

Undergraduate Research Symposium May 17, 2013 Mary Gates Hall

Online Proceedings

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MICRO- AND NANO-MATERIALS IN ACTION

Session Moderator: John Berg, Chemical Engineering

242 MGH

3:45 PM to 5:15 PM

* Note: Titles in order of presentation.

Characterizing the Reducing Potential and Two Proton - Two Electron Transfer Reactions of Titanium Dioxide Nanoparticles

Benjamin Guthrie (Ben) Horst, Senior, Chemistry (ACS Certified), Biochemistry

Levinson Emerging Scholar, Mary Gates Scholar, Undergraduate Research Conference Travel Awardee, Washington Research Foundation Fellow

Mentor: James Mayer, Chemistry

Titanium dioxide (TiO₂) displays a variety of interesting properties and has been intensely investigated for applications in environmental cleanup, photocatalysis, dye-sensitized solar cells, and semiconductor fabrication among others. However, the underlying mechanisms which govern TiO₂ chemistry are not well understood. Here, the tendency for reduced TiO₂ nanoparticles to donate stored electrons to other reagents is being characterized. The reduced ("charged") nanoparticles are made by UV irradiation which excites an electron from the valence band to the higher energy conduction band of the TiO₂ nanoparticles. In the absence of oxygen and other oxidants, the charged TiO₂ nanoparticles are stable and can be easily monitored by their absorption of visible light and blue color. We are exploring the chemical reactions of the charged particles. If the optical spectrum changes after the addition of other reagents, that is an indication that the nanoparticles are reducing the reagents. Removal of the electrons from the nanoparticles has been previously accomplished using aqueous Cu²⁺, but not Zn²⁺ or Mn²⁺. I am repeating this result and extending it to other metal ions such as Cr³⁺ in order to estimate the standard reduction potential of the charged particles. In addition, I am studying optically and via NMR whether dimethyl sulfoxide (DMSO) is reduced to dimethyl sulfide by charged TiO₂ nanoparticles. Because one-electron reduction of DMSO results in extremely unfavorable intermediates we are probing whether the reaction by charged TiO₂ occurs by the direct transfer of two electrons from the TiO₂ nanoparticles to the DMSO. These studies will provide valuable insight into the electronic chemistry of TiO₂

and will aid in the application of TiO₂ to other systems which require the transfer of multiple electrons.

Rheology of Dense Calcium Carbonate Dispersions

Aaron Joseph (Aaron) Johnson, Senior, Chemical Engineering, Bioresource Science and Engineering

Mary Gates Scholar

Mentor: Kevin Hodgson, Bioresource Science & Engr.

Mentor: John Berg, Chemical Engineering

From the fillers that give body to ordinary paper to the antacids that relieve indigestion, calcium carbonate suspensions play an important role in our day-to-day lives. It is often desirable to work with slurries that contain the highest possible fraction of solids. The goal of this research has been to investigate ways to improve the flow of high solids dispersions of calcium carbonate through the use of rheology modifiers. These are chemicals which, when added in small amounts, allow the dense slurries to flow as easily and smoothly as possible. Improving flow characteristics of high solids dispersions has a huge potential for reducing the amount of energy needed for various processes, such as pumping, coating and de-watering. One very promising modifier has been found to be sodium polyacrylate. Both traditional and new products, like nano-sized calcium carbonate particles, have shown significant improvements using this modifier. In this research, the rheological properties such as the viscosity function and the yield stress are determined as functions of additive amount, volume fraction of solids, and pH of the aqueous dispersion medium. All of these have been shown to important parameters in achieving optimum performance.

Battery-Free Gas Sensor Nodes Utilizing Ambient Radio Frequency Energy

*Chen Shi, Senior, Bioengineering, Electrical Engineering
Mary Gates Scholar*

*Mentor: Joshua Smith, Computer Science & Engineering,
Electrical Engineering*

Mentor: Aaron Parks

Gas sensors are widely used in daily life and industry. An important application of gas sensing is the monitoring of environmental factors affecting health, such as the concentration of carbon monoxide, in populated areas. However, most conventional gas sensors are powered by batteries, which need periodic replacement. The goal of this project is to integrate a Wireless Ambient Radio Power (WARP) energy harvesting platform with a new class of amperometric electrochemical gas sensors, provided by KWJ Engineering, Inc, to create novel battery-free gas sensor nodes. The WARP sensing platform, developed in Dr. Joshua Smith's group, utilizes ambient radio frequency (RF) energy from common sources such as cellular towers and TV broadcast stations, which provide a reliable and pervasive 24-hour power source. The gas sensors manufactured by KWJ Engineering possess the advantages of low power, low cost, high sensitivity, and high selectivity. Particularly, the low power requirements of the gas sensors make it possible for them to be powered by the RF energy harvested by the WARP platform. Currently the potentiostat circuit needed to properly bias the gas sensor and acquire the gas concentration is being developed. The gas sensor circuitry will be integrated with the WARP platform to produce the battery-free RF-powered gas sensor nodes, followed by system optimization for reliable and efficient operations. With such gas sensor nodes, long-lived wireless sensor networks with zero maintenance cost could be deployed in continuous toxic gas monitoring applications, including air quality monitoring in cities and process control in industry.

The Charging of Carbon Black Pigments in Apolar Media

Max Grigorovich Kaganyuk, Senior, Chemical Engineering

Mentor: John Berg, Chemical Engineering

Mentor: Matthew Gacek, Chemical Engineering

Electrophoretic displays, such as the Kindle®, currently employ electrostatic effects in apolar media to create a paper-like display. In an electrophoretic display, images are comprised of black and white pixels generated by applying an electric field to reposition charged pigment particles. The optimization of this technology is limited due to the incomplete knowledge of the mechanism(s) by which particles acquire charge in these systems. My project explores the charging behavior of carbon black pigments dispersed in apolar media. Previous studies of mineral oxide particles have provided support for the theory of an acid-base charging mechanism for particles dispersed in apolar media with various charge sta-

bilizing surfactants. My current work looks at the possible extension of the theory of an acid-base charging mechanism to carbon black pigments in apolar systems. I have investigated the charging behavior of four different carbon black pigments by measuring the electrophoretic mobility of each pigment dispersed in solutions of heptane, and a charge stabilizing surfactant at varying weight percentages. Three surfactants were used for charge stabilization: Aerosol OT, SPAN 80 and OLOA 11000. Aerosol OT is a neutral surfactant in water, whereas SPAN 80 is acidic and OLOA 11000 is basic. The surface characteristics of each carbon black pigment were studied by Inverse Gas Chromatography (IGC) and X-ray Photoelectron Spectroscopy (XPS). The preliminary findings of my investigation show the sign of the charge for the carbon black pigments to be dependent on the charge stabilizing surfactant used.

A Study of Optical- and Electron-Induced Plasmons in Nanometal Aggregates

*Alex Vaschillo, Senior, Physics: Comprehensive Physics,
Mathematics (Comprehensive), Chemistry (ACS Certified)*

Mary Gates Scholar, Undergraduate Research

Conference Travel Awardee

Mentor: David Masiello, Chemistry

Collective oscillations of conduction electrons in a metal nanoparticles, known as localized surface plasmon resonances (LSPRs), have been the source of much scientific study over the last decade due to their immediate and significant applications in biosensing, surface-enhanced Raman Spectroscopy (SERS), and light absorption engineering in semiconductor nanodevices used in solar cells. Due to the diffraction limit, many properties of LSPRs are undetectable by optical spectroscopies, creating a need for detection via electron-based probes. LSPRs can be generated as a result of high-energy electrons, such as those in an electron energy-loss (EEL) microscope, transferring energy to a nanometal's electron cloud. This energy can follow a variety of pathways: it can be stored in the electric near-field of the nanoparticle (possibly generating "hot spots" - regions of very high electromagnetic field), radiated into the far field (becoming visible as light), or lost to thermal excitation of the metal. The purpose of this work is to study how nanoparticles distribute energy amongst these decay paths and to quantify the interactions between two adjacent nanoparticles. An interaction of significance is the Fano effect - a destructive interference between the electric fields generated by two adjacent nanoparticles that leads to electromagnetically induced transparency. The Fano effect is studied from a theoretical perspective and is discussed in the context of energy transfer between different modes of a collective LSPR that spans both nanoparticles.

The Impact of Quantum Dot Surface Ligands on the Operation of Hybrid Polymer/Quantum Dot Solar Cells

Wenbi Wu, Junior, Mathematics, Biochemistry

Mary Gates Scholar

Mentor: David Ginger, Chemistry

Mentor: Adam Colbert, Chemistry

Solar technology is a potential way to help meet the growing demand for clean, renewable energy. Hybrid composites of inorganic quantum dots, with organic semiconducting polymers offer a potential means of producing low-cost, solution-processable photovoltaics. The synthesis of quantum dots typically involves the use of large surfactant molecules to facilitate particle growth and solubility. These native ligands act as electrical insulators that impede charge transport in photovoltaic devices. Therefore, it is necessary to exchange these large ligands with small molecules to achieve efficient charge carrier photogeneration and transport. In this research, we examine bulk heterojunction blends of low band gap PbS quantum dots with the conjugated polymer poly((4,8-bis(octyloxy)benzo(1,2-b:4,5-b')dithiophene-2,6-diyl)(2-((dodecyloxy)carbonyl)thieno(3,4-b)thiophenediyl)) (PTB1) treated with different ligands including cetyltrimethylammonium bromide (CTAB), tetrabutylammonium thiocyanate (TBAT), and 3-mercaptopropionic acid (MPA). We aim to elucidate how these different ligands influence the photovoltaic performance of PbS/PTB1 blends by studying the differences in long-lived charge generation and recombination kinetics associated with the quantum dot ligand treatments using transient photovoltage (TPV) and photoinduced absorption (PIA) spectroscopy, respectively. We will also determine whether different ligand treatments influence film morphology using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). We hope to gain a better understanding of how quantum dot ligand treatments may be used to optimize the performance of hybrid photovoltaics.