ABSTRACTS

Undergraduate Research in Chemistry Regional Poster Competition

137 Chemistry-Physics Building

April 5th, 2013

3:00pm - 5:00pm

Department of Chemistry
University of Kentucky
Lexington, KY 40506-0055

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TESTING GRAPHITIC FILLER MATERIALS IN CARBON-BASED ANODES FOR LITHIUM-ION BATTERIES

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☐	Freshman	☐	Sophomore	☐	Junior	X	Senior

Carbon-based anodes are commonly used in lithium-ion batteries due to their low volume expansion, high energy density, and long cycling life. Extensive research has been devoted to understanding and developing existing anode materials for lithium-ion batteries. Graphite has a highly conductive conjugated covalent structure, a high energy density of around 72.9 MJ/L, and a theoretical specific capacity of 372 mAh/g. Filler materials are used to increase electrical conductivity between particles of the active material. In this project, graphitic-based anodes with various filler materials were prepared for testing in full-cell and half-cell batteries to test the capacities and lifetimes of anodes with different filler materials. Electrodes were prepared by mixing mesocarbon microbead (MCMB) graphite as the active material, various graphitic fillers, and a polyvinylidene fluoride (PVDF) binder in an 8:1:1 ratio by weight. Slurries of anode materials in the organic solvents NMP and THF (3:7) were spray coated onto copper current collectors to produce anode films, which were dried in a vacuum oven overnight at 100 °C. Coin-cell batteries were assembled in an argon-filled glove box and cycled on a battery cycler for at least 10 cycles at a rate of C/10. The cycling results are plotted on graphs of capacity vs. cycle number for comparison. Averages and standard deviations of the capacity for each similar battery type were calculated at certain cycles as well as the percent of initial capacity retained at the last cycle. Cycling results show a large standard deviation for most batteries with percent retention mostly in the 65-90% range.

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DINUCLEAR RUTHENIUM COMPLEXES SHOW INCREASED LIGHT ACTIVATED DNA DAMAGE

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Current photodynamic therapy for treatment of cancer uses photosensitizing agents activated by visible to near -IR light to produce cytotoxic singlet oxygen. Oxygen-independent mechanisms can result from using strained metal complexes that covalently bind DNA when activated by light. By introducing two ruthenium centers on the same pro-drug, more effective DNA damage can be achieved. Two novel dinuclear ruthenium complexes have been synthesized and interactions with plasmid DNA characterized. Visible light activation of these compounds produces significantly more damage to plasmid DNA then the mononuclear analogs, indicating that this approach may offer an efficient route to induce DNA damage in cancer cells.

3

ANALYSIS OF THE EFFECT OF PATHLENGTH ON SMALL VOLUME REACTIONS USING THYMINE AND SODIUM PERMANGANATE

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Single stranded deoxyribonucleic acid sequencing is often time-consuming and expensive. Nevertheless, through experimentation, it has been shown that different DNA bases react slightly differently with sodium permanganate. The resulting color change may give clues to less expensive DNA identification and sequencing techniques. Previous work in our lab has developed a colorimetric technique to provide sequence and structural information. One of the challenges of this technique has been the relatively large sample of DNA that must be used. My goal is to analyze the way that the volume of the solution affects color in different types of solution vessels with the hopes of being able to simultaneously run a greater number of reactions at extremely small volumes reducing costs and making the process more efficient. In this experiment, the reaction of sodium permanganate and thymine was done in a 96 well microplate and in capillary tubes. Analysis of the results indicated that there is a way to reduce the scale of the reaction to extremely small volumes without the loss of richness in color.

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CARBONIC ANHYDRASE MIMICS FOR CARBON DIOXIDE CAPTURE

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Greenhouse gases such as carbon dioxide warm the Earth by containing radiation from the sun within the lower atmosphere. Increasing concerns of global climate change have led to the development of new technologies to decrease anthropogenic greenhouse gas emissions. A major source of anthropogenic carbon dioxide emission is the combustion of carbon-based fuels such as coal. Carbon dioxide capture and sequestration significantly decrease the emission of greenhouse gases. The current method of CO2 capture in industrial settings utilizes aqueous solutions of monoethanolamine, MEA. My research project seeks to increase the efficiency of CO2 capture from flue gases utilizing catalyst mimics of the biological enzyme, carbonic anhydrase.

The current state-of-the-art catalyst, Zn-Cyclen, is reported to have a second order rate constant of 2000 M-1s-1. The focus of this research is the synthesis and characterization of a new zinc catalyst, CAER-C2, which I synthesized on a multi-gram scale from the reaction of zinc chloride with a previously reported ligand. The crystalline product was characterized by x-ray crystallography, which shows that it forms a coordination complex that includes three unique zinc atoms in the unit cell, and further testing (mass spectrometry) shows that this complex remains intact in solution. This catalyst has a rate constant for CO2 capture that is approximately two orders of magnitude higher than Zn-Cyclen. This increased activity may have grand implications for the future of carbon capture in industrial settings by increasing the efficiency of CO2 capture and lowering costs. If power plants capture CO2 with better efficiency, greenhouse gas emission into the atmosphere will decrease and reduce the threat of future climate change.

5

EXAMINING OXIDATIVE DAMAGE TO DNA WITH VARIOUS FREE RADICAL SYSTEMS

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Oxidative damage to DNA from reactive oxygen species (ROS) is a common type of damage faced by cells that contributes significantly to carcinogenesis, cellular aging, and genomic instabilities. The production of reactive oxygen species is the consequence of normal body processes such as metabolism but can also arise from toxic sources such as radiation. High rates of oxidative damage to DNA in sperm chromatin have also been linked to infertility in males as well as higher rates of genetic disease in the offspring. In sperm chromatin, the general consensus is that tight packing of DNA in sperm nuclei is necessary to limit DNA damage due to ROS since DNA repair is absent. We hypothesize that protamine chemistries resulting in less efficient packaging, allows increased accessibility of free radical species to the compacted DNA.

Accessibility is not only matter of sterics but also physical chemical interactions. As a first step, agarose gels and fluorescence studies were used to qualitatively assess damage to pUC19 plasmid DNA by different free radical sources including Fenton reagents, 2,2'-azobis(2-amidino-propane) dihydrochloride (AAPH), and N-Nitrosomorpholine (NMOR). For AAPH, comparisons were made between free radical damage to DNA in free solution and protamine packaged DNA. Our long-term goal is to determine quantitatively the interrelationship between DNA packaging densities and the resulting accessibility of DNA to reactive oxygen species (ROS).

6

USE OF BIOCHEMICAL AND GENETIC APPROACHES TO SEARCH FOR ANCESTORS OF MAMMALIAN MANNOLIPID FLIPPASES

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Flippases, a termed originally suggested by Mark Bretscher in 1974, are membrane proteins that play a vital role in membrane biology. Flippases overcome the biophysical barrier, which is imposed by the bilayer common to cellular membrane via the bilayer's hydrophobic core. Flippases facilitate transbilayer movement of the polar head groups of phospholipids and glycolipids. Flippases play a crucial role in the expansion of the bilayer in a uniform manner throughout membrane biogenesis, as well as maintaining and establishing the asymmetric distribution of phospholipids, which reside in the cellular membranes. Flippases are also a crucial component of the transbilayer movement of glycolipid intermediates in the dolichol pathway, which accounts for protein N-glycosylation, C- and O-mannosylation of proteins, biosynthesis of glycosylphosphatidylinositol anchors, the formation of complex glycosphingolipids and cell wall components in yeast and Gram-positive and Gram-negative bacteria.

The topological model (Figure 1) accounts for the assembly of lipomannan, an acidic, branched polymannose chain, which contains 48-50 mannose residues. The mannose residues are attached to the hydroxyl group at position-3 of diacylglycerol (DAG) in M. luteus. In this assembly, GDP-Man acts as the direct mannosyl donor for two mannosyltransferases, catalyzing the biosynthesis of Man1-2-diacylglycerol (Man1-2-DAG). The biosynthesis occurs on the inner face of the cytoplasmic membrane (Figure 1, steps 1,2). Man-P-undecaprenol (Man-P-Undec(C55)) is formed via a mannosyltransferase catalyzing the transfer of mannose from GDP-mannose (GDP-Man) to undecaprenyl phosphate (Undec-P) (Figure 1, step 3). The transverse diffusion of the two mannolipid intermediates is mediated by two flippases, which have not been identified (Figure 1, steps 4,5). From this point, approximately 48 more mannosyl units are donated to Man2-DAG from Man-P-Undec on the outer leaflet of the cytoplasmic membrane (Figure 1, steps 6,7).

The project utilizes two approaches to identify the two mannolipid flippases seen in Figure 1. The first approach uses a collection of temperature-sensitive (TS) mutants in micrococcal lipomannan, which are subjected to screening by effective molecular techniques in a simple genetic background. This process will be utilized to identify this novel class of membrane proteins. The second approach deals with benzophenone-containing photoprobes containing "click chemistry" (CC) handles that introduce minimal structural perturbations to the Man-P-Undec analogues. These analogues are active in the flippase transport assay, and are being utilized to isolate and identify micrococcal membrane proteins involved in the flip-flopping of Man-P-Undec through proteomic analyses. The genetic and biochemical information gained by these studies have the potential to provide clues to the first identification of the membrane protein counterparts in the endoplasmic reticulum. The counterparts are essential for the assembly of vitally important membrane and secretory glycoproteins in human cells.

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MOLECULAR ENGINEERING OF AQUAPORIN TO IMPROVE STABILITY

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Over 30% of the world’s population lives in countries facing water shortage. This figure is predicted to double in 2025. To increase the usable fresh water supply beyond what is available from the water cycle are desalination of sea water, purification of ground water, and recycling of waste water. All these methods depend on the availability of efficient techniques to separate water from solute as well as insoluble substance co-existing with water. Separation involving membranes with high water permeability and selectivity are the method of choice. The development of advanced and innovative membranes by incorporating protein nano-channels in synthetic matrix will drive the progress of finding a technological solution to global water shortages. Water channel proteins called aquaporins in confer high water permeability and selectivity to biological membranes. The goal of this study is to develop molecular engineering strategies to improve the stability of the water channel protein aquaporin. Aquaporin Z (AqpZ) is an integral membrane protein discovered as an effective water channel in Escherichia coli decades ago. Due to its superb specificity and high permeability, AqpZ has been incorporated into artificial membranes used for water filtration and desalination. We are testing the strategy to improve AqpZ stability through the introduction of proline into β-turns. Proline is commonly found in β-turns. Due to its rigid backbone structure, more energy is usually required to unfold protein containing Pro, which leads to protein stabilization. We have created one mutant, T107P, through site directed mutagenesis. The protein was expressed and purified. The structure and stability of the mutant were characterized by circular dichroism spectroscopy. The mutation did not significantly improve protein stability.

We will test more sites and their combinations to determine if the stability of AqpZ could be improved through the introduction of proline into other β-turns.

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INTERACTION OF SYNTHETIC DITHIOL WITH SELENIUM

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Selenium is an essential trace nutrient in biological systems, has antioxidant properties, and prevents the growth of a wide range of cancers. There is a delicate ingestion balance, however, between deficiency (< 40 µg/day) and toxicity (> 400 µg/day) for selenium. The US Environmental Protection Agency (EPA) limit for total selenium in drinking water is 50 ppb[1].

The current study explored the interactions of selenite and selenate with the synthetic, dithiol, metal capture agent N, N'-bis(2-mercaptoethyl)isophthalamide (abbreviated B9). B9 effectively precipitates soft heavy metals such as Cd, Hg, and Pb from aqueous systems through covalent metal-sulfur bonds[2]. It was anticipated that B9 would be effective in precipitating selenium by formation of covalent selenium-sulfur bonds. It was found that selenite actually undergoes a series of reactions rather than formation of a stable covalent bond. This work focused on identifying intermediates in the reaction.

References:
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CHARACTERIZATION AND REACTION OF AN ANALOG ANTICANCER DRUG OXALIPLATIN

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Cisplatin, carboplatin, and oxaliplatin are anticancer drugs that react with deoxyribonucleic acid, ribonucleic acid and proteins both in vitro and in vivo. Cellular reactions involving these compounds have become a major field of study in order to determine the extent to which these drugs' antineoplastic activities exist. Our research focuses on synthesizing analogs of oxaliplatin and understanding how bulky ligand groups affect reaction with amino acids. (R,R)–N,N'–Dimethyl–1,2–diaminocyclohexane platinum (II) oxalate or Pt (Me$_2$dach)(ox) varies from oxaliplatin (Pt(dach)(ox)) in that it has one methyl group attached to each platinum coordinated nitrogen. Theoretically Pt(Me$_2$dach)(ox) has two stereoisomers – RRRR and SRRS – based on the chirality centers of the two platinum coordinated nitrogens and the molecule's C2-symmetry. However, upon synthesis and spectroscopic interpretation, it has been determined that the SRRS conformation is predominant. Nuclear Magnetic Resonance (NMR) spectroscopy has shown that the reactions of N-Acetylmethionine (N-AcMet) with Pt(Me$_2$dach)(ox) and Pt(dach)(ox) react at similar rates suggesting that the methyl groups of Pt(Me$_2$dach)(ox) have little effect on the initial reaction. Whereas reaction of Pt(dach)(ox) and N-AcMet can form 1:1 or 1:2 complexes, Pt(Me$_2$dach)(ox) with N-AcMet can form only 1:1 products. Depending on Pt:N-AcMet ratios, Pt(dach)(ox) has the potential to form either a [Pt(dach)(N-AcMet-S)^2] or [Pt(dach)(N-AcMet-S,N)] complex. The bis product is not found in Pt(Me$_2$dach)(ox) reactions because the formation of a [Pt(Me2dach)(N-AcMet-S,O)]$^+$ product retards the coordination of a second N-AcMet. It has therefore been deduced that the additional methyl groups of Pt(Me$_2$dach)(ox) limit reaction with N-AcMet to a 1:1 molar product.

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INVESTIGATIONS OF THE INHERENT DISTRIBUTION OF DNA PACKAGING IN SPERM CHROMATIN

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The compaction of DNA is a common theme in cell biology. The most tightly packed DNA is found in bacteriophages and vertebrate sperm nuclei. Spermatogenesis, the formation of mature spermatozoa, is a unique multi-step process resulting ultimately in the self-assembly of DNA in sperm to a final volume roughly 1/20th that of a somatic nucleus. The mechanisms underlying sperm chromatin remodeling, however, remain poorly understood especially at the molecular level. DNA compaction in sperm cells is mediated using protamines. Protamines are short, 50-110 residue, highly basic proteins containing from 50-80% arginine. This highly condensed organization of the DNA in sperm is thought crucial for the protection of DNA since all repair mechanisms are shut down. Damage to male sperm has recently been shown to be correlated not only to infertility in men but also to higher miscarriage rates in women and higher rates of genetic diseases in the offspring.As a first step, we must address the inherent distribution of packaging in sperm populations. It is common practice in assisted reproductive technologies (ART) to fractionate sperm by density and to use only the densest fractions. We have gone further and have fractionated isolated salmon sperm nuclei on sucrose density gradients and measured the distribution of DNA spacings for fractions by SAXS. As we anticipated, denser fractions result in more tightly packaged DNA. We are currently working to extend this work to isolating mammalian sperm nuclei from bulls and horses. We plan to systematically progress in complexity from salmon to bull to horse and human sperm with the aim of understanding how cation chemistry dictates DNA packaging in sperm chromatin and determine the interconnection between DNA packaging densities and DNA accessibility to small molecule drugs and reactive oxygen species (ROS).

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2. 2. DeRouchey, J. E.; Rau, D. C., Role of Amino Acid Insertions on Intermolecular Forces between Arginine Peptide Condensed DNA Helices Implications For Protamine-DNA Packaging In Sperm. *Journal of Biological Chemistry* **2011,** *286* (49), 41985-41992.
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ELECTROCHEMICAL PROPERTIES OF EXFOLIATED GRAPHENE NANOPLATELET (XGNP)

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Graphene is a 2-dimensional, honeycomb network of carbon atoms arranged in hexagonal patterns. Graphene-based nanomaterials are receiving significant attentions in electrochemical applications because of their several advantages such as its high surface area, excellent mechanical stability, good electrical conductivity, and easy chemical modification.

Physical and electrochemical properties of xGNPs synthesized by mild chemical oxidation of graphite were studied. First, the morphology and microstructure of xGNPs were characterized by atomic force microscopic (AFM) and Raman spectroscopic techniques. The Raman spectrum of xGNP showed an ID/IG of 0.2-0.4, indicating that it contains exposed edge-planes. Second, electrochemical properties of xGNP powders were studied by cyclic voltammetric measurements. The xGNP powders were placed on a glassy carbon (GC) disk electrode by simply dropping xGNP-dispersed solution and evaporating solvent. After the evaporation of solvent, a thin film of xGNP was formed on GC. The xGNP film was mechanically stable and maintained a good electrical contact with GC which served as a current collector during the electrochemical measurement. Background and redox cyclic volammetric curves were obtained to determine its potential ability in biosensor and energy-related applications. Overall, xGNP showed stable voltammetric responses with a large capacitive current and fast electron transfer kinetics for most of redox systems.

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ENGINEERING A MODERN VECTOR FOR OVEREXPRESSION OF NADH-OXIDASE

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Nitroreductase (NR), an enzyme originally isolated from Enterobacter cloacae in a weapons storage facility, exhibits broad substrate specificity and is capable of reducing a wide variety of nitro-containing aromatic compounds, such as TNT. The ability of NR to metabolize these compounds makes it an excellent candidate for uses in bioremediation and chemotherapy. NADH-oxidase (NADOX) is a homologue of NR, isolated from the extremophile Thermus thermophilus. While more extensive research has been performed on NR and its substrates, we anticipate that NADOX shares the same capability to reduce a broad range of nitro-containing compounds. After overexpressing and purifying NADOX, a comparison will be made of the temperature-dependence of NADOX and NR. Since the optimal efficiency of the NADOX enzyme occurs around 84 °C, vs. 25 °C for NR, NADOX may be able to operate at a broader temperature range than NR for biological applications. A major issue we've encountered is poor overexpression of the of the NADOX gene product with the current genetic construct. The gene is currently in an older plasmid that lacks modern features maximizing transcription and translation. Therefore, we have undertaken the design and engineering of a new expression vector. The poster describes our previous efforts to express the gene and recent progress in cloning the gene into the new vector.

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ENZYMATIC ANALYSIS OF GLUTATHIONE ENZYMES IN WISTAR RATS WITH A MODERATE TRAUMATIC BRAIN INJURY

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It is a well-established notion that imbalances in the production of reactive oxygen species (ROS), reactive nitrogen species (RNS), and native antioxidant mechanisms have been shown to increase oxidative stress. Glutathione is a key antioxidant in the neutralization of ROS and RNS, thereby it is hypothesized that upon administration of γ-glutamyl cysteine ethyl ester (GCEE), a glutathione mimetic, to moderately brain injured Wistar rats, a decrease in oxidative stress will be observed. Glutathione peroxidase (GPx) is the central enzyme used for reduction of the ROS in the brain through the catalyzed reaction with reduced glutathione. Oxidized glutathione is then reduced to allow further protection against oxidative stress via the oxidation of β-nicotinamide adenine dinucleotide phosphate (β-NADPH) by glutathione reductase (GR). GCEE was administered using a time dependent approach, and the statistical significance of each dose was determined by examination of GPx and GR activity. Each animal was treated with 150 mg/kg of body weight of GCEE or saline at a time interval of 30 or 60 minutes post injury. Each brain homogenate was analyzed using a GPx and GR assay by spectrophotometric analysis. Brain samples treated with GCEE had a statistically significant increase in the activity GPx and GR (p values <0.0001 and 0.0359, respectively) compared to those treated with saline at 60 minutes post brain injury. The increased activity of these enzymes correlates with elevated antioxidant capacity, thus lowering overall oxidative stress making this a potential post therapeutic strategy for moderate traumatic brain injury.

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DEVELOPMENT OF AN IN VIVO ASSAY TO MONITOR ACRB TRIMERIZATION IN CELL MEMBRANE

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In Escherichia coli, AcrB is an efflux pump that associates with membrane fusion protein AcrA and outer membrane channel TolC to form a tripartite complex to extrude a variety of noxious compounds from both the cytoplasm and periplasm of the cell. Crystal structures of AcrB have shown that AcrB exists and functions as a trimer. However, the oligomerization process of AcrB remains elusive. To investigate AcrB oligomerization in vivo, the GALLEX system was used to couple the AcrB subunit interaction with the expression of the reporter gene, LacZ. The DNA binding domain of regulator protein LexA was fused at the N-terminus of AcrB. The oligomerization of AcrB leads to LexA dimerization and suppression of LacZ production. The beta -galactosidase activities of strains containing LexA-AcrB (wild type) and LexA-AcrBR780A (a mutant with decreased trimer stability) were compared. The beta-galactosidase activity of the strain containing the mutant construct displayed a small, but reproducible 20% increase in enzyme activity. In addition, the application of McConkey Agar Plate was tested in differentiating AcrB constructs of different trimer affinities. Further optimization will be necessary to improve these assays to make them useful in studying AcrB oligomerization in vivo.

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ELECTROCHEMICAL AND OPTICAL CHARACTERIZATIONS OF NANOCARBON POWDERS

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Carbon based nanomaterials are of a great interest due to their attractive properties and promising roles in many scientific and technological applications including bioimaging, electrochemical sensing and energy storage/conversion devices. We investigated physicochemical, optical and electrochemical properties of sp2- and sp3- bonded carbon powders to understand their structure-function relationships. The electrochemical and optical properties of carbon materials were characterized by cyclic voltammetric and fluorescence spectroscopic methods, respectively. First, background and redox cyclic voltammetric curves of glassy carbon disk electrode were obtained with standard redox systems (Ru(NH3)3+/4+, Fe(CN6)3-/4-, Fe2+/3+, IrCl62-/3-). The heterogeneous electron transfer rate constants were determined by comparing experimental results with simulations.

Secondly, a cavity microelectrode is being under preparation and will be used to monitor capacitive and faradaic behaviors of carbon powder. The cavity microelectrode is fabricated by preparation of a Pt microelectrode surrounded by glass and a subsequent chemical etching of platinum to leave a microliter-volume cavity. This cavity will be filled with carbon powders for electrochemical measurement. Lastly, the optical properties of sp3-bonded nanodiamond were investigated. The fluorescence spectra from the 5 nm diamond nanopowder exhibited stable emissions and the light emitted is dependent upon the excitation wavelength. The mechanism of this photoluminescence is still under investigation for diamond nanoparticles of this size, but the fluorescence properties imply its potential use for bioimaging.

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MWCNT-STUDDED CARBON FIBER COMPOSITES FOR INCREASED THROUGH-THICKNESS THERMAL CONDUCTIVITY - TOWARDS CONTINUOUS SYNTHESIS

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A lightweight and strong alternative to metals are carbon fiber composites. The poor transverse conductivity of composites is counteracted by CVD synthesis of multiwall carbon nanotubes (MWCNT) to the spread-tow fiber surface. Spread-tow is used instead of fiber bundles in order to achieve growth on most fibers. Current methods use batch fabrication which limits production volume. This project was an effort to improve continuous CVD synthesis of MWCNT. Fabrication included spread-tow de-sizing, deposition of silicon dioxide, and MWCNT synthesis under temperature. Modifications to tow speed through the reactor, gas reactants flow rate, temperature, SiO2 precursor, and de-sizing were explored in order to optimize thick and homogeneous MWCNT growth. Scanning electron microscopy was used to analyze MWCNT growth. It was determined that de-sizing was the critical step. Composites from the studded spread-tow were pre-pregged and tested for through-thickness thermal diffusivity using a laser flash apparatus (Netzsch LFA 427). It was shown that the growth of MWCNT increased the through-thickness thermal diffusivity approx 1.5x of the baselines without MWCNT. Normalized conductance of the studded tow showed 1.2x improvement over the baselines.

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ELECTRICALLY CONDUCTIVE PAN/MWCNT FIBERS

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Conventional metal wires made from copper or aluminum provide necessary conductance for electronics applications, but also contribute significantly to the weight of an electronic device. The development and characterization of electrically conductive polymeric fibers can provide a light-weight alternative to relatively heavy metal circuitry.

20 weight-percent multiwall carbon nanotube (MWCNT) to polyacrylonitrile (PAN) was solution spun into fiber continuously in 100 count tows. After a novel heat treatment, these fibers were rendered electrically conductive. To characterize the fibers, circuits were constructed comprised of 100 count MWCNT acrylic fiber tow samples. The circuit configuration included a digital data logger to continuously measure current and voltage-drop data across the fiber as a function of time. A highly sensitive thermocouple was attached to the tow during voltage application to simultaneously measure temperature data. After current equilibrium was reached, internal PAN stabilization took place which increased conductance, commensurately increasing current. Analysis showed distinct regions of increasing current carrying capacity as a function of time of applied voltage. This reaction ultimately led to thermal runaway which resulted in thermal failure.

The average resistivity of MWCNT acrylic tow was reduced 65% before failure while the average current carrying capacity was increased 259% before failure, compared to fiber properties of pre-continuous voltage application.

Further experimentation may be performed to determine whether PAN restructuring is a function of increasing temperature or voltage application. Also, identifying a maximum equilibrium voltage without thermal failure would allow the fiber to be evaluated as a functioning polymeric current carrying wire

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EXTRACTION OF LIPIDS FROM MICROALGAE USING POLAR SOLVENTS

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Given the finite nature of fossil fuel reserves and the negative environmental effects associated with their use, a need for more sustainable fuel sources has risen. Microalgae offer a potential solution in that they are the fastest growing photosynthetically active organisms on the planet and are rich in lipids which can be upgraded into liquid fuels. Lipids, while having high calorific values, are difficult to separate from other cellular components of the microalgae, leading to extraction and purification costs that can exceed the value of the lipids themselves. Traditional solvent extraction methods require a dehydrated and ground algal stock to obtain optimal extraction efficiencies, and employ mixed solvent systems that can complicate solvent recovery. In an attempt to reduce/remove pre-processing costs associated with drying and lysing of the microalgae, polar single solvent systems were used at room temperature to attempt lipid extraction from a wet algal feedstock. The effectiveness of each solvent tested was evaluated according to the weight of extract obtained and the purity of the extract, as determined by GC simulated distillation. Results pertaining to the most promising solvents, as well as plans for future testing, will be presented.

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THE REDUCTION OF PERMANGANATE BY THYMINE AS A COLORIMETRIC ASSAY WITH APPLICATIONS IN NUCLEOTIDE-SPECIFIC DETECTION

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☐	Freshman	☐	Sophomore	☐	Junior	X	Senior

Permanganate (MnO4-) is a strong oxidizer with a distinct purple hue. When reduced, a permanganate solution displays a series of other colors as its oxidation state is lowered from +7 to +6 (green), +4 (yellow/ brown), to +2 (colorless). This range of colors provides an opportunity for permanganate to be used as a colorimetric assay in systems with oxidizable species.

It has been shown that permanganate is able to qualitatively identify nucleotide composition of a DNA sequence due to the varying reactivity of each nucleotide. Our extension of this approach is to apply the known specificity of permanganate for the nucleotide thymine to two possible applications, the first being the determination of PCR endpoint. PCR, polymerase chain reaction, is a technique used to mimic the natural DNA replication process chemically joining free nucleotides together in the order of the target DNA sequence, resulting in the amplification of the target DNA molecule. Our method uses permanganate to measure the amount of free thymine in the PCR solution, indicating the progress of the reaction. This would allow the experimenter to optimize the use of materials and time when using PCR and potentially replace the time consuming methods currently used to measure PCR results.

The second application we are focusing on is the detection of Guanine-Thymine mismatches within a DNA sequence. These mismatches are the result of mutations in the genetic sequence and have the potential to affect the structure of the RNA (ribonucleic acid) and protein molecules that rely on the DNA as a template. The thymine-permanganate reaction detects G-T mismatches by selectively reacting with the thymine of the mismatched pair or possibly with the more unstable DNA containing the mismatch, which is expected to be more reactive than the correctly matched double-stranded DNA.

Our results thus far have shown that the mismatch-containing DNA is more reactive, allowing qualitative identification of the presence of a mismatch in a controlled experiment. This result has lead to further application of this reaction as a way of detecting G-T mismatches in DNA and their effect on the structure of the RNA that is transcribed from them.

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A NEW CLASS OF GOLD NANOANTIBIOTICS- DIRECT COATING OF AMPICILLIN ON GOLD NANOPARTICLES

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Need for novel, innovative strategies for developing antibiotics is becoming a necessity due to an increasing number of rapidly evolving micro-organismal threats. Antibiotic encapsulated gold nanoparticles (GNPs) are one such strategy showing promise. We report the development of ampicillin encapsulated gold nanoparticles (Amp-GNPs) that possess highly effective, dose dependent antibacterial activity. Our method for synthesizing Amp-GNPs is an entirely eco-friendly, single step reaction taking place within an aqueous buffer. We have tested the antibacterial activity of Amp-GNPs against multiple strains of bacteria, both Gram-positive and Gram-negative, and have found Amp-GNPs to be highly efficient against all tested strains. Amp-GNPs have been shown to exhibit significant potential and ability to enter the medical field’s arsenal to fight infectious disease.

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THE EFFECTS OF TEMPERATURE AND TRIFLEUROETHANOL ON THE ACTIVITY OF ALKALINE PHOSPHATASE

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Enzymes typically get inactivated when presented with even minute amounts of organic solvents. However, there are a few enzymes where this is does not seem to be the case. In our study, we examined the enzyme known as alkaline phosphatase, obtained from calf intestines. This enzyme seems to be actually activated by 2,2,2-trifluoroethanol, in the presence of pH 10 carbonate buffer. The focus of this experiment is to determine the dependence of enzyme activity changes on temperature during the activation of the enzyme with the carbonate buffer (pH 10) and the various amounts of trifluoroethanol. The temperatures tested were 45 °C, 65 °C, and 85 °C. The experiment was then extended by utilizing carbonate and Tris buffers, at a pH of 9, and examining their effects. We report on the buffer dependence of the activation of alkaline phosphatase in 2,2,2-trifluoroethanol.

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GREEN SYNTHESIS OF CADMIUM SULFIDE NANOPARTICLES

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This work was designed as a preliminary test to determine if a dithiol ligand could be used to recycle bulk cadmium sulfide (CdS) by forming CdS nanoparticles. It was found that the ligand used actually functionalizes the surface of the nanoparticles, so it was decided to develop a method to tune the optical properties of the particles by changing the size as a function of heating time. A green aqueous based approach was used in this work in hopes that it could possibly be scaled up for industrial production.

The results obtained were fairly reasonable. It was found that different heating times produced particles with different sizes. The ultimate hypothesis that the growth would be linear with heating time was disproven.

This was attributed to the Ostwald ripening process that caused a defocusing of size with longer heating time. Future studies will focus on changing other experimental variables to prevent Ostwald ripening and study the properties that surface functionalization gives the particles.

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ANALYSIS OF MARKERS OF OXIDATIVE DAMAGE IN RAT SPINAL CORD FOLLOWING SPINAL CORD INJURY

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Increased levels of reactive oxygen species (ROS) are believed to contribute to secondary damage after contusion spinal cord injury (SCI) by oxidatively modifying proteins, DNA, and phospholipids. During the secondary biochemical cascade, Ca2+ uptake in the mitochondria is known to increase reactive oxygen species (ROS) production. The current study was designed to assess the levels of markers of oxidative damage in terms of 4-Hydroxynonenal (4-HNE, lipid peroxidation) and protein carbonyls (PC, protein oxidation) following contusion SCI in rats using western blot analysis. Adult female Sprague-Dawley rat spinal cords were contused at the L1/L2 spinal level (250 kdyn) using the IH impactor®. At 24 hr post-injury, tissue homogenate, crude mitochondria (including neuronal and glial mitochondria, synaptosomal membrane, and myelin), and purified neuronal and glial mitochondria were simultaneously isolated from injured spinal cords, as well as naïve animals, in order to assess 4-HNE and PC concentration. Compared to naïve animals, SCI did result in an increase in 4-HNE in the crude mitochondrial sample and the homogenate sample, however not in the purified mitochondria sample.

Additionally, SCI resulted in an increase in PC in the homogenate, however not in the crude mitochondria. In future experiments, the sample size will be increased. Furthermore, the tissue sample size may be decreased to prevent a wash out effect from peripheral non-lesion tissue

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EARLY AGING: THE CHARACTERISTICS GIVEN TO BOURBON IN THE EARLY STAGES OF WHITE OAK AGING

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In the creation of commercial bourbons and whiskeys, the aging process in a usually charred White Oak barrel has the ability to add many flavors and characteristics to the alcohol solution before being bottled and sold to consumers. In this process many of these alcohol solutions are given additional characteristics such as smoky flavors, a distinguishable color, and other traits that help make the samples more desirable. In our research work, we have taken ethanol solutions that range from 45%-65% and aged them with a variety of American and French White Oak wood chips that had different charring preparations. Through analysis with a GC/MS and a UV/Vis Spectrometer, we have been able to determine the initial entrance of chemicals, their concentration changes over time, and the development of a time interval system for specific chemicals as they age our solutions.

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SYNTHETIC APPROACHES TO ORGANOMETALLIC COMPLEXES FOR ELECTRONICS APPLICATIONS

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Organic semiconductor chemistry has the potential for low start-up cost production of electronic devices such as transistors, sensors and organic solar panels. Unfortunately, there are a number of problems with classic organic semiconductors (e.g., polyacenes such as pentacene), including poor solubility and low stability. One possible workaround to these problems is to synthesize organic acenes coordinated with metals (e.g., iron, manganese or ruthenium) to help improve solubility and stability as well as introduce enhanced electrical properties (smaller band gap), redox potentials (electrochemical switches) and new optical properties (electrochromism). This poster will present three projects that explore (with limited success) different possible synthetic pathways to synthesizing metal-coordinated cyclopentadienyl(Cp)-fused acenes in the ferrocene and cymantrene (Cp-Mn(CO)3) systems.

The first project's goal was to find an alternative, high yielding approach for synthesizing 1,2 disubstituted ferrocenes (e.g. [Fe(Cp){1,2-C5H3(CO2H)}]). These compounds are often good precursors for ring homologation reactions (e.g. double aldol or double Friedel-Crafts reactions), but the current approach is low-yielding. This project attempted the Friedel-Crafts reaction with ferrocene and γ butyrolactone followed by subsequent oxidation to the ferrocene 1,2-dicarboxylic acid.1

A second approach to 1,2-disubstituted metallocenes involves the transmetallation of metal salts with 1,2 disubstituted fulvene thallium salts (e.g. [Tl{1,2-C5H3(COCH3)2}]). This approach is well studied in the manganese, iron and ruthenium systems.2,3 The project goal was to synthesize indenyl derivatives of cymantrene by the Diels-Alder reaction with dimethylacetylenedicarboxylate (DMAD) and thiophenes/ pyridazines derived from the corresponding 1,2-diketones (for example [Mn(CO)3{1,2-C5H3(COCH3)2}]) that can be synthesized by the transmetallation approach. The resulting dicarboxylic acid can be used for the same ring homologation reactions as in the first project.

Finally, a third approach involves direct ring addition to metallocenes via the Friedel-Crafts reaction with corresponding acene derivatives (e.g. 2-(CO2CH3)-C6H4COCl). Often ring closure of the anhydride (e.g. phthalic anhydride) is difficult because the first Friedel-Crafts reaction deactivates the Cp ring for subsequent ring closure.3 This is amended by reducing the resultant ketone prior to ring closure. The goal of this ongoing project is to repeat the chemistry that was explored in ferrocene, where the aromatization of the complexes was difficult,3 on cymantrene. Cymantrene may show better success in aromatization due to its more electron-deficient nature.

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