments with the alkali earth metals. Strontium has been selected for the initial alkali earth metal experiments. However, due to strontium having a much higher boiling point than potassium, modifications to the apparatus were necessary. After installing a new, high temperature oven, more experiments were done with potassium to optimize the apparatus. Next, experiments were made to explore the appropriate operating conditions for strontium. Calculations suggest it will be feasible to obtain a beam of strontium, and eventually run cross-beam reactions.

Optimizing Electropolymerization at Methyl, Thienyl, and Mixed Monolayer Surfaces Si(111) Surfaces

Tina Ding

Mentors: Nate Lewis and Leslie O'Leary

Modification of silicon surfaces gives chemical control of semiconductor heterojunctions, which is essential in efficient electronic devices and is applicable to solar cells. A variety of functionalized Si surfaces have been synthesized: Si(111)-CH₃, Si(111)-C₄H₃S (thienyl), and mixed methyl/thienyl. The mixed monolayer could be controllably synthesized with as high as 78.8 ± 9.8% total coverage of Si(111) atop sites as characterized by XPS. The mixed monolayer surfaces also give much lower surface recombination velocities than thienyl surfaces. A three electrode system was used for electropolymerization and obtaining cyclic voltammetry data: reference electrode (Ag/Ag⁺), counter electrode (platinum), and the working electrode (our functionalized Si surface). We desired to oxidize the thiophenes on the Si surface during electropolymerization, and thus form covalent bonds with the polymers. The cyclic voltammetry data did not show a difference in electropolymerization at thienyl surfaces versus methyl, showing that there is possibly noncovalent bonding on these surfaces as well. Thinner films resulted in smoother surfaces than thicker films as looked at under SEM. The oxidation on the Si surface can be controlled with lowering the applied voltage. In the future we hope to electropolymerize using oligomers to further lower the applied voltage to reduce oxidation, and we wish to attach functional groups with lower oxidation potentials to achieve covalent bonding to the deposited polymer. We hope to also determine the bonding nature of the polymers with Si by using the monomer 3-hexylthiophene which dissolves in toluene. Then, we will apply the techniques to mixed monolayer surfaces and compare their device properties with that of the thienylated surface.

Conformational Preferences of Succinic Acid in Media Modeled After the Cell

Kristina Flavier

Mentor: John D. Roberts

Succinic acid exhibits preferences for the gauche conformation that differ from statistical in the diacid, monoanion, and dianion forms, due to hydrogen bonding and the gauche effect. In this project, the conformational preferences of succinic acid were studied in media modeled after conditions found inside cells. Solutions of 0.10 M (2,3-¹³C)-labeled succinic acid in D₂O containing corn syrup, composed of a number of sugars, and gelatin, composed primarily of amino acids, were created, with and without phosphate to regulate pH to cellular pH of about 7.4. ¹H NMR scans were run of these solutions to determine coupling constants, and the Karplus-Altona equation was used to derive the percentage gauche configuration for succinic acid in each solution. In solutions containing only succinic acid and phosphate, the presence of phosphate lowered the percentage gauche in the dianion form, while the percentage remained the same in the case of the diacid. Corn syrup did not significantly change the coupling constants or percentage gauche of succinic acid. Through further study of the effects of gelatin and other molecules, the behavior of succinic acid and like molecules inside cells can be better understood.

Investigating the DNA-Mediated Charge Transport (CT) Pathway of Endonuclease III

Tianjia Jessie Ge

Mentors: Jacqueline Barton and Christine Romano

The base excision repair (BER) pathway is a system of enzymes utilized by the cell to repair DNA lesions. Endonuclease III (Endo III) is a member of the BER family that contains a [4Fe-4S] cluster. The Barton group has shown that BER enzymes may detect their target lesions by means of DNA-mediated charge transport (CT). DNA binding facilitates the oxidation of the [4Fe-4S] cluster of the bound protein, triggering CT to a distally bound protein which is then reduced and dissociates. If a base lesion is present,

CT will be halted and the distal protein will not dissociate. Instead, both proteins will migrate to the area requiring repair. In this study, mutants of Endo III were cloned and expressed with the intention of identifying amino acid residues that mediate CT between the DNA and the [4Fe-4S] cluster of Endo III.

Synthesis of Novel Titanium Complexes for Inexpensive Carbon Dioxide Reduction

Anna Ivanova

Mentor: Christopher Cummins

Carbon dioxide (CO₂) is an exceptionally stable, undesirable byproduct in many organic reactions. On the other hand, the related compound carbon monoxide (CO) is very versatile, showing potential in many applications. Furthermore, the oxygen (O) released in the reduction from CO₂ to CO can be reused. Thus, it is desirable to develop a transition metal compound that can mediate the reduction of CO₂ while not forming a strong oxometal bond. This can be accomplished by binding the CO₂ to a terminal ligand on the compound, rather than to the central metal. Titanium compounds with potential for this bond were synthesized by coordinating a titanium oxoanion with various counteranions, and the efficacy of each compound in the reduction of CO₂ was assessed.

Investigating the Deposition of Metal Catalysts on Structured Semiconductor for VLS Wire Growth and Water Photoelectrolysis

Jessie Ku

Mentor: Nathan Lewis

Silicon wire arrays grown by the vapor liquid solid (VLS) process are promising materials for the creation of high efficiency radial junction energy conversion devices. However, the size of these wires has been limited by the ability to evaporate the metal catalyst of sufficient thickness. The objective of this project is to electrodeposit layers of copper catalyst of controlled thickness onto patterned silicon from which silicon microwires can be grown by the VLS process. Using a three electrode system with the silicon as the working electrode, the parameters for the potentiostatic deposition of copper have been optimized and a relationship between charge density and metal thickness has been determined. Varying the concentrations of CuSO₄ and other additives in the electrodeposition solutions showed that lower concentrations of copper salt in solution resulted in slower and more uniform electrodeposition of copper. Microwires approximately 10 microns in diameter have grown from copper electrodeposited into lithographically patterned 15 micron diameter holes.

Hybrid Conductive Polymer/Silicon Junctions for Solar Energy Conversion

Xueliang (Leon) Liu

Mentors: Nathan S. Lewis and Michael G. Walter

Solar cells offer a promising route for generating clean and renewable energy, but the high cost of current commercial solar cells made from high purity inorganic semiconductors like silicon precludes their widespread adoption today. Solution processible organic polymers offer a potentially cheaper alternative to silicon. Moreover, the versatile range of physical properties of conductive polymers renders them capable of a variety of different applications in solar energy conversion. In this study, the conductive polymer/silicon junction was examined in detail. Poly(3,4 ethylenedioxythiophene) (PEDOT) and poly(3-hexylthiophene) (P3HT) were deposited onto silicon substrates either (photo)electrochemically or by spin-coating. Planar silicon substrates as well as nanowire arrays fabricated by the Vapor-Liquid-Solid mechanism or chemical etching were explored, and chemical surface modifications such as methylation were applied. Furthermore, the electrochemical, optical and morphological properties of the polymer were varied, and comparisons were made on the different device treatments. Results from the study demonstrate facile controllability of the organic/inorganic junction leading to rectifying and ohmic contacts. These junctions can serve as the active layer of photovoltaic or the connection between active layers in multi-junction devices, making conductive polymers a viable alternative to expensive inorganic semiconductors for application in solar energy conversion.

Crystallographic Determination of the Substrate Site(s) in Nitrogenase

Maria A. Luca

Mentors: Doug Rees, Kun-Yun Yang, and Jens Kaiser

Nitrogenase, an enzyme that reduces nitrogen into the biologically relevant form of ammonia, is composed of two proteins. One of these, the molybdenum-iron (MoFe) protein, is thought to be where substrate reduction takes place. The other component is the iron protein which couples ATP hydrolysis and electron transfer. The basic mechanism of the nitrogenase enzyme system consists of: a) the Fe-protein is reduced and forms a complex with two bound ATP and the MoFe-protein; b) hydrolysis of ATP coupled to electron transfer between the Fe-protein and the MoFe-protein; c) the Fe-protein disassociates from the complex and is then reduced again by ferredoxins or flavodoxins while exchanging ATP for ADP and d) this process restarts and continues until enough protons and electrons have been gathered to reduce more substrates. To determine where substrates might bind within the MoFe-protein, the protein was crystallized and

soaked in various solutions of possible substrates and substrate analogs. Future experiments for this project include collecting x-ray diffraction data taken on the 12-2 beamline at the Stanford Synchrotron Radiation Laboratory from these MoFe crystals, and then analyzing this data with the MOSFLM, MOLREP, COOT, and REFMAC programs.

Gallium Phosphide Anodes in Two Junction Semiconductor Microwire Photoelectrochemical Cell for Solar Fuel Generation

Jeanne Y. Peng

Mentors: Nathan Lewis and Gregory Kimball

We have explored the application of gallium phosphide (GaP) *p-n* homojunctions for the photoelectrochemical generation of oxygen from water. We fabricated buried *p-n* homojunction at the wafer surface by diffusing Zn into S-doped (n-type) GaP wafers using dopant sources such as elemental Zn or Zn₃P₂. Contacts to GaP wafers were made with Au-Zn alloy for p-type material and Au for n-type material. The resulting *p-n* junction was characterized with secondary ion mass spectroscopy (SIMS) and spreading resistance profiling (SRP). The performance of the *p-n* junction as a solar cell was examined with a solar simulator.

C-H Bond Activation in the Dimerization of Bisphenolate "Pincer" Compounds of Group IV Metals

Nicholas Rosa

Mentor: John Bercau

Non-metallocene group IV dibenzyl complexes based upon a *bis*(2-*t*-butyl-4-methylphenolate)benzene-diyl (L) "pincer" ligand have recently been shown to exhibit C-H activation and elimination of toluene during a dimerization process upon heating. Initial screenings of kinetics of the Ti complex showed that the most likely process was an alpha-abstraction of a benzylic hydrogen. Moving to Zr and Hf, however, have indicated that this mechanism is not in play for the 2nd or 3rd row metals. Toward understanding the mechanism of the C-H activation, a range of isotopologues of LMBn₂ (Bn=benzyl, M=Zr, Hf) were prepared. The kinetics of dimer formation were followed using ¹H-NMR and the isotopic distribution of the eliminated toluene examined to formulate the mechanisms of these transformations.

Composites of Metalloporphyrins and Carbon Black for Chemical Vapor Sensing

Jordan C. Theriot

Mentors: Nathan Lewis and Edgardo Garcia

Thin-film chemiresistive vapor sensors have been fabricated using composites of carbon black (CB) and metalloporphyrins. The resulting sensors exhibited large, rapid, and reversible relative differential resistance changes upon exposure to a series of test organic vapors. The individual sensor responses, and collective sensor array properties for classification of a series of test organic vapors, were comparable to those of chemiresistor arrays made from composites of metallophthalocyanines. In addition to displaying resistance responses to volatile organic compounds, the CB/metalloporphyrins composite sensors exhibited a high sensitivity towards trace levels of NH₃(g) under ambient temperature and pressure conditions. No degradation in sensor response was observed after nearly 12 h of repeated exposure to 32.4 parts per million of NH₃(g).

Observing the Oxidation of the Iron-Sulfur Cluster in Endonuclease III through DNA Mediated Charge Transport using Transition Metal Complexes

Xida Zheng

Mentors: Jacqueline K. Barton and Eric Olmon

Oxidative stress in cells can cause mutations that result in cancer. The base excision repair (BER) protein endonuclease III (Endo III) is involved in a pathway that corrects mutations in DNA. One possible mechanism that BER proteins use to detect DNA lesions is DNA mediated charge transport (CT). The iron-sulfur clusters in the BER proteins have been shown to be redox active. By triggering DNA CT and recording changes in the absorbance of the system, it should be possible to observe the oxidation of the iron-sulfur cluster in Endo III. Using transient absorption spectroscopy and an intercalated Rhodium photooxidant, we have observed changes in absorbance around the 410nm wavelength that corresponds to the absorbance of the oxidized iron-sulfur cluster. This result suggests that Endo III can participate in DNA mediated charge transport.